

Prepared for: Vale Canada Limited

Prepared by: Stantec Consulting Ltd. 1-70 Southgate Drive Guelph ON N1G 4P5

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CHAPTER ONE - INTRODUCTION



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# **CHAPTER ONE - INTRODUCTION**

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# 1.0 INTRODUCTION

The Port Colborne Community-Based Risk Assessment (CBRA) is the first of its kind in Ontario – a "wide area" risk assessment – which began in the year 2000, after the proponent, Inco Limited (now Vale Canada Limited), accepted accountability for the contamination of soils with nickel, copper, cobalt, and arsenic in the vicinity of Inco's Port Colborne Refinery. Inco further accepted the recommendations of the Ontario Ministry of the Environment (MOE) that the health and environmental risks associated with the elevated soil metal concentrations should be assessed. Inco opted to conduct a risk assessment that would be applicable across the community of Port Colborne and would provide property owners and residents with an understanding of the health risks in their neighbourhoods and the broader community. Inco committed that the management of the risks identified in the CBRA would be addressed in a separate "Integration Report".

The CBRA consists of three component risk assessments, including a Human Health Risk Assessment, an Ecological Risk Assessment on the Natural Environment and an agricultural or "Crops" Risk Assessment. Work on the CBRA was originally conducted by Jacques Whitford Limited (now Stantec) on behalf of the proponent, in consultation with a group of stakeholders, which included among others the MOE, Regional Niagara Public Health Department, the City of Port Colborne and the Public Liaison Committee (PLC – a group of Port Colborne residents who volunteered and were appointed to represent the community as a whole, solicit public input, inform the public and to provide input to the proponent and the MOE on the completion of the CBRA), with results and findings documented in various reports between 2004 and 2007.

At its inception, the CBRA was effectively a pilot for wide-area risk assessment in Ontario, and since then, a second wide-area risk assessment has been conducted in the Sudbury region, the Sudbury Soils Study (SSS) (www.sudburysoilstudy.com), building on the learnings from the CBRA. The Sudbury Soils Study began in 2002 and was completed in 2009 (SARA, 2009), while the CBRA process is only now coming to completion. In part, the differences between these two wide-area risk assessments reflect the learnings that occurred early in the CBRA process. In particular, in the CBRA, the MOE was present largely as an observer, whereas in the SSS, the MOE was an active member of the Technical Committee (TC) that oversaw the technical work of the SSS.

The CBRA process was such that the MOE committed that it would begin its official review of the CBRA component risk assessment reports only after the date that all of the final reports were submitted. Although the MOE received copies of the component risk assessments as they were completed, this official review process began as of August, 2010. The MOE provided review comments, issues of concern, and request for clarification on these reports to Vale on May 11, 2011 (Appendix 1A). The MOE's comments were divided into two types: 1) Global Comments, which were not specific to any one section; and 2) Specific Comments, which were identified by volume, section, and page number.



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The tenor of the MOE comments in the letter of May 11, 2011 reflects that the MOE had many points of concern regarding the conduct of the CBRA. Over the intervening 29 months, the MOE, Vale, and Stantec have had detailed discussions to develop a path forward that would allow the MOE to endorse the CBRA. The discussions reflected several realities that have unfolded over the thirteen years since the CBRA was initiated. First, the MOE staff members involved with the CBRA since its inception have all now retired, and the MOE reviews were conducted by personnel not familiar with the file and the many decisions that were made during the CBRA under its unique circumstances. As just one example, the MOE reviewers questioned how the Chemicals of Concern (CoCs) were selected, which was not done conventionally as per Ontario Brownfields processes, but rather, focused on the specific emissions from the Refinery. This reflected the voluntary nature of the CBRA and the trail-breaking approach of the CBRA. The context of the CBRA CoC selection process had to be understood by the MOE's new reviewers. A second issue for the MOE review was that the CBRA component risk assessments built one upon the other. A third issue which was later revealed after discussions with the MOE is that some of their questions would have been answered if the individual MOE reviewers had received and reviewed the Addendum Reports which reflected preliminary comments from the MOE, and which were meant to be read in conjunction with the main reports. As a result, when the MOE reviewers conducted their reviews in 2010, they were often stymied by the apparent absence of information. The MOE comments in Appendix 1A reflect these issues, and there is no doubt that the component risk assessment reports are exhaustive and can be difficult to understand. This is the essential nature of complex wide-area risk assessments, and is one of the barriers that exist surrounding the dissemination of complex risk assessment information.

Responses to the MOE 2011 comments were presented to the MOE at a meeting held on August 25, 2012. Remaining outstanding issues that could not be resolved by consensus with the MOE required additional analyses of the existing data by Stantec and Vale in an effort to address unresolved/outstanding issues. Findings on these additional analyses of the existing data are presented in individual chapters of this report, i.e. **Chapter 3** for HHRA, **Chapter 4** for the ERA Natural Environment and **Chapter 5** for the ERA Crops Studies.

One of the goals of this Update Report, therefore, is to provide a unified document that will be the primary source of information on the CBRA for all readers. Those readers seeking detailed technical information on the CBRA component risk assessments are referred to the individual risk assessments to supplement the information provided in this Update Report. The original risk assessment reports are "final" reports that reflect the professional judgment of the risk assessment professionals at Jacques Whitford/Stantec who conducted the assessments in consultation with the Proponent and the various stakeholders (see appendices 1G-1M). Nevertheless, this Update Report will provide, under one cover, updated supplemental risk assessment results that reflect the discussions that have taken place with the MOE since the completion of its review of the original risk assessment reports from 2004-2007.

Considerable regulatory activity has taken place, worldwide, since the year 2000 when the CBRA began. In Ontario, the legal framework for contaminated site risk assessment at the time the CBRA began was that of the Guideline for Use at Contaminated Sites in Ontario (GUCSO).



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This was replaced in 2004 by O. Reg. 153/04, the so-called Brownfields Regulation, which included new environmental quality standards and specific risk assessment requirements. Reg. 153/04 has itself undergone two revisions (see **Section 1.10**).

Internationally, the European Union conducted risk assessments for many substances, including Ni and Cu, under its Existing Substances Directive. The EU Ni risk assessment was completed in 2008 (EU 2008). The EU developed a "target value" for Ni in air in 2004 (EU, 2004), which has since been adopted as the basis for Ontario's air quality standard. The World Health Organization (WHO) developed a drinking water guideline for Ni in 2005 (WHO, 2005). California developed a maximum contaminant level (MCL) for Ni in drinking water in 2008 (California, 2008); confirmed by California after its review, four years later, of current toxicological data (California, 2012). Texas has developed an inhalation unit risk for Ni in ambient air (Haney et al. 2012). The Canadian Council of Ministers of the Environment (CCME) has produced a draft soil quality guideline for Ni, which was released for public comment in 2013 (CCME, 2013). Interestingly, this regulatory activity, including the development of new environmental and human health quality standards has been based on scientific data that largely already existed in the year 2000, when the CBRA began. One exception is that of the European water quality guideline for nickel, which is now regulated on a bioavailable basis – the first of its kind in the world. It does take time for the body of scientific knowledge to transfer from the research community to the regulatory community, so this is normal, but much of the recent regulatory activity involves the use of older data. This Update of the CBRA will consider these regulatory changes that have been implemented since the year 2000 and will incorporate them accordingly.

This report by Stantec provides an update to those earlier reports on the Human Health Risk Assessment, the Ecological Risk Assessment and the Crop Studies (collectively referred-to as the CBRA reports).

# 1.1 BACKGROUND TO THE PORT COLBORNE CBRA

The City of Port Colborne, with a population of 18,450 (2001 census), is located on the north shore of Lake Erie in the Regional Municipality of Niagara, Ontario (Figure 1-1). The Welland Canal runs through Port Colborne, dividing the city into east and west sections, and continues north across the Niagara Peninsula to Lake Ontario at the City of St. Catharines. Over 80% of developed areas (commercial/residential) in the City of Port Colborne lie to the west of the Welland Canal. The Port Colborne Refinery (the Refinery) is situated approximately half a kilometer to the east of the Canal, bounded by Nickel Beach and Lake Erie to its south, residential subdivisions to its west and north, and rural agricultural lands to its east and northeast (Figure 1-1).

The Refinery began operating in 1918, with peak commercial production of nickel occurring during the 1940s. Refinery operations during the period 1920 to 1960 were responsible for the majority of airborne particulates emitted by the Refinery operations to the atmosphere. An aerial view circa the 1950s of the Refinery and surroundings is shown in **Figure 1-2**. The Refinery stopped producing nickel in 1984.



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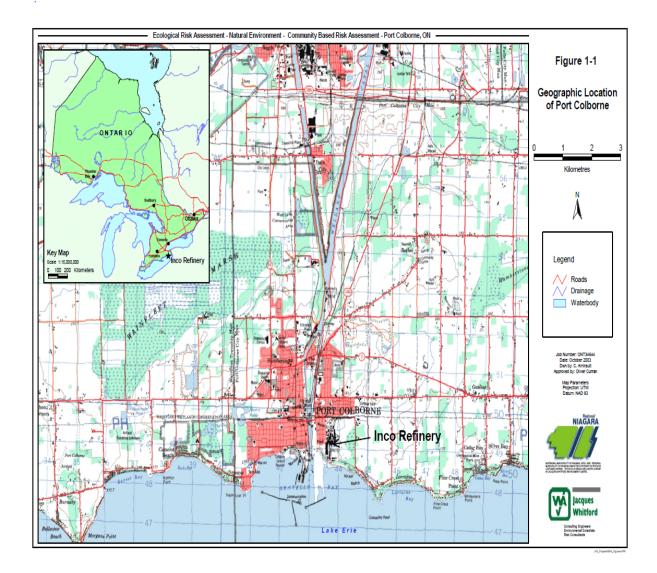
Historical fallout of atmospheric particulates from the Refinery's emissions over time resulted in increased deposition of metal concentrations on surface soils at and near the Refinery and decreasing deposition of metal concentrations on surface soils at distances further away from the Refinery – a phenomenon that is well known around industrial emission sources. The Ontario government has conducted phytotoxicity studies in the area since 1959 (Air Pollution Control Branch, 1959) and the classical depositional plume was presented in the results and findings of the phytotoxicity soil investigations carried out by the Ontario Ministry of the Environment (MOE) in the Port Colborne and surrounding areas between 1998 and 2000.

Soil metals identified by the MOE in their phytotoxicity soil investigations as the primary chemicals of concern (CoCs) related to the deposition of historical Refinery emission particulates included nickel, copper, and cobalt.



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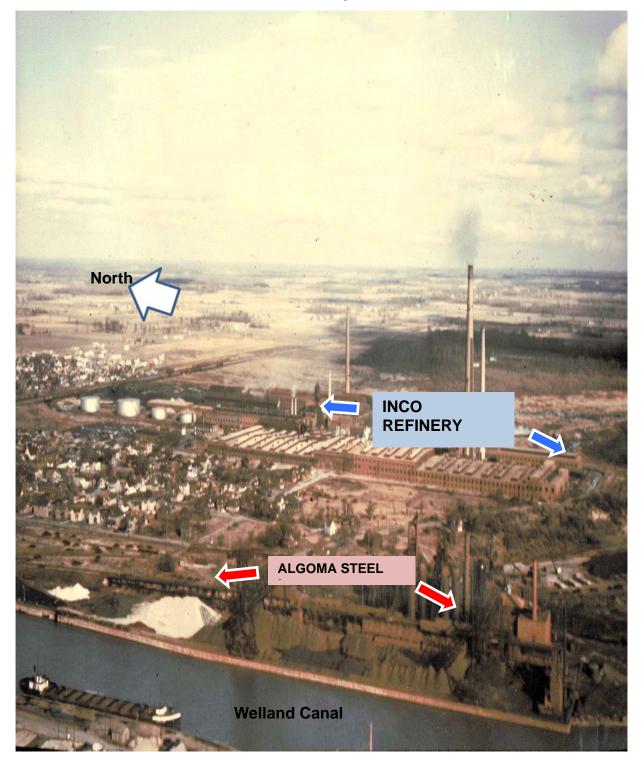






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Figure 1-2 Aerial view of Inco Refinery, circa 1950s





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Mapping by the MOE identified a deposition pattern of atmospherically-dispersed chemicals of concern in soils trending in a southwest-to-northeast manner from the Refinery that coincided with the prevailing southwest-to-northeast wind direction in the area. The footprint of this deposition covered residential lands near the Refinery and to a larger extent, agricultural lands northeast and east of the Refinery.

Further information on the MOE phytotoxicity soil investigations can be found in the reports published by the MOE between 2000 and 2002 (MOE, 2000a, 2000b, 2000c, 2000d; 2002).

Inco acknowledged in 2000 that historical Refinery particulate emissions in Port Colborne was the cause of the southwest-to-northeast depositional plume of soil metal concentrations observed in the MOE phytotoxicity soil investigations. To address any human or environmental health concerns that may have resulted from the historical deposition of the identified CoCs in soil, Inco made a commitment to the community of Port Colborne, the City of Port Colborne, and the MOE, to conduct a CBRA.

#### 1.2 PURPOSE OF THE CBRA

The purpose of the CBRA was to assess, on a comprehensive and community-wide basis, the environmental and human health risks associated with elevated concentrations of the CoCs in Port Colborne soils.

### 1.3 DEVELOPMENT OF CBRA TECHNICAL SCOPE OF WORK, YEAR 2000

The first step in the CBRA process was a presentation to the PLC in May 2000 to explain the proposed Technical Scope of Work (TSOW) to be undertaken in the CBRA and request from the PLC for their support to liaise with the public. An important component of the TSOW was obtaining site characterization information to verify the MOE-identified CoCs and to obtain additional spatial data on concentrations of these CoCs in environmental media. This required the cooperation of property owners to obtain permission to sample on private property. Such cooperation was not always obtained, and gaps in spatial sampling coverage resulted, as noted in the MOE review.

#### A copy of the final TSOW (TSOW, 2000) is found in Appendix 1B.

The CBRA comprised three main risk assessment components:

- 1) A Human Health Risk Assessment (HHRA);
- 2) A Natural Environment Ecological Risk Assessment (ERA); and,
- 3) An Agricultural Crops ERA.

The HHRA quantified the risks of adverse human health consequences and accompanying uncertainties, resulting from CoC exposure. Considerations that CoC exposure may occur simultaneously in several media such as food, air, water, soil or dust and may reach humans through multiple exposure pathways was also examined within the HHRA.



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The Natural Environment ERA quantified risks from exposure to CoCs of non-human, biotic receptors (*e.g.* flora and fauna) and involved an analysis of exposure pathways for CoCs to biotic receptors in the local environment.

The Crops ERA involved both field and greenhouse studies that determined phytotoxic effects of varying concentrations of CoCs on agricultural crops grown on soils within the Port Colborne area.

All these three components of the CBRA are discussed within this Update Report. A fourth component of the CBRA that integrates the findings from the first three components of the CBRA and provides risk management measures can be found in the Vale's "Integration Report", which is a separate document that is not included as part of this Update Report.

The Study Area in this assessment was defined as the City of Port Colborne and adjacent areas where soil concentrations were screened against comparative MOE generic soil standards, which at the start of the CBRA were provided in the MOE *Guideline for Use at Contaminated Sites in Ontario* dated February 1997 (MOE, 1997).

The CBRA developed Risk-Based Soil Concentrations (RBSCs) were intended to provide the equivalent level of protection as the MOE generic soil standards of February 1997 for the specific conditions of the CBRA. Further details on the objectives of the CBRA are found in the TSOW (TSOW, 2000).

The MOE, which participated in the drafting of the Technical Scope of Work in 2000, agreed that a CBRA could be carried out, in which their Ministry's concepts and approach used in individual property risk assessments could also be applied over a large area such as the Port Colborne Study Area.

Field studies for the CBRA data gathering exercise were carried out primarily between the years of 2000 and 2002. When O.Reg.153/04 was later released in October 2004, the MOE confirmed to Inco and the public on their earlier acceptance of the CBRA approach for Port Colborne as developed in 2000. The MOE confirmed that O.Reg.153/04 was not applicable for the CBRA. One of the reasons is that O.Reg.153/04 applies only for properties where the current land use is re-zoned to a more sensitive land use in the future, e.g. from a commercial land use to a residential land use. Another reason is that only the identified chemicals of concerns related to the former Refinery emissions were considered in the CBRA whereas for a property that is to undergo evaluation according to the full O.Reg.153/04 process, other chemicals of concern related to past use(s) or environmental incidents on that property must be considered as well, e.g. petroleum hydrocarbons that may potentially have been released from a leaking heating oil tank on that property to contaminate the underlying soils and groundwater.

### 1.3.1 CBRA Participants

The CBRA proceeded with the scrutiny of internal, external, and third party peer reviews of the scientific methodology used. Additional review and comment input on results and findings that



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flowed from the CBRA came from the MOE, the Regional Niagara Public Health Department, and the general public. The principal CBRA participants included the following:

*Inco Limited* (now Vale), as the proponent of the CBRA process and primary liaison with the Community, the City, and the appropriate government agencies.

The *Ontario Ministry of the Environment (MOE)* as the government agency responsible for ensuring that Inco/Vale conducted the CBRA according to the principles of the risk assessment process. The CBRA "file" rested (rests) with Director of the West Central Region of the MOE, who makes decisions pursuant to the provisions of the *Environmental Protection Act*.

The *Regional Niagara Public Health Department (Public Health Department)* of the Regional Municipality of Niagara as the government agency ensuring that health issues were suitably addressed by the CBRA.

The *property owners* of Port Colborne who were informed of the CBRA progress and invited to comment at the monthly-held public meetings at the City's Municipal building in Port Colborne.

The City of Port Colborne as a participant in the CBRA process.

A *Public Liaison Committee* (PLC), a public body consisting of Port Colborne residents that provided 1) solicitation for public input; 2) dissemination of information to the public; and 3) input to Inco/Vale and to the Director of the MOE on the progress of the CBRA.

*The PLC Consultant*, formerly Beak International Incorporated prior to 2002, provided technical support and advice respecting the CBRA to the City and public residents within the PLC from 2002 to September 2004. Beak's role was replaced later by Watters Environmental Group Inc. in September 2004.

*Jacques Whitford (Stantec after 2009)* was the environmental consultant retained by Inco/Vale to conduct the CBRA from its inception to the present.

A *Technical Sub-Committee* (TSC) of the PLC with members from the PLC, the PLC's consultant, the MOE, the Public Health Department, Jacques Whitford/Stantec and Inco/Vale.

*Third Party Reviewers* included CH2M Hill who reviewed the CBRA's HHRA and ERA reports, SENES Consultants Limited who reviewed the HHRA model spreadsheets, and Dr. Murray McBride who reviewed the Crops Report.

### 1.3.2 Development and Adherence to Protocols

Protocols were established in the CBRA as sets of procedures used to specify how a given testing activity was to be performed. Protocols were developed by Jacques Whitford in 2000 and 2001 for each type of sampling (*e.g.* soil, groundwater, surface water, ambient air, indoor air and dust, local produce, fish, wild game, farm produce, supermarket foods).



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Throughout the Site Characterization stage of the CBRA in 2000 and 2001, all protocols developed by Jacques Whitford were reviewed by the TSC members prior to initiation of any work related to that protocol. If agreement on any one individual protocol was not reached, the contents of that protocol were modified to reach consensus from all TSC members before proceeding.

During the course of conducting CBRA field work and data gathering activities on private properties within the Port Colborne Study Area in the years between 2000 and 2004, one or more representatives of the PLC's consultant accompanied Jacques Whitford staff to observe and witness the techniques employed by Jacques Whitford in the collection of samples of environmental media. This constraint was imposed by the PLC for the entire duration of the CBRA to ensure integrity of sample chain-of-custody.

#### Lands Excluded from the CBRA 1.3.3

Lands associated with the Port Colborne Refinery that are identified within the site's Closure Plan (Inco, 1998), approximately 120 ha, were excluded from the CBRA Scope of Work. The environmental management of these lands is pursuant to the requirements of the Mining Act of Ontario and is outside of the CBRA process.

Further, two large farm properties located approximately a kilometer northeast of the Refinery were excluded from the CBRA due to refusal by the owners to provide access for field sampling of soils and other environmental media on their properties. The inability to access these two properties lying on the centerline of the CoC soil plume was one of the reasons for adopting a zoned approach to the work.

#### **CBRA CHEMICALS OF CONCERN** 1.4

For the CBRA, various studies and soil investigations were done to evaluate all potential relevant Chemicals of Concern (CoCs). The Technical Scope of Work for the CBRA (TSOW, 2000), as found in Appendix 1B, defined a CoC as a chemical found in Port Colborne soils originating from the Inco Refinery where ALL of the following three conditions must be met:

Condition 1)	Chemicals that were historically used or generated by the Inco Refinery or its processes, <b>and</b>
Condition 2)	Chemicals that are present at a community level at concentrations greater than MOE generic effects-based guidelines (MOE, 1997), <b>and</b>
Condition 3)	Chemicals whose presence in soil shows a scientific linkage to the historical operations of the Inco Refinery.

Note that under the above-defined CoC Condition 2, MOE generic effects-based guidelines refer to MOE Table A Generic Guidelines (MOE, 1997). The CoCs identified at the outset of the CBRA in 2001 using the MOE 1997 Guidelines as screening criteria would be the same as those



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that would be identified using the O.Reg.153/04 Table 2 standards that were issued three years later.

Documentation on studies and investigations done by Jacques Whitford that evaluated each of the three CoC Conditions are found in the following appendices:

- **Condition 1**, *CoC Identification using an Emissions Inventory and Dispersion Modelling* dated November 23, 2001 and later updated on March 28, 2008 (Appendix 1C);
- Condition 2, Potential CoC Identification using Soil Chemical Concentration Data in Exceedance of MOE Generic Guidelines dated November 23, 2001 and later updated on March 28, 2008 (Appendix 1D); and
- Condition 3, Potential CoC Identification using Statistical Analyses dated November 16, 2001 and later updated on March 28, 2008 (Appendix 1E) AND CoC Identification using an Emissions Inventory and Dispersion Modelling dated November 23, 2001 and later updated on March 28, 2008 (Appendix 1C).

Evaluation of CoCs in Port Colborne-area soils concluded that these include only nickel, copper, and cobalt as originally determined by the MOE, and, additionally arsenic as determined from the detailed CoC characterization investigations (Appendix 1N). Additional soil metal data from third party sources on subsequent soil investigations carried out in Port Colborne in 2002 and 2003 were examined by Jacques Whitford along with the pre-2002 soil lead data set to determine if lead should be considered as a fifth CoC for the CBRA study. Findings and conclusions are documented in the Jacques Whitford report entitled: Re-Evaluation of Lead as a Potential CoC and dated June 2004(Appendix 1F). The conclusion from this report was that "...lead is not a CoC under the Inco-led Port Colborne CBRA." Lead emissions certainly occurred from the Refinery, as lead is present in the ores mined in Sudbury and is carried over to some extent in the Port Colborne feeds and was therefore processed by the Refinery. However, lead was also used as an anti-knock compound in automotive gasoline for much of the period that the Refinery processed nickel, with unleaded gasoline not being introduced until 1972 and not phased out until 1990 (Health Canada, 2013a). Lead was also used in paints at levels of 10,000-50,000ppm until 1976, when the Federal Hazardous Products Act required lead to not exceed 5,000ppm (Health Canada, 2013b). In older communities, lead can be present in soils due to a combination of industrial sources, historical leaded gas use, and historical paint use (MOE, 2011a). These known contributing sources of soil lead confounded assessment of the Refinery's contribution to soil lead concentrations in Port Colborne. In the final analysis, lead could not be included as a CoC in this community-based risk assessment because all three of the conditions required to be met for a substance to be accepted as a CoC were not met. Studies conducted by Niagara Region Public Health (RNPHD, 2001) indicated that the blood lead concentrations of residents of the Eastside Community were not different from residents of other communities in Niagara. These health studies demonstrated an absence of lead impact in Port Colborne.



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### 1.5 DESIGN APPROACH TO HUMAN HEALTH RISK ASSESSMENT

The HHRA was conducted in general accordance with technical aspects of guidelines from the MOE (MOE, 1996) which includes the tasks presented in **Figure 1-3**. These tasks are similar to those described in *Procedures for the Use of Risk Assessment under Part XV.1 of the Environmental Protection Act* (MOE, 2005), with the primary update to the MOE 2005 document is that the reporting format is more defined than the earlier MOE 1996 document. The CBRA study was not required to conform to this MOE 2005 document nor the other requirements outlined in *Ontario Regulation 153/04* (further stated in **Section 1.10**).

The CBRA's HHRA therefore followed a detailed quantitative assessment approach based on an extensive set of site-specific data of the four CoCs collected from the Port Colborne community. Where site-specific data were not available, existing information found in the literature were used.

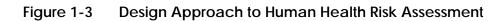
Within the Port Colborne community, potential health risks were evaluated for:

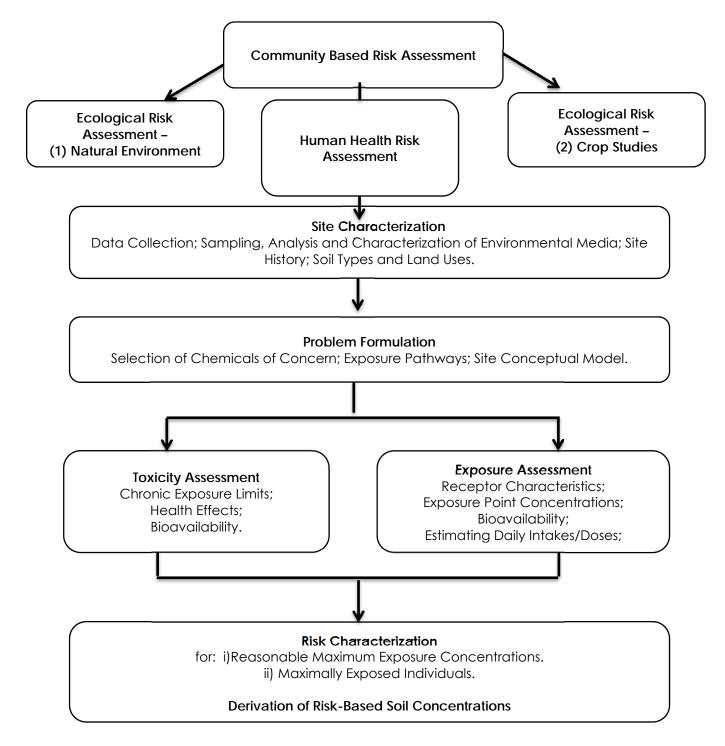
- 1) Typical exposures representative of most people in the community
- 2) Maximally-exposed individuals represented by specific scenarios for the highest measured concentrations at individual properties in the community

Further details on the HHRA are provided in Chapter 3.



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#### 1.6 DESIGN APPROACH TO ECOLOGICAL RISK ASSESSMENT – NATURAL ENVIRONMENT

The ERA examined the risks to both the *natural environment* and to *agricultural crops* (*non-woody vascular plants*) due to elevated concentrations of CoCs in soils. This section discusses the design approach focusing on the Natural Environment. A discussion on the design approach for Agricultural Crops is found in **Section 1.7**.

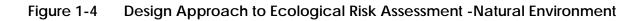
For the ERA that focused on the Natural Environment, an unacceptable risk was defined as an estimated risk linked to the occurrence of soil concentrations of CoCs that prevents sustainable *population(s)* of flora and fauna or a sustainable level of ecological functioning within the defined Study Area. Where an unacceptable risk was estimated, the ERA had the follow-up objective of estimating the levels to which CoCs must be lowered or controlled in order to produce "safe" (acceptable) levels of risk for the natural environment.

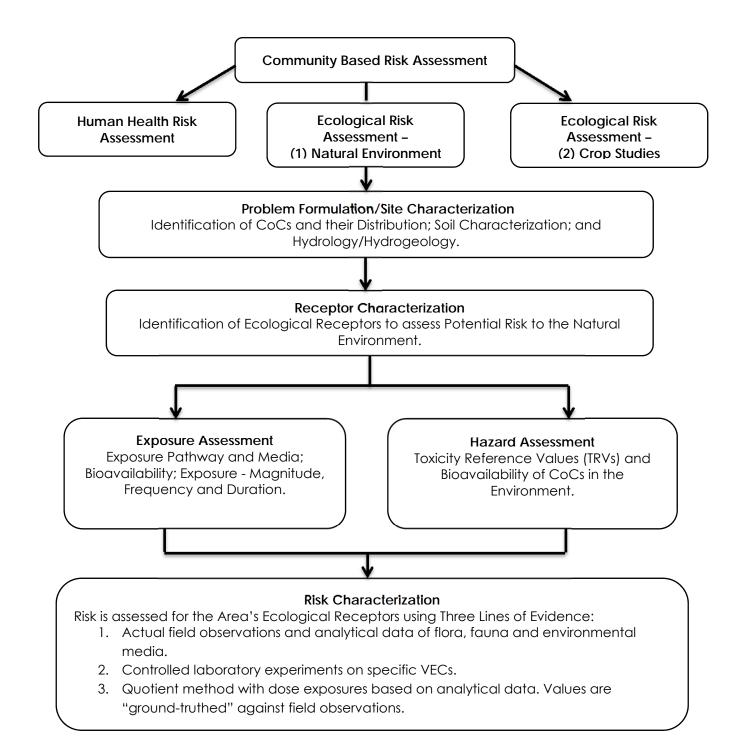
The ERA on the Natural Environment was conducted according to accepted Canadian guidelines (CCME, 1996, 1997) and Ontario guidelines (MOE, 1996). The methodology followed a set process as identified in **Figure 1-4** and included: 1) Problem Formulation and Identification of CoCs; 2) Site Characterization; 3) Receptor Characterization; 4) Exposure Assessment; 5) Hazard Assessment; and 6) Risk Characterization.

Since the ERA focuses on the **natural environment**, human-influenced environments such as parks, playgrounds, gardens, and residential yards were not considered in the ERA. In addition, for assessment of risk to the natural environment, livestock or pets were also not considered as receptors for the ERA. However, a number of mammalian species that were identified as receptors for the assessment of risk can be considered to represent surrogates for pets such as dogs and cats and livestock.



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Initially, only the terrestrial environment had been included for the screening of ecological conditions and potential effects of CoCs. However, as the study progressed, inland water bodies (ponds) and watercourses (municipal drains) were included in the scope of work in direct response to the PLC's concern that aquatic receptors such as amphibians be included.

Specific objectives of the ERA were to:

- Identify receptors (species or species groups, communities, habitats) that allow for an assessment as to whether soil CoCs represent a risk to the natural environment within the defined Study Area;
- Undertake an assessment of risk that is based on the integration of three lines of investigation:
   1) qualitative assessment of the natural environment, 2) quantitative statistical analysis of study area data and 3) quantitative exposure and risk assessment;
- Characterize ecological risk at a population level for ecological receptors found within the Study Area;
- Characterize any potential risks associated with CoCs for the major soil types (clay and organic) and habitat types (woodlots and fields) found in the Study Area; and,
- Identify "safe" (acceptable) soil CoC concentrations for the soil types (clay and organic) and habitat types (field and woodlot) if an unacceptable risk is identified.

A deterministic approach was used for this ERA. Deterministic ERAs use exposure point concentrations which are based on a combination of site-specific, field-collected data as well as information found in the literature. For the CBRA, the ERA followed a detailed quantitative assessment approach based on an extensive set of site-specific data.

Further details on the ERA-Natural Environment are provided in Chapter 4.

### 1.7 DESIGN APPROACH TO ECOLOGICAL RISK ASSESSMENT – CROP STUDIES

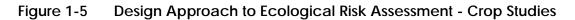
For the ERA-Crop Studies, the risk (phytotoxicity) to non-woody vascular plants due to elevated levels of CoCs in soils was assessed by conducting both field trials on plots of Port Colborne land with CoC-impacted soil, and, greenhouse soil pot experiments using real Port Colborne soils at varying CoC concentrations to grow specific crop plants (oat, soybean, radish and corn).

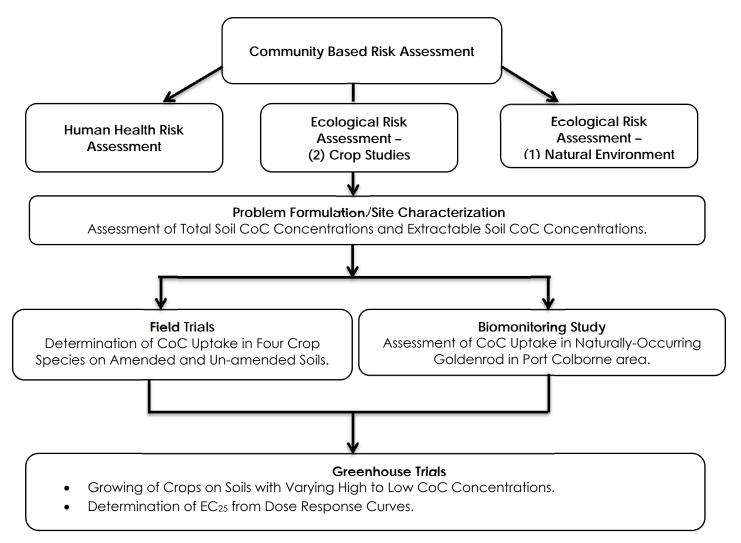
A field program consisting of the collection of goldenrod (*Solidago spp.*) samples throughout the Study Area and the analyses of CoCs in these samples was conducted to determine risk of CoCs in soil to non-agricultural plant species.

The process followed for the Crops Studies is illustrated in Figure 1-5.



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Specific objectives of the Crop Studies were:

- To identify receptors (crop plant species) that allow for an assessment as to whether soil CoCs present a risk to agricultural crops in the Port Colborne area;
- To study the relationship between biomass, plant CoC concentrations and soil CoC concentrations in the Port Colborne area;
- To determine if phytotoxicity attributed to CoC concentrations is different for the area's major soil types (till clay, heavy clay, sand and organic);
- To determine if certain soil amendments influence the yield, biomass and uptake of CoCs by the receptors; and,
- To determine soil CoC concentrations for each of the area's soil types where crops in the Port Colborne area are afforded a safe (acceptable) level of risk.

Further details on the ERA-Crop Studies are provided in Chapter 5.

### 1.8 COMPLETION OF ERA NATURAL ENVIRONMENT AND CROPS REPORTS

In 2004, the ERA reports were finalized and submitted to the MOE for their review. These included:

- Port Colborne Community Based Risk Assessment Ecological Risk Assessment Natural Environment Report by Jacques Whitford Limited and dated September 2004 (Appendix 1G).
- Port Colborne Community Based Risk Assessment Ecological Risk Assessment Crops Report by Jacques Whitford Limited and dated December 2004 (**Appendix 1J**).

Prior to 2004, there had been two draft reports on the Natural Environment study and the Crops study which were circulated for comment to members of the TSC, PLC, and PLC's consultant. All comments were addressed by Jacques Whitford in subsequent draft reports and the final report on the Natural Environment study and the Crops study.

Both the above-mentioned Crops and Natural Environment final reports of 2004 were made available to the general public for their review and comment. Comments from the general public, the PLC, and the PLC's consultant were received and addressed by Jacques Whitford in Addendum Reports entitled:

- Port Colborne Community Based Risk Assessment Ecological Risk Assessment Natural Environment Addendum Report by Jacques Whitford Limited and dated March 2005 (Appendix 1H).
- Port Colborne Community Based Risk Assessment Ecological Risk Assessment Crops Addendum Report by Jacques Whitford Limited and dated September 2006 (Appendix 1K).

The PLC consultant produced an additional round of comments on the two final 2004 ERA reports in a letter dated October 2008. These additional comments from the PLC consultant were formally addressed by Jacques Whitford in the following response reports:



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- Port Colborne Community Based Risk Assessment Ecological Risk Assessment, Natural Environment Response to October 2008 (PLC) Consultant Report by Jacques Whitford Limited and dated January 2009 (**Appendix 1I**).
- Commentary on Watters Environmental Group (PLC Consultant) October 2008 Document CBRA Crops Studies in Port Colborne, Ontario by Jacques Whitford Limited and dated April 2009 (Appendix 1L).

### 1.9 COMPLETION OF HHRA REPORT

Jacques Whitford had produced two draft reports on the HHRA between 2003 and 2004, both of which were sent to members of the TSC, PLC, the PLC's consultant, and the general public for review and comment. All review comments received on these two draft reports were addressed by Jacques Whitford and the HHRA report was finalized in December 2007 and provided to the MOE for its review. The HHRA report was entitled:

• Port Colborne Community Based Risk Assessment – Human Health Risk Assessment Report by Jacques Whitford Limited and dated December 2007 (**Appendix 1M**).

Submission of the 2007 final HHRA report to the MOE also included copies of related reports such as the selection of chemicals of concern.

The key difference between the HHRA final report and the ERA final reports was that all review comments on the HHRA draft reports by general public and all stakeholders were addressed and incorporated in the HHRA final report. The review process by the general public and all stakeholders on the ERA reports on the other hand took place after the finalization of the ERA reports, resulting in Jacques Whitford producing the above-mentioned Addendum Reports.

### 1.10 O.REG.153/04 AND SUBSEQUENT REGULATORY AMENDMENTS

Work on the CBRA data gathering activities, data interpretation and reporting were well underway before the MOE issued, in October 2004, the Province of Ontario's Regulation 153/04 (O.Reg.153/04) made under Part XV.1 of the *Environmental Protection Act* and then later on December 29, 2009, with amendments to O.Reg.153/04 through O.Reg.511/09. Neither O.Reg.153/04 or O.Reg.511/09 are applicable to the CBRA for reasons pointed out earlier in Section 1.3. This point was made clear by MOE representatives at all of the TSC and PLC meetings that were held in Port Colborne.

The design and purpose of the CBRA was never to follow the path of a regular O.Reg.153/04 process, though there are elements of the CBRA that do mirror the requirements under O.Reg.511/09. Instead, the CBRA had been designed in the year 2000 to follow a new community-specific risk assessment process with collaborative input by all members of the Port Colborne community and the various government agencies, including the MOE, Regional Niagara Public Health, and the City of Port Colborne. The CBRA process had more continuous and extensive communication with the Port Colborne public throughout the 2000 to 2007 CBRA duration than would have otherwise occurred if the CBRA had followed the minimal



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requirements for public input under O.Reg.511/09. The CBRA process was and still is voluntary for Inco/Vale.

#### 1.11 **OBJECTIVE OF THE 2014 CBRA UPDATE REPORT**

Objectives of this 2014 CBRA Update Report are two-fold. Firstly to provide written responses to each of the MOE May 2011 comments on the previously-submitted 2004 and 2007 CBRA reports, and secondly, to provide discussion on subject areas in the previously-submitted 2004 and 2007 CBRA reports where 'new science' since 2007 up to 2014 may lead to different conclusions of the earlier work(s).

To reiterate, the goal of this CBRA Update Report is not to rewrite or reproduce contents of all of the original information contained in the 2004 and 2007 CBRA reports. Rather, this CBRA Update Report reflects the outcomes of discussions with the MOE since 2011, summarizes the findings of the risk assessments, and provides discussion on specific areas where changes have been made in the findings and conclusions of the HHRA, ERA Natural Environment, and Crop Studies as a result of application of 'new science' and new data since 2004 and 2007.

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# **CHAPTER 1 APPENDICES 1A to 1N**

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- Appendix 1B: Technical Scope of Work for CBRA, 2000
- Appendix 1C: CoC Evaluation Emissions Study, 2001, 2008
- Appendix 1D: CoC Evaluation Areas of Soil Exceedances, 2001, 2008
- Appendix 1E: CoC Evaluation Statistical Evaluation, 2001, 2008
- Appendix 1F: CoC Evaluation Re-Evaluation of Lead, 2004
- Appendix 1G: ERA Natural Environment Report, 2004
- Appendix 1H ERA Natural Environment Addendum, 2005
- Appendix 1I: ERA Natural Environment Addendum, 2009
- Appendix 1J: ERA Crops Report, 2004
- Appendix 1K: ERA Crops Addendum, 2006
- Appendix 1L ERA Crops Addendum, 2009
- Appendix 1M: HHRA Report, 2007
- Appendix 1N: CoC Summary Evaluation, 2001, 2008



CHAPTER 2 SITE CHARACTERIZATION



Prepared for: Vale Canada Limited

Prepared by: Stantec Consulting Ltd. 1-70 Southgate Drive Guelph ON N1G 4P5

122210662 September 12, 2014

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# 2.0 SITE CHARACTERIZATION

**Chapter 2** summarizes the site characterization information on the Port Colborne CBRA Study Area extracted from the original CBRA documents (**Appendices 1C-1M**). This site characterization information was originally spread amongst each of the component risk assessment reports, as each risk assessment considered aspects that were unique to their purpose (i.e. either as a human health or agricultural or ecological risk assessment). This site characterization information was used as the basis in the development of the Site Conceptual Models for the HHRA and the ERA as later discussed in respective **Chapters 3 and 4** of this text and in the experimental design of the Crop Studies as discussed in **Chapter 5**.

# 2.1 SPATIAL DISTRIBUTION OF CHEMICALS OF CONCERN IN SURFACE SOILS

The total number of data points from all sources on measured CoC concentrations in soils sampled within the Port Colborne CBRA Study Area totals approximately 2,500. Roughly 200 data points came from the MOE 1998 and 1999 phytotoxicity studies carried out prior to the CBRA (MOE, 2000a, 2000b). Approximately 1,500 more data points came from the MOE 2002 Rodney Street investigation. Finally, approximately 800 data points came from the CBRA soils investigations carried out by Jacques Whitford and others between 2000 and 2004, during the active data collection period of the CBRA.

Test pit investigations carried out by Jacques Whitford in 2001 within the Port Colborne CBRA Study Area identified a pattern of high CoC concentration levels in surface soils between 0 and 20 cm, lower CoC concentration levels below 20 cm, and typically, very low background levels below 30 cm. CoC contour maps were generated using a combined data set of 840 soil samples collected from the 0 to 5 cm soil depth interval, which, being the most abundant of datasets of soils collected at other depths, provided the greatest coverage of CoC soil concentration information over the entire Port Colborne CBRA Study Area. **Figure 2-1** in **Appendix 2A** shows the computer-generated soil CoC concentrations maps for nickel, copper, cobalt, and arsenic.

Nickel was the primary metal processed at the Port Colborne Refinery, and this is reflected in the magnitude and extent of contamination in surface soils (0 to 5 cm depth) amongst the maps for the four CoCs (Figure 2-1 in Appendix 2A), which show that nickel is the "fingerprint" contaminant associated with the historical nickel Refinery emissions. Ratios of nickel-to-copper and nickel-to-cobalt in soil identified from the CBRA investigations and the prior MOE investigations were approximately 10 and 50, respectively. The ratio of nickel-to-arsenic soil concentrations from the CBRA investigations was approximately 130.



Maximum measured soil concentrations for the CoCs in open spaces, not including woodlots, were 17,000 µg/g for nickel, 8,400 µg/g for copper, 222 µg/g for cobalt, and 214 µg/g for arsenic. Higher nickel and cobalt concentrations were measured in some woodlots, with Ni, Cu, Co, and As concentrations reaching 33,000, 8,400, 427, and 214 µg/g, respectively, in the Reuter Road woodlot immediately east of the eastern boundary of the Refinery.

The spatial distribution of nickel soil concentrations as mapped on Figure 2-1 in Appendix 2A show the highest nickel soil concentrations on and in the general vicinity of the Refinery lands, with a decreasing soil-nickel concentration gradient relative to increasing distance outwards from the Refinery in the direction of the prevailing wind, namely, to the northeast.

The shape and distribution of the noted contour lines of nickel, copper, cobalt, and arsenic concentrations in soils in Figure 2-1 in Appendix 2A are approximate and reflect statistical interpolation between the 840 data points by the mapping software. These contour maps only infer CoC concentrations and they cannot be used to accurately predict actual soil CoC concentrations.

Figure 2-1 in Appendix 2A was constructed using data points of CoC concentrations in soil samples collected from the open spaces only, and not from samples collected from the woodlots. Figure 2-4 in Appendix 2A shows the locations of all of the soil samples collected from open spaces and woodlots within the Port Colborne CBRA Study Area. Woodlot data were excluded from Figure 2-1 because concentrations of CoCs in soils in some of the woodlots (in particular in soils collected in the woodlot along Reuter Road) were much higher than those in the surrounding open spaces. Hence, any inclusion of the woodlot data would have shown one or more of the woodlots as outliers of high CoC concentrations, incorrectly implying another source of CoCs besides the Refinery.

#### 2.2 **ORIGIN AND TYPE OF CONTAMINATION**

#### 2.2.1 Historical Processes inside the Refinery and associated Speciation of Emissions

The following discussion briefly summarizes the detailed information on historical operations at the Port Colborne Refinery found in Appendix 1F (CoC Evaluation Re-Evaluation of Lead, 2004).

Historical processes associated with Ni production at the Port Colborne Refinery would suggest that the speciation of nickel in air around the calcining and sintering operations would consist mostly of nickel oxides with some sulphidic nickel, while the speciation around the electrolysis tanks would be mostly soluble nickel.



Doll *et al.* (1990) estimated that greater than 60% of nickel in the indoor air in the sinter plant of the Refinery would be present in oxidic species and the remaining 40% of nickel as sulphidic species.

It is important to recognize that the materials processed at the Refinery did not originate in the Port Colborne area. That is, there no mining carried out at Port Colborne. Instead, the metals that ultimately became the CoCs in the CBRA were mined at Inco's Sudbury complex and, after milling and smelting, were enriched into a Ni-Cu matte for further processing. This matte became the feed for the Port Colborne Refinery in its early years of operation, but it is also important to note that the feed to Port Colborne varied in four distinct periods.

In the first period, 1918-1930, Cu-Ni matte was shipped in bulk form from Sudbury to Port Colborne where the Orford process was used to separate Cu from Ni. The Orford process was a high temperature process that had emissions via chimney stacks and generated an alkaline slag. The alkaline slag was further processed in a slag furnace to further remove Ni and produce a final granulated slag product that is stored on-site to this day. Again, because the final slag processing occurred at high temperatures in a blast furnace, there would have been releases via the furnace stack. Vale's recent soil speciation study, discussed in section 2.3.2 below, has identified nickel associated with alkaline slag from this period in soil samples collected for the CBRA. Prior to the existence of electro-refining at Port Colborne (before 1925), the Cu and Ni were firerefined to marketable products. From 1926 to 1930, the Ni product was further processed by electro-refining at Port Colborne. The bulk Cu-Ni matte feed had both Ni and Cu present predominantly as sulphides (some metal was present as well). Grinding the feed would have generated significant dusts of Cu and Ni sulphides (and metals) and some of these likely exited the grinding building as fugitive emissions (fugitive emissions are those arising from windows, doors, and vents, as opposed to process emissions from chimney stacks). When electrolytic operations commenced in 1926, further grinding of the intermediate Ni sulphide had to be done, which would have generated additional Ni sulphide as fugitive emissions. This ground Ni sulphide then had to be calcined (also called roasting or sintering) to form nickel oxide and significant fugitive and stack emissions of both nickel sulphides and oxides (and also some Ni sulphates) would have occurred.

In the second period, 1931-1947, the bulk Ni-Cu matte was no longer sent directly to Port Colborne, but it was first treated for Cu-Ni separation at Sudbury. The intermediate product from this operation was a bulk Ni sulphide and this was sent to Port Colborne. Grinding and calcining was done at Port Colborne and the emissions described above for these operations would have continued to occur.

In the third period, 1948-1961, the processing at Sudbury changed and a finely ground nickel oxide feed was provided to Port Colborne. This feed had to be unloaded and conveyed to feed bins at the Refinery. It is reported by workers present at the time that



significant dusting occurred during this handling and, due to the fine particle size of the oxide, this was swept away by the prevailing winds. There would have been no grinding or calcining carried out at Port Colborne during this period, but the dusting coming from unloading of fine oxide was likely as bad as or worse than the fugitive emissions encountered in the earlier periods.

In the fourth period, 1962-1984, the processing at Sudbury changed once again, this time to provide another nickel oxide to Port Colborne. This new nickel oxide was a fluid bed roaster product and was coarser than the earlier oxide. As a result, dusting of this oxide during unloading and handling would have been far less than for the earlier period. In addition, in 1960, an electrostatic precipitator was commissioned for the main stack, and stack emissions were further reduced.

Throughout the period of electrolytic refining at Port Colborne, fugitive and stack emissions would also have come from the nickel anode furnaces, which reduced nickel oxide with coke to form molten nickel for casting nickel anodes. Emissions from this operation would have been as Ni oxide and metallic Ni.

# 2.2.2 Environmental Fate of Nickel released from the Port Colborne Refinery

Nickel oxide (NiO (bunsenite)) is primarily a synthetic mineral, although its discovery in the 1850s was of a naturally occurring form that is rare in nature (Anthony et al. 2005). Nickel oxide is not naturally occurring in Ontario, and the elevated Ni, primarily as NiO, in the soils of Port Colborne is due to historical emissions from the Refinery. Although the nickel deposited to soil from refinery emissions would have included oxidic nickel and metallic species, there would have been some amounts of sulphidic nickel and soluble nickel (primarily nickel sulphate) deposited as well. The Air Pollution Control Branch (the predecessor of the MOE) reported in 1959 that soluble Ni accounted for 23% of the total Ni in dustfall during the summer months (Air Pollution Control Branch, 1959). This suggests that during the peak production years of the Refinery, soluble metals were a relevant component of total emissions. These soluble metals would have been associated with the surfaces of the deposited particles.

After metal particles were deposited on the soil surface, precipitation events (rain and snowmelt) would have solubilized the highly soluble salts, which released Ni<sup>2+</sup> ions into the soil. Once dissolved, the Ni<sup>2+</sup> ions were available to leach deeper into the soil profile and bind to the numerous anionic sites on clay minerals, organic matter, iron oxides, and so on, in the soil. This is called "ageing" or "weathering". It is well known that fresh additions of nickel salts to soils rapidly age, resulting in the reduction of toxicity of Ni species in the soil, even over a matter of weeks (Oorts et al. 2007, Smolders et al. 2009, Ma et al. 2013). Over longer periods of time (from years to decades), the soluble Ni at the surface of the Ni particles deposited from the Refinery emissions has weathered. What remains in the soil today is, predominantly, residual NiO particles



emitted from the Refinery. These NiO particles are themselves weathering slowly (see Section 2.3.2 and Appendix 2B for details).

It is important to understand that some of these remaining NiO particles may have sulphidic and metallic Ni species in their cores, but that the oxide surfaces of the particles effectively prevent or minimize chemical weathering of the internal Ni. Vale's recent speciation analysis of 13 soil samples (discussed below in Section 2.3.2 and Appendix 2B) supplements the speciation analyses conducted for the CBRA (Appendix 1M (see the file "FINAL VOLUME V REPORT\_Appendix 22 -- 2 of 3.pdf")). The new analyses show that the spherical NiO particles, such as the one seen in Photo 1, have NiO at the exterior of the particle, but could also contain a core with metallic Ni. The Ni metal present in the interior of the NiO particles would be difficult to detect by analytical tools such as scanning electron microscopy (SEM), which cannot penetrate the interior of the NiO particles, although it must be noted that the previous SEM work conducted for the CBRA did detect metallic Ni in 7 of 19 samples. The recent MLA analysis confirms these findings and provides further understanding of the nature of the Ni particles in Port Colborne soils. Other methods, such as high energy X-Ray Absorption Spectroscopy (XAS), can detect Ni species in bulk samples but cannot determine their spatial organization. It would be incorrect to infer from XAS that sulphidic or metallic Ni, though present, would be chemically active or bioavailable.

In summary, the elevated Ni concentrations present today in Port Colborne soils are represented primarily by the residual NiO (bunsenite) particles, ferrite slag, and alkaline slag particles that were originally emitted from the Refinery. Any soluble metals that might have been present at the surfaces of these particles have long been dispersed/weathered. These particles may contain metallic Ni in their interiors, but the predominant environmental reactions of the soil Ni relate to the interactions of NiO with the environment.

# 2.3 SPECIATION OF NICKEL IN ENVIRONMENTAL MEDIA

Supporting information on nickel speciation of environmental media done in 2001 and 2002 during the CBRA is found in Appendix 12 of Volume IV of the HHRA (2007) report as reproduced in **Appendix 1M** of this report.

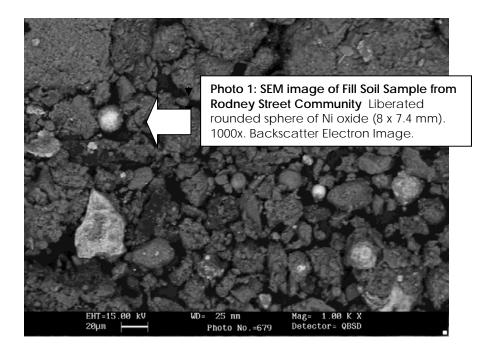
# 2.3.1 Speciation of Nickel in Soils during CBRA

A total of 19 soil samples were examined using various analytical techniques including SEM and XAS in 2001 and 2002. Findings indicated that the speciation of nickel in the analyzed soil samples is primarily as oxidic forms of nickel. This CBRA finding is supported by earlier work done independently by the MOE (MOE, 2002).

The SEM photo shown below of a fill soil sample collected from the Rodney Street Community provide visual evidence of oxidic nickel as either liberated spheres within the soil matrix, or as spheres of oxidic nickel attached to the silicate matrix of the soil. No



evidence of nickel sulphides or sulphates in soil could be found by SEM analyses, or by analyses using XAS.



# 2.3.2 Speciation of Nickel in Soils following CBRA

Vale has recently undertaken a follow-up study of the speciation of CoCs in 13 CBRAarchived soil samples from Port Colborne area using a Mineral Liberation Analyzer (MLA). MLA involves SEM using advanced image analyses software; software that was not available at the time the CBRA speciation work was completed.

The selected samples included fill, clay, and organic soils located along the main depositional gradient NE of the Refinery. There were four key findings from Vale's speciation study. First, the primary Ni species reflecting emissions from the main stack at the Refinery was bunsenite (NiO). A relationship between particle size and distance from the Refinery was apparent in these samples, with finer particles dominating in the more distant samples, and larger particles being dominant nearer to the Refinery. Second, two types of slag particles were found; ferrite slag (residual from the Bessemer matte feed, which contained 1% iron), and an alkaline slag (hydroxycancrinite) from the Orford process. The Ni associated with the alkaline slag particles reflects Ni that is roughly 80 years old, as the Orford process was discontinued at the Refinery in 1931. Third, larger Ni particles in the soil samples could be found with NiO surfaces that surrounded cores with different Ni species. Ferrite slag particles with cores of sulphidic Ni could be found in fill soil from the Rodney Street Community. (These particles reflect



incomplete separation of Ni matte and slag at the time of processing.) Larger spherical bunsenite particles could be found with metallic Ni (present as a Ni:Cu alloy) cores. (These particles reflect losses of unreacted metallic phases from the Bessemer matte to the stack or via fugitive emissions from the Refinery.) Fourth, the nickel oxide particles in soil showed evidence of ageing, in the form of nickel nontronite (nickel clay) at the surfaces of many particles. Ni nontronite is a common mineral in certain subtropical lateritic Ni ore bodies derived from millions of years of weathering of silicate parent materials. The nontronite at the surfaces of the NiO particles in the Port Colborne soils are suggestive of weathering of the NiO particles at contact points with surrounding soil particles. It could also reflect some of the original soluble metals released from the Refinery, which has weathered in-place at the surfaces of the originally deposited particles.

The inter-relationships between these Ni species, as well as those of Cu and Co have been examined in Vale's new speciation analysis. The bunsenite (NiO) content of the soil samples was fairly constant between 25-42% of total Ni, although the size distribution showed larger particles in the soil samples from nearer to the refinery (TP9 and TP206 average NiO particle size of 20 and 25  $\mu$ m respectively) than those farther from the refinery (TPS and TPK2-1average NiO particle size of 7 and 12  $\mu$ m respectively). This reflects the well-known depositional behaviour of particulate air pollutants, with larger particles settling out closer to the emission source and smaller particles being dispersed farther from the source.

The MLA analysis also evaluated copper and cobalt distribution among the soil particles. Further details on the results and findings of the MLA study by Vale is found in **Appendix 2B** of this report.

# 2.3.3 Speciation of Nickel in Ambient Air

Fifteen filters (five each of TSP,  $PM_{10}$  and  $PM_{2.5}$ ) were submitted to SGS Lakefield Research for nickel speciation analysis using scanning electron microscopy. In the ambient air filter samples, oxidic forms of nickel were found to be dominant. Nickel oxide/hydroxide was found to be the dominant constituent (about 80%) in nickelcontaining particulates. Metallic nickel was detected in particles greater than 2.5  $\mu$ m size fraction and ranged up to 11.9%. Sulphate complexes containing nickel were identified in the control samples (up to 30%) and in some samples from stations within the CBRA Study Area.

# 2.3.4 Speciation of Nickel in Indoor Air

Four indoor air filters (two each of TSP and PM<sub>10</sub>) were submitted to SGS Lakefield Research for particulate nickel speciation using Scanning Electron Microscopy (SEM). No indoor air filter samples were submitted for analyses by X-Ray Absorption Spectroscopy (XAS). The purpose of this limited SEM analysis was to estimate the amount and type of nickel-bearing particulates in some of the samples.



Oxidic nickel and oxides with nickel and other metals were the dominant constituents in indoor air PM<sub>10</sub> in most homes surveyed.

# 2.3.5 Speciation of Nickel in Attic Dust

Two attic dust samples were submitted to SGS Lakefield Research for nickel speciation by SEM analysis. One was a grab sample, obtained from a residence north of the Inco property. The other was a swipe sample from a home in the Rodney Street community to the west of the Inco property.

Oxidic nickel compounds appear to be the dominant constituents (85% and 95%) of the attic dust samples collected from these residences. Approximately 11% nickel sulphide was estimated in the sample collected to the north of the Inco refinery. It is possible that this minor amount of nickel sulphide in attic dust is related to accumulation of historical dust in the rafters blown in from the outside of the home when the Refinery was in operation and that the environment of the inside of the attic was not conducive for its complete oxidation to oxidic nickel.

# 2.4 SOIL CHARACTERIZATION

Supporting information on soil characterization for the CBRA study area as summarized below is found in Volume IV of the ERA Crops (2004) report as reproduced in **Appendix 1J** of this report.

## 2.4.1 Soil Types

The geology of Port Colborne consists of clayey silt to stoney silt till and glaciolacustrine sediments overlying limestone bedrock.

Six generic soil groups identified within the Port Colborne CBRA Study Area included the following:

- heavy clay (clay of glaciolacustrine origin; referred as *Welland Clay* in Crop Studies)
- shallow clay (a till clay; referred as *Till Clay* in Crop Studies)
- clay loam (another till clay and containing more clay content than shallow clay)
- organic muck
- sand
- fill

Locations of the geographic boundaries of each of the six soil groups within the Port Colborne Study Area and the locations of the soil samples collected from within each soil group are found on **Figure 2-2** in **Appendix 2A**.

Fill is identified in Figure 2-2 in Appendix 2A as built land south of the Refinery. Though not shown on Figure 2-2 in Appendix 2A, fill is also the prevalent soil type in the area of



the Rodney Street Community immediately west of the Refinery. During the Jacques Whitford 2001 test pitting investigation within the Rodney Street Community, fill material was encountered to a maximum depth of one metre below grade. Field description in 2001 identified fill material as soil mixed with waste rock fragments, slag, coal pieces and iron pellets; the source of these man-made wastes was likely the former Algoma Steel facility that once operated immediately west and south of the Rodney Street Community. Historical Inco-archived photos from the early 1900's during early development of Rodney Street Community show evidence of infilling of low-lying areas immediately west of the Refinery's western boundary; areas later developed with residential homes.

# 2.4.2 Leaching Characteristics of Soil

The CoCs are distributed primarily in upper soil horizons; hence, the leaching capacity of soils is an important consideration in assessing availability of CoCs for uptake by plants and into garden and farm produce. The leaching capacity of clay and organic soils in the Study Area was investigated by carrying out sequential chemical extraction work on two representative soil samples collected from the Study Area.

The sequential extraction procedure determines the solid-phase association of metals. The procedure involves digesting a soil sample in successively more aggressive extracting solutions to mobilize metal fractions with decreasing mobility in the following sequence: exchangeable, linked to carbonates, iron/manganese oxides, organic matter and residual form.

Sequential extraction results of percentages of CoCs measured in the five abovementioned solid-phase fractions in one organic muck soil with a total soil nickel concentration of 4,810 µg/g and in one mineral type soil with a total soil nickel concentration of 8,910 µg/g are found in **Table 2-1** in **Appendix 2A**. The organic muck soil was collected in a woodlot area east of Reuter Road and the mineral soil sample was collected on the Refinery property. Percentages of exchangeable-nickel and other exchangeable-CoCs that would be readily available for uptake by plants in the clay and organic soil samples were noted to be less than 5%. As expected, findings from the sequential extraction tests showed most of the CoCs were found complexed with organic matter in the organic muck soils and with iron and manganese oxides in the mineral soils.

Table 2-1	Percentages of Extractable CoCs in Various Soil Components
	recentages of Extractable 0005 in Validas soli Components

		Percentage of CoC			
Soil CoC Fraction	Extractant	Soil Type	Nickel	Copper	Cobalt
Exchangeable-CoC	Strontium Nitrate	Organic	3	<0.2	<3
Carbonate-CoC	Sodium Acetate	Organic	4	1	<4
Iron/Manganese Oxides-CoC	Sodium Hypochlorite	Organic	7	4	19



Organic-CoC	Oxalic Acid	Organic	41	88	46
Residual-CoC	Strong Acid*	* Organic 45 7		7	35
Exchangeable-CoC	Strontium Nitrate	Mineral	5	<0.2	<2
Carbonate-CoC	Sodium Acetate	Mineral	5	3	<2
Iron/Manganese Oxides-CoC	Sodium Hypochlorite	Mineral	25	38	67
Organic-CoC	Oxalic Acid	Mineral	13	53	13
Residual-CoC	Strong Acid*	Mineral	52	6	20

Notes:

\* Strong Acid consisted of a mixture of hydrochloric, hydrofluoric and nitric acids

Subsequent sequential extractions on Port Colborne organic muck soils and mineral soils were carried out by others after the completion of the CBRA field work (Everhart et al. 2006). Percentages of exchangeable-nickel in organic muck soils calculated using data from Everhart et al. (2006) were 3% for one organic muck soil sample with total soil nickel concentration at 2,006  $\mu$ g/g, 3% for a second organic muck soil sample with total soil nickel concentration at 4,902  $\mu$ g/g, and 2% for a third organic muck soil sample with total soil nickel concentration at 22,444  $\mu$ g/g.

Percentages of exchangeable-nickel in mineral soils were 14% for one mineral soil sample with total soil nickel concentration at 2,115 µg/g and 1% for another different mineral soil sample with total soil nickel concentration at 4,700 µg/g (Everhart et al. 2006). Overall, the CBRA-reported values on percentages of exchangeable-nickel in mineral soils and organic muck soils agree with those reported in Everhart et al. (2006). One last observation from Everhart et al. (2006) was that nickel bioavailability decreased as the pH of the soil increased when soils were amended with lime. Liming had been identified as the key method for remediation of affected agricultural soils in the Port Colborne area.

## 2.4.3 Plant-bioavailable Soil Nickel

Over many years following deposition of particulates from the Refinery, the CoCs in soils in the Port Colborne Study Area have been naturally weathered by biological, geochemical and physical processes acting on soil particles; processes influenced by variations in seasonal temperature and precipitation. A certain proportion of nickel in these soils when dissolved in soil water solution were made available for uptake by plant roots. The actual amount of nickel uptake in plants is dependent on Ni bioavailability which is related not only to the magnitude of nickel concentrations present in soil, but also to the chemical form of the metal within the soil matrix and the physical properties of the soil matrix itself. Nickel in the Port Colborne soils is predominantly in the chemical form of insoluble nickel oxides (as established in the preceding sections) therefore, its presence in soil solution is low because of its low



solubility and the corresponding nickel bioavailability in these soils is also low, generally less than 5% total Ni in soil.

Soil extractions using diluted neutral salts such as calcium chloride or strontium nitrate are procedures indicative of metal availability to plants. Strontium nitrate extractions were shown to be successful in the prediction of nickel phytoavailability (ref: Siebielec and Chaney, 2000).

Port Colborne clay and organic soils samples collected from various test pits during the CBRA at locations in the agricultural area approximately one km north east of the Refinery were extracted with strontium nitrate extractions. Percentages of strontiumnitrate extractable nickel were found between 0.04% and 0.7% in clay type soils with pH values ranging from pH 5.4 to pH 6.9 and between 0.04% and 0.1% in organic type soils with pH values ranging from pH 5.8 to pH 6.8.

The MOE extracted soil samples collected from the residential area immediately west of the Refinery during their 2002 Rodney Street investigation with ammonium-acetate as a measure of plant bioavailable soil nickel (MOE, 2002). The MOE had selected ammonium acetate, a dilute neutral salt, as the soil extractant to simulate the leaching of nickel from soil by natural rainfall, soil movement, and normal soil microbial activities.

Findings of the MOE ammonium acetate extractions showed that plant-bioavailable nickel in pH-neutral mineral soils (e.g. fill and clay soils) averaged 0.22%, whereas plantbioavailable nickel in pH-slightly acidic (pH values less than 6.0) organic muck soils averaged 8.49% (MOE, 2002). The higher value of ammonium-acetate extractable nickel in the organic soils compared to that found in the mineral soils was believed by the MOE to reflect the higher solubility of nickel in slightly acidic organic muck soils.

The MOE concluded from their findings (MOE, 2002) that the potential for soil nickel to dissolve into soil solution and be available for uptake by vegetation (plant bioavailability) is very small for the mineral soil type that predominates the Port Colborne area. MOE's conclusion was corroborated by their observation of the CBRA findings of a lack of relationship between soil nickel concentrations and nickel concentrations of residential garden produce (Appendix 17 Volume V of the HHRA (2007) report (copy in **Appendix 1M** of this report).

# 2.5 LAND USES

Land use zoning in Port Colborne include:

- Commercial/Industrial
- Recreational,
- Residential, Schools,
- Woodlots and Parkland,
- Agricultural.



Locations of the geographic boundaries of each of the above-mentioned land use types within the Port Colborne Study Area and the locations of the soil samples collected from each land use are found on **Figure 2-3** in **Appendix 2A**.

As stated earlier, the industrial property encompassing the Refinery lands was excluded from the CBRA, as it is an active industrial site with its own closure plan, as required by law. Nevertheless, limited sampling of soil and other environmental media on the Refinery lands was carried out to better understand and characterize the spatial extent and depth distribution of CoCs in soil.

# 2.6 WOODLOTS AND FIELD HABITAT

The Niagara Region represents a part of Canada that was settled by European immigrants early in the country's history. As a result of settlement over the past two centuries, most of the Niagara Region's natural forests have been cleared and drained for agriculture. The Port Colborne area is representative of much of the Niagara Region's natural landscape, where only small pockets of historically cut and logged woodlots remain. In this respect, from an ecological perspective, the Port Colborne area is typical for the region, with a highly altered and significantly fragmented natural landscape remaining.

As stated earlier, woodlots have generally elevated levels of CoCs in comparison to surrounding fields and agricultural lands. These elevated levels are a result of trees and their leaves acting as traps for the atmospheric particulate matter, which, once trapped, is conveyed to the forest floor by rain and leaf fall. This phenomenon gives rise to a 'patchy' distribution of CoCs in soil across the landscape, with any one woodlot representing a 'hot spot' in a local area. **Table 2-4** in **Appendix 2A** shows examples of soil nickel concentrations in several selected woodlots and adjacent fields at different distances from the Refinery.

Fields at Vario	ous Distances from the	e Inco Refinery.	
Approximate Linear Distance of woodlot from	Woodlot Soil Ni Concentration (mg/kg)	Approximate Linear Distance of Woodlot from	Adjacent Field Ni Concentration
Refinery (km)		Adiacent Field (km)	(ma/ka)

0.35

0.7

0.4

1,860

145

156

33,000

709

550

# Table 2-2A Comparison of Soil Nickel Concentrations in Woodlots and AdjacentFields at Various Distances from the Inco Refinery.

Although woodlot soil CoC levels are elevated when compared with adjacent fields in any one area, woodlots and fields both follow the same concentration gradient in



1.0

4.2

4.8

relation to distance from the Refinery, with woodlots and fields closer to the Refinery having higher CoC soil levels than those further away from the Refinery.

Finally, in addition to woodlots having higher CoCs levels, sampling and testing of soil from woodlots has identified that surface (0-5 cm) soil CoC concentrations in woodlots also have a patchy distribution. Generally, for woodlots near the Refinery, CoC concentrations are highest along the windward (western) edge of the woodlot. These levels then decline through the woodlot to the downwind, eastern edge. However, even within this general distribution pattern, soil CoCs are still locally patchy due to the past/present occurrence of tall, large-crowned trees, which acted/act as highly efficient local filters.

Soils and Valued Ecological Components (VECs) in the woodlot and open field habitats were examined in the ERA. Geographic boundaries of the woodlot and open field habitats within the Port Colborne Study Area and the locations of the soil samples collected from both types of habitats are found on **Figure 2-4** in **Appendix 2A**.

# 2.7 AGRICULTURAL SETTING

A large portion of the defined study area to the north and east of the Inco Refinery consists of rural agricultural lands. Within the study area, an estimated 1,500 hectares of agricultural land is potentially impacted with greater than 200 mg Ni/kg. As such, the impact of historical contamination on the agricultural soils and on the crops grown on these soils today is of key importance.

In the summer of 2001, a visual survey of crops growing on agricultural fields in the Port Colborne area was conducted (see Section 3.3 of Volume I of the ERA Crops (2004) report as reproduced in **Appendix 1J** of this report). This survey showed the major crops growing at the time to be corn (*Zea mays*) and soybean (*Glycine max*). In addition, many fields were planted with red clover (*Trifolium pratense*) or were being prepared/worked as part of crop rotation schedule that is typical farming practice in the region.

# 2.8 WATER QUALITY

Supporting information on water quality for the CBRA study area as summarized below is found in Section 2.6 of Volume I of the HHRA (2007) report as reproduced in **Appendix 1M** of this report.

# 2.8.1 Residential Well Water Sampling

The Ontario Drinking Water Standards or ODWS (MOE, 2001a; 2003) provided an appropriate basis of comparison for data on the unfiltered tap water samples. The U.S. EPA Region III Risk Based Concentrations (RBC) for cobalt and nickel (U.S. EPA, 2002) in drinking water were used as comparative criteria in the absence of MOE criteria.



Samples collected directly from well heads or other locations other than taps (e.g., bailed) were considered representative of drinking water only if the samples were filtered in the field.

The maximum measured concentrations in dug wells (excluding unfiltered samples taken directly from the well) were all below the ODWS (arsenic and copper) and the U.S. EPA Region III RBC (cobalt and nickel).

The maximum concentrations of CoCs measured in drinking water from drilled wells (excluding unfiltered samples taken directly from the well) were below the ODWS, the U.S. EPA MCL (U.S. EPA, 2002a) (arsenic), and U.S. EPA Region III Risk Based Concentrations (nickel and cobalt).

All maximum concentrations of CoCs measured in drinking water from cisterns were below the ODWS for arsenic and copper, the U.S. EPA MCLs and the U.S. EPA Region III Risk Based Concentrations (RBC) for cobalt and nickel.

#### 2.8.2 Port Colborne Municipal Drinking Water

The City of Port Colborne obtains treated water from the Regional Municipality of Niagara's water treatment plant located on King Street, Port Colborne, which in turn obtains raw water from the Welland Canal and treats it using conventional technology. The municipal water distribution system services the residential areas of Port Colborne, including those immediately west and north of the Inco Refinery. The areas to the east and northeast of the Inco Refinery are not serviced by the water distribution system and instead rely on private water wells, some of which are supplemented by cisterns. Some residents use bottled water for drinking.

#### 2.8.3 Surface Water

The landscape of the Study Area and surrounding areas consist mainly of agricultural lands that are hydrologically manipulated through agricultural drainage tiles, ditches, and municipal drains. No naturally occurring (unaltered) streams or creeks occur in the Study Area. The main surface water drainage features are the Wignell Drain and Beaverdam Drain that drain the lands from north to south. Each of these drains function as such, and should therefore not be considered natural water courses.

The Wignell drain, which runs parallel to Snider Road 400 m east of the Refinery property boundary, has a watershed of approximately 1200 ha and is connected to the majority of the Study Area's agricultural ditches and smaller drains between Reuter Road and Weaver Road.

The Beaverdam Drain has a watershed of approximately 1400 ha and collects surface water from lands in and around Miller Road to the eastern limits of the Study Area. Both



the Wignell and Beaverdam drains empty into Lake Erie with flood gate and pump controls at the mouth of the drains at the Lake Erie shore.

The use of municipal drains for draining the agricultural lands in the Port Colborne surrounding areas is historical. The Wignell and Beaverdam drains were established over one hundred years ago, with associated records of the drains dating back to the early 1900s. As a result of surface water management practices, the landscape is efficiently drained; only a small percentage of ditches and drains contain flowing or standing surface water during comparatively dry summer months.

In a similar fashion, the combined result of ditching surrounding clay soils has resulted in shallow standing water in woodland swamps only being present in early spring and typically drying by early June. A Department of Fisheries and Oceans (DFO) review of the drainage systems in the Study Area identified all branches to the Wignell and Beaverdam Drains as intermittent in nature and accordingly concluded that neither of the drain systems support fish populations (reported by City of Port Colborne, 2000). Based on DFO assessment, the potential effects of CoCs on inland fisheries are not a concern. Surface water that persists year round is present only in man-made farm ponds dug deep into the clay soil and at the very lower sections and mouth of the larger collector municipal drainage ditches that feed directly into Lake Erie. In 2013, Stantec conducted a water quality sampling and testing of surface water samples collected from the Wignell and Beaverdam Drains to allow re-assessment of the CoCs in the drains using the biotic ligand models developed for Ni, Cu, and Co; details on results and findings can be found in Chapter 4 of this report.

# 2.8.3.1 Lake Erie Nearshore

Although Lake Erie surface water and sediments could represent a potential CoC exposure route to human receptors swimming or wading in Gravelly Bay and Lorraine Bay, the nearshore area and beach along the lakeshore represent a zone of dynamic wave action. In this area, significant wave action during high water periods and winter months results in continual replacement and movement of sediments and sands along the lake shore. The sediments, sands and bare limestone bedrock of the nearshore environments have been continually subjected to these natural processes, being continually washed, mixed, and replaced over the period of Refinery operations.

# 2.9 AIR QUALITY WITHIN PORT COLBORNE COMMUNITY

# 2.9.1 Ambient Air Monitoring

An ambient air monitoring program was conducted in the Port Colborne community to estimate the concentrations of particulate matter and metals in the ambient air. Monitoring was conducted between August 11<sup>th</sup>, 2001 and September 15<sup>th</sup>, 2001, during one of the hottest and driest summers (drought conditions) ever reported for this area of Ontario. The measured concentrations of both particulate matter and CoCs in air



during this monitoring program are therefore considered to represent a worst possible scenario.

The ambient air sampling program focused on the measurement of all dust in air (total suspended particulate matter, TSP), fine dust particles in air small enough to be reach the lungs (PM<sub>10</sub>), and very fine dust particles, small enough to reach the deepest parts of the lungs (PM<sub>2.5</sub>). Laboratory analysis of collected particulate matter involved the quantification of the four CoCs as well as 24 additional elements.

Important criteria in the evaluation of ambient air quality include the MOE (2001b) Ambient Air Quality Criteria (AAQC). The AAQC quantify the maximum concentrations of various elements in ambient air that are deemed acceptable and safe by the MOE. These criteria therefore provide maximum air concentration limits over a 24-hour period that are directly comparable to the results from the ambient air monitoring program conducted in Port Colborne. All ambient air CoC concentrations obtained from the Port Colborne ambient air sampling program were below the associated AAQC guidelines (ref: Section 2.7.1 of Volume I in HHRA (2007) report as reproduced in **Appendix 1M** of this report).

# 2.9.2 Monitoring of Farming Activities

Ambient air quality was monitored during staged agricultural activities to estimate the concentrations of particulate matter and CoCs in Port Colborne ambient air. The purpose of the staged agricultural activities was to obtain scientifically credible worst-case air quality measurements, in particular those related to potential community-wide CoC exposure resulting from airborne dust generated by agricultural activities. The sampling program focused on the measurement of TSP, PM<sub>10</sub> and PM<sub>2.5</sub>. The monitoring program was conducted from October 1<sup>st</sup> to October 7<sup>th</sup>, 2001.

All of the measured CoC concentrations in the vicinity of the farming activities were above background ambient air CoC concentrations, but below the MOE ambient air quality criteria (ref: Section 2.7.2 of Volume I in HHRA (2007) report as reproduced in **Appendix 1M** of this report).

# 2.9.3 Indoor Air Quality

The indoor air quality of Port Colborne residences was investigated by a communitywide study (ref: Section 2.7.4 of Volume I in HHRA (2007) report (copy in **Appendix 1M** of this report)). The study involved the sampling of PM<sub>10</sub> and TSP in indoor air in 30 residences divided in three study zones in Port Colborne. The first air study zone included areas in which soil nickel concentrations exceeded 5,000 mg/kg, while the second zone consisted of areas of the community with soil nickel concentrations falling between approximately 200 and 5000 mg/kg, and the third zone contained soil nickel concentrations less than 200 mg/kg.



Results of the study for both indoor TSP and PM<sub>10</sub> samples showed that none of the measured maximum CoC concentrations in indoor air exceeded the applicable MOE AAQC. Nickel concentrations in indoor air were found to be lower than concentrations of nickel in ambient air.

# 2.9.4 Indoor Settled Dust

Concentrations of indoor settled dust were measured as a component of the indoor dust sampling program (ref: Section 2.7.4.2 of Volume I in HHRA (2007) report (copy in **Appendix 1M** of this report)). Samples of dust were collected from both hard and fabric surfaces in 30 randomly chosen residences in Port Colborne. Attic dust samples were collected from these same houses if the attic space was accessible. Samples were collected in each of the same three zones described for indoor air quality, and the results of the indoor settled dust sampling are provided in the earlier HHRA report (HHRA, 2007). There are no criteria for comparison and evaluation of CoCs in dust.

# 2.10 HHRA STUDY AREA

The HHRA Study Area was defined as the City of Port Colborne and adjacent areas where soil concentrations are greater than one or more of the applicable MOE Table A guidelines (MOE, 1997; or Table 2 standard, Ontario, 2004b) for the CoCs in soil. As soil nickel was established as the fingerprint CoC, the HHRA study area became defined in the year 2000 as all areas where soil nickel concentrations exceeded 200 mg/kg (MOE Table A 1997 Guideline for nickel). The areal extent of the HHRA Study Area was estimated to be approximately 29 km<sup>2</sup>. The entire City of Port Colborne was considered in the HHRA to account for those residents who may frequent areas both inside and outside of the Study Area.

The HHRA examined risks to human receptors in five zones, Zones A to E as shown on **Figure 2-5** in **Appendix 2A**. Zone A is the residential area on relatively-unimpacted nickel in soil area west of the Welland Canal. Zone B is the Rodney Street Community residential area immediately west of the Refinery's western boundary and east of the Welland Canal. Zone C is the mainly residential area located North of the Refinery. Zone D is largely agricultural lands with some residential. Zone E is the background or reference areas with no soil nickel impacts.

For the HHRA assessment, woodlots and parkland were evaluated as one land use, namely recreational, recognizing that these areas are frequented by a variety of people for hiking, etc.

Beaches were evaluated in the HHRA separately from the recreational land uses in the assessment due to the unique nature of beach sands compared to other soils.



Some residentially-zoned areas also exist within largely agricultural areas such as in Zone D. Residential and agricultural land uses in these combined areas were pooled for the purposes of the HHRA.

# 2.11 ERA STUDY AREA

The ERA Study Area was considered in the year 2000 to be representative of all natural areas for lands where soil nickel values exceed 200 mg/kg (MOE Table A 1997 Guideline for nickel). The ERA Study Area was partitioned into a primary ERA Study Area, which included lands where soil nickel concentrations were found to exceed 500 mg/kg, and a Secondary ERA Study Area, which included lands where soil nickel concentrations ranged between 200 mg/kg and 500 mg/kg. Additionally, sampling was conducted in background areas west and east of the ERA Study Area where soil nickel concentrations were below 200 mg/kg. These background areas are referred in the ERA as the Reference Area.

Residential areas, the Refinery site property, and a large quarry located northeast of the Refinery were excluded from the ERA.

Although Primary and Secondary ERA Study Areas were identified to ensure that field data collection was structured and data were representative of the areas where soil CoC concentrations were high to moderate, characterization of risk to VECs was based on potential exposures to VEC populations.

Nickel concentrations in some of these VECs, where measured, were mapped along with the corresponding soil nickel concentration to determine any evident relationships. As an example of one of these maps, earthworms was designated as one of the VECs and **Figures 2-6** and **2-7** in **Appendix 2A** show nickel earthworm concentrations and corresponding nickel soil concentrations for specific sampling locations within the Study Area and the Reference Area, respectively.

A VEC's population was defined as all individuals of a species (plant or animal) that inhabit or occur within the Primary and Secondary Study Areas. For the characterization of risk for the ERA, an unacceptable risk to a VEC population was defined as an estimated risk linked to the occurrence of soil concentrations of CoCs that prevents sustainable population(s) of flora and fauna or a sustainable level of ecological functioning within the defined Study Area.

Separate risk characterization was not undertaken for sub-populations represented by the Primary and Secondary Study Areas, or other specific areas within the Study Area.

## 2.12 CROPS STUDY AREA

The Study Area used for the Crops Studies included areas from which soil samples were collected and field plots established within the soil-nickel footprint, as well as reference



areas (i.e., those areas with representative of background concentrations of nickel) outside and west of this footprint.

Nickel-impacted soils located in areas down wind and northeast of the Refinery were collected to provide representative soil samples of high nickel concentrations for crop dose-response studies carried out in greenhouses. Reference soils with CoC concentrations representative of background were collected from areas west of the soil-nickel footprint that were not impacted by atmospheric deposition of historical Refinery emissions. These reference soils served as negative control soils for the same crop dose response studies.

Field plots were established for the phytotoxicity studies on lands in three designated areas with varying soil nickel concentrations ranging from very high, to high, and to moderate concentrations. All of these three areas were located along the centre line of the defined soil nickel plume northeast of the Refinery.

Figures 2-8 and 2-9 in Appendix 2A show specific soil sampling and field plot locations within the Study Area and the Reference Area, respectively.

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using calibrated bioavailability models to set ecological standards. *Environ. Toxicol. Chem.* 28: 1633-1642.



Appendix 2A:

Figures



Appendix 2B:

# Quantitative Mineralogy of Port Colborne Soils



#### CHAPTER THREE – HUMAN HEALTH RISK ASSESSMENT

Project Number: 122210662



Prepared for: Vale Canada Ltd.

Prepared by: Stantec Consulting Ltd. 1-70 Southgate Drive Guelph ON N1G 4P5

September 12, 2014

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#### **CHAPTER THREE – HUMAN HEALTH RISK ASSESSMENT**

# 3.0 Human Health Risk Assessment

# 3.1 BACKGROUND

Inco Limited (now Vale Canada Limited (Vale)) commissioned a Community-Based Risk Assessment (CBRA) that was completed by Jacques Whitford Limited (now Stantec) in 2004 (Jacques Whitford, 2004). One component of the CBRA was to undertake a Human Health Risk Assessment (HHRA) to estimate the concentrations of historically deposited chemicals of concern (CoCs) in Port Colborne soil that may present an unacceptable risk to residents of Port Colborne. As discussed in Chapter 1, two drafts of the report were produced in 2003-2004 and were provided to relevant stakeholders (including members of the Public Liaison Committee [PLC], the Technical Sub-Committee to the PLC [TLC], the PLC's consultants) and the general public for review and comment. All comments were addressed and the HHRA report was finalized during December 2007 and subsequently submitted to the Ontario Ministry of the Environment (MOE) for its review. The HHRA component of the CBRA dated December 2007 is herein referred to as the "original HHRA" and is provided in Appendix 1M in its entirety. Figure 3-1 presents the design approach for the original HHRA.

An updated HHRA was carried out to address the MOE's key review concerns. This updated HHRA relies on information from the original HHRA report and any updates on toxicological and certain other information received from 2007 to 2013. Stantec's responses to MOE's comments on the original HHRA are found in Appendix 3A.

This chapter on the updated HHRA is not intended to be a stand-alone document and relies substantially on the wealth of information provided in the original HHRA. Instead, the focus of this HHRA chapter is to examine any required modifications to the original HHRA and, if required, provide updates to the original risk estimates. Where additional information on a given topic was previously provided in the original HHRA, the location of that information within the original HHRA has been identified. Finally, a Sensitivity Analysis was conducted to review how the assumptions adopted in this updated HHRA are likely to impact on the results and conclusions of the assessment.

A number of changes have been undertaken in the development of this current updated HHRA, so the details of the original HHRA will not be re-presented here.

## 3.2 DESIGN APPROACH FOR THE HHRA

As discussed in Chapter 1, the CBRA consists of three component risk assessments, including an Ecological Risk Assessment on the Natural Environment, an agricultural, or "Crops" Risk Assessment and the Human Health Risk assessment (HHRA). The HHRA, in particular, was conducted in general accordance with technical aspects in MOE (1996 and 2005). It should be understood that the CBRA was completed under a voluntary process and that this HHRA is intended to address risk across a wide area rather than providing a Record of Site Condition



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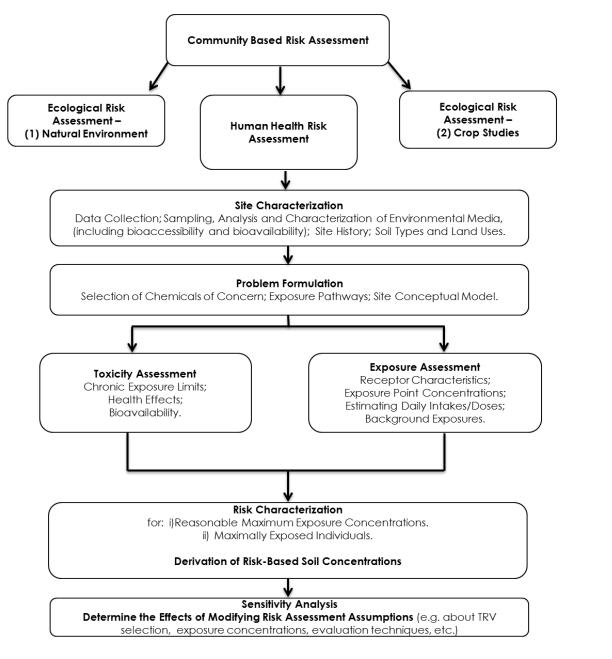
(RSC) for individual properties. As such, it is not required to strictly conform to MOE (1996 and 2005), nor is it required to conform to requirements outlined in Ontario Regulation 153/04.

The process followed for the HHRA is outlined in Figure 3-1 and includes the following:

- Site Characterization- A review and compilation of existing data and a summary of past activities. Site characterization information used in this HHRA includes information presented in the original HHRA as well as additional experiments on the bioaccessibility/bioavailability of soil conducted in 2013;
- **Problem Formulation** Identification of the on-site chemical hazards that may pose a health risk (Contaminants of Concern (CoCs)), identification of potential human receptors and the relevant exposure pathways for the receptors. The exposure pathways used in this updated HHRA are the same as those used in the original HHRA. The original HHRA included human receptors of multiple age ranges including infants, toddlers, children, teenagers and adults; the updated HHRA focuses the evaluation on two critical receptor age groups, the toddlers and adults. The lifetime receptor has been retained for the evaluation of carcinogenic risk. The original HHRA evaluated exposures across the entire community and in background areas which were divided into Zones based on land use (Zones A through F). The updated HHRA only evaluates exposures in the two most sensitive Zones (B and D).
- **Exposure Assessment**-A qualitative or quantitative evaluation of the likelihood or degree to which potential receptors will be exposed to CoC. The approaches for evaluating exposure are generally consistent with those used in the original HHRA, but exposures values have been recalculated due to changes in exposure-point concentrations (e.g., concentration in garden produce), changes in exposure factors (e.g., soil ingestion rate) and the new bioaccessibility/bioavailability information obtained in 2013;
- Toxicity Assessment-Identification of the toxicity of the CoC present on the Site. The toxicity of CoCs were re-evaluated as part of this updated HHRA. Alternate toxicological reference values (TRVs) have been selected where appropriate (see Table 3-1, Table 3-5, and Table 3-6);
- Risk Characterization- A quantitative assessment of the health risk of each CoC to each receptor, based on the degree of exposure and the toxicity of the CoC. As with the exposure assessment, the approaches used for estimating risk are generally consistent with those in the original HHRA, however the values have been recalculated due to changes in exposure point concentrations, exposure factors, bioaccessibility/bioavailability and TRV selection. Consistent with the original HHRA, following the risk characterization, a Risk-Based Soil Concentration (RBSC) was derived as the maximum concentration of a CoC in soil that would not result in an unacceptable risk to receptors, when considering all other exposure pathways.
- Sensitivity Evaluation- A qualitative and quantitative assessment of how the output of the Risk Characterization could change based on changes in assumptions and input data. This updated sensitivity evaluation only reviews assumptions that were not evaluated in the Sensitivity analysis for the original HHRA.



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## Figure 3-1 Design Approach to Human Health Risk Assessment

#### 3.3 CHANGES FROM THE ORIGINAL HHRA

As discussed, the updated HHRA contains many items that differ from the original HHRA; these are summarized below with more detail provided in Table 3-2.

#### Regarding general aspects:

• It focuses on Zone B (the highest soil Ni concentrations in residential properties) and Zone

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D (residences on agricultural properties);

- It focuses on human life stages of the toddler and the adult for non-cancer risks and on the entire lifetime for cancer risks; and
- It uses a revised spreadsheet structure, as requested by the MOE, to minimize the potential for data input errors that could have been present in the multiple spreadsheet approach of the original HHRA.

#### Regarding changes to input data:

- The original soil ingestion rate for toddlers of 100 mg/day was re-evaluated with updated literature, as requested by the MOE. The soil + dust ingestion rate was changed to 110 mg/day (50 mg/day from soil; 60 mg/day from dust), consistent with recommendations by the US EPA (2011);
- Dust exposures from surface area measurements were omitted to avoid double counting;
- The concentrations of each CoC in dust were taken as the higher value between the measured concentrations in vacuumed samples and the empirically derived concentration ratio;
- Garden produce concentrations for the RBSC scenario were taken to be the 90<sup>th</sup> percentile concentration instead of the maximum observed. This results in a more robust statistical approach;
- Data from the house with the maximum measured levels of nickel in indoor air has been excluded due to concerns about the data quality;
- Through improved statistics, as well as the most recent Health Canada Total Diet Studies, the intake of Ni from supermarket food for a Port Colborne toddler was increased from 95 µg/day to 142 µg/day. The intake of 142 µg/day is in the midrange of the intakes estimated from the seven Health Canada TDS;
- Exposures to CoCs in ambient air were based on long term monitoring results where available (i.e., for arsenic, cobalt and copper in Zone B); in the absence of long term monitoring data, exposures were estimated using modelled data. Where measured data were available, the maximum annual average was used for both the RME and maximum exposure scenarios. Monitoring results from short term sampling (i.e., 24 hours) were incorporated into the ambient air model, but were not used directly to estimate exposure;
- Dermal absorption of nickel ions arising from soil in contact with the skin is important for two health endpoints: one is the amount that passes completely through the skin and is



#### **CHAPTER THREE – HUMAN HEALTH RISK ASSESSMENT**

absorbed by the bloodstream, which can cause systemic health effects; the second is the amount of Ni that stays within the skin, which is linked to allergic contact dermatitis. A new comprehensive review of scientific literature in this area was carried out as part of the updated HHRA. The highest fraction of Ni on the skin (as a solution of nickel chloride), which was able to penetrate all the way to the bloodstream was 0.5%. The fraction was taken as the fraction of soluble Ni from soil on skin that contributes to systemic effects. Likewise, the fraction of soluble nickel on the skin that is absorbed into the skin only was found to be 2.8%. This value was used for estimating risks of allergic contact dermatitis; and

• The relative bioavailability (ROB) or the bioaccessibility of all the CoCs in the gastrointestinal tract caused much discussion between the MOE and Vale Canada and Stantec. For example, the MOE favored using its in vitro Ni results from the Rodney Street Risk Assessment (MOE, 2002) for fill soils. Stantec was reluctant to do this because the MOE's data were restricted to fill and it would mean a rejection of the *in vivo* data generated for the CBRA. It was clear that more testing, both *in vitro* and *in vivo*, of all types of soils were required and these were carried out as part of the updated HHRA. The results clearly show that the ROB is different for different soil types. The ROB of 4% for nickel in soil adopted in the original HHRA was in agreement with the ROB of 5.8% determined for fill soil. The clay soil and the organic soil, 9% and 22%, respectively, were considerably higher than the original value used. Accordingly, these new values were used for evaluating the ingestion risks for each type of soil.

#### Regarding changes in Toxicity Reference Values (TRVs):

 Selection of TRVs is a very important part of any risk assessment because these values typically represent broad international regulatory science consensus of safe thresholds for a specific toxic response through a specific route of exposure. A TRV is the number to which a calculated exposure is compared to estimate risk. Since TRVs are highly protective (i.e., many factors applied to account for scientific uncertainties), a calculated exposure that is less than the TRV is widely accepted as entirely without risk for the specific health endpoint in question.

During discussions with the MOE, it became evident that their opinions on which TRVs were acceptable had changed since issuing their comments on the original HHRA in 2011. The MOE requested that there be a review of the TRVs selected in the original HHRA. A review was undertaken for this updated HHRA, which considered the most current science available. TRVs adopted for this updated HHRA as a result of this review are provided in Table 3-1.



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CoC	Endpoint	Pathway	Original HHRA	Updated HHRA
Nickel	Non-carcinogenic	Ingestion	0.020 mg/kg-day: All receptors	0.020 mg/kg-day: Toddlers 0.011 mg/kg-day: Adults- reproductive age
		Inhalation	0.09 µg/m <sup>3</sup>	0.06 µg/m <sup>3</sup>
	Carcinogenic	Inhalation	4.0E-05 (µg/m³)-1	Unchanged
Copper	Non-carcinogenic	Ingestion	0.13 mg/kg-day	Unchanged
		Inhalation	2.4 µg/m <sup>3</sup>	Unchanged
Cobalt	Non-carcinogenic	Ingestion	0.02 mg/kg-day	0.03 mg/kg-day
		Inhalation	0.1 µg/m³	Unchanged
Arsenic	Non-carcinogenic	Ingestion	0.0003 mg/kg-day	Unchanged
		Inhalation	None selected	0.03 µg/m <sup>3</sup>
	Carcinogenic	Ingestion	1.5 (mg/kg-day)-1	Unchanged
		Inhalation	4.3 (µg/m³)-1	Unchanged

#### Table 3-1 TRVs used in this Updated HHRA

All of these values adopted for the updated HHRA are tabulated in Table 3-2 and each is described in more detail in the sections that follow below.

In addition to the changes summarized in Table 3-2, revised estimates of exposure, risk, and riskbased soil concentrations (RBSCs) have been completed. Consistent with the original HHRA, exposure estimates have also been completed for the reasonable maximum exposure scenario (RME) and maximum exposure scenarios. A summary of the revised exposure estimates for the RME scenario are provided in Appendix 3F; risk estimates for the RME scenario, risk estimates for the maximum scenario and revised RBSC estimates are provided in Sections 3.10, 3.11, and 3.12, respectively. The results of the Sensitivity Analysis are provided in Section 3.1 with additional detail given in Appendix 3H.

In discussions with the MOE, it was suggested that the "RME" (reasonable maximum exposure) scenarios be renamed as "CTE" (central tendency estimate). This suggestion has not been adopted in this updated HHRA for the reasons outlined below.

The concept of RME was proposed by the U.S. EPA for use in EPA Superfund Risk Assessments (US EPA 1989). US EPA (1989) states that, "The reasonable maximum exposure (RME) is the maximum exposure that is reasonably expected to occur at a site. Under this approach, some intake



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variables may not be at their individual maximum values but when in combination with other variables will result in estimates of the RME." What constitutes "reasonable" cannot be based solely on quantitative information, but also requires the use of professional judgment (US EPA, 1989).

Exposure scenarios include three main components, chemical-related factors (exposure point concentration), receptor-specific factors (e.g. incidental soil ingestion rate, inhalation rate, body weight, skin surface area, soil adherence factors, and so on), and assessment-determined factors (exposure duration or averaging time) (US EPA, 1989). Under the US EPA Risk Assessment Guidance for Superfund (RAGS) approach, the exposure-point concentration is considered to be the arithmetic average of the concentration that is contacted over the exposure period. Although this concentration does not reflect the maximum concentration that could be contacted at any one time, it is regarded as a reasonable estimate of the concentration likely to be contacted over time, because in most situations, assuming long-term contact with the maximum concentration is not reasonable. The RAGS approach considers that because of the uncertainty associated with any estimate of exposure concentration, the upper confidence limit (i.e., the 95th percentile upper confidence limit) on the arithmetic mean (UCLM) should be used in an RME exposure scenario (US EPA, 1989). The UCLM is extremely valuable in this regard, as the confidence limits are influenced by the sample size. As sample coverage increases at a site, the UCLM will tend to decrease towards the arithmetic mean as a function of the square root of the sample size. When the sample size is low, the UCLM could conceivably be above the maximum detected value. In these cases, the maximum detected value should be used to estimate the exposure point concentration. The US EPA regards this approach as reasonable (US EPA, 1989). The use of the UCLM rewards thorough site characterization in terms of increased soil sample number (n).

The US EPA RME exposure approach contrasts with earlier risk assessment approaches, which evaluated an average and an upper-bound exposure case, rather than a single exposure case. The advantage of the two-case approach is that the resulting range of exposures provides some measure of the uncertainty surrounding these estimates. The disadvantage of that approach is that the upper-bound estimate of exposure may be above the range of possible exposures, whereas the average estimate is lower than exposures potentially experienced by much of the population. The intent of the RME is to estimate a conservative exposure case (i.e., well above the average case) that is still within the range of possible exposures (US EPA, 1989).

In this updated HHRA, the RME approach is used. Exposure-point concentrations are either based on the UCLM, upper percentiles or the maximum measured value, depending on the individual scenario. Receptor-specific exposure factors include a range of mid- to high-percentile values that are believed to result in a RME scenario.



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#### Table 3-2: Changes from the original HHRA included in this report.

Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA	Page   3
Changes to Exposure/Risk Assessment Approach				
Reduction in number of study Zones.	The original HHRA considered six receptor zones including three residential zones (A, B and C), a farm/residential Zone (Zone D) and two background Zones (E and F). Residential Zones A and C have lower levels of exposure than Zone B. Risk estimates for background Zones are for comparative purposes only.	The number of zones evaluated has been reduced from six to two. These zones include Zone B (the residential Zone closest to the refinery) and Zone D (the agricultural Zone).	Section 3.4.1	
Life stages Evaluated	The original HHRA evaluated five life stages including infant, toddler, child, teen, and adult. Typically, risk assessments in Ontario only evaluate the toddler (the most sensitive receptor) and the adult or lifetime (for cancer risks).	The number of life stages considered was reduced from five to two (i.e., the toddler and the adult) for non- cancer endpoints plus lifetime for cancer risks.	Section 3.4.2	
Spreadsheet Model Structure	Using a spreadsheet model for each zone and each sensitivity analysis independently can result in introducing errors or inconsistencies into the various model versions.	The spreadsheet model structure was altered to accommodate evaluations of all zones within the same spreadsheet model by using a process of toggling options and automatically selecting input values corresponding to the correct zone or scenario. The final product is considered a more robust tool.	Section 3.4.3	
	Changes to Input A	ssumptions		
Soil and Dust Ingestion Rate	The MOE recommends that the toddler ingestion rate be increased to reflect current scientific information.	The US EPA combined soil and dust ingestion rate of 110 mg/day (50 mg/day soil and 60 mg/day dust) has been adopted for this updated HHRA. This value is supported by recent studies completed by (Ozkaynak, 2011; US EPA, 2011) and exceeds the values recommended by Health Canada (Health Canada, 2012) and Wilson <i>et al.</i> (2013).	Section 3.5.1 and Appendix 3B	

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Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA
Concentration in Dust	Exposure to dust was counted twice, because dust was included once in the combined soil-dust ingestion rate and again in an assessment of contact with surfaces. The area-based exposure was static and did not change with changing soil concentrations. This is unlikely.	Exposure to dust was only assessed as part of the combined soil and dust ingestion rate; area-based measurements were not considered. This eliminated double counting of dust exposures.	Section 3.5.2 and Appendix 3B
	When evaluating the exposure to dust as part of the overall soil ingestion rate of 100 mg/day, the concentration in indoor dust was assumed to be the same as in outdoor soil. This is unlikely.	The concentration in dust used in the HHRA is the higher of the measured concentrations from the gravimetric vacuum samples or the concentration predicted using empirically-derived concentration ratio curves.	
	Dust ingestion was only evaluated for the infant and the toddler.	Dust ingestion was evaluated for exposures of the toddler, adult and lifetime receptor.	
Concentration in Garden Produce	The maximum concentrations in garden produce (i.e., fruits and vegetables) obtained from backyard gardens were used in the estimation of the RBSC. This resulted in an apparent overestimation of the contribution of garden produce to the overall intake of CoCs in food. Use of the maximum concentration also implies that the highest produce concentration corresponds to the highest soil concentration. This is not the case in Port Colborne. The maximum concentration also assumes that only one type of produce is grown. This is also unlikely.	The 90 <sup>th</sup> percentile concentration in backyard fruits and vegetables was taken as adequately conservative (i.e., representative of a maximum home soil/produce combined scenario and was used for the estimation of the RBSC. However, the Zone B data set was too small and had to be combined with data from Zones A and C. This combined dataset was used to generate concentrations for the RME scenario, the maximum scenario and the RBSC scenario for application in Zone B.	Section 3.5.3 and Appendix 3B
Concentration in Supermarket Food	In the original HHRA, the concentrations in supermarket food were based on the results of the site-specific food basket survey of Port Colborne. The MOE raised concerns that these site-specific concentrations were not sufficiently conservative as they resulted in an intake of nickel in supermarket food of 95 µg/day for the toddler, which is significantly less than the intake of 190 µg/day reported by the MOE (2002).	The food categories with a small numbers of samples from the Port Colborne specific study were augmented with data from seven <i>Total Diet Studies</i> (TDSs) conducted by Health Canada. The concentrations in the augmented dataset are comparable to the average concentrations from the Health Canada TDS indicating that they are sufficiently conservative for evaluating exposure to CoC in supermarket food. The resulting intake of nickel in supermarket food for the toddler has increased to142 µg/day.	Section 3.5.4 and Appendix 3B

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Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA
	In addition some food categories had a small number of samples which was a concern to the MOE.		
Concentrations in Ambient Air	Potential risks were estimated by using a combination of both the modelled and measured results. The MOE expressed concern over using measured values from a 24-hour sampling event to estimate chronic risk.	Risk estimates for all scenarios (i.e., RME, maximum and RBSC) were based on the modelled data, other than Zone B which considered the MOE's long term monitoring results for nickel, cobalt and arsenic.	Section 3.5.5
Maximum Concentration of Nickel in Indoor Air	The maximum concentration of nickel in indoor air was reported to be $0.15 \ \mu g/m^3$ in Indoor Air Sample (IAS) 102. This concentration was identified as a statistical outlier relative to the study population. In addition, the occupant of IAS 102 was uncooperative and was unwilling to allow for adequate sampling. A report conducted by the PLC's Independent Consultant that was intended to provide further assessment of the risks associated with this residence was not completed. As a result the data and the risks associated with this residence remain unresolved.	Indoor air data from IAS 102 was not evaluated.	Section 3.5.6
	Changes to Toxicity Assessr	ment/TRV Selection	
Non-Carcinogenic TRV	Nickel Oral: In their formal comments on the original HHRA, the MOE recommended that the TRV of 0.020 mg/kg-day based on the feeding study by Ambrose (1976) be used instead of the TRV of 0.020 mg/kg-day based on the Springborn (2000a,b ) study. In 2012, the MOE suggested that a TRV of 0.011 mg/kg-day based on an alternate interpretation of Springborn (2000a, b) be considered.	<b>Nickel Oral:</b> For the updated HHRA the TRV based on Ambrose et al. (1976) (i.e., 0.020 mg/kg-day) was used for assessing risk for the toddler life stage while the TRV based on Springborn (2000a, b) (i.e., 0.011 mg/kg-day) was used for assessing risk for the adult life stage. Sensitivity analyses were performed using a TRV based on Springborn (2000a,b) corrected for nickel in the rat diet (i.e., 0.013 mg/kg-day)and a TRV for nickel dermatitis, based on Nielson (1999) (i.e., 0.012 mg/kg-day).	Section 3.6 and Appendix 3C
	Nickel Inhalation: Selected TRV was 0.09 μg/m <sup>3</sup> based on ATSDR (2005). MOE recommended a TRV of 0.06 μg/m <sup>3</sup>	<u>Nickel Inhalation:</u> Used TRV of 0.06 μg/m <sup>3</sup> provided in MOE (2011a).	

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#### **CHAPTER THREE – HUMAN HEALTH RISK ASSESSMENT**

Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA
	Nickel Dermal Absorption: The MOE asked that the nickel dermal absorption term be reviewed and updated.	<b>Nickel Dermal Absorption:</b> Dermal absorption of nickel is now handled as 3 separate values: 1) nickel available for absorption; 2) absorption of available nickel into the dermal layers; and, 3) absorption of nickel into the bloodstream. The second factor is presented in the report, but only used in the evaluation of nickel contact dermatitis. The other 2 factors are input into the spreadsheet model and the product of these factors is the dermal absorption into the bloodstream. All of these factors have been reviewed and updated.	Section 3.7.3 and Appendix 3D
	Nickel Contact Dermatitis: The MOE commented that the assessment of Ni dermatitis in the report was insufficient and outdated. The MOE requested that this assessment be updated based on additional review of the literature. The MOE provided information to assist in the expanded assessment.	Nickel Contact Dermatitis: A limited update has been undertaken to consider more recent information on nickel absorption and nickel contact dermatitis. Many of the references that the MOE requested be reviewed contained information arriving at similar conclusions of a type more focused on aspects of nickel release from jewelry, with limited applicability to the current study; the review focused on recent studies which added value to this updated HHRA.	Section 3.7.4 and Appendix 3D
	<b>Cobalt Oral:</b> Selected TRV was 0.02 mg/kg-day based on recommendations by US EPA Region III (2001). The US EPA no longer supports this value. The MOE recommends using the value of 0.001 mg/kg- day as provided in MOE (2011a).	<b><u>Cobalt Oral:</u></b> Used a TRV of 0.030 mg/kg-day derived by Finley et al. (2012). This value is considered more robust than the value recommended by the MOE (2011a).	Section 3.6 and Appendix 3C
	<b>Copper Oral:</b> The TRV used in the original HHRA was 0.130 mg/kg-day derived by IOM (2001). The MOE recommended a TRV of 0.030 mg/kg-day provided by Health Canada (2004a) and included in MOE (2011a). The MOE indicated that if the TRV of 0.130 mg/kg-day is also used in the updated HHRA, then a more substantial explanation should be provided.	<b><u>Copper Oral:</u></b> The TRV of 0.130 mg/kg-day derived by IOM (2001) was also used in the updated HHRA and further rationale has been provided.	

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Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA
	Arsenic Inhalation: Inhalation risk for arsenic was not evaluated, as an acceptable TRV could not be identified. The MOE recommended the use of the chronic inhalation TRV of 0.03 µg/m <sup>3</sup> provided in MOE (2011a).	Arsenic Inhalation: Used the MOE recommended TRV of 0.03 $\mu$ g/m <sup>3</sup> .	
Carcinogenic TRV	Nickel Cancer: The evaluation included three approaches with three different TRVs. Approach I and II were based on a non-threshold approach using unit risks. Approach I was specific to nickel refinery dust, while Approach II was specific to nickel oxide dust. Approach III was a threshold approach which relied on a limit value, below which cancers are not observed. The MOE recommended that a quantitative risk evaluation should be conducted using Approach I and II to bracket the potential range of effects. The MOE did not support the threshold approach for evaluating the carcinogenic inhalation endpoint of nickel.	<b>Nickel Cancer:</b> Used Approach II to evaluate the carcinogenic risk associated with inhalation of nickel. Approach II is based on exposure to nickel oxide, which is the major nickel species in air at Port Colborne. The TRV based on Approach II is supported by a recent study by Conard and Seilkop (2011)	Section 3.6 and Appendix 3C
	Changes to Bioavailability	y/Bioaccessibility	
Relative Oral Bioavailability of Nickel	One of the most critical parameters in the estimation of the RBSC is the relative oral bioavailability (ROB) used to estimate the fraction of nickel in ingested soil, which is available for absorption. The MOE did not support the ROB of 4% for nickel in all soil types based on a limited in vivo study of Port Colborne soil, but instead recommended the use of a bioaccessibility of 19% based on in vitro studies conducted by the MOE (2002). The limited size of the <i>in vivo</i> dataset (n=3) was identified as the major issue with the MOE.	In vivo experiments are considered the preferred method for estimating the fraction of a metal available for absorption; <i>in vitro</i> bioaccessibility experiments are only a simplified extreme approach of the complex <i>in vivo</i> processes and thus provide only a rough estimate of the actual bioavailability. Vale conducted additional <i>in vivo</i> experiments on 20 soils from Port Colborne to strengthen the statistical power of the <i>in vivo</i> datasets for nickel. When the <i>in vivo</i> ROB results from the original HHRA are considered along with the more recent experiments, the datasets for fill, clay and organic have sample sizes of n= 6, n=8 and n=7, respectively. These datasets are sufficiently large to estimate soil-type specific ROB for nickel of 5.8%, 9.4% and 21.7% for fill, clay, and organic, respectively. These values were used for exposure	Section 3.8 and Appendix 3E

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Parameter	MOE identified issue (s) in the original HHRA	Response to issue in updated HHRA	Relevant section of HHRA
		calculations in this updated HHRA.	
Bioaccessibility of Nickel, Cobalt, Copper and Arsenic	The original HHRA conducted bioaccessibility testing on only three soil samples (one each of fill, clay and organic). Overall bioaccessibility values for cobalt, copper and arsenic were estimated by combining the results of the analyses with data from the MOE (2002) <i>in vitro</i> analyses of 10 fill soils. This resulted in bioaccessibility values for each CoC that were applicable to all soil types. Soil type specific bioaccessibilities could not be derived for clay or organic soil as each had only one data point.	Vale conducted additional bioaccessibility testing on soil from Port Colborne, including 6 samples of fill, 12 samples of clay and 11 samples of organic. These data were combined with the previous data collected by Jacques Whitford (now Stantec) as well as the data collected by the MOE (2002) in order to develop conservative estimates of bioaccessibility by soil type. It is noted that the bioaccessibility results for nickel are considered in the sensitivity analysis as the ROB estimated from the <i>in vivo</i> studies are used for risk estimation within the report. For the updated HHRA, soil exposure is estimated based on the specific soil type for a given scenario or land use and the soil-type specific ROB/bioaccessibility. The ROB/bioaccessibility of sand was not measured, but is conservatively assumed to be the higher of the ROB/bioaccessibility for fill or clay soil, depending on the CoC.	Section 3.8 and Appendix 3E

<u>Notes:</u>

NA Not Applicable. The modification applies to the entire HHRA, but does not require detailed discussion in any particular section of the HHRA.

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#### 3.4 CHANGES FROM THE ORIGINAL RISK ASSESSMENT

#### 3.4.1 **Reduction in the Number of Study Zones**

The original HHRA considered six receptor zones, including three residential zones (A, B and C), a combined farm/residential zone (Zone D) and two background Zones (E and F). Zones A through Page | 3.15 E are identified in Figure 2-5 in Chapter 2. In this updated HHRA, risks have only been estimated for receptors in Zones B and D. Zone B contains the highest concentration of nickel in a residential area (i.e., 17,000 mg/kg) and Zone D is considered the most sensitive zone as it is largely agricultural and the exposure scenarios for the specific soil types for this zone result in the lowest estimated RBSC of all zones in the Port Colborne area. The results of the original HHRA indicated that likely exposure scenarios for Zones A and C were less sensitive than those of Zone B and D. For this reason, Zones A and C were not evaluated in this updated risk assessment.

Two background Zones were included in the original HHRA (i.e., Zone E and Zone F). Zones E and F were primarily used for comparative purposes only; Zone E represented local background and Zone F represented a more general background in Ontario. As these results were not expected to change in a significant way, a comprehensive estimate of background risk in these zones was not included in the updated HHRA. However, risks due to background exposure have been evaluated for select scenarios including for oral and inhalation exposure to arsenic (Section 3.10.1.7 and Section 3.10.1.9) and for estimating vacation exposures for receptors in Zone D, as they are assumed to vacation for two weeks a year in Zone F. As requested by the MOE, the mean soil concentrations for widespread background have been used to estimate RME exposures while vacationing in Zone F, as opposed to the 98<sup>th</sup> percentiles of the Ontario dataset, which were used in the original HHRA.

It is noted that, consistent with the approach in the original HHRA, receptors in Zone B are assumed to vacation within Port Colborne, and are thus assumed to be exposed to media from Port Colborne throughout the year.

#### 3.4.2 Life Stages Evaluated

The original HHRA considered receptors from all age groups from infant through adult for a 70year life span. This updated HHRA only reports non-cancer risk for two receptors, the toddler and the adult. These are the two receptors that are typically considered in risk assessments in Ontario. Toddlers represent the most sensitive receptor, as they have the highest exposure rates per unit body weight of any life stage and because their organ systems are actively developing during this life stage. Consequently, the Toddler is used as the most sensitive receptor for RBSC estimation. Consistent with the original HHRA, receptors are assumed to move within Zones in the community, to go to work or the beach, according to the Zone in which they are most likely to receive the highest exposures. Cancer risks, on the other hand, are reported for an entire lifetime, based on a combination of all life stages from infant through adult.



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# 3.4.3 Spreadsheet Model Structure

The version of the Microsoft Excel model spreadsheet used in the original HHRA required that new versions be used for each zone and each sensitivity analysis, leading to a higher risk of introducing errors or inconsistencies into the various spreadsheet model versions. The spreadsheet model structure was consequently augmented to accommodate evaluation of all zones and sensitivity scenarios within the same model by using a process of toggling options and automatically selecting input values corresponding to the correct zone or scenario. The final product is considered a more robust tool.

# 3.5 CHANGES TO INPUT ASSUMPTIONS

# 3.5.1 Soil and Dust Ingestion Rate

The combined soil and dust ingestion rate used in the original HHRA for the sensitive receptor (i.e., the toddler) was 110 mg/day; this ingestion rate is assumed to include contributions of 50 mg/day from soil and 60 mg/day from dust resulting in the total ingestion rate of 110 mg/day. This rate was selected based on recommendations in US EPA (1997; 2002a; 2006) and is consistent with current recommendations (US EPA, 2008; 2011). Additional studies have been published recently in the peer reviewed scientific literature and these, along with recommendations from Health Canada, support the use of the ingestion rates selected in the current evaluation.

The total soil and dust ingestion rate of 110 mg/day for the toddler is less than the value of 200 mg/day recommended by the MOE (2011a). The ingestion rate of 200 mg/day (all soil ingestion rates include soil and dust) was reported to be a conservative estimate of the mean based on historical US EPA analysis of the tracer studies (US EPA, 1997). The soil/dust ingestion rate of 400 mg/day was reported in US EPA (1997) as the upper percentile, and 100 mg/day was the recommended ingestion rate for estimating exposure. Since 1997, new information has become available, including computer modelling studies that have brought into question the accuracy of a mean soil ingestion rate of 200 mg/day. Since 1997 the US EPA has refined its recommended soil ingestion rates based on a refined meta-analysis of available tracer studies as well as computer modelling using its Stochastic Human Exposure and Dose Simulation (SHEDS). The US EPA maintained their recommendation of 100 mg/day for the toddler (includes soil and dust) ingestion rate, but 200 mg/day is now reported to be the upper percentile (95<sup>th</sup> percentile) ingestion rate (US EPA, 2011). The value of 100 mg/day for the toddler (110 mg/day in this HHRA) is in reasonable agreement with the soil/dust ingestion rate of 80 mg/day recommended by Health Canada as the average intake rate for a toddler.

This HHRA was conducted using the combined soil and dust ingestion rates provided in US EPA (2011) and shown in Table 3-3. Consistent with the approach in the original HHRA, the total soil and dust ingestion rate for the toddler used for risk estimates in this updated HHRA is 110 mg/day (60 mg/day dust and 50 mg/day soil), or 100 mg/day if rounded to one significant figure. Additional information related to the selection of the soil and dust ingestion rates used in this updated HHRA is provided in Appendix 3B.



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	Soil/Dust Ingestion Rate (mg/day)				
Receptor	Original	MOE (2011a) Includes	US EPA (2	2011)	
	HHRA	Soil and Dust	Soil	Dust	
Toddler	100ª	200ª	50	60	
Adult	20ª	50ª	20	30	

#### Table 3-3: Soil/dust ingestion rates to be used in this Updated HHRA.

<u>Notes:</u>

Bold Values used in updated HHRA.

<sup>a</sup> Dust exposures are included in the ingestion rates.

# 3.5.2 CoC Concentration in Dust

In the original HHRA, the toddler (i.e., the most sensitive receptor) was evaluated for exposure to dust based on a combined soil/dust ingestion rate of 100 mg/day as well as through the use of area based measurements from vacuum samples and swipe samples collected as part of the Indoor Air and Dust study of 30 houses in Port Colborne (Volume II, Appendix 1.7 of the original HHRA-provided in Appendix 1M of this report). There are several potential drawbacks to this approach:

- The approach results in a double counting of the dust exposure;
- When evaluating the exposure to dust as part of the overall soil/dust ingestion rate of 100 mg/day, the concentration in dust is assumed to be the same as the concentration in outside soil. This is inconsistent with information in the literature which suggests that only 20-30% of household dust is derived from outdoor soils (Rutz, 1997, Calabrese, 1992);
- The magnitude of the area-based exposure was static and did not change, even when modeling the higher soil concentrations of the RBSC scenario. This underestimates exposure since the concentration in indoor dust is expected to increase with the concentration in outdoor soil; and
- When estimating exposure in the context of risk assessment, CoC concentrations based on mass basis, rather than area basis, are preferred in order to be consistent with the intake rates established by regulators including the MOE.

In order to address these drawbacks, the following approaches for estimating the concentration of nickel in dust samples have been adopted in this updated HHRA:

- Exposure to dust is assessed as part of the combined soil and dust ingestion rate; area-based measurements were excluded. This eliminates double counting of dust exposures.
- The concentration in dust used in this updated HHRA is the maximum of the measured concentrations from the gravimetric vacuum samples or the concentration predicted using empirically-derived concentration ratio curves:



 $[As]_{dust} = 5 \times [As]_{soil}$  $[Co]_{dust} = 1 \times [Co]_{soil}$  $[Cu]_{dust} = 2 \times [Cu]_{soil}$ 

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#### [Ni]<sub>dust</sub> = 0.2 x [Ni]<sub>soil</sub>

Detailed rationale for the selection of the approach used for evaluating exposure to dust in this updated HHRA is provided in Section 1.2, Appendix 3B.

#### 3.5.3 Concentration in Garden Produce

In the estimation of an RBSC in the original HHRA, receptors in each Zone were assumed to be exposed to maximum concentrations of CoC in garden produce (i.e., fruits and vegetables). There are several problems with this assumption:

- It asserts that there is a significant correlation between concentrations of CoCs in soil and concentrations of CoCs in produce. However, site specific sampling of soil and produce (part of the original HHRA) demonstrated that this was not the case for most produce types and CoCs.
- The maximum only represents one type of produce;
- The maximum measured concentration in different types of produce is not consistently associated with the maximum soil concentration;
- Use of the maximum concentration of nickel for exposure estimates resulted in an apparent overestimation of the exposure. For example, the Zone D RBSC yielded an estimated nickel dose for the toddler of approximately 10 µg/kg-day, which represents nearly double the dose estimated from supermarket foods (~5.5 µg/kg-day). This is very difficult to understand, particularly when the contribution of local foods to the overall intake of vegetables and fruits for a toddler in Zone D was assumed to be only 23% and 5.0%, respectively; and,
- The scenario of a person eating garden produce exclusively at the maximum measured concentration has a very low probability of happening. Residents would not be expected to have a steady diet of the single highest produce sample from their garden, but rather would eat a variety of produce grown throughout their garden.

In order to address these concerns, the 90<sup>th</sup> percentile concentration was used instead of the maximum concentration in the estimation of the RBSC. Consistent with the approach in the original HHRA, the RME concentration based on the UCL statistic (or other statistic selected based on the statistical approach outlined in the original HHRA) was used for risk estimation for the RME scenario. For this updated HHRA, the produce data from Zone B has been combined with the produce data from Zones A and C in order to develop a larger dataset, more suitable for the statistical analysis required to estimate the 90<sup>th</sup> percentile concentrations. The produce data used for Zone D has not been modified from the original HHRA. The garden produce concentrations used in this updated HHRA, as well as the rationale for the selection of these values is provided in Section 1.3, Appendix 3B. Based on the revised approach presented in this updated HHRA, the estimated CoC dose from garden produce for a Zone D toddler under the RBSC scenario is approximately 2.6 µg/kg-day, which is about one third of the dose estimated



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from supermarket food (8.3  $\mu$ g/kg-day). This lower estimate for intake of nickel from local foods seems more reasonable than the intake of approximately 10  $\mu$ g/kg-day reported in the original HHRA.

# 3.5.4 CoC Concentration in Supermarket Food

Supermarket foods are one of the principal sources of CoC exposure for residents of Port Colborne. Shops and supermarkets, including those in Port Colborne, obtain the majority of their food from central distribution centers (a review was conducted in the original HHRA); thus the CoC concentrations in foods from Port Colborne are assumed to be comparable to CoC concentrations in foods in other cities in southern Ontario. In the original HHRA, the concentrations of CoCs in supermarket foods were obtained from a site-specific food basket survey of Port Colborne supermarkets and shops conducted by Jacques Whitford. Jacques Whitford also conducted surveys of local produce and eggs, which were identified in a community food basket survey of residents. The supermarket survey also controlled for nickel that might otherwise have been introduced through laboratory processing of samples (e.g. grinding), in order to obtain representative results and avoid nickel contamination of the food that would not be associated with typical household food preparation. Information, data and calculations related to the exposure to nickel from supermarket (i.e. store-bought) foods in Port Colborne was originally presented in Volume V, Appendix 19 of the original HHRA (provided in Appendix 1M of this report).

The dietary intake of a CoC depends on both the concentration of the CoC in the food and the amount of the food that is consumed. While the concentration in foods is estimated using food basket surveys and total diet studies, the amount of each type of food that is consumed is estimated based on dietary intake studies. The intake study used in the original HHRA and this updated HHRA was the United States Department of Agriculture (USDA) intake survey of the North Eastern United States conducted from 1994-1996. While a relevant Canadian intake survey would be preferred over the USDA survey, the only available Canadian-specific food intake data was from the Nutrition Canada Intake Survey (NCS) conducted from 1970-1972, which is considered outdated. Using the USDA intake survey, the average daily intake of nickel in supermarket food for the toddler in the original HHRA was estimated to be 95 µg/day. This value was significantly below the intake of 190 µg/day based on the concentrations in the Health Canada Total Diet Study (TDS) conducted in Montreal between 1986-1988 by Dabeka and McKenzie (Dabeka, 1995) and used by the MOE in the Rodney Street Report (MOE, 2002). The higher intake estimated by the MOE was due to the higher concentrations reported in Dabeka (1995); some of these higher concentrations (i.e. for the meat and poultry group) may have been caused by nickel contamination during food preparation. Due to the discrepancy between these nickel intakes, the approach for determining the concentrations in supermarket food was reevaluated and included the most recent Health Canada diet studies (2001-2007).

The approach adopted in the updated HHRA relies on the same food group categories and site-specific Food Basket study that were presented in the original HHRA, but also incorporates a more conservative statistical approach. The approach for selecting exposure point



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concentrations for the various food groups in the updated HHRA incorporates the following assumptions:

- For categories with fewer than 10 samples (n<10), concentrations are based on the higher of the UCLM/UCLGM (where applicable) and the 75<sup>th</sup> percentile. This is consistent with the statistical approach presented in Vol.5, Appendix 20 of the original HHRA (provided in Appendix 1M of this report).
- For categories with n>10, concentrations are based on the average of the Port Colborne study and the seven Health Canada TDS (overall n=8). The average is considered appropriate based on the large sample sizes of the Health Canada TDSs (Table 3B.9, Appendix 3B).

The market basket concentrations used in this updated HHRA, as well as the rationale for the selection of these values, are provided in Section 1.4, Appendix 3B. Based on the revised approach presented in this updated HHRA, the concentrations of CoCs for the various food groups are generally comparable to the values from the Health Canada TDSs. One important exception is the concentration of nickel in in meat and poultry. The nickel concentrations for this food category reported in the Health Canada TDSs are higher than the value in this updated HHRA; however, this may be related to nickel contamination during sample processing for the Health Canada TDS.

Through the use of more conservative statistics and the addition of Health Canada TDS data for smaller food categories (i.e., N<10), the estimated nickel intake for a Port Colborne toddler increased from 95  $\mu$ g/day (as estimated in the original HHRA) to 142  $\mu$ g/day in this updated HHRA. The intake of 142  $\mu$ g/day is in the midrange of the intakes estimated from the seven Health Canada TDS, and is only marginally below the Health Canada cumulative average of 160  $\mu$ g/day. Additional information is provided in Section 1.4 of Appendix 3B.

# 3.5.5 Concentrations in Ambient Air

Both Jacques Whitford and the MOE have conducted 24-hour air sampling events in Port Colborne in order to measure CoC concentrations in ambient air. Jacques Whitford conducted short-term air sampling in areas throughout Port Colborne for a period of three months; the MOE collected long-term data from the Rodney Street area only (Zone B) between 2001 and 2006. No long-term data was collected for Zone D. The data from both Jacques Whitford and the MOE were used to calibrate a predictive model which was used to model the long term (i.e., 5 year) CoC concentrations in ambient air for Zone B and Zone D. In the original HHRA, these modelled data were used to estimate chronic risk due to inhalation of ambient air.

A comparison of the maximum annual average concentrations from the modelled data to the maximum measured annual concentration from long-term measured data for Zone B is provided in Table 3-4 (reproduced from Volume III, Appendix 9, Section 6.0 of the original HHRA-provided in Appendix 1M of this report). The long-term measured data for copper was determined to be unreliable and was not included in this updated HHRA. In general, modelled concentrations exceeded measured concentrations, with the ratio between the two ranging from 3x for nickel



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to 7.5x for arsenic. Based on this comparison, the modelled data appear to significantly overestimate the concentrations of CoCs present in ambient air in Zone B and are thus not appropriate for estimating risk when long-term site-specific measured data is available. In addition, measured values are anticipated to result in a more robust estimate of risk than modelled values. In this updated HHRA, inhalation risks related to arsenic, cobalt and nickel in ambient air in Zone B were estimated using long-term measured data. Inhalation risks related to copper in Zone B and all CoCs in Zone D are estimated using modelled data.

# Table 3-4Comparison of Maximum Annual Average CoC Model Predictions to MOEMeasurements at Rodney Street (µg/m³)

Parameter	Arsenic	Cobalt	Copper	Nickel
Modelled Concentration	2.79E-02	1.33E-02	3.44E-03	6.3E-02
Long-term Measured Concentration	3.74E-03	2.80E-03	N/Aª	2.04E-02

Notes:

<sup>a</sup> The MOE data for copper includes many instances where the copper in PM<sub>10</sub> exceeds the copper in TSP, which may be indicative of data quality issues. As a result, measured data was not used in this Updated HHRA. Inhalation risk estimates due to exposure to copper in ambient air were completed using modelled concentrations.

In the original HHRA, potential risks were estimated by using a combination of both the modelled and 24-hour measured results. These measured results refer to short-term sampling events conducted by Jacques Whitford, not from the long-term sampling conducted by the MOE over the course of 6 years. The MOE expressed concern over using measured values from a 24-hour sampling event to estimate chronic risk. For this updated HHRA, risk estimates for all exposure scenarios (i.e., RME, maximum and RBSC) are not based directly on the 24-hour sampling data but rather are based on either the long-term measured data, or modelled data where long-term measured data is unavailable.

Additional changes include the following:

- In the original HHRA, the modelled concentration of copper from Zone B was used for risk estimates for all Zones. In this updated HHRA the risk estimates for a given Zone are based on the modelled/measured concentrations from that Zone.
- In the original HHRA, the highest year average concentrations of CoCs in Zone B were selected as both the RME and maximum concentrations. In this updated HHRA, the approach for selecting appropriate concentrations based on the exposure scenario differs for measured concentrations versus modelled concentrations. Where long-term measured data are available, risk estimates for the various scenarios (RME, RBSC and maximum) are based on the maximum annual average (Table 3-4). Where risk estimates are based on modeled data, the RME and RBSC scenarios are evaluated based on the maximum 5 year average concentration, while the maximum scenario is evaluated based on the highest year average for that Zone.



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# 3.5.6 Maximum Concentrations of Nickel in Indoor Air

In the original HHRA, risks were evaluated for the maximum concentration of nickel in indoor air, which was reported to be 0.15 µg/m<sup>3</sup> in Indoor Air Site (IAS) 102. This value was based on the average of two 24-hour sampling events and was identified as a statistical outlier relative to the study population. No other home sampled from the entire study population showed a concentration in the same order of magnitude as IAS 102. For example, the next highest value measured in a house was 0.023 µg/m<sup>3</sup>. In addition, the occupant of IAS 102 was uncooperative and was unwilling to allow for additional sampling, thus it is unknown if the measured concentration is reflective of the long-term concentration of nickel in indoor air of home IAS 102. A report conducted by the PLC's Independent Consultant that was intended to provide further assessment of the risks associated with this residence was not completed. As a result, the data and the risks associated with this residence remain unresolved, thus data from this residence was not evaluated in this HHRA.

# 3.6 CHANGES IN TOXICITY REFERENCE VALUE SELECTION

If the MOE did not comment on a particular TRV selection in the original HHRA, then that TRV was maintained in the updated HHRA and no additional rationale was deemed necessary. In some cases, however, (e.g., oral TRV for copper) the TRV selection in the original HHRA was maintained but additional rationale was provided based on requests by the MOE made in either their comments on the original HHRA or in meetings with Vale (2011-2013).

If a TRV selection was modified to be consistent with recommendations in MOE (2011a), then further rationale was deemed unnecessary and only a brief summary of the TRV derivation is provided. If an alternate TRV has been selected, which is not recommended in MOE (2011a), or if the TRV in MOE (2011a) has been modified then detailed rationale is provided. However, it is reiterated that this is a voluntary HHRA, thus it is not required that MOE (2011a) be the primary source of TRVs.

The selection of TRVs for non-carcinogenic endpoints for the updated HHRA can be summarized as follows:

#### Ingestion of Nickel

- The TRV for toddlers remains 0.020 mg/kg/d as in the original HHRA; and,
- The TRV for reproductive toxicity (adverse pregnancy outcomes) was recommended by the MOE as 0.011 mg/kg/d; this value was used to evaluate risk for a specific receptor, a female of reproductive age. The experiments used to derive this TRV did not account for the background nickel present in the experimental food. When the nickel in food is accounted for the TRV becomes 0.013 mg/kg/d. The effects of using this adjusted TRV on the estimated risk are examined in the Sensitivity Analysis (Section 3.1).

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• The use of life-stage-specific non-carcinogenic TRVs in this updated HHRA is exclusive to the ingestion of nickel.

#### Inhalation of Nickel

• The TRV has been decreased from 0.09  $\mu$ g/m<sup>3</sup> to 0.06  $\mu$ g/m<sup>3</sup>, in accordance with the Page | 3.23 MOE recommendation.

#### Ingestion of Copper

• The TRV remains unchanged.

#### Inhalation of Copper

• The TRV remain unchanged.

#### Ingestion of Cobalt

• The TRV for all life stages has been taken as 0.03 mg/kg based on Finley (2012).

#### Inhalation of Cobalt

• The TRV remains unchanged.

#### Ingestion of Arsenic

• The TRV remains unchanged.

#### Inhalation of Arsenic

• The TRV remains unchanged.

The selection of TRVs for carcinogenic endpoints for the updated HHRA can be summarized as follows:

#### Inhalation of Ni:

• A TRV developed explicitly for oxidic Ni in air (i.e., Approach II) has been adopted because air sampling in Port Colborne showed oxidic Ni to be the predominant nickel species in ambient air. This TRV is supported by a recent study by Conard and Seilkop (2011). This TRV remains unchanged since the original HHRA.

#### Ingestion of As:

• The TRV remains unchanged.



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#### Inhalation of As:

• The TRV remains unchanged.

The non-carcinogenic and carcinogenic TRVs used in the original HHRA and the updated HHRA are tabulated in Table 3-5 and Table 3-6. Detailed rationale for the selection of the TRVs identified in Table 3-5 and Table 3-6 is provided in Appendix 3C.

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#### Non-Carcinogenic TRVs selected for use in the original HHRA and Updated RA Table 3-5:

0-0	Route of		Original HHRA				Up	odated HHRA	
CoC	Exposure	TRV	Endpoint	Reference	MOE (2011a) TRV	Approach	TRV	Endpoint	Reference
				Springborn et al. (2000a,b) Nickel	MOE (2011a) currently recommends a TRV of 0.020 mg/kg-day based on Ambrose (1976), however the MOE has indicated that it now supports a TRV 0.011mg/kg-day based on an interpretation	<b>Toddler:</b> Use TRV based on Ambrose (1976) from MOE (2011a)	<b>Toddler:</b> 0.020 mg/kg-day	Decreased body weight.	Pag Ambrose (1976) and MOE (2011a)
Nickel	Ingestion	0.02 mg/kg-day	Reproductive Toxicity	Working Group, (2007)	of Springborn (2000a,b). The interpretation of Springborn (2000a,b) provided in the original HHRA resulted in a TRV of 0.022 mg/kg-day. This interpretation is no longer supported.	Adult-Reproductive Age: Use TRV based on Springborn (2000a,b)	Adult-Reproductive Age: Use TRV of 0.011 mg/kg-day.	Reproductive Effects	Springborn (2000a,b)
	Inhalation	0.09 µg/m <sup>3</sup>	Chronic active inflammation in lungs of rats	ATSDR (2005)	0.06 µg/m <sup>3</sup> based on modification from TERA (1999).	Use TRV recommended in MOE (2011a)	0.06 µg/m3	Chronic active inflammation in lungs of rats.	TERA(1999) and MOE (2011a).
-	Ingestion	0.13 mg/kg-day	Liver Function	IOM (2001)	0.030 µg/kg-day based on Health Canada(1992)	Use TRV from the original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA
Copper	Inhalation	2.4 µg/m <sup>3</sup>	Respiratory Effects	CAPCOA (1993)	None	Use TRV from original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA
<b>.</b>	Ingestion	0.02 mg/kg-day	Increased hemoglobin in anemic dialysis patients	US EPA (2001)	0.001 mg/kg-day based on modification of ATSDR (2004)	Use TRV from Finley et al (2012)	0.030 mg/kg-day	Thyroid effects	Finley et al (2012)
Cobalt	Inhalation	0.1 µg/m³	Decreased respiratory function in exposed workers	ATSDR (2004)	5.0E-04 mg/m <sup>3</sup> from RIVM (2001)	Use TRV from original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA
Arsenic	Ingestion	0.0003 mg/kg-day	Increased rate of Blackfoot disease in exposure human population	US EPA (2002b)	0.0003 mg/kg-day based on US EPA (IRIS) (2002b);	Use TRV from original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA
	Inhalation	No suitable value identified	NA	NA	$0.03 \ \mu\text{g/m}^3$ based on Cal EPA (2000)	Use TRV recommended in MOE (2011a)	0.03 µg/m <sup>3</sup>	Skin Cancer	CalEPA (2000)

Notes:

a

The MOE recommended a TRV of 0.020 mg/kg (based on Ambrose) in their comments on the original HHRA, but later changed that recommendation in 2012 to 0.011 mg/kg (based on Springborn(2000a,b). Not Applicable NA

MOE (2011a) MOE Rationale Document, 2011.



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# Table 3-6: Carcinogenic TRVs selected for use in the Original HHRA and Updated RA

			Original H	HRA				Rev	ised RA						
CoC	Route of Exposure	TRV	Type of TRV	Endpoint	Reference	MOE (2011a) TRV	Approach	TRV	Endpoint	Reference					
	Inhalation- Approach I Nickel Refinery Dust Unit Risk	2.4E-4 (µg/m³) <sup>-1</sup>	Unit Risk	Lung Cancer- Midpoint of range for refinery workers	US EPA (1986; 2003)	0.24 (mg/m <sup>3</sup> ) <sup>-1</sup> from US EPA (IRIS)(1991) Use Approach II, supported by Conard and Seilkop (2011)	2003) epicard et , (1997), ported by nard and top (2011) 0.24 (mg/m <sup>3</sup> ) <sup>-1</sup> from US EPA (IRIS)(1991) Use Approach II, supported by Conard and Seilkop (2011)								
Nickel	Inhalation- Approach II Oxidic Nickel Unit Risk	4E-5 (µg/m³)-1	Unit Risk	Lung Cancer	EU, Lepicard et al., (1997), supported by Conard and Seilkop (2011)			4E-5 (μg/m³)- 1	Lung Cancer	EU, Lepicard, et al, (1997) supported by Conard and Seilkop (2011).					
	Inhalation- Approach III Nickel Refinery Dust Limit Value	0.6 µg/m³	Limit Value	Lung Cancer	EC (2001); Lewis and Caldwell (1999)						Selikop (2011)				
	Conard and Seilkop (2011)- Oxidic Nickel	5.1E-5 (µg/m³) <sup>-1</sup>	Unit Risk	Lung Cancer	Conard and Seilkop (2011)										
Arsenic	Ingestion	1.5 (mg/kg-da) <sup>-1</sup>	Slope Factor	Skin Cancer	US EPA(1998)	1.5 (mg/kg-da) <sup>-1</sup> based on Cal EPA (2005)	Use TRV from original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA					
Arsenic	Inhalation	4.3 (mg/m <sup>3)-1</sup>	Unit Risk	Lung Cancer	US EPA(1998)	1.5 (mg/m <sup>3)-1</sup> based on WHO (2000)	Use TRV from original HHRA	Same as original HHRA	Same as original HHRA	Same as original HHRA					

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# 3.7 CHANGES IN APPROACH FOR EVALUATING DERMAL EXPOSURE TO NICKEL

# 3.7.1 Nickel Dermal Bioavailability

The dermal exposure and associated risk to nickel in soils is related to the three main factors: the amount of nickel in soils that can come into contact with the skin and that is available for absorption; the proportion of nickel absorbed into the dermal layer; and the proportion of the dermally absorbed nickel that is absorbed into the bloodstream. Nickel absorption into the skin is related to the solubility (in sweat) of the nickel species, which depends on the nickel speciation as well as the characteristics of the soil. The ability of the nickel to penetrate into the dermal layers is critical in assessing contact dermatitis. The ability of the nickel to penetrate deeper and ultimately reach the blood stream is important in assessing systemic effects. Each of these has been examined separately in Appendix 3D and is summarized in this section.

# 3.7.2 Availability of Nickel for Dermal Absorption

Extraction tests of nickel from Port Colborne soils were conducted as a component of the crops study for the CBRA and by Everhart *et al.* (2006). Bioaccessibility of nickel in Port Colborne soils was also investigated through the application of tests based on physiological processes that may occur in the stomach and intestine during the digestion of incidentally ingested soils. However, the data provide very limited information on skin solubility due to significant differences in the physio-chemical conditions encountered in the GI tract and the skin. The available site-specific data were reviewed. It was concluded that the intestinal phase extraction conducted by ESG (2002a,b) was a conservative estimate for the bioaccessibility of nickel for skin. Based on this study, 10.9% of the nickel in Port Colborne soil, when adhered to human skin, is assumed to be leached from the soil into human sweat and made accessible for absorption into the skin.

# 3.7.3 Dermal Absorption

Limited information on nickel absorption through the skin is available. Nieboer *et al.* (1992) reported that dermal absorption is not a major source of nickel exposure in humans. It is important to distinguish between the nickel that is available for absorption, the nickel actually absorbed into the skin, and the fraction of that absorbed nickel that reaches the blood stream. For a systemic reaction to occur, the nickel must reach the blood stream. To cause a dermatological contact reaction, the nickel need only be absorbed by the skin (Horowitz and Finley 1994).

Researchers have typically used nickel chloride to study absorption of nickel into and through the skin. However, a significant difference exists in the solubilities of nickel chloride and oxidic nickel, which are the predominant species of Ni in Port Colborne soils. Nickel chloride solubility is over five orders of magnitude greater than that of nickel oxide. Fullerton *et al.* (1986) report that nickel chloride has a dermal absorption 50 times that of nickel sulphate. Since most of the nickel in Port Colborne soils is oxidic, use of nickel chloride derived absorption rates is considered very conservative for application to absorption of nickel from Port Colborne soils.



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Table 3-7 summarizes results of studies that investigated the absorption of nickel through the dermal layers into the blood stream. These included studies that used artificial means of simulating absorption and those that included soil in the nickel solution. The purpose of this table is the examination of absorption of nickel into the blood stream. Studies that did not examine the blood stream or simulation of this have been excluded from the table. Additional studies that did not include the use of soil are summarized in Appendix 3D.

# Table 3-7 Summary of Literature - Fraction of Nickel Reaching Bloodstream

Study Study Type		Absorption into Bloodstream	Time
Moody et al. 2009	In vitro study with human skin	0.5% of the contained Ni as NiCl2 in aqueous solution with sand	24 hours
Turkall et al. 2008a In vitro study with pig skin		<0.5% NiCl2 in ethanol alone or with soil	16 hours
Turkall et al. 2008b In vitro study with pig skin		<0.5% NiCl <sub>2</sub> in ethanol alone or with soil	16 hours
MOE 2002	Adjusted human in vitro study	0.038%	24 hours

The highest absorption from all studies was 0.5% from Moody *et al.* (2009). This value was selected for evaluating the absorption of nickel into the bloodstream for the following reasons:

- the presence of sand is relevant to the Port Colborne assessment of nickel in soil;
- the results of this study are applicable to the exposure scenario (i.e., higher absorption without soil in other studies); and,
- the nickel was in a soluble form in the solution.

Table 3-8 summarizes results of studies that investigated the total dermal absorption of nickel from soil, or the nickel recovered dermally, where the total was not specifically measured.

# Table 3-8 Summary of Literature - Fraction of Nickel Dermally Absorbed

Study	Study Type	Dermal Absorption	Time
Turkall et al. 2008a	In vitro pig skin, nickel chloride in ethanol	2.8% aged soils (skin dose of nickel chloride of 0.113 µg/cm²)	16 hours
Turkall et al. 2008b	In vitro study with pig skin, nickel chloride in ethanol	1.8% and 2.8% aged sand solutions (skin dose of nickel chloride of 0.113 μg/cm²)	16 hours
Moody et al. 2009	In vitro study with human skin	1% NiCl <sub>2</sub> in aqueous solution with sand (skin dose of nickel of 0.89 μg/cm <sup>2</sup> from a 5.7 μg/mL nickel solution)	24 hours



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A more comprehensive review of the literature on dermal absorption of nickel is included in Appendix 3D. The results shown that a significant fraction of soluble nickel when applied alone is absorbed by the skin (up to 58% after 16 hours). The results also indicate that the presence of soil has a significant effect on reducing the amount of nickel absorbed. With nickel present in soil, up to 2.8% of nickel was absorbed.

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Since the presence of soil is the focus of this assessment, the highest absorption with soil (excluding freshly spiked) was selected for the evaluation of nickel contact dermatitis, namely 2.8%.

# 3.7.4 Nickel Allergic Contact Dermatitis

Nickel ranks as the most common cause of allergic contact dermatitis, particularly affecting females due to its frequent use in jewellery. The immunogenic form of nickel is its divalent ion. Thyssen and Menne (2009) state the prevalence of nickel allergy is up to 17% in females and 3% in men. Thyssen and Menne (2009) attribute the higher prevalence of nickel sensitivity in women to ear piercing which is reported to be 8 times more common in women than in men.

School children were included in a few of the studies and they displayed the same high prevalence rate of nickel sensitization as adults. The prevalence studies also revealed that the vast majority of nickel-sensitive patients have light and intermittent problems with contact dermatitis, while only a minority of the total number of sensitized patients develop severe dermatitis leading to sick leave (Menne, 1992).

Simonsen *et al.* (2011) reviewed 20 studies from the literature on reaction rates in past testing of patients for contact allergens and found that all but one of the reviewed studies only gave information on populations already suspected of having allergic contact dermatitis. In other words, the statistics resulting from these studies do not reveal any information on the prevalence of nickel contact dermatitis in the general population. Nickel was the top allergen in 16 of the 20 studies reviewed. A more detailed review of the literature on nickel contact dermatitis is provided in Appendix 3D.

# 3.7.4.1 Elicitation Threshold

In the current assessment, the most recent work by Fischer *et al.* (2011), Gawkrodger *et al.* (2012) and supporting studies were selected as the most appropriate studies on which to base a benchmark value for a screening evaluation of nickel contact dermatitis. The findings indicate that the 10% elicitation rate for sensitive individuals of 0.835 µg/cm<sup>2</sup> is appropriately protective of sensitive individuals and accounts for an occluded skin condition. The studies that this value is based on were reviewed and determined to meet specific testing protocol requirements determined by Fischer *et al.* (2011). The benchmark value notably is not expected to take into account atopic dermatitis which may not be a direct result of dermal exposure to nickel and may lead to reactions at lower thresholds. Further information on studies investigating a threshold of elicitation can be found in Appendix 3D.



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It is noted that sensitization and elicitation are different processes. Sensitization is an increased susceptibility that a subject may have when exposed to a chemical over time. In the case of nickel dermatitis, the sensitization phase, also referred to as the induction phase, involves the sensitization of the immune system to an allergic dermal response. Sensitization to nickel dermatitis could be brought on by repeated exposure to nickel on the skin. Elicitation is the triggering of a response in a sensitized individual i.e., an individual whose immune system is predisposed to generate an allergic response to nickel due to previous exposures. In the case of nickel dermatitis, exposure of a nickel-sensitized individual to nickel via oral or dermal route can result in elicitation of a response such as a skin rash.

# 3.8 CHANGES TO RELATIVE ORAL BIOAVAILABILITY AND BIOACCESSIBILITY

One of the most critical parameters in the estimation of the RBSC is the relative oral bioavailability (ROB) or bioaccessibility used to estimate the fraction of a CoC in soil that is available for absorption. ROB is estimated using *in vivo* tests which are considered the preferred method for evaluating bioavailability, while bioaccessibility is estimated using simpler *in vitro* tests that attempt to simulate complex *in vivo* processes. As part of the CBRA, Jacques Whitford conducted *in vivo* ROB testing and *in vitro* bioaccessibility testing on three soils from Port Colborne (i.e. fill, clay and organic). The MOE also conducted *in vitro* bioaccessibility testing on 10 samples of fill soil as part of their Rodney Street Report (MOE, 2002). In the original HHRA, the *in vitro* data for arsenic, cobalt and copper from the Jacques Whitford evaluation was combined with the *in vitro* data from the MOE evaluation to estimate mean bioaccessibility values for the CoCs (Table 3-9). The *in vivo* data collected by Jacques Whitford was used to estimate the ROB of nickel (4%). The MOE has identified concerns regarding use of the limited *in vivo* dataset (n=3) to estimate the ROB for nickel.

6.6	Soil	ROB/BA (%)					
CoC	2011	Method	Original HHRA	Updated HHRA			
	Fill	In vitro BA		33			
As	Clay	In vitro BA	36	30			
	Organic	In vitro BA		48			
	Fill	In vitro BA		25			
Со	Clay	In vitro BA	26	21			
	Organic	In vitro BA		35			
	Fill	In vitro BA		35			
Cu	Clay	In vitro BA	36	36			
	Organic	In vitro BA		32			
NE	Fill	In vivo ROB	1	5.8			
Ni	Clay	In vivo ROB	4	9.4			

# Table 3-9:ROB and Bioaccessibility Values used in the Original HHRA and in the<br/>Updated HHRA



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CoC	انوع	ROB/BA (%)				
	Soil	Method Original HHRA Updated HHRA				
	Organic	In vivo ROB		22		

Notes:

BA Bioaccessibility

ROB Relative Oral Bioavailability

As part of this updated HHRA, Vale has conducted additional *in vitro* testing for all CoCs and additional *in vivo* testing for nickel. The goal of this testing was to increase the size of the datasets in order to estimate soil type specific ROB/bioaccessibility for each CoC. When the datasets from the original HHRA are combined with the datasets from the supplemental testing, the *in vivo* datasets for fill, clay and organic have samples sizes of n=6, n=8 and n=7, respectively, while the *in vitro* datasets for the same soil types have sample sizes of n=16, n=13 and n=12, respectively. It is noted that the bioaccessibility datasets include the MOE data. The ROB/bioaccessibility values used in this updated HHRA are based on the averages of these datasets and the values selected for each soil type and CoC are provided in Table 3-9. In general, the values are either comparable to or exceed the values in the original HHRA.

Additional rationale on selection of the ROB/bioaccessibility value for each CoC is provided in Appendix 3E. Appendix 3E also contains a discussion of the bioaccessibility of nickel including the decreasing relationship between soil nickel concentration and bioaccessibility identified for fill soil. The effect of using this relationship on the estimated risk was examined in the Sensitivity Analysis (Section 3.13). Based on the Sensitivity analysis of the bioaccessibility data for nickel that is presented later in Section 3.13, the *in vivo* bioavailability data for nickel was concluded to be adequately supported for use in this updated HHRA.

In the original HHRA, risk estimates for soil exposure were differentiated by location (e.g., Zone D Farm versus Zone D Residential) and soil type (clay versus organic soil); however only one ROB value (i.e., 4% for nickel) was used to adjust ingestion exposure for all soil types. The additional *in vivo* and *in vitro* analyses conducted by Vale as part of this updated HHRA have demonstrated that the ROB of nickel, in particular varies considerably depending on soil type. The ROB of nickel in fill soil of 5.8% is comparable to the previous ROB of nickel of 4%, however the ROBs of clay and organic soils are considerably higher. The use of a single ROB of 4% for clay and organic soils may result in a significant underestimation of the ingestion dose from these soil types. As a result, for this updated HHRA, oral exposure to each CoC in soil was adjusted by the specific ROB/bioaccessibility for the soil type.

# 3.9 EXPOSURE ESTIMATES FOR THE RME SCENARIO

Exposure estimates for the RME scenario are provided in Appendix 3F.

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# 3.10 RISK ESTIMATES FOR RME SCENARIO

The methods and equations used for risk estimates in this updated HHRA are consistent with those used in Volume I, Chapter 6 of the original HHRA (Appendix 1M of this report), with the exception of the risk estimates for carcinogenic compounds. In the original HHRA, risk characterization for carcinogenic compounds included estimates of both incremental lifetime cancer risk (ILCR) and the total lifetime cancer risk (TLCR) and an inhalation exposure ratio. The ILCR was defined as the difference between the cancer risk for an individual exposed to contaminated soil in Port Colborne and an individual exposed to background concentrations. The TLCR was simply the cancer risk for an individual exposed to contaminated soil in Port Colborne that was not adjusted to account for the background risk. In typical risk assessments in Ontario, a consistent approach to background risks is not followed. Risk estimates are typically based on measured concentrations in specific media which may or may not include contributions associated with background (naturally occurring) or other sources. Further correction of the estimated cancer risk due to background exposure is not generally undertaken, though the risk estimate is still identified as an ILCR. In order to satisfy the MOE request, cancer risk estimates have not been corrected for background exposure in the updated HHRA, and are referred-to as ILCR. This is considered a conservative approach as removing the correction for background leads to a higher risk estimate.

For detailed examples of quantitative risk estimates for this HHRA, please refer to Volume I, Chapter 6 and Volume III, Appendix 6 of the original HHRA (provided in Appendix 1 M of this report). All estimated ILCRs and HQs in the following sections have been rounded to two significant figures, as requested by MOE. Notably, the degree of uncertainty in most of the measured concentrations and toxicity values on which the risk estimates are based is plus or minus 30 to 50% or plus or minus an order of magnitude, respectively. Receptor characteristics and other input factors also tend to have large associated uncertainties. The reader is cautioned that the presentation of two significant figures for the computed risk estimates should not be interpreted as providing a greater degree of accuracy as these values are considered estimates and not precisely computed values.

It is noted that inhalation risk related to nickel, arsenic and cobalt in ambient air in Zone B were estimated based on long-term measured concentrations (i.e., maximum annual concentrations), while inhalation risks for copper in Zone B and all CoCs in Zone D were estimated based on modelled concentrations.

# 3.10.1 Results and Discussion

#### 3.10.1.1 Nickel Inhalation

Inhalation exposure to nickel was assessed for both carcinogenic and non-carcinogenic risks. The non-carcinogenic risk (the HQ), was estimated based on the total exposure and is provided in Table 3-10.



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7	R	eceptor
Zone	Toddler	Adult
B (measured air)	0.27	0.24
D - Farm	0.19	0.19
D - Residential	0.19	0.24

#### Table 3-10: Hazard Quotients for Inhalation Exposure to Nickel

The results of the non-cancer risk estimation indicate that the highest estimated risk is 0.27 for the toddler receptor in Zone B. The HQs for all receptors are well below the MOE benchmark of one.

The ILCRs were estimated using the Approach II unit risk (Lepicard, 1997, EC 2001) based on oxidic nickel. For results of the ILCR estimations for nickel inhalation refer to Table 3-11. ILCRs were below the MOE benchmark of 1.0E-06 indicating that potential health risks are not expected.

 Table 3-11:
 Lifetime Cancer Risks for Inhalation Exposure to Nickel

Zone	Cancer Risk Approach II: Oxidic Nickel Unit Risk (Lepicard, 1997 and European Union)
	ILCR
B (measured data)	0.59E-06
D – Farm	0.47E-06
D – Residential	0.55E-06

# 3.10.1.2 Systemic Nickel Intake (Ingestion and Dermal)

The ingestion and dermal dose for nickel was assessed as a threshold, non-carcinogenic response. The ingestion dose is the sum of the doses for all ingestion-related pathways including soil/dust ingestion, drinking water ingestion, surface water ingestion, secondary ingestion after inhalation, supermarket food ingestion and backyard/local food ingestion. HQs were estimated for the total nickel ingestion dose and dermal dose and are provided in Table 3-12.

#### Table 3-12: Hazard Quotient for Nickel Ingestion and Dermal Dose

7	Toddler			Adult		
Zone	Ingestion	Dermal	Total	Ingestion	Dermal	Total
В	0.48	0.019	0.50	0.23	0.0042	0.23
D - Farm, Clay	0.50	0.0088	0.51	0.24	0.0018	0.24



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7000	Toddler			Adult		
Zone	Ingestion	Dermal	Total	Ingestion	Dermal	Total
D – Farm, Organic	0.55	0.019	0.57	0.25	0.0036	0.25
D - Residential	0.48	0.0098	0.49	0.22	0.0017	0.23

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Overall, there is very little difference in the estimated HQs among the various scenarios (Table 3-12). The highest estimated HQ was 0.57 for a toddler receptor in the Zone D Farm area with organic soils. Based on the RME scenario and exposure pathway assumptions adopted in this HHRA, systemic human health risks from ingestion and dermal exposure to nickel in Port Colborne are below the MOE's benchmark HQ of one (MOE 1996; 2002).

# 3.10.1.3 Copper Inhalation

Copper is assessed as a non-carcinogen via the inhalation pathway; HQs based on the total exposure were estimated and are provided in Table 3-13.

#### Table 3-13: Hazard Quotients for Inhalation Exposure to Copper

Zene	R	eceptor
Zone	Toddler	Adult
B (modelled data)	0.0010	0.00093
D - Farm	0.00061	0.00061
D - Residential	0.00061	0.00061

The highest HQ estimated for copper inhalation pathways was 0.0010 for the Zone B toddler, which is well below the acceptable benchmark of one.

# 3.10.1.4 Systemic Copper Intake (Ingestion and Dermal)

For the estimated HQs for total ingestion dose (includes all ingestion routes) and dermal dose of copper, see Table 3-14.

#### Table 3-14: Hazard Quotients for Ingestion and Dermal Dose of Copper

7		Toddler			Adult	
Zone	Ingestion	Dermal	Total	Ingestion	Dermal	Total
В	0.44	9.4E-05	0.44	0.15	1.4E-05	0.15
D - Farm, Clay	0.45	0.00012	0.45	0.15	1.3E-05	0.15
D – Farm, Organic	0.45	0.00020	0.45	0.15	2.1E-05	0.15
D - Residential	0.52	0.00012	0.52	0.18	1.9E-05	0.18



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The highest estimated HQ was 0.52 for the toddler in the Zone D Residential area. Based on the RME scenario and exposure pathway assumptions, human health risks from exposure to copper in Port Colborne are below the benchmark of one.

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# 3.10.1.5 Cobalt Inhalation

The inhalation exposure of cobalt is assessed as a non-carcinogenic effect; HQs were estimated based on total inhalation exposure (see Table 3-15).

Table 3-15:	Hazard Quotients for Inhalation Exposure to Cobalt
-------------	--

7	Rec	eptor
Zone	Toddler	Adult
B (measured data)	0.022	0.019
D - Farm	0.023	0.024
D - Residential	0.023	0.023

A maximum HQ of 0.024 was estimated for the adult in the Zone D-Farm scenario. This HQ value is well below the acceptable benchmark of one.

#### 3.10.1.6 Systemic Cobalt Intake (Ingestion and Dermal)

For the estimated HQs for total ingestion dose (includes all ingestion routes) and dermal dose of cobalt, see Table 3-16.

Table 3-16: Hazard Quotients for Ingestion and Dermal Dose of Cobalt

7.000		Toddler			Adult	
Zone	Ingestion	Dermal	Total	Ingestion	Dermal	Total
В	0.027	0.000038	0.027	0.0081	0.0000058	0.081
D - Farm, Clay	0.030	0.000043	0.030	0.0092	0.0000047	0.0092
D – Farm, Organic	0.032	0.000057	0.032	0.0094	0.000006	0.0094
D - Residential	0.027	0.000047	0.026	0.0080	0.0000049	0.0080

The highest estimated HQ was 0.032 for the toddler receptor in the Zone D Farm area with organic soil. This HQ value is below the acceptable benchmark of one. All of the HQs estimated for cobalt ingestion and dermal exposure were below the threshold effects benchmark of one.

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# 3.10.1.7 Systemic Arsenic Intake (Carcinogenic and non-carcinogenic)

Non-carcinogenic and carcinogenic exposures to arsenic via ingestion and dermal contact were not evaluated in the original HHRA. The reader is referred to Volume I, Section 6.2.4 of the original HHRA (provided in Appendix 1M of this report) for additional information. The conclusions of that section included the following :

- The arsenic data from a variety of media from Port Colborne contained a large number of non-detect samples, such that oral and dermal exposure estimates were found to have an uncertainty that was greater than the computed differences between the zones. This uncertainty was concluded to be too large to reliably estimate exposures or risks due to arsenic in media from Port Colborne.
- Three health studies for arsenic involving bioassays (including arsenic-urine studies) have been conducted in Ontario for the communities of Wawa, Deloro and Falconbridge. Information related to these studies was provided in Volume III, Appendix 7, Attachment B of the original HHRA (provided in Appendix 1M of this report). These communities have historical metal refining activities that are comparable to those in Port Colborne. The health studies for these communities did not identify health effects due to exposure to arsenic that exceeded those that might be expected for the general population. The arsenic concentrations in soil from the Falconbridge study in particular are equivalent to or exceeded the levels identified in Port Colborne. No health effects above background were identified for human receptors in the Falconbridge study, thus, health effects are not expected for residents of Port Colborne.

In their comments on the risk assessment (MOE, 2011- provided in Appendix 3A) the MOE indicated the uncertainty surrounding the sample concentrations was insufficient reason to not undertake a quantitative evaluation of risk due to exposure to arsenic. In addition the MOE noted that the urinary studies from Wawa, Deloro and Falconbridge could not be used to make claims of no health effects due to exposure to arsenic.

In order to address the first of these concerns, a limited quantitative assessment of risk due to ingestion/dermal exposure to arsenic in Port Colborne is provided in this section. Risks for residents of Port Colborne are compared to risks expected for background receptors outside of Port Colborne.

The urinary studies are no longer used here to make health claims about residents of Port Colborne; however these studies do provide context for exposure to arsenic. For instance the largest and most comprehensive of these studies was conducted in the Village of Deloro where the average arsenic concentration in the soil in the community was 111 mg/kg and the maximum reported concentration was 605 mg/kg (MOE, 2002). This study measured arsenic levels in the urine of people in the Deloro community and compared the result to those collected from a control community where the arsenic levels in the soil were not elevated. The



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study found that there was no essential difference in the arsenic concentrations in urine between the two study groups. In addition, the Deloro study found no association between arsenic concentrations in the soil and those in the urine (MOE, 2002). Excretion in the urine is the primary route of elimination of arsenic that has been absorbed into the body, typically accounting for more than 95% of the elimination of absorbed arsenic (ATSDR, 2007). Therefore, the finding that urinary arsenic levels did not differ between residents of Deloro and residents of the control community indicates that arsenic in the soil does not make a measurable contribution to exposure.

To provide comparison to the Deloro study, the average, 95th percentile and maximum concentration of arsenic in surficial soil in Port Colborne (non-detects were considered to be present at the detection limit) are 11.6 mg/kg, 29.8 mg/kg and 213.5 mg/kg, respectively. Based on these concentrations, the concentrations of arsenic in Port Colborne soil are lower than those in Deloro and by extension; the arsenic is soil in Port Colborne is not expected to make a measurable contribution to exposure. The results of the other bioassays (Volume III, Appendix 7, Attachment B of the original HHRA (provided in Appendix 1M of this report)) also suggest that the exposure to arsenic in these communities as well as in Port Colborne are not significantly different than estimated exposures for typical residents of Ontario.

It is noted that in their Rodney Street Report (MOE, 2002) the MOE made a decision to exclude arsenic from the quantitative RA based on the results of the three bioassay studies and concluded the following:

- Wawa: This study did not produce evidence that Wawa residents were at an increased risk of cancer due to exposures to arsenic (MOE, 2002)
- Deloro: Estimated arsenic exposures are not measurably higher than those of typical Ontario residents (MOE 2002)
- Port Hope (Falconbridge): Estimated intakes from contact with these soils yields risk estimates in the range generally considered negligible and below the WHO permissible intake (MOE 2002)

Based on the results of these studies the MOE concluded that it is unlikely that soil arsenic concentrations in Port Colborne will result in increased exposures to Rodney Street community residents (MOE, 2002). The MOE also concluded that measured levels of arsenic in the soil are unlikely to pose an undue health risk to residents of this community based on consideration of (Section 7.2 of MOE, 2002):

- 1) comparison of typical levels found elsewhere in Ontario; and
- 2) knowledge of outcomes of health studies involving arsenic in soil exposure in other Ontario communities where the average and maximum soil arsenic levels were higher than those found in Port Colborne.

3.10.1.7.1 Urinary Arsenic Levels from the Nucrotechnics Rat In vivo Dosing Study

The claim that the arsenic in soil does not contribute significantly to the overall exposure of arsenic is supported by the results of the *in vivo* rat dosing study conducted by Nucrotechnics (on behalf of Vale) in 2013. The rat *in vivo* model has been widely used by researchers to study



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the metabolism of arsenic and its excretion into urine (Adair, 2007; Castellino, 1985; Gegus, 2000; Inoue, 1996, Kenyon, 2005; Ng, 1998; Yoshida, 1997; Yoshida, 1998). In the 2013 Nucrotechnics study, rats were gavaged a single oral dose of Port Colborne soil, which included a range of soil types and arsenic concentrations. Besides the treatment groups, additional control groups were gavaged blank solutions or blank solutions containing food. Rats in both the treatment and control groups were administered a standard lab diet. Arsenic is naturally present in food, and the levels in the standard lab diet are assumed to be comparable to levels in typical human food. Following administration of the soil or control dose, urine and feces were collected daily for 72 hours; the levels in urine are an indication of the absorbed dose (ATSDR, 2007). The measured concentrations provided on the x-axis are the concentrations in the gavaged solution. The actual soil concentrations for the treatment groups are approximately 2.5x the concentrations in the gavaged solutions. For example the soil with the maximum arsenic concentration (i.e., TP6) was 65 mg/kg. It is noted that this concentration exceeds the UCLM concentration of arsenic in Port Colborne of 13.9 mg/kg (Section 3.10.1.7.2).

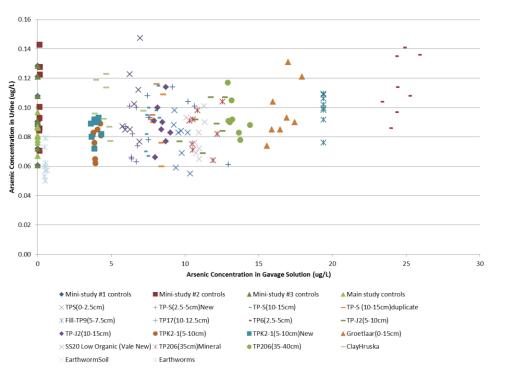
Based on Figure 3-2, the concentration of arsenic in the gavaged dose did not have a significant effect on the concentration of arsenic in the urine. Considering that the concentrations in the control doses (blanks) were orders of magnitude lower than the concentrations in the treatment groups, exposure to arsenic in soil did not have a significant effect on the overall absorbed dose of arsenic. This conclusion is consistent with the conclusions of the community bioassays.

Further details related to the methods and the results of the dosing study are provided in Appendix 2B, Appendix 3C and Appendix 3E.



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Notes:

Concentrations of arsenic in the gavaged solutions are provided in the x-axis. Concentration in soil for the non-control groups are approximately 2.5x the concentrations in the gavaged solution. This multiplication factor includes unit conversion from µg/L to mg/kg.

3.10.1.7.2 Quantitative Evaluation of Systemic Arsenic Risk

Exposure to arsenic in food typically accounts for the majority of overall exposure, regardless of whether the person is in Port Colborne or in a community that does not have a history of metal refining. The typical individual obtains the majority of his/her food from a supermarket. The concentrations in food from supermarkets in Port Colborne are expected to be comparable to the concentrations in food from supermarkets from the surrounding area (e.g., the Niagara area) since supermarkets obtain their food from centralized distribution centers. As a result residents of Port Colborne are assumed to be exposed to similar levels of arsenic as the general population. In order to demonstrate this, the risk model used in this updated HHRA was used to estimate the health risks for three scenarios, which include:

• Exposure to the UCLM concentration of arsenic in Port Colborne soil, which is 13.9 mg/kg based on analysis using the US EPA's Pro UCL software. This value is below the guideline of

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18 mg/kg recommended in MOE (2011b) for residential land use and potable groundwater conditions. For this analysis, the UCLM concentration was assumed to be present in soil throughout Port Colborne.

- Exposure to 11 mg/kg of arsenic in soil, which is the Table 1 (i.e., background) guideline for arsenic in soil for agricultural properties in Ontario. This is the lowest soil quality guideline for arsenic provided in MOE (2011b). This guideline is equivalent to the 98<sup>th</sup> percentile concentration of arsenic in rural parkland soil in Ontario (CCME, 1997). This concentration is less than the 98<sup>th</sup> percentile concentration in old urban parkland in Ontario of 17 mg/kg (CCME, 1997), which is applicable to Port Colborne This scenario represents the estimated risk if concentrations of arsenic in soil throughout Port Colborne were remediated to a level that meets the lowest applicable guideline. This calculation also functions as an estimate of background risk.
- Exposure to arsenic in supermarket food only. For this scenario, the proportion of the food intake from local/backyard food assumed in the other two scenarios was added to the intake for supermarket food. This scenario represents the background risk of the general population due to exposure to arsenic in supermarket food alone.

The non-carcinogenic and carcinogenic risk estimates for these scenarios are provided Table 3-17 and Table 3-18, respectively. The proportion of the arsenic intake from each source is illustrated in Figure 3-3 and Figure 3-4. The following conclusions are made based on this information:

- The calculated non-carcinogenic and carcinogenic risks for each scenario exceed the applicable MOE benchmarks of HQ=1 and ILCR= 1E-06, respectively. The carcinogenic risk in particular is more than three orders of magnitude greater than the benchmark. This finding suggests that if the TRVs for arsenic are accurate then one would expect to find widespread health effects due to arsenic exposure in Port Colborne and the surrounding areas (e.g., the Niagara area), however, this is not the case. This finding makes it difficult to interpret the meaning of these risk estimates;
- The majority of the calculated risks are due to exposure to arsenic in supermarket foods;
- There is only a small difference in the estimated non-carcinogenic risk for Port Colborne residents exposed to the UCLM concentration in soil and a member of the general population that is only exposed to arsenic in supermarket food. There is little to no difference in the carcinogenic risk calculated for someone in Port Colborne and a member of the general population exposed to arsenic in supermarket food only.
- Remediating the arsenic in Port Colborne to the lowest applicable guideline would not significantly change the calculated risk. In fact no amount of soil remediation could achieve and HQ<1 or an ILCR < 1E-06.

These conclusions are consistent with those provided in the Sudbury Area Risk Assessment (SARA) (2008), which was a comprehensive risk assessment of another Ontario community where similar metal refining has occurred and arsenic was one of the CoCs. Overall this evidence supports the conclusion that residents of Port Colborne are not expected to be at greater risk of health effects due to exposure to arsenic than typical Ontario residents.



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#### Table 3-17 Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact with Arsenic- Toddler Receptor

		Risk Scenario	
Zone	RME Scenario (No Modification)	[As] <sub>soil</sub> = 11 mg/kgª	Supermarket Food Only
Zone B	6.0	6.0	5.3
Zone D	6.2	6.0	5.5

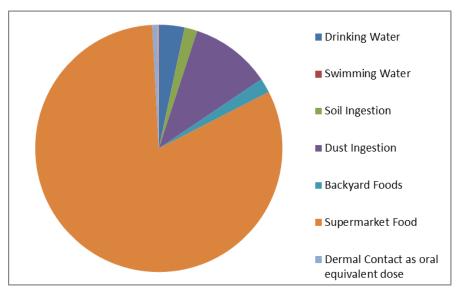
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#### Notes:

<sup>a</sup> Risk estimates completed assuming concentration of arsenic in soil throughout Port Colborne was 11mg/kg which is the MOE's lowest applicable guideline for soil. (Guideline is for Full Depth Background assuming Agricultural Property Use (MOE, 2011b).)

**Bold** Calculated hazard quotient exceeds benchmark of 1.0.

# Figure 3-3 Toddler Arsenic Ingestion - Zone D Organic Farm Receptor- RME Scenario



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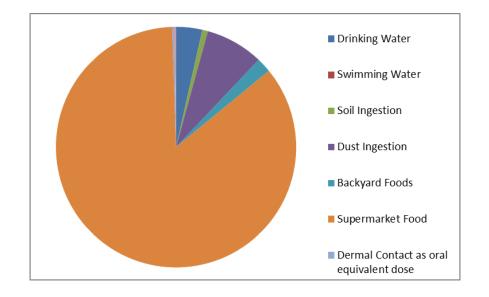


Figure 3-4 Toddler Arsenic Ingestion - Zone D Organic Farm Receptor-11 mg/kg Arsenic throughout Port Colborne

#### Table 3-18 Carcinogenic Risk Estimates for Ingestion/Dermal Contact with Arsenic

Zone	RME Scenario (No Modification)	[As] <sub>soil</sub> = 11 mg/kgª	Supermarket Food Only
Zone B	1.2E-03	1.2E-03	
Zone D	1.3E-03	1.2E-03	1.2E-03

Notes:

<sup>a</sup> Risk estimates completed assuming concentration of arsenic in soil throughout Port Colborne was be 11mg/kg which is the MOE's lowest applicable guideline for soil. Guideline is for Full Depth Background assuming Agricultural Property Use (MOE, 2011b).

Bold Calculated ILCR exceeds benchmark of 1.0E-06

#### 3.10.1.8 Arsenic Inhalation (Non-Carcinogenic Approach)

HQs for inhalation of arsenic associated with non-carcinogenic effects were estimated based on total inhalation exposure (see Table 3-19).

#### Table 3-19: Hazard Quotient for Inhalation Exposure to Arsenic

7	Receptor		
Zone	Toddler	Adult	
B (measured data)	0.097	0.087	
D - Farm	0.16	0.16	



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7000	Receptor		
Zone	Toddler	Adult	
D - Residential	0.16	0.15	

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A maximum HQ of 0.16 was estimated for the toddler in the Zone D area and the adult in the Zone D Farm scenario. This HQ value is well below the acceptable benchmark of one.

# 3.10.1.9 Arsenic Inhalation (Carcinogenic Approach)

The maximum annual measured concentrations of arsenic in Zone B and Zone D, as well as typical background concentrations in Ontario are provided in Table 3-20. Maximum measured and modelled concentrations in ambient air in Zone B and D respectively are within the range of typical background concentrations in Ontario. Carcinogenic risk estimates were completed for a lifetime receptor in Zone B and Zone D (Table 3-20). Carcinogenic risk estimates representative of the range of background exposures were also conducted using the model and assuming that the receptor was in Zone B, but was exposed to typical Ontario ambient air concentrations. For these scenarios the indoor air concentration was estimated as 0.6x the concentration in ambient air.

ILCRs calculated for all scenarios exceeded the benchmark of 1.0E-06. The ILCRs calculated for Zone B and Zone D were in the range of those estimated based on typical concentrations in Ontario. As a result, residents of Port Colborne are not expected to be at greater risk of carcinogenic inhalation effects due to exposure to arsenic than a typical resident in Ontario.

Table 3-20	ILCR for Inhalation Exposures to Arsenic
------------	--

Zone	Statistic	Concentration in Ambient Air (µg/m³)°	ILCR
В	Maximum measured	0.00374	1.2E-05
D	Maximum modelled	0.00811	2.4E-05
Typical 24 hour Ontario Air Concentrations (PM10) from Environment Canada (MOE, 2002)ª	Minimum	0.003a	9.2E-06 <sup>b</sup>
	Maximum	0.02a	6.10E-05 <sup>b</sup>
	Average	0.002a	6.10E-06 <sup>b</sup>

Notes:

**Bold** Calculated ILCR exceeds benchmark of 1.0E-06



<sup>&</sup>lt;sup>a</sup> Data reproduced from Volume I Table 6-10 of the original HHRA, provided in Appendix 1M of this report.

<sup>&</sup>lt;sup>b</sup> Calculations conducted based on a receptor in Zone B exposed to identified ambient concentrations in all outdoor locations.

Concentration in indoor air was assumed to be 0.6x concentration in ambient air.

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# 3.10.2 Summary of Risk Characterization for RME Concentrations of All CoCs

#### 3.10.2.1 Non Cancer Risks

See Table 3-21 for the highest HQs estimated in Port Colborne for the RME concentration scenarios. With the exception of ingestion of arsenic, none of the estimated HQs exceed the MOE recommended benchmark of one. The HQ for the ingestion of arsenic was comparable to that estimated for a background receptor outside of Port Colborne.

Chemical	Exposure Route	Hazard Quotient (HQ)	Zone	Receptor
Nickel	Inhalation	0.27	Zone B	Toddler
	Ingestion/Dermal	0.57	Zone D Farm Organic	Toddler
Commer	Inhalation	0.0010	Zone B	Toddler
Copper	Ingestion/Dermal	0.52	Zone D-Res	Toddler
Cobalt	Inhalation	0.024	Zone D-Res	Adult
	Ingestion/Dermal	0.032	Zone D Farm Organic	Toddler
Arsenic	Inhalation	0.16	Zone D Farm Toddler/Adult	Toddler/Adult
	Ingestion/Dermal	6.2	Zone D Farm Organic	Toddler

Table 3-21: Maximum Estimated Hazard Quotients

#### 3.10.2.2 Cancer Risks

The estimated cancer risks for nickel inhalation were concluded to be below the MOE benchmark of one in one million. The estimated cancer risks for arsenic inhalation were concluded to lie in the range of arsenic risks calculated for a typical Ontario resident.

#### Table 3-22: Maximum Estimated Incremental Lifetime Cancer Risks

Chemical	Exposure Route	Zone of Maximum ILCR	Slope Factor	ILCR
Nickel	Inhalation (Lifetime)	Zone B (measured air concentrations)	Approach II: Oxidic Nickel (European Commission)	5.9E-07
Arsenic	Inhalation (Lifetime)	Zone D (modelled air concentrations	4.3 (mg/m <sup>3</sup> ) <sup>-1</sup>	2.4E-05

Notes:

Risk estimates completed assuming concentration of arsenic in soil throughout Port Colborne was be 11 mg/kg



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which is the MOE's lowest applicable guideline for soil. Guideline is for Full Depth Background assuming Agricultural Property Use (MOE, 2011b). Bold Calculated hazard quotient exceeds benchmark of 1.0.

#### 3.10.3 Summary of the Risk Estimates for the RME Scenario

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The risks estimated for RME exposures are considered representative of typical residents of Port Colborne and are within the range considered acceptable by MOE. Overall, no adverse effects to human health are expected for most people living in, working in, or visiting Port Colborne.

This evaluation does not account for potential maximally exposed individuals where specific characteristics of their homes, properties, or contaminants on their properties might result in exposures higher than those that are typical for most residents; these potential maximally exposed individuals are investigated in Section 3.11.

# 3.11 RISK ESTIMATES FOR MAXIMUM EXPOSURE SCENARIO

#### 3.11.1 Introduction

Consistent with the approach in the original HHRA (Volume I, Chapter 7- provided in Appendix 1M of this report) seven scenarios of maximally exposed individuals, exposed to maximum CoC concentrations in one or more particular sampled media and to RME CoC concentrations in all other remaining exposure media (except where noted) were selected for evaluation. These maximum exposure scenarios included:

- Maximum soil CoC concentrations (any depth);
- Maximum home for nickel in indoor dust;
- Maximum garden produce CoC concentrations combined with maximum soil CoC concentrations in gardens (any depth);
- Maximum well water CoC concentrations;
- Maximum home for nickel in drinking water;
- Maximum location ambient air CoC concentrations and correspondingly higher indoor air CoC concentrations;
- Maximum home indoor air CoC concentrations based on short term measurements.

In each case, the risk estimated for the maximum scenario is compared to the risk estimated for the RME scenario. The risk values for the maximum scenario have changed from the original HHRA due to the changes in input assumptions, bioavailability values, and TRVs, as discussed previously.

# 3.11.2 Maximum Concentrations in Soil at Any Sample Depth

For each of the four exposure scenarios (i.e., Zone B, Zone D Farm Clay, Zone D Farm Organic and Zone D Residential), the maximally exposed individual was evaluated for exposure to the maximum soil concentration for each land use. This approach is considered conservative as it



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assumes that the resident is exposed to the maximum soil CoC concentrations in all activities (e.g., home, work, gardening, play, etc.).

Maximum soil concentrations were adopted from the dataset provided in Volume V, Appendix 20 of the original HHRA provided in Appendix 1M of this report). RME and maximum CoC concentrations measured at all sampled depths, as presented in Table 3-23, were used in the maximum concentrations in soil scenario. Overall these concentrations are consistent with the maximum concentrations provided in the original HHRA for each Zone and land use (Volume I, Chapter 7, Table 7-1- provided in Appendix 1M of this report). However, risk estimates for this revised maximum exposure scenario include specific adjustments for ROB/bioaccessibility for different soil types. The relevant soil types for each scenario and land use as well as the corresponding maximum concentration in soil are provided in Table 3-23.



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		Concentration of CoCs in Soil, All Sample Depths (mg/kg)						(g) <sup>b</sup>
Zonec	Soil Type / Location	Soil type	Nickel		Copper		Cobalt Page	
			RME	Maximum	RME	Maximum	RME	Maximum
	Residential	Fill	2500	17,000	260	2,700	39	260
	Recreational	Fill	1300	9,300	120	720	23	180
В	Work (Zone B and D residential receptors)	Fill	410	16,000	770	8,400	20	270
	Garden	Fill	1100	6,700	228	570	37	100
C (school zone)	School (all Zone B, D receptors)°	Clay	240	240	11	11	15	15
D (all)	Beach (all Zone B, D receptors)	Sand	240	240	11	11	15	15
	Recreational woodlot scenario ; all Zone B, D receptors)	Organic	1900	33,000 °	730	3,900	88	430
	Residential	Clay	620	5,900	94	710	19	120
D-Farm, Clay	Work (on Farm)	Clay	620	5,900	94	710	19	120
	Garden	Clay	435	2,700	81	360	13	54
	Residential	Organic	2300	5,900	380	710	38	120
D-Farm, Organic	Work (on Farm)	Organic	2300	5,900	380	710	38	120
	Garden	Organic	435	2,700	81	360	13	54
D Posidont d	Residential	Clay	780	3900	100	360	24	74
D-Resident d	Garden	Clay	435	2,700	81	360	13	54

### Table 3-23: Maximum Concentrations of CoCs in Soil at All Sample Depths, by Zone and Land Use.

Notes:

• This concentration was measured in organic soils in the Reuter Road woodlot during CBRA tree study. The woodlot is fenced off from the general public, thus exposure to this area is expected to be minimal.

<sup>b</sup> Since 24 properties were remediated to 8,000 mg Ni/kg soil after the sampling campaigns took place, the current maxima may be less than those shown here.

c All Zone B and D receptors attend schools in Zone C and visit the beach in Zone D.

<sup>d</sup> Zone D non-farm receptor was assumed to work in Zone B.

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Consistent with the original HHRA, this maximum soil concentration scenario does not account for potential increased concentrations of CoCs in garden produce that may occur simultaneously in relationship to increased soil concentrations. Based on Section 1.3, Appendix 3B, CoC concentrations in soils were poorly predictive of the concentration in garden produce, thus actual measured concentrations in garden produce are considered the more reliable and appropriate measure of maximum receptor exposures. For this reason, maximum measured garden produce and their corresponding soil concentrations are evaluated in an additional scenario, detailed in Section 3.11.4.

The estimated risk from exposure to the maximum soil concentrations for nickel, copper and cobalt at all sample depths, as well as the predicted risks based on the RME concentrations, are presented in Table 3-24 through Table 3-26.

	Toddler I	Receptor	Adult Receptor		
Zone	HQ, Based on RME Nickel Concentration	HQ, Based on Maximum Nickel Concentration	HQ, Based on RME Nickel Concentration	HQ, Based on Maximum Nickel Concentration	
В	0.51	0.74	0.23	0.28	
D – Farm, Clay	0.51	0.94	0.24	0.30	
D – Farm, Organic	0.57	1.0	0.25	0.32	
D – Resident	0.49	0.88	0.23	0.29	

### Table 3-24: Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on Exposure to Maximum Concentrations of Nickel in Soil.

The use of maximum nickel soil concentrations had a more substantial effect on the ingestion/dermal HQ for Zone D receptors than for Zone B receptors. This large change for toddlers in Zone D is due to the change in concentration in recreational soil from 1,900 mg/kg nickel in the RME scenario to 33,000 mg/kg nickel in the maximum scenario. Recreational soil (excluding beach soil) is assumed to be organic, which has the highest ROB for nickel of all soil types. The change was less drastic for the adult receptor because the adult is assumed to consume less soil per unit of bodyweight than the toddler receptor. All HQs in Table 3-24 show an acceptable risk.

Ingestion/dermal exposure to the maximum concentrations of copper in soil did not result in an appreciable increase in HQs compared to exposure to RME concentrations (Table 3-25). This is due to the lower soil concentrations of copper in comparison to nickel and the fact that the dietary intake of copper has a larger proportional influence on the overall ingestion/dermal dose than the dietary intake of nickel.

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## Table 3-25:Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on<br/>Exposure to Maximum Concentrations of Copper in Soil.

	Toddler	Receptor	Adult Receptor		
Zone	HQ, Based on RME Copper Concentration	HQ, Based on Maximum Copper Concentration	HQ, Based on RME Copper Concentration	HQ, Based on Maximum Copper Concentration	
В	0.44	0.50	0.15	0.16	
D – Farm, Clay	0.45	0.47	0.15	0.16	
D – Farm, Organic	0.45	0.46	0.15	0.16	
D – Resident	0.52	0.53	0.18	0.18	

Ingestion/dermal exposure of a toddler receptor to the maximum concentrations of cobalt in soil results in moderately higher HQs than a toddler exposed to RME concentrations via the same pathways (Table 3-26).

## Table 3-26:Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on<br/>Exposure to Maximum Concentrations of Cobalt in Soil.

	Toddler I	Receptor	Adult Receptor		
Zone	HQ, Based on RME Cobalt Concentration in Soil	RME Cobalt Concentration in Concentration in		HQ, Based on Maximum Cobalt Concentration in Soil	
В	0.028	0.038	0.0084	0.0094	
D – Farm, Clay	0.030	0.036	0.0092	0.0096	
D – Farm, Organic	0.032	0.039	0.0094	0.010	
D – Resident	0.026	0.030	0.0080	0.0085	

All HQs predicted for the maximum soil concentration scenario are either equivalent to or below the MOE benchmark of one, thus no elevated risks are expected for receptors exposed to maximum soil concentrations under the scenarios evaluated.

### 3.11.3 Residence with Maximum Nickel Concentration in Indoor Dust

A maximally exposed individual was evaluated for exposure to the maximum measured concentration of nickel in house dust from the gravimetric samples collected as part of the Indoor Air and Dust study of 30 houses in Port Colborne (Volume II, Appendix 1.7 of the original HHRA-provided in Appendix 1M of this report). The highest measured concentration of nickel in

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dust was 775 mg/kg. This sample was collected from a house in Zone B. The maximally exposed individual was assumed to be exposed to this maximum concentration in dust, as well as the concentration in soil of 625 mg/kg reported for the co-located soil sample. The data provided in Table 3-27 indicate that exposure of a receptor to maximum nickel concentrations in dust and concurrent exposure to the measured concentration in the co-located soil sample does not result in a substantial change in estimated risk in comparison to the RME exposure scenario.

# Table 3-27Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on<br/>Exposure to Maximum Measured Concentrations of Nickel in Dust and<br/>Measured Concentration of Nickel co-located Soil.

	Toddler R	eceptor	Adult Receptor		
Zone	HQ, Based on RME Nickel Concentration	HQ, Based on Maximum Nickel Concentration	HQ, Based on RME Nickel Concentration	HQ, Based on Maximum Nickel Concentration	
В	0.51	0.49	0.23	0.23	

### 3.11.4 Maximum Garden Produce Concentrations

The sensitivity of the ingestion/dermal HQ to maximum garden produce CoC concentrations and concurrent maximum concentration in garden soil was examined. The maximum home fruit and vegetable concentrations, as measured in the garden produce sampling program for each Zone, were adopted for receptors. As discussed in Section 3.5.3 the garden produce datasets for Zone B were combined with the datasets from Zone A and C in order to generate larger overall datasets.

Zone D contains multiple soil types (e.g. organic, clay, sand). However, in an effort to be conservative, the maximum concentrations of CoCs in all garden soils in Zone D have been adopted for all scenarios in Zone D, irrespective of soil type. This is consistent with the approach in the original HHRA.

The maximum garden produce concentrations scenario was seen as a conservative approach as it assumes that the maximum fruit and vegetable concentrations occur at the same location, though this was not generally observed in the garden produce study. The resulting maximum vegetable and fruit concentrations as measured in each zone are presented in Table 3-28.



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Zone	CoC	Concentration in Fruits (mg/kg)		Concentration in Vegetables (mg/kg)		Concentration in Garden Soils (mg/kg)		
		RME	Maximum	RME	Maximum	RME	Maximum	Page   3.5
	Со	0.037ª	0.037	0.006	0.054	37	37	
Ba	Cυ	1.0	1.9	0.720	2.1	228	180	
	Ni	0.53	2.2	0.450	4.1	1100	6700	
	Со	0.0088	0.051	0.0058	0.26	13	54	
D	Cυ	0.82	2.1	0.78	2.9	81	360	
	Ni	0.32	2.7	0.37	6.4	435	2700	

## Table 3-28:Maximum Concentrations of Nickel, Copper and Cobalt in GardenVegetable and Fruit Samples and Garden Soil.

Notes:

RME concentration based on UCLGM of 31 samples (0.12 mg/kg) exceeded the maximum concentration (0.037 mg/kg). The maximum concentration was adopted as the RME concentration.

The resulting HQs estimated based on exposure to the RME or maximum concentrations of nickel, copper and cobalt in garden produce and concurrent exposure to RME or maximum concentrations of nickel, copper and cobalt in garden soil are presented in Table 3-29, Table 3-30 and Table 3-31.

# Table 3-29:Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on<br/>Exposure to Maximum Concentrations of Nickel in Garden Produce and<br/>Maximum Concentration of Nickel in Garden Soil.

	Toddler I	Receptor	Adult Receptor		
Zone	HQ, based on RME Nickel Concentrations in Garden Produce and Garden Soil	HQ, based on Maximum Nickel Concentrations in Garden Produce and Garden Soil	HQ, based on RME Nickel Concentrations in Garden Produce and Garden Soil	HQ, based on Maximum Nickel Concentrations in Garden Produce and Garden Soil	
В	0.51	0.60	0.23	0.41	
D Farm- Clay	0.51	0.96	0.24	0.67	
D Farm- Organic	0.57	1.0	0.25	0.68	
D Residential	0.49	0.75	0.23	0.47	

The maximum HQ for ingestion/dermal exposure of a toddler to the maximum concentration of nickel in garden produce (concurrently with the maximum concentration of nickel in garden soil) was 1.0 for the toddler in the Zone D Farm Organic scenario (Table 3-29). Adverse health effects are not expected for these exposure scenarios.



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The difference between the RME concentration exposure scenario and the maximum garden produce concentration exposure scenario is lowest for Zone B, which also has the lowest estimated HQs. The lower HQs for Zone B are related to the lower bioaccessibility of the fill soil in comparison to clay and organic soil and the proportion of produce assumed to come from backyard gardens, which is lower for the Zone B receptor than for the Zone D receptor. For example, based on the site-specific food basket survey, the fraction of intake of fruits and vegetables from backyard gardens for a toddler in Zone D are approximately 5% and 23%, respectively, while for a toddler in Zone B the values are approximately 3% and 15%, respectively.

The data provided in Table 3-30 indicate that exposure of a receptor to maximum copper concentrations in garden produce and concurrent exposure to maximum garden soil copper concentrations does not result in a substantial increase in estimated risk in comparison to the RME exposure scenario.

Table 3-30:	Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on
	Exposure to Maximum Concentrations of Copper in Garden Produce and
	Maximum Concentration of Copper in Garden Soil.

	Toddler	Receptor	Adult Receptor		
Zone	HQ, based on RME Copper Concentrations in Garden Produce and Garden Soil HQ, based on Maximum Copper Concentrations in Garden Produce and Garden Soil		HQ, based on RME Copper Concentrations in Garden Produce and Garden Soil	HQ, based on Maximum Copper Concentrations in Garden Produce and Garden Soil	
В	0.44	0.46	0.15	0.16	
D Farm-Clay	0.45	0.48	0.15	0.17	
D Farm- Organic	0.45	0.48	0.15	0.17	
D Residential	0.52	0.54	0.18	0.19	

The data provided in Table 3-31 indicate that exposure of a receptor to maximum cobalt concentrations in garden produce and concurrent exposure to maximum garden soil cobalt concentrations does result in an increase in estimated risk in comparison to the RME exposure scenarios. The changes are larger for the Zone D scenarios as receptors in these scenarios are assumed to obtain a larger proportion of their produce intake from backyard produce than receptors in Zone B. Regardless, the resulting HQ values indicate that no elevated risk is expected for receptors exposed to the maximum cobalt concentrations in garden produce and concurrent exposure to the maximum cobalt concentrations in garden soil.



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Table 3-31:Non-Carcinogenic Risk Estimates for Ingestion/dermal Contact based on<br/>Exposure to Maximum Concentrations of Cobalt in Garden Produce and<br/>Maximum Concentration of Cobalt in Garden Soil.

	Toddler R	eceptor	Adult Receptor		
Zone	HQ, based on RME Cobalt Concentrations in Garden Produce and Garden Soil	HQ, based on Maximum Cobalt Concentrations in Garden Produce and Garden Soil	HQ, based on RME Cobalt Concentrations in Garden Produce and Garden Soil	HQ, based on Maximum Cobalt Concentrations in Garden Produce and Garden Soil	
В	0.028	0.028	0.084	0.0088	
D Farm-Clay	0.030	0.041	0.0092	0.016	
D Farm- Organic	0.032	0.043	0.0094	0.016	
D Resident	0.026	0.033	0.0080	0.012	

HQs estimated for exposure to maximum CoC concentrations in garden produce and concurrent exposure to maximum CoC concentrations in garden soil are less than the MOE benchmark of one, thus adverse effects on health are not anticipated.

### 3.11.5 Maximum Drinking Water Concentrations

The effects on the ingestion/ dermal HQs as a result of the concentrations of CoCs in drinking water were examined. Zone B is serviced by a municipal drinking water system; consistent with the approach in the original HHRA, variation in municipal concentration is not considered significant and Zone B is not addressed in this maximum drinking water concentrations scenario analysis.

The focus of this maximum drinking water concentration scenario is on concentrations of CoCs in drinking water samples collected from drilled wells and dug wells in Zone D and their impact on the HQs estimated for receptors from Zone D. The maximum concentration of CoCs as measured in drilled and dug wells in Port Colborne are presented in Volume I, Chapter 3, Table 3-11 in Appendix 1M of this report. Detailed information related to concentrations of CoCs in well water from Zone D is provided in Volume V, Appendix 15 of the original HHRA (provided in Appendix 1M of this report). The resulting HQs for exposure to the maximum well water concentrations of nickel, copper, and cobalt for the Zone D receptors are presented in Table 3-33, Table 3-34 and Table 3-35.

## Table 3-32:RME and Maximum Concentration of Nickel, Copper and Cobalt in<br/>Drinking Water in Drilled and Dug Wells in Zone D

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Medium	Concentrations of Chemicals of Potential Concern in Drinking Water from Drilled and Dug Wells (mg/L)						
	Cobalt		Co	opper	Nickel		
	RME	Maximum	RME	Maximum	RME	Maximum	
Drilled Wells (Zone D Farm)	0.0022	0.035	0.059	0.76	0.0080	0.076	
Dug Wells (Zone D Residential)	0.0003	0.0012	0.196	0.84	0.0049	0.017	

# Table 3-33:Non-Carcinogenic Risk Estimates for Ingestion/ Dermal contact based on<br/>Exposure of the Zone D Receptor to Maximum Concentrations of Nickel in<br/>Drinking Water

	Toddler Receptor		Adult Receptor		
Zone	HQ, Based on RME Nickel Concentration in Drinking Water	HQ, Based on Maximum Nickel Concentration in Drinking Water	HQ, Based on RME Nickel Concentration in Drinking Water	HQ, Based on Maximum Nickel Concentration in Drinking Water	
D – Farm Clayª	0.51	0.73	0.24	0.37	
D – Farm Organicª	0.57	0.79	0.25	0.38	
D – Residential <sup>b</sup>	0.49	0.53	0.23	0.25	

Notes:

<sup>a</sup> Based on maximum drilled well nickel concentrations

<sup>b</sup> Based on maximum dug well nickel concentrations

The data provided in Table 3-33 toTable 3-34 reveal that the well water concentrations may have a significant impact on the estimated HQs for nickel, copper and cobalt, respectively; however, the estimated HQ values are below the MOE benchmark of one, indicating that adverse effects to human health are not expected under this maximum drinking water concentrations scenario.



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### Table 3-34 : Non-Carcinogenic Risk Estimates for Ingestion/ Dermal contact based on Exposure of the Zone D Receptor to Maximum Concentrations of Copper in Drinking Water

Toddler		Receptor	Adult Receptor		
Zone	HQ, based on RMEHQ, based onCopperMaximum CoppConcentrations inConcentration iDrinking WaterDrinking Water		HQ, based on RME Copper Concentrations in Drinking Water	HQ, based on Maximum Copper Concentrations in Drinking Water	
D – Farm Clayª	0.45	0.80	0.15	0.27	
D – Farm Organicª	0.45	0.80	0.15	0.27	
D – Residential <sup>b</sup>	0.52	0.85	0.18	0.28	

Notes:

<sup>a</sup> Based on maximum drilled well copper concentrations

<sup>b</sup> Based on maximum dug well copper concentrations

# Table 3-35:Non-Carcinogenic Risk Estimates for Ingestion/ Dermal contact based on<br/>Exposure of the Zone D Receptor to Maximum Concentrations of Cobalt in<br/>Drinking Water

	Toddler I	Receptor	Adult Receptor		
Zone	HQ, based on RMEHQ, based onCobaltMaximum CobConcentrationsConcentration		HQ, based on RME Cobalt Concentrations	HQ, based on Maximum Cobalt Concentrations	
D – Farm Clayª	0.030	0.10	0.0092	0.032	
D – Farm Organicª	0.032	0.10	0.0094	0.032	
D – Residential <sup>b</sup>	0.026	0.028	0.0080	0.0086	

Notes:

b

Based on maximum drilled well cobalt concentration.

Based on maximum dug well cobalt concentration.

### 3.11.6 Residence with Highest Nickel in Well Water

Results of the maximum scenarios evaluated for drinking water concentrations and garden produce concentrations suggest that if concentrations in both of these media were maximized at the same time, the total hazard quotient to the Zone D Farm area toddler would be representative of maximum exposure. For this assessment, one home was selected as having a measured well water nickel concentration above all other homes measured. Of note for this particular home was the condition of the well reported by MOE as not meeting proper well construction standards and thus a candidate for well contamination. This home is therefore expected to be atypical, and similar conditions are unlikely to be found at other homes. The data for the particular home is consistent with data previously provided in Volume I, Section 7.4.1 of the original HHRA (provided in Appendix 1M of this report).



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Well and tap water from this home were only sampled by the MOE, but no samples of soil or garden produce from that same home were collected by the MOE. A nearby home (Site 526) was sampled for both soil and produce. For the maximum case evaluation, the maximum of the measured drinking water concentrations at this home (MOE site), and the maximum concentrations of each of garden fruits, vegetables and soil from the nearby residence (Site 526) were selected, as summarized in Table 3-36. Review of well water and garden produce concentrations indicated that the combination of these parameters selected for this home was expected to result in the highest potential exposure of nickel to residents.

AA o diumo	Selected Nickel Concentrations		
Medium	Value	Units	
Well Water	.076	mg/L	
Fruits	0.076	mg/kg	
Vegetables	0.88	mg/kg	
Soil	302	mg/kg	

### Table 3-36: Home with Highest Nickel Concentrations in Well Water

The resulting HQ for the toddler in this home (MOE site) with maximum concentrations from all environmental media is 0.75, indicating that adverse effects to the most sensitive receptor at this home using maximum concentrations are not expected.

### 3.11.7 Maximum Modelled Ambient Air Concentration

As part of the risk characterization for maximally exposed individuals, the effects on the inhalation HQ as a result of varying air concentrations of CoCs in different locations in the community were examined. More specifically, maximum concentrations of the CoCs in ambient air were used instead of the RME concentrations in order to determine the effect on the risk estimates.

In the original HHRA, the maximum modelled concentrations in ambient air were identified in Zone B; maximum concentrations in Zone B were adopted as maximum concentrations for risk estimates for all other zones (including Zone D). The approach for evaluating this scenario has changed from the original risk assessment in two ways:

• Long-term measured data has been used where available to estimate maximum annual averages in ambient air. Measured data is available for arsenic, cobalt and nickel in Zone B; and

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• The maximum yearly concentrations of CoCs in ambient air for Zone D are based on modelled data from that Zone.

The ambient air concentrations selected for use in the maximum ambient air concentrations scenario are presented in Table 3-37.

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### Table 3-37: Maximum Concentrations of Nickel, Copper, and Cobalt in Ambient Air

_	Selected Concentrations (µg/m³)					
Zone	Nickel Copper Cobalt				obalt	
	RME	Maximum	RME	Maximum	RME	Maximum
B (measured air)	0.020	0.020	NA	NA	0.0028	0.0028
B (modelled air)	NA	NA	0.0032	0.0034	NA	NA
D (modelled air)	0.015	0.019	0.0020	0.0029	0.0031	0.0038

Notes:

NA Not Applicable

Consistent with the approach for the RME scenario, receptors are assumed to move freely among the Zones, and thus, depending on the particular activity (e.g., home, school, beach, etc.), may be exposed to the maximum concentrations in ambient air in multiple Zones. The same time activity patterns used for risk estimates in the RME scenario were also used for risk estimates in the maximum scenario. Since indoor air concentrations were evaluated as being proportional to ambient air, these were also increased accordingly for this maximum ambient air concentrations scenario.

Nickel inhalation cancer risk estimates for receptors exposed to maximum concentrations of CoCs in indoor air are provided in Table 3-38.

# Table 3-38:Carcinogenic Risk Estimates for Inhalation of Maximum Modelled Nickel<br/>Concentration in Ambient Air, Approach II: European Union, Oxidic Nickel<br/>Unit Risk

		ILCRs
Zone	Based on RME Nickel Concentrations	Based on Maximum Nickel Concentrations
B (measured air)	5.9E-07	5.9E-07
D – Farm	4.7E-07	4.7E-07
D – Residential	5.5E-07	5.6E-07

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Based on the results presented in Table 3-38, exposure to the maximum concentrations of nickel in ambient air does not result in a significant increase in the ILCRs. This is expected as the concentrations under the RME scenario are comparable to the concentrations for the maximum scenario. The ILCRs for nickel exposure for receptors in both Zone B and Zone D are below the risk threshold of 1.0E-06, indicating that carcinogenic health effects are not expected.

Nickel inhalation HQs based on nickel as nickel sulphate are provided in Table 3-39. There is very little variation between the HQs for the RME scenario and HQs for the maximum scenario, which reflects the small variation in nickel concentration between the two scenarios (Table 3-39). All HQs are below the benchmark of one indicating that exposure to maximum concentrations of nickel in ambient air is not expected to result in non-carcinogenic health risks.

## Table 3-39: Non-Carcinogenic Risk Estimates for Inhalation Exposure to Maximum Concentrations of Nickel in Ambient Air

Toddler Receptor			Adult Receptor		
Zone	HQ, Based on RME Concentrations of Nickel	HQ, Based on Maximum Concentrations of Nickel	HQ, Based on RME Concentrations of Nickel	HQ, Based on Maximum Concentrations of Nickel	
B (measured air)	0.27	0.27	0.24	0.24	
D – Farm	0.19	0.24	0.19	0.24	
D – Resident	0.19	0.24	0.24	0.29	

Table 3-40 and Table 3-41 provide comparisons of HQs for copper and cobalt, respectively, for RME and maximum concentrations. All resulting HQs are below the target benchmark of one.

### Table 3-40:Non-Carcinogenic Risk Estimates for Inhalation Exposure to Maximum<br/>Modelled Concentrations of Copper in Ambient Air

Toddler Receptor		Adult Receptor		
Zone	HQ, Based on RME Copper Concentration	HQ, Based on Maximum Copper Concentration	HQ, Based on RME Copper Concentration	HQ, Based on Maximum Copper Concentration
B (modelled air)	0.0010	0.0011	0.00093	0.0010
D – Farm	0.00061	0.00089	0.00061	0.00089
D – Resident	0.00061	0.00089	0.00061	0.00084



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### Table 3-41: Non-Carcinogenic Risk Estimates for Inhalation Exposure to Maximum Concentrations of Cobalt in Ambient Air

	Toddler Receptor		Adult R		
Zone	HQ, Based on RME Cobalt Concentration	HQ, Based on Maximum Cobalt Concentration	HQ, Based on RME Cobalt Concentration	HQ, Based on Maximum Cobalt Concentration	Page   3.59
B (measured air)	0.022	0.022	0.019	0.019	
D – Farm	0.023	0.029	0.024	0.029	
D – Resident	0.023	0.029	0.030	0.035	

Overall, the results of the assessment of maximum ambient air concentrations indicate that inhalation health risks associated with the highest evaluated maximum ambient air concentrations (*i.e.*, highest location) are not expected.

### 3.11.8 Maximum Indoor Air Concentrations

Changes to risk estimates as a result of the maximum concentrations of CoCs in indoor air were examined in this section. The indoor air nickel concentrations adopted for the maximum indoor air concentrations scenario analysis are presented in Table 3-42. As discussed in Section 3.5.6 data from IAS 102 was excluded from this assessment.

Risk estimates for cobalt and copper were conducted for receptors in Zone B and Zone D, assuming that the receptors in these Zones were exposure to the single highest concentration of the CoC, measured in indoor air. Conversely, risk estimates for nickel were conducted assuming a Zone B receptor is exposed to one of the two highest concentrations in indoor air, which were both in houses located in Zone B. Consistent with the approach in the original HHRA, ambient air concentrations are assumed to be those used in the RME scenario.

### 3.11.8.1 Nickel

Two scenarios were run for the highest indoor air nickel concentrations measured in Port Colborne. The two highest indoor air nickel concentrations were input into the exposure spreadsheets; outlier data were not considered. Zone B was conservatively chosen as the base case for comparison due to the highest indoor air concentrations being measured in Zone B. The maximum measured concentrations of nickel in indoor air are provided in Table 3-42.

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### Table 3-42: Maximum Concentration of Nickel in Indoor Air PM<sub>10</sub> Samples Measured in Port Colborne (Outliers not included)

Zone	CoC	Maximum Concentration (μg/m³)
B, Highest Value	Nickel	0.023 1
B, Second Highest Value	Nickel	0.00822

Note:

1. Average of two 24-hour samples

2. Single 24-hour sample

The resulting HQs and lifetime cancer risk, based on the maximum concentrations of nickel in indoor air as well as the RME concentrations are presented in Table 3-43 and Table 3-44. For these scenarios risk has been estimated based on exposure to the maximum measured concentrations of nickel in indoor air and RME concentration of nickel in ambient air based on measured data.

## Table 3-43:Non-Carcinogenic Risk Estimates for Inhalation Exposure to Maximum<br/>Concentrations of Nickel in Indoor Air

Ambient Air Assumptions	Indoor Air Assumptions	Concentration			
	-	Toddler	Adult	Toddler	Adult
Measured Air	B, Highest Measured Value	0.07	0.24	0.36	0.35
	B, Second Highest Measured Value	0.27	0.24	0.23	0.19

HQ based on both the highest and second highest concentrations were below the benchmark of 1.0. It is noted that the predicted risks for the second highest home are lower than the risk for the RME scenario, as the concentrations predicted under the RME scenario based on a mean indoor/outdoor ratio of 0.6 for PM<sub>10</sub> are higher than the measured concentrations in Table 3-42.



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# Table 3-44:Carcinogenic Risk Estimates for Inhalation Exposure to the Maximum<br/>Concentrations of Nickel in Indoor Air, Approach II: European Union,<br/>Oxidic Nickel Unit Risk

		ILCRs	
Ambient Air Assumptions	Zone	Based on RME Concentration	Based on Maximum Concentration
Measured Air	B, Highest Value		0.84E-06
B, Second Highest Value		0.59E-06	0.49E-06

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ILCR based on the highest and second highest concentrations in indoor air and measured concentrations in ambient air were below the benchmark of 1.0E-06, indicating that health risks related to inhalation of nickel are not expected.

### 3.11.8.2 Copper and Cobalt

Maximum indoor air concentrations of copper and cobalt were selected and applied for each specific Zone. Table 3-45 summarizes copper and cobalt concentrations chosen for the maximum scenario analysis.

Table 3-45: Maximum	Indoor Air	<b>Concentrations o</b>	f Copper and Cobalt
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Zone	CoC	Maximum Concentration (µg/m³)
D	Copper	0.0021
В	Cobalt	0.00168
5	Copper	0.0017
U	Cobalt	0.0023

Variation of HQs for copper with indoor air concentrations are provided in Table 3-46.



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		Rece	ptors			
	Todo	ller	A	Adult		
Zone	HQ Based on RME Copper Concentration HQ, Based on Maximum Copper Concentration		HQ Based on RME Copper Concentration	HQ, Based on Maximum Copper Concentration		
В	0.0010	0.0011	0.00093	0.0097		
D – Farm	0.00061	0.00074	0.00061	0.00074		
D – Resident	0.00061	0.00074	0.00069	0.00083		

## Table 3-46: Non-Carcinogenic Risk Estimates for Inhalation Exposure to the Maximum Concentrations of Copper in Indoor Air

Table 3-47 summarizes the variation of HQs for cobalt with indoor air concentrations. All resulting HQs in both Table 3-46 and Table 3-47 are below the benchmark of one.

## Table 3-47: Non-Carcinogenic Risk Estimates for Inhalation Exposure to the Maximum Concentrations of Cobalt in Indoor Air

	Receptor								
	Tode	dler	Ad	ult					
Zone	HQ Based on RME Cobalt Concentration	Cobalt Maximum Cobalt		HQ, Based on Maximum Cobalt Concentration					
В	0.022ª	0.022ª	0.019ª	0.019ª					
D – Farm	0.023	0.026	0.024	0.026					
D – Resident	0.023	0.026	0.038	0.040					

Since HQs are below the applicable benchmark of one, no adverse health effects from copper or cobalt are expected to residents of the homes with maximum measured indoor air concentrations.

### 3.11.9 Summary of the Risk Estimates for the Maximum Scenarios

Risk estimates based on exposure to maximum CoC concentration in media did not result in unacceptable risk.

Additional factors that may affect the outcome of the assessment that were not specifically evaluated as maximum scenarios, are considered further in the Sensitivity Analysis that follows in Section 3.13.

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### 3.12 RBSC ESTIMATES

The approach for deriving RBSCs in this updated HHRA is generally consistent with the approach in the original HHRA however the values of the RBSC have changed due to modifications to the input parameters, ROB/bioaccessibility and TRV selection. These modifications are discussed below. The reader should refer to Volume I, Chapter 9 of the original HHRA (provided in Appendix 1M of this report) for detailed information on the derivation of the RBSC.

In the original HHRA the maximum concentration in garden produce was used to derive the RBSC based on an HQ of one. For the updated HHRA, the 90<sup>th</sup> percentile concentrations in garden produce are used to estimate the RBSCs. For further rationale for the selection of the 90<sup>th</sup> percentile as an appropriate statistic, refer to Section 3.5.3. The equations and model used for the derivation of the RBSCs are identical to those used for the RME and maximum scenarios. An iterative solution was used to achieve the target HQ of one while changing the assumed soil concentration for all areas within a Zone until the desired HQ was achieved.

Key modifications that have been carried through the RBSC derivation and are discussed in previous report sections include:

- Reanalysis of garden produce data to pool Zones A, B and C and provide a more robust data set for application to Zone B analyses;
- Reanalysis of representative background concentrations of the CoCs in supermarket foods by using a more robust statistical approach and combining data from Health Canada for food groups with small data sets;
- Use of soil type specific nickel ROBs derived using additional *in vivo* testing of Port Colborne soils. These soil type specific ROBs are used to estimate soil-type specific RBSCs in this updated HHRA;
- Use of soil type specific cobalt and copper bioaccessibility estimates derived using additional *in vitro* testing of Port Colborne soils; and,
- Use of alternate oral/dermal TRVs selected for nickel and cobalt.

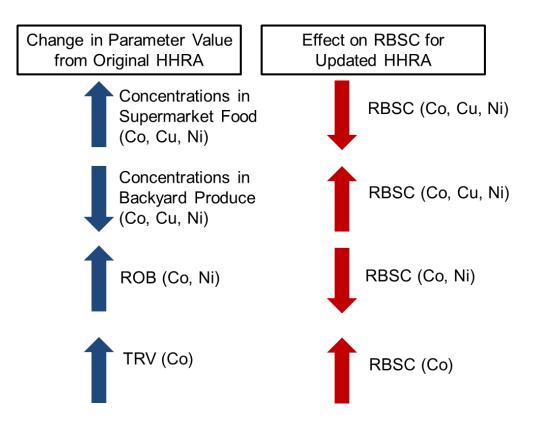
The major changes in this updated HHRA and their effect on the RBSC derivation are summarized in Figure 3-5. The affected CoCs are identified in brackets. Note that a decrease in the RBSC is a more conservative outcome.



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Figure 3-5: Effects of Modifying Parameter values on the RBSC Derivation for Updated HHRA



Notes:

- Blue Arrows Indicates how the parameter value has changed from the original HHRA. An upward arrow indicates an increase since the original HRHA, while a downward arrow indicates a decrease.
- (Co, Ni) Indicates the relevant CoCs to which the indicated change in parameter value applies.

### 3.12.1 Systemic Nickel

For each Zone and soil type scenario, all soil concentrations were started at the same value, which was varied until a target HQ of one was obtained for the toddler life stage, based on the reference dose (RfD) of 0.02 mg/kg-day (Ambrose, 1976). The toddler was the most sensitive life stage. The endpoint of the toxicity study was reduced weight gain, which is considered a relevant endpoint for assessing non-carcinogenic health risks related to a toddler ingesting soil. For target soil nickel concentration for each of the scenarios considered in this assessment, refer to Table 3-48. An example calculation for the derivation of the RBSC for nickel is provided in Appendix 3G.

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			RBSC	: (mg/kg)	Full Depth: Zone/Soil type	
Zone	Receptor	Major Soil Type	Original HHRA	Updated HHRA (current	Maximum Measured Concentrations (mg/kg)	Page   3.65
				approach)	(119/kg)	1 uge   3.03
В	Toddler	Fill	60,000	48,000	17,000	
D Farm Clay	Toddler	Clay	20,000	20,500	<b>33,000ª</b> organic woodlot 5,900 <sup>b</sup> residential/farm	
D Farm Organic	Toddler	Organic	20,000	11,900	<b>33,000ª</b> organic woodlot 5,900 <sup>b</sup> residential/farm	
D Residential	Toddler	Sand	40,000	24,000	<b>33,000ª</b> organic woodlot 3,900 <sup>b</sup> residential	

### Table 3-48: Risk-Based Soil Concentrations for Nickel

Notes:

<sup>a</sup> Sample located in Vale owned woodlot, none of which is farmed.

<sup>b</sup> Maximum concentration outside of the woodlot.

The variation in RBSCs among the various scenarios is primarily attributed to the ROB/bioaccessibility of the major soil type in that scenario. The highest estimated RBSC is for Zone B, which contains fill soil. The higher RBSC for fill soil is due to the lower ROB of fill soil (i.e. 5.8%) compared to the ROB of clay and organic soils of 9.4% and 22%, respectively. Zone D contains both clay soil and organic soil; organic soil has the higher ROB, which results in the Zone D Farm Organic scenario having a lower target than the Zone D Farm Clay scenario. The Zone D Residential scenario contains sand as the primary soil type, but the ROB is assumed to be that of clay.

Based on the information provided in Table 3-48, the maximum measured concentration of fill soil in Zone B of 17000 mg/kg is below the RBSC of 48,000 in Zone B (i.e., for fill soil). The maximum concentration of nickel in soil in Zone D of 33,000 mg/kg, which is in the Vale Inco Ltd. (Inco) owned woodlot exceeds the RBSCs for Zone D. This woodlot is adjacent to the Inco lands and not readily accessible to the public. Direct and prolonged exposure of toddlers to the woodlot soils is considered highly unlikely, since they are not currently residential and are fenced and signed to prohibit public entry. This localized area would not be considered suitable for residential development unless concentrations were reduced. The soil type specific maximum concentrations of nickel in soil for the various scenarios are lower than the predicted RBSCs for each scenario, suggesting that the proposed soil-type and Zone specific RBSC do not violate the current conditions in Port Colborne. Remediation of the Vale woodlot is not considered and signed to minimize public access.

### 3.12.2 Copper

For each Zone and soil type scenario, soil concentrations were given the same value, which was varied until a target HQ of one was obtained for the most sensitive life stage (i.e., the toddler),

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based on the Toxicity Reference Value (TRV) of 0.13 mg/kg-day. For the copper soil concentrations corresponding to target HQs of one for the toddler receptor, see Table 3-49.

Zone	Receptor	Major Soil Type	Estimated Copper RBSC (mg/kg)	Full Depth: Zone Maximum Measured Concentrations (mg/kg)
В	Toddler	Fill	19,600	8,400
D Farm (Clay)	Toddler	Clay	18,500	3,900ª organic woodlot
D Farm (Organic)	Toddler	Organic	20,500	3,900ª organic woodlot
D Residential	Toddler	Sand	14,500	3,900ª organic woodlot

### Table 3-49: Risk-Based Soil Concentrations for Copper

Notes:

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Sample located in Vale owned woodlot exceeds all Zone D soils outside the woodlot.

The lowest (most stringent) RBSC value is for the residential area of Zone D. The differences among the scenarios are primarily due to the concentration of copper in drinking water, which vary significantly. Zone D Residential receptors were evaluated as obtaining their drinking water from dug wells, where the selected RME concentration for copper was 0.20 mg/L. Zone D Farm receptors were assumed to obtain their drinking water from drilled wells, where the selected RME concentration selected for municipal water in Zone B was 0.022 mg/L. Copper bioaccessibilities for fill, clay and organic soil were 35%, 36% and 32%, respectively. Since the bioaccessibility of copper does not vary appreciably among the different soil types, it is only a minor contributor to the differences identified in Table 3-49.

The RBSCs estimated for copper are at least two fold higher than the respective concentrations in soil for each specific Zone and soil type scenario; therefore, no health risks are expected based on the highest concentrations of copper in soil present in Port Colborne.

### 3.12.3 Cobalt

The toddler receptor was selected as the most sensitive receptor for the derivation of the cobalt RBSC based on a target HQ of one.

For each zone and soil type scenario, all soil concentrations were given the same value, which was varied until a target HQ of one was obtained for the toddler life stage based on the TRV of 0.030 mg/kg-day. The resulting RBSCs for cobalt in soil are provided in Table 3-50.



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Zone	Receptor	Major Soil Type	Estimated Cobalt RBSC (mg/kg)	Full Depth: Zone Maximum Measured Concentrations (mg/kg)	age   3.67
В	Toddler	Fill	18500	270	ago   0.0/
D Farm (Clay)	Toddler	Clay	22000	430ª organic woodlot 120 <sup>b</sup> residential/farm	
D Farm (Organic)	Toddler	Organic	13400	430ª organic woodlot 120 <sup>b</sup> residential/farm	
D Residential	Toddler	Sandy Soil	17800	430ª organic woodlot 74 <sup>b</sup> residential	

### Table 3-50: Risk-Based Soil Concentrations for Cobalt

<u>Notes:</u>

<sup>a</sup> Sample located in Vale owned woodlot

Maximum concentration outside of the woodlot.

The variation in RBSCs among the various scenarios is primarily attributed to the ROB/bioaccessibility of the major soil type in that scenario. For instance, the major soil types in Zone B, Zone D Farm Clay and Zone D Residential are fill, clay and sand (assumed to be fill like), respectively. Cobalt bioaccessibilities of fill and clay are fairly close at 25% and 21%, respectively, and as a result the RBSC for the Zone B, Zone D Farm Clay and Zone D Residential scenarios are comparable. On the other hand, the bioaccessibility of the organic soil of 35% is significantly higher than the bioaccessibilities of cobalt in fill or clay soil, resulting in a lower RBSC for the toddler receptor in a Zone D Farm Organic area.

The most conservative RBSC for a toddler recommended based on this supplemental analysis is 13400 mg/kg. The RBSC exceeds the RBSC of 10000 mg/kg estimated in the original HHRA due to the higher TRV adopted in this HHRA.

The RBSCs estimated for cobalt are at an order of magnitude higher than the respective concentrations in soil for each specific Zone and soil type scenario; therefore, no health risks are expected based on the highest concentrations of cobalt in soil present in Port Colborne.

### 3.12.4 Arsenic

Based on the information presented in Section 3.10.1.8, ingestion/dermal risk due to exposure to arsenic for residents of Port Colborne is comparable to risk estimated for background receptors (typical residents of Ontario). The majority of the calculated risk is due to exposure to arsenic in supermarket food. Carcinogenic and non-carcinogenic health risks for Port Colborne receptors and background receptors were estimated to be far greater than regulatory benchmarks of ILCR=1.0E-06 or HQ =1. In addition it was concluded that no amount of soil remediation could reduce risk estimates to regulatory levels. As a result, RBSC were not estimated for arsenic.

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### 3.13 SENSITIVITY ANALYSIS

Based on comments from MOE and other updates considered in this updated HHRA, several aspects of the risk assessment were identified for further review of the input parameters or assumptions made in the assessment. Each of these assumptions was reviewed for its potential to significantly impact on the results or conclusions of the risk assessment. Table 3-51 summarizes the various assumptions considered in this updated HHRA and summarizes the selection of scenarios for further (quantitative) evaluation.

Numerous additional assumptions made in the original HHRA were evaluated in Volume 1, Section 8.5 of the original HHRA (provided in Appendix 1M of this report). If the sensitivity of the model to the assumption in question is not expected to have changed significantly from the original HHRA, then they were not re-evaluated. Assumptions that were assessed in the original HHRA, but have been modified in the updated HHRA include the effects of going to school in Zone D, the evaluation of nickel contact dermatitis and the evaluation of a pica child. These assumptions are re-evaluated in this section.

This sensitivity analyses also functions as an uncertainty analysis as it incorporates an evaluation of the effect of the various assumptions on the outcome of the risk assessment. Based on the results provided in Table 3-51, the conclusions of the risk assessment are not affected by the assumption of uncertainty.



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### Table 3-51: Selection of Scenarios for Further Evaluation in the Sensitivity Analysis.

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion	 Page   3.69
		Problem Formulation a	Ind Site Characterizatio	on			
Soil concentrations assumed to be applicable while on vacation were based on Zone F in the original HHRA. The MOE commented that the basis of the assumed concentrations, namely 98 <sup>th</sup> percentile concentrations of typical Ontario concentrations (OTR <sub>98</sub> ) may overestimate background and may not be appropriate.	Because these concentrations contribute to the total exposure, the higher values are considered conservative.	The assumption is conservative, tends to overestimate exposures and risks, and does not alter the assessment conclusions. No further analysis is proposed.	NA	NA	NA	Assessment outcome not affected by assumption of uncertainty.	
At the time that the original HHRA was conducted, there	In the future, a school could operate in Zone D	Perform quantitative assessment of youth attending school in	Nickel HQ, child, Zone D organic soil, RME scenario	HQ = 0.31	HQ = 0.31	Assessment conclusions not affected by	
were no schools operating in Zone D. Zone B and D residents were	and may be attended by Zone D residents. The effect of this assumption is	Zone D.	Nickel HQ, teen, Zone D organic soil, RME scenario	HQ = 0.19	HQ = 0.19	assumption of uncertainty	
assumed to go to school in Zone C.	unknown.		Cobalt HQ, child, Zone D organic soil, RME scenario,	HQ = 0.018	HQ = 0.018		

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion
			Cobalt HQ, teen, Zone D organic soil, RME scenario,	HQ = 0.011	HQ = 0.011	
			Nickel RBSC, Zone D organic soil	RBSC = 11,900	RBSC = 11,900	
The indoor air concentration is based on a ratio to ambient air. The assessment uses a	oncentration is ased on a ratio to mbient air. Thesensitivity analysis using a ratio of 1 instead of 0.6 to testassessment. Note that the maximum and RBSC scenarios	Nickel inhalation HQ, toddler, Zone B, RME scenario	HQ = 0.27 (measured air)	HQ = 0.34 (measured air)	Assessment conclusions not affected by assumption of uncertainty	
ratio of 0.6.	assumption.		Nickel inhalation ILCR, Zone B, RME scenario	ILCR = 0.59 x 10 <sup>-6</sup> (measured air)	ILCR = 0.82 x 10 <sup>-6</sup> (measured air)	Uncertainty
The indoor settled dust concentration is based on a ratio to outdoor soil. The ratio varies for different CoCs but is 0.2 for nickel. Other CoCs have ratios greater	MOE requested a sensitivity analysis using a ratio of 0.39. The assumptions used for arsenic, cobalt and copper are more conservative. The	The ratio may have a significant effect on indoor settled dust concentrations of nickel. Perform quantitative assessment for nickel. The	Ni HQ, toddler, Zone B	HQ = 0.50	HQ = 0.51	The uncertainty has a minor effect on the numerical results. The assessment conclusions are not affected by the assumption
than or equal to 1, suggesting that indoor sources are more significant than outdoor soil.	assumption used for nickel is less conservative.	assumption is conservative for other CoCs and the comment does not alter the assessment conclusions. No further analysis is	Ni HQ, toddler, Zone D organic soil	HQ = 0.57	HQ = 0.59	of uncertainty.

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion	
		proposed for CoCs other than nickel.	Ni RBSC, Zone D organic soil	RBSC = 11,900	RBSC = 9,750		Page   3.
Drinking water concentrations for Zone B (and previously evaluated Zones A, C and E) are based on samples from within the distribution system and at the tap. Zone D samples include both tap and well samples, as per MOE sampling protocols.	The effect of the non-tap samples on the results for copper is unknown. Since the database includes both tap and non- tap samples, a sensitivity analysis using the maximum measured concentrations would bracket the range of potential impacts of this assumption.	Perform Zone B sensitivity analysis based on maximum measured concentrations. Sensitivity analysis for Zone D included in original HHRA does not require redoing.	Cu HQ, toddler, Zone B	HQ = 0.44	HQ = 0.73	The uncertainty has a noticeable effect on the numerical results. The assessment conclusions are not affected by the assumption of uncertainty.	
The MOE raised questions about the Port Colborne supermarket data. The previous HHRA used averages of Port Colborne specific data. The current HHRA combined some	The statistical approach used differs from the manner in which dietary intake is usually evaluated, namely using averages.	Conduct quantitative evaluation using average concentrations instead of UCLMs and 75 <sup>th</sup> percentiles.	Nickel HQ, toddler, Zone D organic soil	HQ = 0.57	HQ = 0.43	The uncertainty has a noticeable effect on the numerical results. The resulting HQ is less conservative indicating that the assessment conclusions are	

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion
datasets with Health Canada data and selected averages of those data sets. For the other data sets, alternate (higher, more conservative) statistics were used.			Nickel RBSC, Zone D, organic soil	RBSC = 11,900	RBSC = 15,700	not affected by the assumption of uncertainty.
		Exposure	Assessment			
The assessment uses a combined soil and dust ingestion rate of	The MOE (2011a) recommends a combined soil and dust ingestion rate of	Perform quantitative assessment of uncertainty.	Nickel HQ, toddler, Zone D organic soil, RME	HQ = 0.57	HQ = 0.63	The uncertainty has a noticeable effect on the numerical results.
110 mg/day based on US EPA recommendations, supported by more	200 mg/day.	Nickel RBSC, Zone B	RBSC = 48,000	RBSC = 27,000	The assessment conclusions are not affected by	
recent publications.			Nickel RBSC, Zone D organic soil	RBSC = 11,900	RBSC = 8,100 (this value is lower than the maximum concentration outside the woodlot- see Section 3.12.1)	the assumption of uncertainty.
The quantitative assessment does not consider a child with pica.	The US EPA (2011) provides a short term soil pica exposure for 1000 mg/day. They note that this is appropriate for	Perform quantitative sensitivity analysis of acute soil ingestion rate of 1000 mg/day. Estimate toddler's HQ for this acute	Nickel HQ, toddler, Zone B	HQ = 0.50	HQ = 0.81	The uncertainty affects the numerical results. HQ>1 was estimated for the toddler in Zone D

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion	
	evaluation of an acute exposure scenario. No acute nickel ingestion TRV is available for the evaluation of this scenario.	exposure using chronic TRV of 0.020 mg/kg-day. Assume dust intake remains at 60 mg/day.	Nickel HQ, toddler, Zone D organic soil (most sensitive soil ingestion scenario)	HQ = 0.57	HQ = 1.7	with soil pica behaviour, however the validity of these results are questionable due to risk for this acute exposure being estimated using exposure frequencies and a TRV more reflective of chronic exposure. Actual risks are likely overestimated and when this is considered along with the infrequent nature of soil pica behavior, health risks in Port Colborne are not expected (Comment 35, Appendix 3A).	Page   3.73
		Toxicity A	Assessment				
The updated HHRA uses a nickel oral non-cancer TRV	The Springborn (2000a,b) TRV was not corrected for	Perform quantitative assessment of uncertainty of TRV	Nickel HQ, adult, Springborn TRV, Zone B, RME	HQ = 0.23	HQ= 0.19	The results indicate that the use of the TRV	

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion
based on Springborn (2000a,b) (0.011 mg/kg-day) for assessment of an	(2000a,b)         (0.011         food         (Section 1.1.3.2, Appendix 3C).         (2000a,b)	based on Springborn (2000a,b) that has been corrected for background nickel	Nickel HQ, adult, Springborn TRV, Zone D organic soil	HQ = 0.25	HQ= 0.21	corrected for background would yield a less conservative
adult of reproductive age.	nickel in food is incorporated into the derivation of the TRV, the TRV becomes 0.013 mg/kg-day.	background nickel levels in food. Conduct calculations for both the RME scenario (Zone B and D) and the Maximum garden Scenario (Zone D only). This latter scenario for Zone D is the most conservative scenario for soil ingestion.	Nickel HQ, adult, Springborn TRV, Zone D organic soil, maximum garden scenario	HQ = 0.68	HQ= 0.57	RBSC.
The updated HHRA uses a nickel oral non-cancer TRV based on Ambrose, 1976, (0.020 mg/kg- day) for assessment of a general	An alternate TRV of 0.012 mg/kg-day has also been proposed based on a drinking water study conducted by Neilsen et al. (1999).	Perform quantitative assessment of uncertainty of TRV based on Nielsen et al (1999) for both a toddler and an adult. It is noted that	Nickel HQ, toddler, Neilsen TRV: Zone B, RME	HQ = 0.49	HQ = 0.11	The results indicate that the use of the TRV based on Neilsen (1999) would yield a less conservative
receptor (toddler is the most sensitive).	a general Neilsen et al. (1999). adult. It is noted that eptor (toddler is This TRV applies to all since the TRV was	Nickel HQ, toddler, Neilsen TRV, Zone D organic soil, RME	HQ = 0.57	HQ = 0.17	RBSC due to bioavailability assumptions for this specific scenario.	

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion			
		much higher than in food or soil. As a result the relative bioavailability of nickel used in the risk estimate was adjusted to 5% for food and 26% in water.	Nickel HQ, toddler, Nielsen TRV, Zone D organic soil, maximum garden scenario	HQ = 1.0	HQ = 0.26		Page   3.7		
The updated HHRA uses a cobalt oral non-cancer TRV based on Finley,	The MOE recommends an oral TRV for cobalt of 0.001 mg/kg-day	Perform quantitative assessment of uncertainty of TRV of 0.001 mg/kg-day	Cobalt HQ, toddler, MOE TRV, Zone B, RME	HQ=0.027	HQ=0.8	The results indicate that use of the MOE TRV has a substantial effect on the estimated risk, but would not change the conclusions for the RME scenario as HQ was less than one.	indicate that use of the MOE TRV has a substantial effect on the estimated risk, but would not change the conclusions for the RME scenario as HQ was less	indicate that use of the MOE TRV has a substantial effect on the estimated risk, but would not change the conclusions for the RME scenario as HQ was less	-
2012, (0.030 mg/kg- day) for assessment of a general receptor (toddler is the most sensitive).	based on production of polycythemia in humans.	recommended by the MOE. Conduct calculations for the RME scenario (Zone B and D). Risk estimates were completed for the sensitive receptor (i.e., the toddler)	Cobalt HQ, toddler, MOE TRV, Zone D organic soil, RME (most sensitive RME scenario for ingestion)	HQ=0.032	HQ=0.96				estimated risk, but would not change the conclusions for the RME scenario as HQ was less
The updated HHRA uses a nickel oral non-cancer TRV based on Springborn (2000a,b) which has reproductive	ses a nickel oral on-cancer TRV ased on Springborn 2000a,b) which has	Perform a quantitative assessment of uncertainty of the developmental receptor (adult female of reproductive age) using the nickel oral TRV. Conduct	Nickel HQ, adult female, Springborn (2000a,b) TRV Zone B, RME	HQ=0.23	HQ=0.26	The results indicate that health effects are not expected for the adult female			
endpoints. This TRV was used to evaluate ingestion exposure for the for			Nickel HQ, adult female, Springborn TRV, Zone D organic soil, RME	HQ=0.25	HQ=0.28	developmental receptor exposed to nickel.			

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion
assessment of the generic adult of reproductive age.		calculations for both the RME scenario (Zone B and D) and the Maximum garden Scenario (Zone D only). This latter scenario for Zone D is the most conservative scenario for soil ingestion. The body weight (63.1 kg) and skin surface area (total of 16750 cm <sup>2</sup> ) of the adult female was used for risk estimates. Receptors were assumed to be present in Port Colborne throughout the year which satisfies the requirement for assessing continuous exposure for the developmental receptor (MOE, 2011a).	Nickel HQ, adult female, Springborn(2000a,b) TRV, Zone D organic soil, maximum garden	HQ=0.68	HQ=0.76	

Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion	
The nickel relative oral bioavailability used in the updated HHRA is based on recent <i>in vivo</i> rat studies. The MOE previously requested that the results of earlier <i>in vitro</i> studies be used for assessing this parameter.	The <i>in vivo</i> studies are considered the gold standard for this type of investigation; however, like all other approaches, they have inherent uncertainties. The MOE <i>in vitro</i> data was combined with Jacques Whitford data (see Appendix 3E) for fill soils, for which a large database exists. Statistical	Use the <i>in vitro</i> bioaccessibility equation relating to soil in a quantitative sensitivity analysis. (ROB% = -9.8 ln [Ni] (soil) +101) In this sensitivity analysis, the upper confidence limit on the equation was selected for estimating bioaccessibility.	ng to ative sis. per t on as	in UU Si O C W	The results indicate that the uncertainty has a significant effect on the conclusions and would yield a less conservative RBSC.	Page   3.77	
	methods were used to derive an empirical relationship between nickel bioaccessibility and fill soil concentration.		Nickel RBSC, Zone B	RBSC = 48,000	RBSC = 225,000		

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Assumption	Discussion	Recommendation	Parameter	Previous Result	Result of Sensitivity Analysis	Conclusion
		Risk Char	acterization			
Nickel contact dermatitis was identified as a potential health outcome from direct contact exposure to soil.	Methods for assessing this endpoint are not well developed.	Evaluation nickel contact dermatitis.	See Appendix 3H for detailed evaluation.	NA	HQs ranging from 0.001 to 1 with maximum HQ for scenario of Zone B toddler/child playing in mud. The Zone D woodlot scenario resulted in an HQ of 3, however this scenario was excluded as it was determined to be highly improbable.	The assessment conclusions are not affected by the assumption of uncertainty.

Notes:

<sup>a</sup> Risk estimate includes both ingestion and dermal exposure.

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### 3.14 CONCLUSIONS

A number of modifications were made to the HHRA approach based on comments by the MOE and through consideration of new science. These included the following:

- Changes to the approach to dust ingestion;
- Re-evaluation of dietary intakes includes supermarket foods and backyard produce;
- Changes to the approach for interpreting ambient air modeling and monitoring results within the assessment;
- Changes to the toxic reference value (TRV) selection for the cobalt and nickel oral RfDs and the nickel inhalation cancer TRV;
- Expansion of, and revision to the evaluation of dermal exposure to nickel including nickel contact dermatitis and absorption both into the bloodstream and into the skin;
- Inclusion of new nickel bioavailability data and CoC bioaccessibility data; and,
- Conduct of additional sensitivity analyses.

Revised risk estimates were completed for the RME and Maximum Scenarios:

- All hazard quotients were less than or equal to the MOE benchmark of 1.0 applicable to a multimedia pathway assessment. Although consumer products were not specifically included in the quantitative exposure assessment, a qualitative assessment previously concluded that this was not expected to be a significant contributor to exposure or risk and would not be expected to impact on the results or conclusions of the risk assessment;
- Estimated cancer risks for arsenic inhalation were below the MOE benchmark of one in one million;

RBSCs were developed for cobalt, copper and nickel in soil for Zones B and D, including soil type specific values as summarized below:

Zone	Nickel (mg/kg)	Copper (mg/kg)	Cobalt (mg/kg)	
Zone B (fill soil)	48,000	21,000	18500	
Zone D (farm, clay soil)	20,500	20,500	22000	
Zone D (farm, organic soil)	11,900	22,500	13400	
Zone D non-farm (not organic soil)	24,000	17,800	17800	

### Table 3-52 RBSC for Specific Zones and Soil Types.

The RBSCs notably do not cover every possible contingency for soil type, although the Zone D Farm exposure scenarios are considered to be conservative. Exposure scenarios for other soil

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types would result in lower risk estimates, as the highest bioavailability and soil concentrations were measured for the organic soils in Zone D. The Zone D Farm Organic risk estimates would therefore result in a more conservative RBSC than for the other soil types within and around Port Colborne.

The only exceedances of the soil type specific RBSC is for nickel in a woodlot owned by Vale (in Zone D). As long as this woodlot remains fenced and signed to limit trespassing, remediation is not considered warranted.

A supplemental sensitivity analysis on the results of the risk assessment indicated that modification of some of the assumptions would have a significant effect on the numerical results; however, these modifications did not affect the conclusions of the assessment. Overall, the sensitivity analysis results indicate that the RBSCs are sufficiently robust for application to Port Colborne soils.



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Port Colborne Community-Based Risk Assessment 2014 Update Report Chapter 4 - Natural Environment Risk Assessment

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Prepared for: Vale Limited

Prepared by: Stantec Consulting Ltd. Suite 1 – 70 Southgate Drive Guelph, ON N1G 4P5

September 12, 2014

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# **Abbreviations**

ADD	Average Daily Dose
BCF	Bioaccumulation factor
BSAF	Biota-Sediment Accumulation Factors
CBRA	Community-Based Risk Assessment
CCME	Canadian Council of Ministers of the Environment
CEPA	Canadian Environmental Protection Act
CoC	Chemical of Concern
COSEWIC	Committee On the Status of Endangered Wildlife In Canada
dw	dry weight
EC	Environment Canada
EPC	Exposure Point Concentration
ERA	Ecological Risk Assessment
HQ	Hazard Quotient
LOAEL	Lowest Observed Adverse Effects Level
LOE	lines of evidence
MOE	Ontario Ministry of the Environment
MECC	Ministry of the Environment and Climate Change
NOAEL	No Observed Adverse Effects Level
PEL	Probable Effect Level
SARA	Species At Risk Act
SedQG	Sediment Quality Guideline
SW	Surface Water
TDI	Total Daily Intake
TOC	Total Organic Carbon
TRV	Toxicity Reference Value
UCLM	Upper Confidence Limit of the Mean
UF	Uptake Factor
USEPA	United States Environmental Protection Agency
USEPA EcoSSL	USEPA Ecological Soil Screening Level
VEC	Valued Ecological Component
WOE	Weight Of Evidence
ww	wet weight



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# 4.0 CHAPTER 4 NATURAL ENVIRONMENT RISK ASSESSMENT

# 4.1 INTRODUCTION

Vale (formerly Inco) commissioned a Community Based Risk Assessment (CBRA) that was completed by Jacques Whitford Ltd. in 2004 (Jacques Whitford Ltd., 2004). One component of the CBRA was to undertake an Ecological Risk Assessment (ERA) to determine if historical emissions from the refinery present an unacceptable risk to the natural environment of the Port Colborne area. The ERA is provided in its entirely in Appendix 1J of the CBRA Update Report and was comprised of five volumes.

Volume I was the primary document, detailing the findings and results of the ERA. The other four volumes are appendices that presented supporting documentation, including technical information for the exposure assessment and risk characterization, additional support studies, data collection protocols, and raw data for field and laboratory sample analyses. For a comprehensive technical review of the original ERA – Natural Environment, the reader should consult all five volumes of the report in Appendix 1J of the 2004 CBRA.

The main ERA report (Volume I in Appendix 1J of this Update Report) also included four appendices (Appendices A-D) that addressed peer review comments, public comments, the PLC's Independent Consultant's comments, and maps (Appendix D).

In May, 2011, the Ontario Ministry of Environment (MOE) provided review comments, identified issues of concern, and requested clarification of specific aspects of the ERA (refer to Appendix 4A of this Report). The focus of this report is to provide a brief synopsis of the ERA from 2004 and then to resolve the outstanding issues related to the ERA component of the Port Colborne CBRA, as identified by the MOE review.

#### 4.1.1 Ecological Risk Assessment objectives and scope

The primary objective of the ERA completed in 2004 was to determine if historical emissions of CoCs from the refinery and deposited in soil present an unacceptable risk to the natural environment of the Port Colborne area. An unacceptable risk was defined as an estimated risk linked to the occurrence of soil concentrations of CoCs that would prevent sustainable population(s) of flora and fauna, or a sustainable level of ecological functioning within the defined Study Area.

Specific objectives of the study were to:

• Identify receptors (species or species groups, communities, habitats) that allowed for an assessment as to whether soil CoCs represent a risk to the natural environment within the defined Study Area;



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- Undertake an assessment of risk that is based on the integration of three lines of investigation:
   1) qualitative assessment of the natural environment, 2) quantitative statistical analysis of study area data and 3) quantitative exposure and risk assessment;
- Determine ecological risk at a population level for ecological receptors found within the Study Area;
- Determine if any potential risks associated with CoCs are different for the major soil types (clay and organic) and habitat types (woodlots and fields) found in the Study Area; and,
- Determine "safe" (acceptable) soil CoC concentrations for the soil types (clay and organic) and habitat types (field and woodlot) if an unacceptable risk were found to occur.

The ERA focused on the natural environment; human-influenced environments such as parks, playgrounds, gardens and residential yards were not considered. Livestock or pets were also not considered as receptors for the original ERA. However, a number of mammalian species that were identified as receptors for the assessment of risk, such as the fox, could be considered to represent conservative surrogates for pets such as dogs and cats.

Initially, only the terrestrial environment had been included for the screening of ecological conditions and potential effects of CoCs. However, as the study progressed, inland water bodies (ponds) and watercourses (municipal drains) were included in the scope of work. This was in direct response to the PLC's concern for aquatic receptors such as amphibians. Although the shoreline of Lake Erie lies within the Study Area, the near-shore aquatic environment did not fall within the scope of the ERA.

Lands associated with the Inco Port Colborne Refinery that were identified within the site's Closure Plan, approximately 120 ha, were also excluded from the ERA's Scope of Work. The environmental management of these lands is pursuant to the requirements of the Mining Act of Ontario and is outside of the CBRA process. However, a limited number of samples were collected from the eastern portion of the lands covered under the Closure Plan, where soil CoC concentrations were known to be high and the simple presence of a road and a fence would not present a barrier to the movement of avian and mammalian receptors.

The objective of this revised ERA report in 2014 is to provide the newly re-named Ministry of the Environment and Climate Change (formerly the OMOE) and the public with an up-dated and revised evaluation of whether the Ni, Cu, Co, and As present in the environment due to the historical emissions from the refinery present an unacceptable risk to the natural environment of the Port Colborne area. This document is a **complete risk assessment** that still relies on the information presented in the Jacques Whitford Ltd. (2004) report but has incorporated additional data, analyses and risk calculations. Effort was made to incorporate technical advances in the area of risk assessment as well as to address the main concerns of the Ministry associated with the 2004 report.



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### 4.2 ECOLOGICAL RISK ASSESSMENT

### 4.2.1 Ecological Risk Assessment Framework

The purpose of the ERA is to evaluate the potential for ecological receptors to experience negative health effects from exposure to chemicals of concern (COCs) found in the environment as a result of historical emissions from the refinery in Port Colborne. The applied risk assessment framework has remained consistent over the years and is constructed from the following three elements:

- 1. Presence of a receptor.
- 2. Potential for exposure.
- 3. Potential for a hazard.

All chemicals (from either anthropogenic or natural sources) have the potential to cause toxicological effects. However, the magnitude of the effect (i.e., the risk) depends on the quantity and duration of the dose or exposure, the presence of a receptor (such as wildlife) to be exposed, and the hazard (e.g., reproductive impairment) caused by the chemical at a specified dose. If all of these components are present (i.e., receptor, exposure and hazard), and exposure is sufficiently high to surpass the threshold for effects, then the possibility of a toxicological risk exists. It is important that all three components be present. If one or more are missing, then there is no potential risk.

The approach used to apply this framework may differ but the ERA was conducted according to widely accepted risk assessment methodologies and followed guidance published and endorsed by regulatory agencies including the Ontario Ministry of the Environment and Climate Change (OMOECC), Canadian Council of the Ministers of the Environment (CCME), Environment Canada, and the United States Environmental Protection Agency (USEPA). Generally, the following framework is used in a risk assessment:

- Site Characterization
- Problem Formulation
- Exposure Assessment
- Toxicity Assessment
- Risk Characterization

Each of these elements is presented in the following sections.

#### 4.2.2 Site Characterization

The purpose of the Site Characterization is to understand the source of potential chemicals of concern (CoCs), and the nature of the receiving environment such that it might influence or modify the potential risks. This includes information on the physical, chemical, and biological nature of the site and the surrounding area.



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Site characterization information and data used in the ERA were obtained from the initial CBRA that was completed by Jacques Whitford Ltd. in 2004. It was further revised and presented within Chapter 2 of this CBRA Update Report. The following sections provide a brief summary of this information and note any additional site information that was incorporated and relevant to the ecological component of the risk assessment.

# 4.2.2.1 Site Description

Inco began operations in the City of Port Colborne in 1918. Historical operations at the Inco Refinery produced particulate emissions that subsequently deposited on soils surrounding the Inco Refinery. Based on an assessment of historic emissions from the Inco Refinery, peak particulate air emissions occurred during the operation period from 1918-1930, during which nickel emissions were as much as 700 tonnes annually. By the 1960s and 1970s particulate emissions had been significantly reduced (< 60 tonnes annually). Further reductions in particulate air emissions continued through 1970s until Ni refining ceased in 1984.

The local natural environment predominantly downwind (northeast) of the Refinery was exposed to the greatest atmospheric deposition of particulates for a period of approximately forty years (1918-1960). It is during this period that the particulate matter principally accumulated in the local soils. Refinery emissions were significantly reduced from 1960 until closure in 1984, and through the 1990s to the present, potential harmful environmental effects on local biota due to direct atmospheric depositions have been greatly reduced compared to past-elevated levels. However, the levels of historic accumulated particulate matter in the local surface soils have remained unchanged from the late 1970s through to the present (McLaughlin and Bisessar 1994).

The Study Area for the ERA was considered to be representative of all natural areas for lands where soil nickel values exceed 200 mg/kg, which was the applicable environmental quality guideline at the time. The Study Area was partitioned according to soil nickel concentrations reported by MOE (2000a,b) to structure sampling efforts within areas of high levels of soil nickel and moderate levels of soil nickel. The Primary Study Area includes land within the ERA's Study Area where soil nickel concentrations exceeded 500 mg/kg, according to MOE (2000a,b). The Secondary Study Area includes land within the ERA's Study Area where soil nickel concentrations lie between 200 mg/kg and 500 mg/kg.

A test-pitting program was conducted and determined that the zone of potential adverse effects of soil CoCs on the area's biota and ecological processes is from the soil surface to a lower depth of approximately 20 cm. The 0-5 cm horizon was considered to represent the area of primary interaction of soil CoCs with most biological receptors and most soil samples were obtained and chemically analyzed in the upper 5 cm of the soil profile throughout the study area.

The woodlots in the Study Area represented a unique aspect to the ecological risk assessment in Port Colborne. Against the broader depositional gradient present to the northeast of the Refinery, woodlots represent areas of patchiness of CoC concentrations, typically containing



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elevated levels of CoCs in comparison to surrounding fields and agricultural lands (MOE 2000c). This pattern reflects the role of trees and their leaves acting as "traps" for the atmospheric particulate matter that is conveyed to the forest floor by rain and leaf fall. For the woodlots having higher CoCs levels (closest to the Refinery), CoCs levels are highest along the windward (western) edge of the woodlot. These levels then decline through the woodlot to the downwind, eastern edge, although the spatial patchiness of CoCs due to the past/present occurrence of tall, large-crowned trees, which acted/act as highly efficient local filters.

# 4.2.2.2 Ecological Setting

Prior to settlement, the Port Colborne area is located at a point where the Carolinian forest to the south overlaps with the Great Lakes-St. Lawrence Forest Region to the north. Tress from both regions can still be seen in the region. However, the Regional Municipality of Niagara also represents a part of Canada that was settled by European settlers early in the country's history. As a result of settlement over the past two centuries, most of Niagara's natural forests have been cleared and drained for agriculture. Undisturbed natural areas remain in very few, small patches within the region. The Port Colborne area is representative of much of the region's natural landscape, where much of the area has been cleared and developed and only small areas of secondary growth woodlots remain. In this respect, from an ecological perspective, the Port Colborne area is dominated by a highly altered and significantly fragmented natural landscape.

# 4.2.2.3 Data used in the ERA

#### Terrestrial Environment

The total number of data points from all sources on measured CoC concentrations in soils sampled within the Port Colborne CBRA Study Area amounted to approximately 2,500. However, in order to ensure that the calculations for the revised ecological risk assessment are representative of actual site conditions, the 95% Upper Confidence Limit of the Mean (95% UCLM) was calculated for arsenic, cobalt, copper and nickel using a select number of soil samples appropriate to the exposure scenarios assessed. Specifically, soil samples used to calculate the 95% UCL values were limited to those collected in woodlots and open spaces (field habitat) in the primary and secondary study areas. A summary of the data is provided in Appendix 4B.

Given the complexity of the project, with site characterization spanning three study areas, each with its own unique land-uses and habitat types, it was not possible to ensure perfect spatial coverage of the ecological communities (e.g. CoCs in soil and biota as well as population characteristics). In the original Natural Environment Risk Assessment (Jacques Whitford, 2004), the data collected from the primary and secondary study areas were pooled as if the nickel were distributed randomly across the study area, when in fact these study areas were highly heterogeneous. However, in order to reduce the bias in the statistical analyses that might result from such variable CoC concentrations along the depositional gradient northeast of the



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Refinery, the calculations of risks were revised to incorporate the 95% UCLM from data reported for a reasonable worse-case woodlot and adjacent field area. Although this will often result in an overly conservative prediction of the potential exposure and subsequent risk, it helps to ensure that the risks to VECs are not underestimated in the ERA due to any perceived influence of unequal distribution of sampling. Detailed site characterization information is provided in Chapter 2 of this Update Report.

The need for primary and secondary study areas was necessitated by the fact that some property owners did not permit access to their properties for the collection of environmental quality data. This underscores that the CBRA is not a traditional risk assessment for an individual parcel of land owned by the proponent. The inability to obtain samples in specific locations prevented the use of a simple gradient approach for the risk assessment in relationship to the deposition plume, and made it necessary to consider discrete primary and secondary study areas.

Maximum measured soil concentrations for the CoCs in the field habitat that were used to calculate the 95% UCLM, were 4310  $\mu$ g/g for nickel, 577  $\mu$ g/g for copper, 77  $\mu$ g/g for cobalt, and 28.5  $\mu$ g/g for arsenic. Higher nickel and cobalt concentrations were measured in some woodlots, up to 33,000  $\mu$ g/g for nickel and 427  $\mu$ g/g for cobalt in the Reuter Road woodlot immediately east of the eastern boundary of the Refinery.

The spatial distribution of nickel soil concentrations as mapped on Figure 2-1 in the 2004 CBRA Report (JWL, 2004 Appendix 1J) show the highest nickel soil concentrations on and in the general vicinity of the Refinery lands and a decreasing soil-nickel concentration gradient with increasing distance away from the Refinery. Figure 2-1 was constructed using data points of CoC concentrations in soil samples collected from field habitat samples only and not from samples collected from the woodlots. Figure 2-4 of the 2004 CBRA Report (JWL, 2004) shows the locations of all of the soil samples collected from the field habitat and woodlots within the Port Colborne CBRA Study Area.

The reason for excluding the woodlot data from Figure 2-1 was because concentrations of CoCs in soils in some of the woodlots, in particular in soils collected in the woodlot along Reuter Road, were much higher than those in the surrounding field habitat. The woodlots represent unique depositional areas within the broader depositional zone to the northeast of the Refinery that should be considered separately from the open field areas.

As stated earlier, woodlots have generally elevated levels of CoCs in comparison to surrounding fields and agricultural lands. These elevated levels are a result of trees and their leaves acting as traps for the atmospheric particulate matter that once trapped is transferred to the forest floor by rain and leaf fall. This phenomenon gives rise to a 'patchy' distribution of CoCs in soil across the landscape, with any one woodlot representing a 'hot spot' in a local area. **Table 4-1** shows examples of soil nickel concentrations in several selected woodlots and adjacent fields at different distances from the Refinery.



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# Table 4-1A Comparison of Soil Nickel Concentrations in Woodlots and Adjacent Fields at<br/>Various Distances from the Inco Refinery

Approximate Linear Distance of woodlot from Refinery (km)	Woodlot Soil Ni Concentration (mg/kg)	Approximate Linear Distance of Woodlot from Adjacent Field (km)	Adjacent Field Ni Concentration (mg/kg)
1.0	33 000	0.35	1860
4.2	709	0.7	145
4.8	550	0.4	156

Due to the difference in soil concentrations between the woodlot and field habitats, two separate scenarios were evaluated in the revised ERA. Woodlot #3 was chosen and evaluated in the ERA due to its proximity to the refinery, and consequently, the highest soil concentrations were measured in Woodlot #3. The 95% UCLM values for CoC in woodlots were calculated from soil data collected at 9 sampling points within this woodlot. Although 11 soil samples were collected, soil data for only 9 of the samples were included in the calculation of the 95% UCLM values. The remaining 2 soil samples were excluded from consideration, as they were located toward the eastern (downwind) end of the woodlot and had the lowest measured CoC concentrations. As a result, the 95% UCLM values calculated for Woodlot #3 is considered to represent the most conservative evaluation of potential risk to ecological receptors that may be present in a woodlot habitat in the Port Colborne area.

The field habitat was evaluated in the revised ERA using the 95% UCLM value for CoCs measured in soil samples collected from open spaces within the primary and secondary areas. Due to an inadequate amount of samples needed to provide a separate representative value for the primary and secondary areas, the soil data was grouped together and a single 95% UCLM value was calculated for CoCs measured across all field samples. The soil data used for the calculation of the 95% UCLM was limited to those collected during the ecological risk assessment field program.

Soils and Valued Ecological Components (VECs) in the woodlot and open field habitats were examined in the ERA. Geographic boundaries of the woodlot and open field habitats within the Port Colborne Study Area and the locations of the soil samples collected from both types of habitats are found on **Figure 2-4** of the 2004 CBRA report (JWL, 2004 – Appendix 1J of this Update Report).

#### Aquatic Environment

The landscape of the Study Area and surrounding areas consist mainly of agricultural lands that are hydrologically manipulated through agricultural drainage tiles, ditches, and municipal drains. No naturally occurring (unaltered) streams or creeks occur in the Study Area. The main surface water drainage features are the Wignell Drain and Beaverdam Drain that drain the



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lands from north to south. Each of these drains functions as such, and should therefore not be considered natural water courses.

The Wignell drain runs parallel to Snider Road 400 m east of the Refinery property boundary. It drains approximately 1200 ha of farmland, and is connected to the majority of the Study Area's agricultural ditches and smaller drains between Reuter Road and Weaver Road.

The Beaverdam Drain drains approximately 1400 ha of farmland and collects surface water from lands in and around Miller Road to the eastern limits of the Study Area. Both the Wignell and Beaverdam drains empty into Lake Erie with flood gate and pump controls at the mouth of the drains at the Lake Erie shore.

The use of municipal drains for draining the lands in the Port Colborne surrounding areas is historical. The Wignell and Beaverdam drains were established over one hundred years ago, with associated records of the drains dating back to the early 1900s (AMEC, 2001c). As a result of surface water management practices, the landscape is efficiently drained; only a small percentage of ditches and drains contain flowing or standing surface water during comparatively dry summer months.

In a similar fashion, the combined result of clay soils and ditching has caused shallow standing water in woodland swamps to be present in early spring but typically drying by early June. Prior to the construction of the drains, these woodland swamps would have retained standing water later into the year. A Department of Fisheries and Oceans (DFO) review of the drainage systems in the Study Area identified all branches to the Wignell and Beaverdam Drains as intermittent in nature, and accordingly, concluded that neither of the drain systems supports fish populations (reported by City of Port Colborne, 2000). Based on DFO assessment, and further supported by CBRA field investigations (Jacques Whitford 2004b), the potential effects of CoCs on inland fisheries are not a concern. Surface water that persists year round is present only in man-made farm ponds dug deep into the clay soil and at the very lower sections and mouth of the larger collector municipal drainage ditches that feed directly into Lake Erie.

Data characterizing the water quality within the Beaverdam Drain and the Wignell Drain was most recently collected in 2013. This data was used to represent the characteristics of the surface water quality evaluated within the ERA and is provided in Appendix 4B).

#### 4.2.3 Problem Formulation

The role of the Problem Formulation was to develop a focused understanding of the soil distribution of CoCs and how ecological receptors inhabiting contaminated areas may be exposed to these CoCs. The level of protection afforded an ecological receptor resulting from an exposure or assessment endpoint is also defined. Therefore, the main points addressed in the Problem Formulation were the following:

CoC screening



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- Receptor identification
- Exposure pathway screening
- Definition of assessment endpoints
- The results of these activities were summarized in a conceptual site model (CSM) that provides a visual depiction of the relevant pathways linking the source of CoCs in various environmental media to the receptors of interest.

# 4.2.3.1 Identification of CoCs

The CoCs identified in the ERA completed by Jacques Whitford Ltd. in 2004 were arsenic, cobalt, copper and nickel. At that time, the definition of a CoC was a chemical found in Port Colborne soils originating from the Inco Refinery where the following conditions were met:

Condition 1 -	Chemicals that were historically used or generated by the Inco Refinery or
	its processes, and

- Condition 2 Chemicals that are present at a community level at concentrations greater than MOE generic effects-based guidelines, and
- Condition 3 Chemicals whose presence in soil show a scientific linkage to the historical operations of the Inco Refinery.

These conditions remain valid and were central to the CBRA process. The approach used to identify the CoCs has not changed for this Update Report. Therefore, the list of CoCs was not altered for this updated ERA.

#### 4.2.3.2 Identification of Receptors

An initial site characterization of the natural environment was undertaken in the summer of 2000 (Jacques Whitford 2001d). Based on the results, the diversity of wildlife within the study area around Port Colborne was considered to be typical and representative of the Region. A subset of these species was selected as suitable VECs for the ERA based on the following criteria.

- The potential VEC represents organisms in a major trophic level;
- The potential VEC is prevalent in, and typical of, the Study Area;
- The potential VEC represents a major vegetation component in the Study Area; and/or,
- For animals in higher trophic levels, life history and metabolic data necessary for quantitative risk assessment are either readily available or could be estimated using recognized (standard) equations.



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The following table provides a list of the VECs selected for the ecological risk assessment.

Group	Valued Ecosystem Component	
Decomposers	Earthworms	
	Leaf litter	
Amphibians	Frogs, general (adults/tadpoles)	
	Fowler's Toad	
Plants	Maple (leaves/seeds)	
	Woodlots	
Mammals	Meadow Vole	
	Raccoon	
	Red Fox	
	White-tailed Deer	
Birds	Red-tailed Hawk	
	American Woodcock	
	American Robin	
	Red-eyed Vireo	

Table 4-2	List of the 14 VECs for which risk of exposure to CoCs was assessed in 2004.

In 2007, and then further revised in 2011, the MOE developed additional guidance for the conduct of ecological risk assessments in Ontario. Included in the approach were standardised VECs. Similar to the criteria listed above, these receptors were chosen as representative of each trophic level in the food web, and which represent "groups of species that are typical of agricultural and natural ecosystems in Southern Ontario". **Table 4-3** lists the VECs chosen by the MOE.

# Table 4-3 List of VECs used in the 2011 MOE Ecological Risk Assessment Guidance Document Document

Group	Valued Ecosystem Component	
Plants and Soil Invertebrates	Assessed as a group. No specific species is selected.	
Aquatic Species (plants, invertebrates, fish and amphibians)	Assessed as a group. No specific species is selected.	
Mammals	Meadow Vole	
	Short-tailed shrew	
	Red Fox	
	Domestic Sheep	
Birds	Red-tailed Hawk	
	American Woodcock	
	Red-winged Blackbird	



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For the revised ERA, the standard MOE VECs were adopted. A comparison of **Tables 4-2 and 4-3** did not indicate any significant differences. The American robin and the red-eyed vireo were omitted with secondary consumers of terrestrial invertebrates represented by the American woodcock. The raccoon was also omitted, with the red fox representing an omnivorous small mammal. A short-tailed shrew was added to represent a small insectivorous mammal. The MOE's review identified that the domestic sheep should be assessed to address the potential of copper as a risk, so sheep have been added as a VEC specifically for this Update Report.. Finally, specific species were not selected for terrestrial plants and invertebrates as these are assessed as a group. This reflects both the measure of exposure and the available toxicity data. This is also standard practice for aquatic species such as plants, invertebrates, fish and amphibians. However, the primary surface water features within the study area were classified as agricultural ponds, drains and ditches. They would not represent significant habitat except for amphibians which would use the ephemeral surface water for breeding and early development. Therefore, only amphibians such as frogs and the Fowler's toad were maintained as VECs.

# 4.2.3.3 Identification of Exposure Pathways

An exposure pathway describes the movement of a CoC from the source to the eventual point of intake by the VEC. Identifying the potential exposure pathways involves consideration of several factors. The life history traits of each VEC (e.g., habitat, diet), features of the site (e.g., biota, habitat suitability) and environmental fate and transport properties of each CoC comprise the most common components taken into account when identifying potential pathways.

As previously discussed, a detailed assessment of exposure pathways is not necessary for terrestrial plants, soil invertebrates, and the amphibians since their exposure is based on the chemical concentration reported in the soil, surface water or sediment. However, pathways analysis is important for the avian and mammalian VECs.

 Table 4-4 provides a summary of potential exposure media for mammalian and avian

 ecological receptors and pathway-specific rationale for inclusion or exclusion from the ERA.

#### Table 4-4 Rationale for Avian and Mammalian Exposure Pathway Inclusion

Potential Exposure Route	Carried Forward for Further Assessment?	Justification
Soil Ingestion	Yes	Uptake from incidental ingestion of soil will constitute potential sources of exposure to wildlife receptors.



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Potential Exposure Route	Carried Forward for Further Assessment?	Justification
Terrestrial Biota Ingestion	Yes	The consumption of contaminated biota such as terrestrial plants, soil invertebrates, or prey (through their potential uptake of COC in soil and groundwater) can often provide a major source of exposure to ecological receptors depending on the environmental fate and transport properties of the COC.
Soil Dermal Absorption/Contact	No	Dermal absorption of COCs is not expected to provide a relevant source of exposure to mammalian and avian receptors due in most part to the presence of fur or feathers which can significantly reduce skin surface area available to directly contact contaminants.
Soil Particulate Inhalation	No	Standard RA practice does not consider inhalation as a significant ecological exposure pathway. There are data limitations for exposure via inhalation (e.g. VOCs or soil particulate) and soil ingestion is considered significantly more important than inhalation.

#### Table 4-4 Rationale for Avian and Mammalian Exposure Pathway Inclusion

Each of the exposure pathways identified for further assessment within **Table 4-4** are consistent with those used in the 2004 ERA prepared by Jacques Whitford.

#### 4.2.3.4 Review of Assessment Endpoints

The focus of an ERA is to identify potential risks to ecological receptors at the population level (rather than at the individual level), with the notable exception being for species protected under the *Species at Risk Act* or other legislation protective of threatened or endangered wildlife. Therefore, the ERA evaluated the potential for chemical-specific effects that could directly result in the reduction of either the abundance or diversity of populations and communities. These endpoints are difficult to evaluate directly, but were extrapolated from comparison of average daily doses to toxicological reference values (food chain modelling for birds and mammals), comparison to appropriate guidelines (surface water exposure to aquatic life) and from studies focused on the survival and growth effects within toxicity tests (where available). These endpoints were used for the evaluation of risk with the assumption that if a significant proportion of the community was unaffected by chemical exposure (i.e., not significantly affected in terms of its ability to grow and survive), and its abundance and diversity was acceptable, then the health of the community as a whole would also be unaffected (i.e., there will be an insignificant effect on the abundance and diversity of other species).

The ERA evaluated risk to VECs as per normal ecological risk assessment practice. For the characterization of risk for the ERA, an unacceptable risk to VEC populations is defined as an estimated risk linked to the occurrence of soil concentrations of CoCs that prevents sustainable



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population(s) of flora and fauna or a sustainable level of ecological functioning within the defined Study Area. Separate risk characterization was not undertaken for sub-populations represented by the Primary and Secondary Study Areas, or other specific areas within the Study Area.

# 4.2.4 Exposure Assessment

The interaction between the CoCs and VECs in the Study Area was evaluated in the Exposure Assessment. The main objective was to develop a quantitative estimate of exposure for each VEC to each COC, based on the empirical data. This data is used to support Exposure Point Concentrations (EPCs) for soil, and surface water, which are used directly or integrated with biological uptake factors to predict concentrations in food items such as forage plants and prey species. These are then incorporated into the multi-pathway exposure modelling for birds and mammals.

## 4.2.4.1 Exposure Point Concentrations

The EPC is intended to represent a conservative yet reasonable estimate of the CoC concentration to which an ecological receptor is assumed to be exposed during their time at the site. It is not reasonable to assume that long-term contact with soil CoCs will be with the maximum concentration, so the mean of the available CoC concentrations data was used. To be conservative, the upper 95% confidence limit of that mean (95% UCLM) was adopted as the EPC. Compared to the maximum value, the 95% UCLM is a better measure of the exposure that an organism may experience while moving around the Site, as well as what a population of sessile organisms may experience. The EPCs applied to each of the study areas are shown in **Table 4-5**. The data is provided in Appendix 4B.

сос	Soil EPC (mg/kg)	
Arsenic	114	
Cobalt	320	
Copper	3035	
Nickel	22861	
Adjacent Field Habitat		
Arsenic	20	
Cobalt	43	
Copper	379	
Nickel	2404	

#### Table 4-5 Exposure Point Concentrations in Soil



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For water, there was insufficient data collected for the Beaverdam Drain and the Wignell Drain to calculate a 95% UCLM, so the EPC was derived from the maximum concentration recently reported in samples taken in 2013. These were, however, adjusted to account for site-specific factors that would influence the potential exposure to amphibians and other aquatic receptors.

In order to consider the site-specific characteristics of the surface water and the potential influence on exposure to amphibians, the metal concentrations were assessed using the internet-based "bio met tool" (www.bio-met.net), which is based on biotic ligand models (BLMs) that predict the bioavailability of copper and nickel with consideration of the site-specific pH, DOC, and hardness of the surface water. The potential exposure to cobalt was addressed using the BLM developed for Co, but not yet incorporated into the bio-met software with a separate but similar tool (W. Stubblefield, Cobalt Development Institute, pers. comm.).

Results and findings of surface water samples collected from the Beaverdam Drain and Wignell Drain habitats in 2013 are provided in **Table 4-6**. The pH, DOC and hardness for the Beaverdam Drain were 7.85, 36 mg/L, and 123 mg/L, respectively. For the Wignell Drain, the pH, DOC and hardness were 7.51, 4.7 mg/L, and 285 mg/L, respectively.

сос	Concentration in Surface Water (ug/L)	Bioavailable in Surface Water (ug/L)
Beave	er Dam	
Arsenic	3.0	NC
Cobalt	1.2	NC
Copper	1.9	0.01
Nickel	19	1.41
Wigne	ll Drain	
Arsenic	<1.0	NC
Cobalt	<0.5	NC
Copper	<1.0	0.04
Nickel	8.2	3.53

#### Table 4-6 Exposure Point Concentrations in Surface Water

NC – Not calculated

For both copper and nickel, the predicted bioavailability of the metals in the surface water was more than an order of magnitude lower than the reported total concentrations, with the exception of nickel in the Wignell Drain, which was approximately 2-fold lower. The hardness values in the Wignell Drain are outside of the calibrated range. However, they are not expected to make the results unreliable. The following explanation is provided from the Biomet Guidance document (Bio met, 2011).



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"Hard waters, where the calcium ion concentration exceeds the BLM application range, especially for the nickel BLM, can be treated relatively easily. The upper limit to the applicable range of calcium ion concentrations exists because there is a limit to the "protective" effect from calcium ions as a competitor for binding sites on the "Biotic Ligand". Increases in calcium ions concentrations beyond the boundary do not result in further reductions in metal bioavailability/toxicity. This situation can be adequately handled by limiting the input data to the maximum allowable calcium ion concentration, and BLM predictions performed by doing so should continue to be reliable."

For cobalt, the BLM was also used but was applied in conjunction with published chronic toxicity data (provided by the Cobalt Development Institute) to produce a Predicted No Effect Concentration (PNEC) based on the specific characteristics of the Beaverdam and Wignell Drains. This modeling was conducted by Dr. William Stubblefield of the Cobalt Development Institute and the results presented in the Toxicity Assessment (Section 2.5).

# 4.2.4.2 Calculation of Tissue Residues for Food and Forage

For the terrestrial avian and mammalian receptors, the predicted exposure was represented by the sum of each of the contributing exposure pathways. For the ingestion of food, concentrations in forage material and prey species (e.g. terrestrial plants, invertebrates and small mammals) were estimated with the use of CoC-specific uptake factors (UF). The generalized equation used to calculate a CoC concentration in biotic tissue from a media concentration is as follows:

 $EPC_i = EPC_{media} \times UF_i$ 

where:

EPCi	<ul> <li>Exposure point concentration in target biotic tissue i (mg/kg wet weight)</li> </ul>	l

EPC<sub>media</sub> = Exposure point concentration in media (mg/kg dry weight or mg/L)

UF<sub>i</sub> = Uptake factor from media to wet weight target biotic tissue i (dimensionless)

Site-specific uptake factors were calculated in the 2004 risk assessment based on an analysis of tissue residues for a variety of plants, soil invertebrates, and small mammals. These UFs were applied instead of the generic BAFs provided by the MOE (2011). The resulting tissue residues predicted for woodlot #3 and the adjacent fields are provided in **Table 4-7**.



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CoC	Terrestrial Plant (mg/kg ww)	Terrestrial Invertebrates (mg/kg ww)	Small Mammals (mg/kg ww)
Woodlot #3			
Arsenic	6.38E-01	1.21E+00	1.21E-01
Cobalt	3.60E-01	6.25E+00	3.91E+00
Copper	6.90E+00	1.61E+01	9.33E+00
Nickel	3.64E+01	3.87E+03	2.36E+02
Adjacent Field			
Arsenic	1.12E-01	3.20E-01	2.91E-02
Cobalt	4.84E-02	8.41E-01	5.02E-01
Copper	3.04E+00	4.10E+00	5.81E+00
Nickel	5.48E+00	4.07E+02	2.48E+01

#### Table 4-7 Exposure Point Concentrations in Plant and Animal Tissues

# 4.2.4.3 Calculation of Average Daily Dose for Birds and Mammals

For birds and mammals, the exposure from each pathway is expressed as a rate of CoC intake with units of mg/kg/day basis (referred to as the average daily dose, or ADD). For each VEC, the ADD was calculated for each CoC by considering the intake from each applicable exposure pathway (e.g., sediment ingestion, water ingestion, food ingestion). The generalized form for the ADD calculation is as follows:

 $ADD_j = IF_j \times AF_j \times EPC_j$ 

where:

ADDj	= Average daily dose (mg chemical/kg body weight-day)
IFj	= Intake factor (kg contaminated media/kg body weight-day)
AFj	= Absorption factor (default value of 1, unless otherwise specified)
EPCj	= Exposure point concentration (mg chemical/kg media)

The intake factor is not specific to each COC, but is dependent on the exposure media. It is calculated for each exposure pathway using the media-specific ingestion rate (IR), the fraction of the total ingestion rate from the Site ( $f_{Site}$ ), and the receptor's body weight (BW) as follows:

 $IF_j = (IR_j \times f_{Site}) / BW$ 

The absorption factor was revised to include more current predictions of metal bioavailability (previously discussed in Appendix 3.E of Chapter 3 of this Update Report). Additional exposure



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factors for each of the avian and mammalian VECs such as body weight, and diet composition (plant, invertebrate and prey are summarized in Appendix 4C. Calculated ADDs for each mammalian and avian VEC are also summarized in Appendix B and total ADDs are presented for the woodlot and adjacent field in **Table 4-8** and **Table 4-9**.

		Total Average Daily Dose (mg/kg-day) for each VEC								
сос	Short- tailed Shrew	Meadow Vole	Domestic Sheep	Red Fox	Red-winged Blackbird	American Woodcock	Red-tailed Hawk			
Arsenic	1.36E+00	5.38E-01	9.67E-01	1.55E-01	7.38E+00	1.55E+00	1.86E-01			
Cobalt	2.74E+00	1.35E+00	2.42E+00	4.02E-01	1.83E+01	3.11E+00	4.58E-01			
Copper	3.18E+01	2.31E+00	4.61E+00	6.74E+00	4.19E+01	3.68E+01	7.04E+00			
Nickel	9.01E+01	4.50E+00	1.05E+01	1.30E+01	1.16E+02	9.81E+01	1.60E+01			

#### Table 4-8 Summary of Total ADDs for Mammals and Birds in Woodlot #3

Table 4-7 Solution of total ADDs for Maining and birds in the Adjaceth field	Table 4-9	Summary of Total ADDs for Mammals and Birds in the Adjacent Field
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		Total Average Daily Dose (mg/kg-day) for each VEC								
сос	Short- tailed Shrew	Meadow Vole	Domestic Sheep	Red Fox	Red-winged Blackbird	American Woodcock	Red-tailed Hawk			
Arsenic	6.46E+00	2.66E-02	5.15E-02	2.73E-02	4.47E-01	8.13E+00	3.27E-02			
Cobalt	1.39E+01	1.04E-01	1.89E-01	5.40E-02	1.48E+00	1.75E+01	6.16E-02			
Copper	6.77E+01	4.87E-01	9.22E-01	8.41E-01	7.72E+00	8.50E+01	8.80E-01			
Nickel	1.65E+02	1.04E+00	2.09E+00	1.37E+00	1.93E+01	2.07E+02	1.68E+00			

# 4.2.5 Toxicity Assessment

The objective of the Toxicity Assessment was to identify the potential adverse effects associated with chronic exposure of ecological receptors to each CoC and use this dose-response information to derive exposure limits or toxicological reference values (TRVs). The TRV represents the amount of a substance that can be tolerated, below which adverse environmental effects are not expected to be observed in a population. For the revised ERA, the TRVs for mammals, birds, terrestrial plants and invertebrates were obtained from the MOE Rationale Document



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(2011) with the application of the Modified Ecological Protection Approach. The TRVs for amphibians were derived from suitable toxicological literature with the application of the biotic ligand model, in order to account for the properties of the environment.

# 4.2.5.1 Modified Ecological Protection

The MOE has developed a modified ecological protection (MEP) option that is intended to promote the preservation of existing ecological habitat while still allowing for the effective management of a contaminated site. Where potential risks are identified using the more traditional assessment methods, the approach provides an alternative to large scale soil removal or paving over of ecological habitat that may produce more harm than good. It has been recognized by the MOE that the established natural habitat is valued even though it may not be comparable in quality to habitat in an uncontaminated setting but instead is habitat comprised of assemblages of species that are adapted or less sensitive to the CoCs at the property.

The use of the MEP may allow a contaminant concentration that will result in adverse effects to some plants, soil organisms and wildlife that might reside in or frequent the site. The degree to which this might occur was assessed further with the use of a qualitative habitat assessment as an additional line-of-evidence. The objective of the risk assessment was to identify those areas of the Site where soil remediation would not be warranted from the perspective of protecting the health and viability of the environment. The scope is limited to those contaminants that are associated with the Site and do not include those from other historical sources.

For plants and soil invertebrates under all land uses, the MEP approach applies a multiplier of 1.9 to the industrial component value. This provides a concentration in soil that is equivalent to the 75th percentile value for the dose-response data set. That is, it is theoretically protective of 25% of the indigenous plant and invertebrate species. In contrast, the residential/parkland values are protective of 75%, and the industrial/commercial values are protective of 50% of the plant and invertebrate species. The level of protection offered by the MEP is considered acceptable because the presence of a valued habitat, in spite of contaminant concentrations above the industrial/commercial standards, is a testament to the level of conservatism inherent in the standards. The MOE also acknowledges that at some sites the higher soil concentrations might not cause adverse ecological impacts due to ameliorating site-specific conditions, such as decreased bioavailability due to soil physicochemical characteristics or due to the site-specific speciation of the contaminant, differential sensitivity of species at a site relative to those used to generate ecotoxicity values, and plasticity or adaptation of the species at the site.

Under the MEP approach, birds and mammals are essentially removed from the ecological risk assessment. A multiplier of 1000 is applied to the TRV. Given the interest in these VECs, this approach was not applied. Instead, the 1.9 multiplier was applied to the TRVs available from the MOE (2011) in their document titled "Rationale for the Development of Soil and Ground Water Standards for Use at Contaminated Sites in Ontario" released on April 15, 2011.



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The industrial/commercial component soil standards for plants and invertebrates are provided in the following table along with the adjustment for the MEP. The original and adjusted TRVs for birds and mammals are also included. For arsenic, the component standard for plants and invertebrates was derived based only on plant data and does not include data for invertebrates. Environment Canada (1995) did conduct a study with earthworms where they found a no observable adverse effect limit (NOAEL) for arsenic of 83 mg/kg; however, this data was considered insufficient to properly support a standard. It does suggest that invertebrates are less sensitive to arsenic such that values protective of plants will also be protective of soil invertebrates.

CoC	Terrestrial Plants and Invertebrates (mg/kg)		Mam (mg/kg b			ds bw-day)
	Generic	MEP	Generic	MEP	Generic	MEP
Arsenic	40	76	1.3	2.5	7.4	14.1
Cobalt	80	152	8.8	16.7	7.8	14.8
Copper	230	437	15	29	62	118
Nickel	270	513	80	152	107	203

#### Table 4-10 Summary of TRVs for the Terrestrial VECs

# 4.2.5.2 Surface Water

In 2004, a Hazard assessment conducted for tadpoles, frogs and toads found effects levels, particularly for nickel and copper that was below the natural background surface water concentrations for southern Ontario. As a results, the determination of TRVs considered the 20% effects level (EC20), or 10% lethal concentration (LC10). The final values are summarised in the following table.

Since that time, surface water standards or Aquatic Protection Values (APVs) have been developed by the MOE (2011a) to provide a scientifically defensible and reasonably conservative level of protection for most aquatic organisms. These have replaced the PWQOs for the protection of aquatic life, which are conservative values that, when met, are protective of all forms of aquatic life and all aspects of the aquatic life cycle during indefinite exposure to the water. PWQOs were not used in the final assessment because the MOE has concluded that some of the assumptions made in the development of PWQOs are not considered appropriate for the assessment and potential remediation of contaminated sites (MOE, 2011a). The following table lists the APVs for the CoCs.



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CoC	Tadpole TRVs (EC20s) (JWEL, 2004)	Aquatic Protection Value (ug/L)	Adjusted based on the BLM (ug/L)	
Arsenic	10	150	NC	
Cobalt	10	5.2	7.3	
Copper	8	6.9	NC	
Nickel	10	39	NC	

#### Table 4-11 Summary of TRVs for Aquatic Life (Amphibians)

For cobalt, the Biotic Ligand Model (BLM) was used in conjunction with published chronic toxicity data to estimate the Predicted No-Effect Concentration PNEC) for cobalt in the Beaver Dam and Wignell Drain based on the site specific characteristics (pH, hardness and DOC). The influence was similar between the two surface water features with the TRV ranging from 7.3 to 7.6 ug/L. The lower of the two was adopted.

The calculation can be described as resulting from three steps. In the first step, the BLM predicts bioavailability effects to adjust observed chronic toxicity threshold values (NOECs or EC10 values) to values appropriate for a new water body. In the second step these individual observations are combined to generate Species Mean NOECs for each aquatic species' endpoint, defined as the geometric mean of individual NOECs for each species' endpoint (e.g., mortality, growth, reproduction). Where multiple toxicity endpoints have been measured for a species, the most sensitive species mean endpoint is used as the species mean NOEC (SM NOEC). Finally, a PNEC is derived from the species mean NOECs, using a log-normal distribution.

As discussed in Section 2.4, the BLM was used to adjust the EPC for copper and nickel, so it was not used again to adjust the TRV. A separate model was used for cobalt, which uses the predicted bioavailability to adjust the TRV.

# 4.2.6 Risk Characterization

Risk Characterization evaluates the evidence linking CoCs with adverse ecological effects by combining information from the Exposure and Toxicity Assessments.

The potential for adverse effects to birds and mammals is quantified by comparing the amount of a substance that can be tolerated, below which adverse environmental effects are not expected (e.g., TRV or toxicity benchmarks), to the amount of a CoC an organism is expected to be exposed to, or come into contact with, on a daily basis. This is defined as the Hazard Quotient:



HQ = <u>ADD (mg/kg-d)</u> TRV (mg/kg-d)

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In the ERA, for the assessment of potential risk to community-based receptors (e.g., terrestrial plants, soil invertebrates, and amphibians), the HQ is calculated by dividing the EPC (rather than the ADD) of the CoC by an appropriate TRV.

In either case, the magnitude by which values differ from parity (e.g., TRV = EPC or daily dose, HQ = 1.0) is used to make inferences about the possibility of ecological risks. A HQ less than 1.0 indicates that the exposure concentration is less than the threshold of toxicity and there is a low probability that adverse environmental effects might occur. However, a HQ value of greater than 1.0 does not automatically indicate that there is an unacceptable level of risk, only that there is a possibility of adverse ecological effects. HQ values greater than 1.0 should be examined carefully and further, more focused, investigations may be required to reduce conservatism and provide a more accurate assessment of the actual level of risk. If it is ultimately determined that the HQ is indeed indicating unacceptable risk, then mitigation or remediation activities may be appropriate in order to reduce risks to ecological receptors.

## 4.2.6.1 Assessment of Risks to Plants and Invertebrates

Hazard Quotients representing the potential risk to terrestrial plants and invertebrates were calculated by taking the EPC, which was based on the 95% UCLM of the CoC concentration reported within the woodlot and field, and dividing it by the TRV adjusted for the MEP. The results are provided in **Table 4-12**.

сос	Hazard Quotients				
202	Woodlot #3	Adjacent Field			
Arsenic	1.5	0.3			
Cobalt	2.1	0.3			
Copper	6.9	0.9			
Nickel	44.6	4.7			

#### Table 4-12 Hazard Quotients for Plants and Invertebrates

Notes: Highlighted values exceed applicable HQ benchmark of 1

The HQs calculated for the CoCs in the field habitat ranged from 0.3 to 4.7, with the former representing an acceptable risk and the latter representing only a marginal risk to plants and invertebrates. An HQ of 4.7 is well within the inherent uncertainty associated with the risk assessment method. For example, the 95% UCLM provides a conservative estimate of exposure at the population level and a significant proportion of the plants and invertebrates experience a much lower concentration. However, in areas where the soil concentration of nickel exceeded the modified soil standard, the flora and fauna might be dominated by more tolerant species or those less susceptible to being exposed via direct soil contact. This impact would be limited to areas within the worst-case field. Field habitats further from the source had concentrations of



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nickel that were more than 10-fold lower, producing HQs that were less than 1. The plants and invertebrates in these areas would not be at a significant risk.

In contrast to the field habitat, the HQs for all of the CoCs in the woodlot exceeded 1 with values ranging from 1.5 for arsenic to almost 45 for nickel. The latter HQ represents a potentially significant risk. In areas where the concentration of nickel in soil is this high, one would expect a noticeable effect on both the abundance and diversity of plants and soil invertebrates. However, as was discussed for the field habitat, only areas of high CoC concentrations within the woodlot would be adversely affected. The woodlots further from the source, which had concentrations of nickel more than 50-fold lower, would produce HQs that were less than 1. Although the modified ecological standards are intended to be protective of only the 25<sup>th</sup> percentile of species, the existing plants and invertebrates in these latter areas would not be at a significant risk.

Reported literature data from toxicity tests conducted with cultured earthworms indicated that there was potential for concern if soil Ni concentrations exceeded the TRV of 3,000 mg/kg (Jacques Whitford, 2004 – see Appendix 1J). For organic soil, EC20 values from the chronic reproduction test ranged between 2,000 to 3,000 mg Ni/kg soil for progeny production, progeny biomass (wet and dry), and hatched and unhatched cocoons. The range of EC20s in clay soil was even lower (84 to 1,200 mg/kg). If these EC20s were accepted as the lowest-observed-adverse-effect level (LOAEL), a TRV based on this information would be lower than 3,000 mg/kg (which was based on an estimated NOAEC) thereby resulting in even higher HQs, and potentially greater risk. However, other lines of site-specific evidence indicated that there were no significant differences in survival of earthworms during either the acute or chronic tests in either the organic or clay soils relative to the reference control soils. The results of the field survey demonstrated that there were healthy earthworm populations reproducing in the Port Colborne area even at a location on the site with soil Ni concentrations > 20,000 mg/kg. The field survey results (578 worms reported at 10 sites from the study area (averaging 58 worms per site); 108 worms at 4 sites from the reference area (27 worms per site)) demonstrates that variability in worm numbers can be large, and the lower numbers at reference sites show that this variability can be independent of soil Ni. There were no significant differences in numbers of worms in soil as soil nickel concentrations increased from 2,000 mg/kg to 5,000 mg/kg (Figure 8-12; Jacques Whitford Ltd., 2004a). In addition, field data for areas with lower nickel concentrations indicated a slight increase in earthworm numbers was associated with increasing nickel concentrations (pp. 8-33; Jacques Whitford Ltd., 2004a).

In 2001, earthworms were absent from a sample location adjacent to the Inco Refinery, which had much higher soil CoC concentrations (e.g., nickel = 18,500 mg/kg) than all other sample sites. This site was re-sampled in June 2002 to confirm that the location was devoid of earthworms. Earthworms were found at each sample site in the Reuter Road and Snider Road Woodlots in 2002 (Table 8-19; Jacques Whitford Ltd., 2004a). Numbers of earthworms within each woodlot increased as one moved to the east (i.e., further away from the presumed CoC source), but individuals were present at the western edge of each woodlot, including juveniles. At the western edge of the Reuter Road Woodlot, adjacent to the Inco Refinery, soil nickel



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concentrations were 21,100 mg/kg, soil, copper concentrations were 3,620 mg/kg, and soil arsenic concentrations were 129 mg/kg. Two adults and three juveniles of two species were found at this site. This evidence indicates that the earthworms could inhabit and were reproducing in soils located in areas with high levels of CoC, although the numbers of individual worms were reduced in the areas of greatest contamination.

Another important assumption used when applying the TRV for calculating HQs was that the adult and juvenile worms at the on-site sampling locations received a constant exposure concentration. In situ, juveniles of earthworm species (e.g., Lumbricus terrestris, L. rubellus, and Apprectodea tuberculata – the three dominant species found in the Port Colborne soils) tend to disperse from parental clusters into neighboring areas (at least 30 m away) (Valckx et al., 2009), and adult L. terrestris, an anecic or deep burrowing species form permanent burrow systems in soil and selectively feed on organic material from the surface which can be drawn into their burrows or combined with cast material to form middens. The burrows are lined with chlorogenous exudates and cast which form a protective, stabilizing barrier for the worms. Collectively, field populations of endogeic species (surface soil dwellers) are estimated to produce 1000 km/ha of new burrows each week (Cook and Linden, 1996 as cited in Simonsen et al., 2010). Moreover, L. terrestris is known to disperse over the soil surface significant distances at night (Mather and Christensen, 1988). These levels of activity coupled with the inherent capacity (e.g., chemoreceptors) of earthworms to avoid contaminants in soils (Stephenson et al., 1998; Spurgeon et al., 2006; Yeardley et al. 1995) could explain, in part, the presence of the earthworms observed in the field soil, even in soils where Ni concentration exceeded 20,000 mg/kg. These observations could also be explained, in part, by an earthworm's ability to adapt to soils with elevated metal levels (Hobbelen et al., 2006; Peijnenburg et al., 1999; Spurgeon and Hopkin, 1999).

The apparent contradiction between the predicted HQs and the observed abundance and diversity of earthworms within areas where the CoC concentrations in soil were above soil quality standards demonstrates the conservative nature of the predicted exposure and exposure limits used to calculate the HQs. As stated by Chapman (2005), if data from a habitat assessment or site-specific toxicity test contradicts the chemistry-based HQ prediction of risk, then the latter is wrong. The interpretation of the results from the HQ calculations should be limited to a trigger for further exploration of potential impact of elevated soil Ni (and other CoC) concentrations on earthworm survival and reproduction. HQ values are more appropriately used to trigger awareness for potential concern rather than set policy for managing potential risk (Tannenbaum et al., 2003). The ERA carried this concern forward by using the toxicity testing and field survey to assess the impact of elevated soil Ni concentration.

It is important to note that the field observations do not completely dismiss the potential concerns that soil Ni concentrations exceeding the TRV of 3,000 mg/kg might pose risk to earthworm survival and reproduction. Rather, one would interpret the field study results to indicate that the earthworm populations in Port Colborne are unlikely to be exposed to soil Ni concentrations at or exceeding the TRV for durations that might adversely affect their survival or reproduction.



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### 4.2.6.2 Assessment of Risks to Birds and Mammals

As discussed in Section 2.5, within the MEP approach, the MOE considers the potential risk to birds and mammals to be an irrelevant endpoint. The generic TRVs are multiplied by 1000 and thus only extreme CoC concentrations in the soil would be considered unacceptable. However, concern has been expressed over the potential risks to these species and so a more conservative approach was adopted, where the same adjustment applied to the plant and invertebrate TRVs was applied to the mammalian and avian TRVs. Therefore, instead of being protective of the most sensitive birds and mammals (i.e. the 5<sup>th</sup> percentile of species distribution), it is protective of between the 25<sup>th</sup> or 50<sup>th</sup> percentile. The HQs derived from this approach are listed in **Table 4-13** for the worse-case woodlot and **Table 4-14** for the field habitat.

		Hazard Quotients for each VEC								
CoC	Short- tailed Shrew	Meadow Vole	Domestic Sheep	Red Fox	Red-winged Blackbird	American Woodcock	Red-tailed Hawk			
Arsenic	0.55	0.22	0.39	0.06	0.53	0.11	0.01			
Cobalt	0.16	0.08	0.14	0.02	1.23	0.21	0.03			
Copper	1.12	0.08	2.73	0.24	0.36	0.31	0.06			
Nickel	0.59	0.03	0.07	0.09	0.57	0.48	0.08			

#### Table 4-13 Hazard Quotients for each VEC in Woodlot #3

Notes: Highlighted values exceed applicable HQ benchmark of 1

Within the woodlot, a marginal potential for risk was identified for the short-tailed shrew (Cu), the domestic sheep (Cu) and the red-winged blackbird (Co). Sheep are not expected to reside in the woodlots but this VEC acts as a surrogate for all ungulates, including white-tailed deer. The same is true for the red-winged blackbird, which acts as a surrogate for seed-eating birds such as the sparrow and chickadee, both of which would also be prevalent within the woodlots.

The HQs for the short-tailed shrew, the domestic sheep and the red-winged blackbird ranged from 1.12 to 2.73 and thus represent only a marginal risk to these groups of birds and mammals. An HQ of 2.73 is well within the inherent uncertainty associated with the risk assessment method and the conservatism associated with both the exposure assessment and the hazard assessment. The mobility of these receptors and their flexibility to inhabit areas where there is a greater abundance and diversity of food should bias their exposure to the lower CoC concentrations where plants and invertebrates are also less impacted. However, in areas where the soil concentration of metals was elevated, the smaller more sedentary mammals might be dominated by more tolerant species and more sensitive species like the short-tailed shrew might be absent. This impact would be limited to areas within the worse-case woodlot. Woodlots further from the source had concentrations of metals that were 10 to 50-fold lower,



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producing HQs that were much less than 1. The birds and mammals in these areas would not be at a significant risk.

		HQ for each VEC									
CoC	Short- tailed Shrew	Meadow Vole	Domestic Sheep	Red Fox	Red-winged Blackbird	American Woodcock	Red-tailed Hawk				
Arsenic	2.62	0.01	0.02	0.01	0.03	0.58	0.00				
Cobalt	0.83	0.01	0.01	0.00	0.10	1.18	0.00				
Copper	2.37	0.02	0.55	0.03	0.07	0.72	0.01				
Nickel	1.09	0.01	0.01	0.01	0.09	1.02	0.01				

Notes: Highlighted values exceed applicable HQ benchmark

The potential risks to birds and mammals in the field habitats showed much the same trends as those in the woodlot. Given the similar magnitude of the HQs, the potential risks were also expected to be negligible.

The intent of the MEP is to promote the preservation of existing ecological habitat while still allowing for the effective management of a contaminated site. Where potential risks are identified using the more traditional assessment methods, the approach provides an alternative to large scale soil removal or paving over of ecological habitat that may produce more harm than good. It has been recognized by the MOE that the established natural habitat is valued even though it may not be comparable in quality to habitat in an uncontaminated setting but instead is habitat made up of assemblages of species that are adapted or less sensitive to the CoCs.

The assessment of domestic sheep was added in this section to address the issue raised by the MOE review that sheep (which are known to be sensitive to copper toxicity) might be raised by landowners in the study area. Based on the results in Table 4-14, it is seen that the risk to sheep of copper toxicity is not expected to be a significant concern.

# 4.2.6.3 Assessment of Risks to Amphibians

As with the assessment of terrestrial plants and invertebrates, the potential risk to communitybased receptors such as amphibians and other aquatic life was calculated by dividing the EPC (rather than the ADD) of the CoC by the appropriate TRV. The results are provided in **Table 4-15**.



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CoC	Hazard Quotient		
	Beaver Dam	Wignell Drain	
Arsenic	0.30	0.10	
Cobalt	0.16	0.068	
Copper	0.001	0.006	
Nickel	0.14	0.35	

#### Table 4-15 Hazard Quotients for each VEC Woodlot Area

Notes: Highlighted values exceed applicable HQ benchmark

Based on the HQs, there are not predicted risks expected for amphibians inhabiting either the Beaver Dam reservoir or the Wignell Drain. The HQs were based on the most conservative TRV between the APV and those initially developed to be protective of indigenous amphibians such as the Fowler's toad, and the EPC was represented by the maximum reported metal concentrations in the water (adjusted for bioavailability). With this inherent conservatism, there would be a high degree of certainty with this conclusion.

Additional information regarding the characteristics of the indigenous amphibian populations was gleaned from frog calling studies. Based on the data generated from these field surveys, chorus frogs, spring peepers, and the American toad appear to be common across the entire study area. However, the expected high densities of spring peepers and chorus frogs at quality breeding sites were not encountered. It was also stated that there may be some suppression in population numbers but not at levels that affect long term persistence of frog and toad populations in the Study Area. In addition, the American Toad was not found at sites 17 or 26 on any of the 4 visits. The MOE concluded that since the American Toad was found at every other site from across the study area, the absence of the toad at these sites within the primary study area should be noted and discussed. Concern was also raised by the MOE regarding the design of these studies. Specifically, the calling sites were unequal between the primary (n=10) and the secondary study area (n=20). Two sites within the primary study area were located in the Rodney Street community that should not be flagged based on poor habitat suitability (i.e., it was an urban environment). Hence, frog calling sites within the Primary study area were limited to Sites 17 to 22 and 26 (n=7).

However, the objective of the ERA was to identify if CoC concentrations in the Study Area pose an unacceptable risk to VECs (defined as an occurrence of CoC that prevents sustainable populations of flora and fauna or a sustainable level of ecological functioning). Based on the predicted bioavailability of copper, cobalt and nickel, risks to aquatic species are not expected, and poor frog calling survey results do not necessarily indicate that risk thresholds have been exceeded. Missing frog calls might simply reflect spatial and seasonal variation of frog distribution. For example, American Toad was absent from sites 17 and 26, yet site 17 had the highest code value (3) and frequency (3 or 4 of 4 samplings) recorded for Chorus Frog and



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Spring Peeper. In addition, both species were present at site 26 during at least 2 of the 4 samplings but absent from some sites (e.g., 1, 14, 23, 27, and 28) where the American Toad was present. All surveyed sites supported frog communities, as at least one frog species was detected at least once at all surveyed sites. In addition, the bioavailability-adjusted potential risk as determined by the HQ method for amphibians also indicated that potential risk to frog and toad populations is not expected.

# 4.3 CONCLUSIONS

The primary objective of this study was to revise the 2004 ecological risk assessment that was conducted to determine if historical emissions of nickel, copper, cobalt and arsenic from the Inco Port Colborne Refinery and deposited in the local soil present an unacceptable risk to the natural environment. To conduct this assessment, two worse-case study areas (woodlot and adjacent field) were identified based on their proximity to the refinery, and where previously collected data showed soil nickel concentrations of 200 mg/kg or greater (i.e., exceeding the MOE generic guideline for soil nickel). Data used to represent the soil quality within these areas was taken from an extensive sampling and inventory program that was undertaken to collect qualitative and quantitative data for the natural environment.

The MOE had identified a number of issues with the original 2004 risk assessment. These have been resolved where possible and based on the additional lines of evidence presented in this Update Report, and the revised risk calculations where 95% UCLM of reported CoC concentrations were considered, the findings presented in the 2004 CBRA – Natural Environment report (Jacques Whitford Ltd., 2004a) were confirmed to be valid. The "safe" soil CoC concentrations (the concentrations at which adverse health effects to ecological receptors are not expected) are as follows (**Table 4.16**):

Soil Type	Safe Soil CoC Concentration (mg/kg)				
	Nickel	Copper	Cobalt	Arsenic	
Organic	3500	550	3000	40	
Clay	3000	350	3000	25	

#### Table 4-16 "Safe" Soil CoC Concentrations

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# Appendix A

# **MOE** Comments

(to be provided at a later date)



Appendix B

**Data Tables** 



Sample Name		Chemical Conce	entration (mg/kg)		Source
Sample Name	Arsenic	Cobalt	Copper	Nickel	Source
RS-H-1	129	340	3620	21100	JWEL Earthworn 2002
RS-H-2	109	181	2520	13800	JWEL Earthworn 2002
RS-H-3	81.4	190	2020	12600	JWEL Earthworn 2002
A1	27.4	93	827	5400	JWEL Trees - Hig Woodlots
A2	97.3	356	2910	24500	JWEL Trees - Hig Woodlots
A3	137	427	3930	33000	JWEL Trees - Hig Woodlots
A4	82.9	224	1870	14200	JWEL Trees - Hig Woodlots
A5	78.1	249	2100	18900	JWEL Trees - Hig Woodlots
LL18	99.8	248	2270	18250	JWEL Leaf Litte Study Soils
Number of samples	9	9	9	9	
Min concentration	27.4	93	827	5400	
Mean concentration	93.5	256.4	2451.9	17972.2	NA
Max concentration	137	427	3930	33000	
95 UCLM	113.5	320	3035	22861	Calculated usin ProUCL



Sample Name —		Chemical Conc	entration (mg/kg)		Source
	Arsenic	Cobalt	Copper	Nickel	300100
CS-H-4	8	40	367	2460	JWEL Earthworm 2002
CS-H-5	12.4	36	346	2000	JWEL Earthworm 2002
CS-H-7	3.2	12	66	364	JWEL Earthworm 2002
CS-H-8	5.3	13	71	410	JWEL Earthworm 2002
CS-H-9	5.2	13	58	355	JWEL Earthworm 2002
I-H-1	-	-	-	-	JWEL Field Insec Soils
-H-3	21	29	333	1860	JWEL Field Insec Soils
I-H-5	21	73	566	4310	JWEL Field Insec Soils
OS-H-1	20.2	23	257	1350	JWEL Earthworm 2002
OS-H-2	13.4	26	371	1550	JWEL Earthworm 2002
OS-H-26	21.6	39	345	1770	JWEL Earthworm 2002
OS-H-27	14.5	16	169	935	JWEL Earthworm 2002
OS-H-28	21.6	34	300	2000	JWEL Earthworm 2002
OS-H-29	21.6	34	300	2000	JWEL Earthworm 2002
OS-H-3	26.7	46	453	2900	JWEL Earthworm 2002
OS-H-6	28.5	77	577	3820	JWEL Earthworm 2002
Number of samples	16	16	16	16	
Min concentration	3.2	12	58	355	
Mean concentration	16.3	34.1	305.3	1872.3	NA
Max concentration	28.5	77	577	4310	
95 UCLM	19.95	43.06	379.2	2404	Calculated using ProUCL

Note: Primary and Secondary Areas were combined when calculating 95 UCLM values as there was an insufficient number (N<10) of discrete samples for separate calculations



Table B-3: Primary and Secondary Study Areas, and Control Area Sediment Concentrations Used in Revised Risk	
Calculations	

Sample Name		Seuree					
Sample Name	Arsenic	Cobalt	Copper	Nickel	Source		
Primary and Second	ary Study Areas						
F-H-1	4.4	14.25	56.25	251.75			
F-H-2	3.6	11	57	193			
F-H-3	12.4	24	171	1040			
F-H-3 (replicate)	11.9	24	170	1050			
F-H-4	4.7	16	85	429			
F-H-5	4	14	62	242	From 2004 Report Bio-Physical Data		
F-M-1	4	11	66	195	Tab 27		
F-M-2	2.3	5.5	30	60	100 27		
F-M-3	3	11	41	81			
F-M-4	3.6	10	29	65			
F-M-5	4	10	34	37			
F-M-6	4.7	9	25	25			
Number of samples	12	12	12	12			
Min concentration	2.3	5.5	25	25			
Mean concentration	5.2	13.3	68.9	305.7	NA		
Max concentration	12.4	24	171	1050			
95 UCLM	6.9	16.3	105.7	654.3	Calculated using ProUCL		
Control Area							
F-C-1	7.15	9	50	40.5			
F-C-2	7.3	7	41	44	E 000 / D		
F-C-3	2.5	8	24.5	21.5	From 2004 Report Bio-Physical Data		
F-C-4	2.4	5	33	21	Tab 27		
F-C-5	3.6	10	24	27	10.0 2.		
F-C-6	4.5	9	31	26			
Number of samples	6	6	6	6			
Min concentration	2.4	5	24	21			
Mean concentration	4.6	8.0	33.9	30.0	NA		
Max concentration	7.3	10	50	44			
95 UCLM		Not Calcu	lated (n<10)				

Note: Primary and Secondary Areas were combined when calculating 95 UCLM values as there was an insufficient number (N<10) of discrete samples for separate calculations



	condary, and Control	Chemical Concern					
Sample Name	Arsenic	Cobalt	Copper	Nickel	Source		
Primary Słudy Area				MCKCI			
51	0.0005	0.0377	0.0125	0.101			
52	0.038	0.0178	0.08195	0.884			
53	0.004	0.01175	0.0721	0.626			
54	0.0005	0.00005	0.0003	0.029			
\$8	0.002	0.0003	0.0031	0.019	From 2004 Report		
\$19	0.0005	0.0004	0.0052	0.018	Bio-Physical Data		
\$20	0.001	0.00075	0.00365	0.028	Tab 32		
\$22	0.0005	0.0006	0.0026	0.004			
\$28	0.0005	0.0001	0.0013	0.004			
\$31	0.0005	0.00053	0.0032	0.01525			
\$32	0.00075	0.005	0.0079	0.0165			
Number of samples	11	11	11	11			
Min concentration	0.0005	0.00005	0.0003	0.004			
Mean	0.004	0.007	0.018	0.159	NA		
Max concentration	0.038	0.038	0.082	0.884	Calculated using		
95 UCLM	0.019	0.026	0.053	1.063	ProUCL		
Secondary Study Arec		0.0007	0.00/7	0.000			
\$5	0.002	0.0027	0.0067	0.092			
\$6		0.0011					
S9	0.0005	0.0019	0.0048	0.05			
S11	0.0005	0.0009	0.0046	0.029			
\$13	0.0005	0.0042	0.0124	0.078			
S14	0.0005	0.0039	0.0108	0.07	From 2004 Report		
S15	0.0005	0.0034	0.0102	0.053	Bio-Physical Data Tab 32		
S16	0.0005	0.002	0.0102	0.041	100.02		
S17	0.0005	0.00035	0.0046	0.028			
\$18	0.001	0.0012	0.0042	0.029			
S21 S29	0.0005	0.0012	0.005	0.009			
\$33			0.0014	0.003			
333	0.0005	0.0007	0.004	0.005			
Number of samples	13	13	13	13			
Min concentration	0.001	0.0002	0.001	0.003	NA		
Mean concentration	0.001	0.002	0.006	0.040			
Max concentration	0.002	0.004	0.012	0.092			
95 UCLM	0.001	0.002	0.008	0.054	Calculated using ProUCL		
Control Area							
\$7	0.0005	0.007	0.0018	0.0105			
\$10	0.002	0.00695	0.00905	0.096			
\$12	0.0005	0.002	0.0156	0.103			
\$23	0.004	0.0025	0.0019	0.013			
S24	0.0005	0.0002	0.0007	0.0005			
S25	0.0005	0.0001	0.00051	0.0005	From 2004 Report		
\$27	0.006	0.0013	0.00305	0.019	Bio-Physical Data		
\$26	0.001	0.0006	0.0043	0.004	Tab 32		
\$30	0.002	0.0041	0.0179	0.053			
\$34	0.002	0.0041	0.0137	0.011			
\$35	0.0005	0.0002	0.0053	0.002			
\$36	0.0005	0.0007	0.0082	0.002			
\$37	0.0005	0.0004	0.0015	0.001			
Number of samples	13	13	13	13			
Min concentration	0.0005	0.0001	0.00051	0.0005			
Mean	0.0016	0.0023	0.0064	0.0244	NA		
concentration Max concentration	0.006	0.007	0.0179	0.103	_		
				0.103	Calculated using		
95 UCLM	0.004	0.004	0.009				



		Distance from					Me	asured Parame	ers				
Sample Name	Sampled Drain	Refinery of Sampling Location (km)	Dissolved Arsenic (µg/L)	Total Arsenic (µg/L)	Dissolved Cobalt (µg/L)	Total Cobalt (µg/L)	Dissolved Copper (µg/L)	Total Copper (µg/L)	Dissovled Nickel (µg/L)	Total Nickel (µg/L)	рН	Dissolved Organic Carbon (mg/L)	Hardnes (µg/L)
W15 A - unfiltered	Beaverdam	3.5	NM	3.4	ИМ	1.5	NM	3.2	ИМ	21	7.76	35	370
SW15 C - ïeld filtered (0.45μ)	Beaverdam	3.5	3	NM	1.2	NM	1.9	NM	19	NM	7.85	37	350
SW15B - lab iltered 0.2µ)	Beaverdam	3.5	2.8	NM	0.61	NM	2.3	NM	18	NM	7.81	36	350
SW20 - Unfiltered	Wignell	1	NM	1.2	NM	0.98	NM	4.1	NM	15	7.52	4.2	790
SW20 - field iltered (0.45µ)	Wignell	1	<1.0	NM	<0.50	NM	<1.0	NM	8.2	NM	7.52	4.7	760
SW20 - lab iiltered (0.2µ)	Wignell	1	<1.0	NM	<0.50	NM	<1.0	NM	8.1	NM	7.5	3.7	740
SW20 - unfiltered Duplicate)	Wignell	1	NM	<1.0	NM	<0.50	NM	1.7	NM	8.1	7.54	3.7	800
W20 - field iltered 0.45µ) Duplicate)	Wignell	1	<1.0	NM	<0.50	NM	<1.0	NM	7.3	NM	7.54	4.3	750
W20 - lab iltered 0.2µ) Duplicate)	Wignell	1	<1.0	NM	<0.50	NM	<1.0	NM	6.5	NM	7.56	3.8	740
°WQO	N	A	NV	100	NV	0.9	NV	5	NV	25	NV	NV	NV



	A B C I	DE	F	G H I J K	I
1			•	ensored Full Data Sets	<u> </u>
2					
2	User Selected Options				
3	Date/Time of Computation 8/19/2	2014 9:39:59 AM			
4 5		e-case UCLM_b.xls			
5 6	Full Precision OFF				
6 7	Confidence Coefficient 95%				
8	Number of Bootstrap Operations 2000				
<u> </u>					
9 10					
	Arsenic				
12					
13			General	Statistics	
14	Total Numb	er of Observations	9	Number of Distinct Observations	9
				Number of Missing Observations	0
15 16		Minimum	27.4	Mean	93.54
16		Maximum	137	Median	97.3
		SD	32.23	Std. Error of Mean	10.74
18 19	Сое	fficient of Variation	0.345	Skewness	-0.794
20					
20 21	Note: Sample siz	e is small (e.g., <1)	0), if data ar	e collected using ISM approach, you should use	
			-	SM (ITRC, 2012) to compute statistics of interest.	
22 23		-		rshev UCL to estimate EPC (ITRC, 2012).	
	•		-	nparametric and All UCL Options of ProUCL 5.0	
24 25		· ·	-	· · · · · · · · · · · · · · · · · · ·	
26			Normal (	GOF Test	
20	Shapiro	Wilk Test Statistic	0.934	Shapiro Wilk GOF Test	
27	5% Shapiro	Wilk Critical Value	0.829	Data appear Normal at 5% Significance Level	
20 29	Lilli	efors Test Statistic	0.205	Lilliefors GOF Test	
30	5% Lillie	efors Critical Value	0.295	Data appear Normal at 5% Significance Level	
31		Data appea	ar Normal at	5% Significance Level	
32					
33		As	suming Nori	nal Distribution	
34	95% Normal V	JCL		95% UCLs (Adjusted for Skewness)	
35	95	% Student's-t UCL	113.5	95% Adjusted-CLT UCL (Chen-1995)	108.2
36				95% Modified-t UCL (Johnson-1978)	113.1
37				I	
38			Gamma	GOF Test	
39		A-D Test Statistic	0.608	Anderson-Darling Gamma GOF Test	
40	5%	A-D Critical Value	0.722	Detected data appear Gamma Distributed at 5% Significance	e Level
41		K-S Test Statistic	0.266	Kolmogrov-Smirnoff Gamma GOF Test	
42	5%	K-S Critical Value	0.28	Detected data appear Gamma Distributed at 5% Significance	e Level
43	De	tected data appear	Gamma Di	stributed at 5% Significance Level	
44					
45			Gamma	Statistics	
46		k hat (MLE)	6.516	k star (bias corrected MLE)	4.418
40		Theta hat (MLE)	14.36	Theta star (bias corrected MLE)	21.17
47		nu hat (MLE)	117.3	nu star (bias corrected)	79.52
40 49	MLE Me	an (bias corrected)	93.54	MLE Sd (bias corrected)	44.51
		,		Approximate Chi Square Value (0.05)	59.97
50					

	A B C D E	F	G	н	JK	<del></del>
51	A B C D E Adjusted Level of Significance		G	п	Adjusted Chi Square Value	56.41
52						<u> </u>
53	As	suming Gam	nma Distribu	tion		
54	95% Approximate Gamma UCL (use when n>=50))	124		95% Ad	justed Gamma UCL (use when n<50)	131.9
55						
56		Lognorma	I GOF Test			
57	Shapiro Wilk Test Statistic	0.783		Shap	iro Wilk Lognormal GOF Test	
58	5% Shapiro Wilk Critical Value	0.829		Data Not I	ognormal at 5% Significance Level	
59	Lilliefors Test Statistic	0.304		Lill	iefors Lognormal GOF Test	
60	5% Lilliefors Critical Value	0.295		Data Not I	ognormal at 5% Significance Level	
61	Data Not I	Lognormal at	t 5% Signific	ance Level		
62						
63		-	al Statistics			
64	Minimum of Logged Data				Mean of logged Data	
65	Maximum of Logged Data	4.92			SD of logged Data	0.474
66						
67		uming Logno	ormal Distrib	oution		
68	95% H-UCL				90% Chebyshev (MVUE) UCL	
69	95% Chebyshev (MVUE) UCL				97.5% Chebyshev (MVUE) UCL	. 190.8
70	99% Chebyshev (MVUE) UCL	. 247.4				
71						
72	-	etric Distribu				
73	Data appear to follow a	Discernible	Distribution	at 5% Signifi	cance Level	
74	News					
75	-	rametric Dist		e UCLs	050/ 1	110 5
76	95% CLT UCL				95% Jackknife UCL	
77	95% Standard Bootstrap UCL				95% Bootstrap-t UCL	
78	95% Hall's Bootstrap UCL 95% BCA Bootstrap UCL				95% Percentile Bootstrap UCL	108.8
79	95% BCA Boolstrap UCL 90% Chebyshev(Mean, Sd) UCL				95% Chebyshev(Mean, Sd) UCL	. 140.4
80	97.5% Chebyshev(Mean, Sd) UCL				99% Chebyshev(Mean, Sd) UCL	
81		100.0				200.5
82		Suggested	UCL to Use			
83	95% Student's-t UCL					T
84		110.0				
85	Note: Suggestions regarding the selection of a 95%	& UCL are pr	ovided to he	In the user to	select the most appropriate 95% UC	<u> </u>
86	These recommendations are based upon the res	•		•		
87	and Singh and Singh (2003). Howev					
88	For additional insig					
89						
90	Note: For highly negatively-skewed data, confi	idence limits	(e.g., Chen	, Johnson, Lo	ognormal, and Gamma) may not be	
91	reliable. Chen's and Johnson's m					
92 93		· · ·	-	•	-	
93 94						
-	Cobalt					
95 96						
90 97		General	Statistics			
97 98	Total Number of Observations	9			Number of Distinct Observations	9
		+			Number of Missing Observations	; 0
	Minimum	93			Mean	
99 100	Minimum	93				

	А	В		С	D		E	F	G		Н		1	T	J	<b>—</b>	К	
101	7			0			Maximum	427	<u> </u>			-			0		Median	248
102							SD	102.5							Std.	Error	of Mean	34.15
102					Coeffic	cient of	f Variation	0.4								Sł	kewness	0.21
104																		
105			N	ote: Sam	ple size is	s sma	<b>ll (e.g., &lt;</b> 1	0), if data a	are collect	ed using	g ISM a	approa	ich, you	ı shou	uld us	e		
106			gui	idance pr	ovided in	ITRC	; Tech Re	g Guide on	ISM (ITRO	C, 2012)	) to con	npute	statistic	cs of i	intere	st.		
107				For	example,	you n	nay want f	o use Chel	oyshev UC	CL to est	timate l	EPC (	ITRC, 2	2012).				
108			С	hebyshe	VUCL car	n be c	omputed	using the N	onparame	etric and	I All UC	CL Opt	ions of	ProU	CL 5.	0		
109																		
110								Normal	GOF Tes	t								
111				S	hapiro Wi	ilk Te	st Statistic	0.97				Sha	piro Wi	ilk GC	OF Te	st		
112				5% S	hapiro Wi	ilk Crit	ical Value	0.829		D	ata app	oear N	ormal a	nt 5% 3	Signif	icance	Level	
113					Lilliefo	ors Tes	st Statistic	0.196				Li	lliefors	GOF	Test			
114				5	% Lilliefor	rs Crit	ical Value	0.295		D	ata app	oear N	ormal a	nt 5% 3	Signif	icance	Level	
115						I	Data appe	ar Normal a	at 5% Sigr	nificance	e Level	I						
116																		
117							As	suming No	rmal Distr	ibution								
118				95% N	ormal UC	L					95%	% UCL	.s (Adju	usted <sup>·</sup>	for Sk	ewne	ss)	
119					95% :	Stude	nt's-t UCL	320				95%	Adjuste	ed-CL	T UCI	_ (Che	en-1995)	315.2
120												95%	Modifi	ed-t U	JCL (J	ohnso	on-1978)	320.4
121																		
122								Gamma	GOF Tes	st								
123					A-	-D Tes	st Statistic	0.241			Ande	erson-	Darling	Gam	ima G	OF Te	əst	
124					5% A-	-D Crit	ical Value	0.723	Dete	ected da	ta appe	ear Ga	mma Di	istribu	uted a	t 5% S	Significan	ce Level
125					K	-S Tes	st Statistic	0.142			Kolmo	ogrov-	Smirno	ff Gar	mma (	GOF 1	ſest	
126					5% K-	-S Crit	ical Value	0.28	Dete	ected da	ta appe	ear Ga	mma Di	istribu	uted a	t 5% S	Significan	ce Level
127					Detec	cted d	ata appea	r Gamma D	istributed	at 5% S	Signific	ance l	evel					
128																		
129								Gamma	a Statistics	5								
130						k	hat (MLE)	6.236					k :	star (t	bias c	orrect	ed MLE)	4.231
131					7	Theta	hat (MLE)	41.13					Theta	star (t	bias c	orrect	ed MLE)	60.61
132						nu	hat (MLE)	112.2						nu s	star (b	ias co	orrected)	76.16
133				М	LE Mean	(bias	corrected)	256.4						MLE	Sd (b	ias co	orrected)	124.7
134												Appr	oximate	e Chi S	Squar	e Valu	ue (0.05)	57.06
135				Adjus	sted Level	l of Si	gnificance	0.0231					A	djuste	ed Chi	Squa	re Value	53.59
136																		
137							As	suming Ga	mma Distr	ribution								
138	95	5% Appr	oximat	e Gamma	a UCL (us	e whe	n n>=50))	342.3			95% A	djuste	d Gamr	ma U(	CL (us	se whe	en n<50)	364.5
139								1										
140								Lognorm	al GOF Te	est								
141				S	hapiro Wi	ilk Te	st Statistic	0.937			Sha	apiro V	Vilk Log	gnorm	nal GC	OF Te	st	
142				5% S	hapiro Wi	ilk Crit	ical Value	0.829		Dat	ta appe	ear Log	Inormal	at 5%	6 Sigr	ifican	ce Level	
143					Lilliefo	ors Tes	st Statistic	0.168			L	illiefor	s Logno	ormal	GOF	Test		
144				5	% Lilliefo	rs Crit	ical Value	0.295		Dat	ta appe	ear Log	normal	at 5%	% Sigr	ifican	ce Level	
145						Da	ata appea	r Lognorma	l at 5% Si	gnifican	ice Lev	el						
146																		
147								Lognorm	al Statistic	cs								
148					Minimum	of Lo	gged Data	4.533						Ν	/lean o	of logg	jed Data	5.465
149				1	Maximum	of Lo	gged Data	6.057							SD o	of logg	jed Data	0.454
150								1										

	А	В	С	D	E	F	G H			J		K	
151	Α	U	0	D		-	rmal Distribution			0		IX I	L
152					95% H-UCL	371.8		ç	0% Cheby	yshev (N	MVUE	) UCL	377.3
153			95%	Chebyshev	(MVUE) UCL	431.1		97.	5% Cheby	yshev (N	MVUE	) UCL	505.8
154			99%	Chebyshev	(MVUE) UCL	652.4							
155													
156					Nonparam	etric Distribut	tion Free UCL Statist	ics					
157				Data appea	ar to follow a	Discernible [	Distribution at 5% Sig	nificance L	.evel				
158													
159					Nonpa	rametric Dist	tribution Free UCLs						
160				9	5% CLT UCL	312.6			ç	95% Jao	ckknif	e UCL	320
161			95%	Standard B	ootstrap UCL	309.5			95	5% Boot	tstrap-	-t UCL	325.2
162				95% Hall's B	ootstrap UCL	322.2		9	5% Percer	ntile Bo	otstra	p UCL	308.1
163				95% BCA B	ootstrap UCL	312.3							
164			90% C	nebyshev(Me	ean, Sd) UCL	358.9		95%	6 Chebysh	nev(Mea	an, Sd	J) UCL	405.3
165			97.5% C	nebyshev(Me	ean, Sd) UCL	469.7		99%	6 Chebysh	nev(Mea	an, Sd	לג) UCL	596.3
166													
167						Suggested	UCL to Use						
168				95% Stu	udent's-t UCL	320							
169													
170	١	Note: Sugges	tions regar	ding the sele	ction of a 95%	6 UCL are pro	ovided to help the use	r to select t	he most ap	ppropria	ate 95	% UCL	•
171		These reco	mmendatic	ns are based	d upon the res	sults of the sir	mulation studies sumr	narized in S	Singh, Sing	gh, and	laci (2	2002)	
			and Singl	and Singh (	2003). Howe	ver, simulatio	ns results will not cov	er all Real V	Norld data	sets.			
172			and enigr	i ana omgir (									
172 173							ay want to consult a s	tatistician.					
173							ay want to consult a s	tatistician.					
173 174							ay want to consult a s	tatistician.					
173 174 175	Copper						ay want to consult a s	tatistician.					
173 174 175 176	Copper						ay want to consult a s	statistician.					
173 174 175 176 177	Copper							statistician.					
173 174 175 176 177 178	Copper			For ad		ht the user m			mber of Di	stinct O	bserv	'ations	9
173 174 175 176 <b>C</b> 177 178 179	Copper			For ad	dditional insig	ht the user m		Nu	mber of Dia				9
173 174 175 176 177 177 178 179 180	Copper			For ad	dditional insig	ht the user m General S 9		Nu					
173 174 175 176 177 177 178 179 180 181	Copper			For ad	dditional insig	ht the user m General S 9		Nu			)bserv	ations	0
173 174 175 176 177 177 178 179 180 181 182	Copper			For ad	dditional insig	ht the user m General S 9 827 3930		Nu			)bserv N	vations Mean Median	0 2452
173 174 175 176 177 178 178 179 180 181 182 183	Copper			For ad	dditional insig Observations Minimum Maximum	At the user m General 3 9 827 3930 941.1		Nu		ssing O	bserv N rror of	vations Mean Median	0 2452 2270
173 174 175 176 177 177 178 179 180 181 182	Copper			For ad	dditional insig Observations Minimum Maximum SD	At the user m General 3 9 827 3930 941.1		Nu		ssing O	bserv N rror of	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 177 178 179 180 181 181 182 183 184	Copper		Tota	For ac	Observations Minimum Maximum SD nt of Variation	General 3           9           827           3930           941.1           0.384		Nur	nber of Mis	ssing O Std. Er	bserv N rror of	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 178 180 180 181 182 183 184 185	Copper		Tota Note: Sarr guidance p	For ac For ac I Number of ( Coefficier aple size is s rovided in IT	Observations Observations Minimum Maximum SD nt of Variation mall (e.g., <1 rRC Tech Re	General S         9         827         3930         941.1         0.384         0), if data and g Guide on IS	Statistics e collected using ISM SM (ITRC, 2012) to c	Nur Nur	nber of Mis	Std. Er	bserv M rror of Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 179 180 180 181 182 183 183 184 185 186	Copper		Tota Note: Sarr guidance p	For ac For ac I Number of ( Coefficier aple size is s rovided in IT	Observations Observations Minimum Maximum SD nt of Variation mall (e.g., <1 rRC Tech Re	General S         9         827         3930         941.1         0.384         0), if data and g Guide on IS	Statistics	Nur Nur	nber of Mis	Std. Er	bserv M rror of Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 177 178 179 180 181 182 183 183 184 185 186 187	Copper		Tota Note: Sam guidance p For	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo	Observations Observations Minimum Maximum SD It of Variation Imall (e.g., <1 RC Tech Resource)	ht the user m General \$ 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby	Statistics e collected using ISM SM (ITRC, 2012) to c	Nur Nur I approach, ompute sta	you shou tistics of ir	Std. Er	bserv M rror of Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 178 179 180 181 182 183 184 185 186 187 188	Copper		Tota Note: Sam guidance p For	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo	Observations Observations Minimum Maximum SD It of Variation Imall (e.g., <1 RC Tech Report	ht the user m General \$ 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby	Statistics e collected using ISM SM (ITRC, 2012) to c rshev UCL to estimate	Nur Nur I approach, ompute sta	you shou tistics of ir	Std. Er	bserv M rror of Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 178 179 180 181 182 183 184 185 185 186 187 188	Copper		Tota Note: Sam guidance p For	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo	Observations Observations Minimum Maximum SD It of Variation Imall (e.g., <1 RC Tech Report	General S 9 827 3930 941.1 0.384 0), if data arr g Guide on IS to use Cheby using the Not	Statistics e collected using ISM SM (ITRC, 2012) to c rshev UCL to estimate	Nur Nur I approach, ompute sta	you shou tistics of ir	Std. Er	bserv M rror of Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 179 180 180 181 182 183 184 185 185 186 187 188 188 188	Copper		Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier ple size is s rovided in IT example, yo v UCL can b	Observations Observations Minimum Maximum SD It of Variation Imall (e.g., <1 RC Tech Report	ht the user m General S 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Nor Normal C	Statistics e collected using ISM SM (ITRC, 2012) to co rshev UCL to estimate nparametric and All L	Nur Nur I approach, ompute sta e EPC (ITR JCL Option	you shou tistics of ir	Std. Er Ild use Interest.	Normal Skev	vations Mean Median f Mean	0 2452 2270 313.7
173 174 175 176 177 178 178 179 180 180 181 182 183 184 185 185 186 187 188 188 188 188 188	Copper		Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of C Coefficier ple size is s rovided in IT example, yo v UCL can b Shapiro Wilk	dditional insig Observations Minimum Maximum SD at of Variation mall (e.g., <1 RC Tech Rep ou may want to be computed	ht the user m General S 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Nor Normal C 0.962	Statistics e collected using ISM SM (ITRC, 2012) to co shev UCL to estimate nparametric and All U GOF Test	Nur Nur I approach, ompute sta e EPC (ITR JCL Option	you shou tistics of in C, 2012). s of ProU( o Wilk GO	Std. Er Id use nterest. CL 5.0	Dbserv M rror of Skev	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 178 179 180 180 181 182 183 184 185 185 186 187 188 188 188 188 188 188 188 188 188	Copper		Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier ple size is s rovided in IT example, yo v UCL can b Shapiro Wilk (	dditional insig	ht the user m General S 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Nor Normal C 0.962 0.829	Statistics e collected using ISM SM (ITRC, 2012) to co shev UCL to estimate nparametric and All U GOF Test	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapiro ppear Norm	you shou tistics of in C, 2012). s of ProU( o Wilk GO	Std. Er Id use Interest. CL 5.0	Normal Skew	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 179 180 180 181 182 183 184 183 184 185 186 187 188 188 188 188 188 189 190 191 192 193	Copper		Tota Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo v UCL can b Shapiro Wilk shapiro Wilk chapiro Wilk	Dbservations Minimum Maximum SD Int of Variation mall (e.g., <1 RC Tech Rep bu may want f recomputed Test Statistic Critical Value	ht the user m General 3 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Nor Normal C 0.962 0.829 0.157	Statistics e collected using ISM SM (ITRC, 2012) to construction rshev UCL to estimate nparametric and All U GOF Test Data a	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapiro ppear Norm	you shou tistics of in C, 2012). s of ProU( D Wilk GO hal at 5% S fors GOF	Std. En Id use Id use Iterest. CL 5.0 F Test Significa Test	Norror of Skey	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 178 178 180 180 181 183 183 184 185 183 184 185 188 188 188 188 188 189 190 191 192 193 194 195	Copper		Tota Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo v UCL can b Shapiro Wilk shapiro Wilk chapiro Wilk	dditional insig	General \$         9         827         3930         941.1         0.384         0), if data are         g Guide on IS         to use Cheby         using the Normal G         0.962         0.829         0.157         0.295	Statistics e collected using ISM SM (ITRC, 2012) to construction rshev UCL to estimate nparametric and All U GOF Test Data a	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapir ppear Norm Lillie ppear Norm	you shou tistics of in C, 2012). s of ProU( D Wilk GO hal at 5% S fors GOF	Std. En Id use Id use Iterest. CL 5.0 F Test Significa Test	Norror of Skey	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 178 179 180 180 181 182 183 183 184 185 185 186 187 188 188 189 190 191 192 193 193 194 195			Tota Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo v UCL can b Shapiro Wilk shapiro Wilk chapiro Wilk	dditional insig	General \$         9         827         3930         941.1         0.384         0), if data are         g Guide on IS         to use Cheby         using the Normal G         0.962         0.829         0.157         0.295	Statistics  e collected using ISM GM (ITRC, 2012) to c shev UCL to estimate nparametric and All L GOF Test Data a Data a	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapir ppear Norm Lillie ppear Norm	you shou tistics of in C, 2012). s of ProU( D Wilk GO hal at 5% S fors GOF	Std. En Id use Id use Iterest. CL 5.0 F Test Significa Test	Norror of Skey	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 178 178 180 180 181 182 183 184 183 184 185 186 187 188 188 189 190 191 192 193 194 195 196			Tota Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo v UCL can b Shapiro Wilk shapiro Wilk chapiro Wilk	dditional insig	ht the user m General 3 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Not 0.962 0.962 0.829 0.157 0.295 ar Normal at	Statistics  e collected using ISM GM (ITRC, 2012) to c shev UCL to estimate nparametric and All L GOF Test Data a Data a	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapir ppear Norm Lillie ppear Norm	you shou tistics of in C, 2012). s of ProU( D Wilk GO hal at 5% S fors GOF	Std. En Id use Id use Iterest. CL 5.0 F Test Significa Test	Norror of Skey	vations Mean Aedian f Mean wness	0 2452 2270 313.7
173 174 175 176 177 178 178 178 180 180 181 182 183 184 185 188 188 188 188 188 188 188 188 188	Copper		Tota Tota Note: Sam guidance p For Chebyshe	For ac For ac I Number of ( Coefficier aple size is s rovided in IT example, yo v UCL can b Shapiro Wilk shapiro Wilk chapiro Wilk	dditional insig	ht the user m General 3 9 827 3930 941.1 0.384 0), if data are g Guide on IS to use Cheby using the Not 0.962 0.962 0.829 0.157 0.295 ar Normal at	Statistics  e collected using ISM GM (ITRC, 2012) to c shev UCL to estimate nparametric and All L GOF Test Data a Data a 5% Significance Lev nal Distribution	Nur Nur I approach, ompute sta e EPC (ITR JCL Option Shapir ppear Norm Lillie ppear Norm	you shou tistics of in C, 2012). s of ProU( b Wilk GO hal at 5% S fors GOF hal at 5% S	Std. En Id use Id use Iterest. CL 5.0 F Test Bignifica Bignifica	Normal Skew	vations Mean Aedian f Mean wness 	0 2452 2270 313.7

	A	В		С	1	D		E	F	G	н		1		.1		К	
201	χ	D		0		D		<u> </u>		Ğ		95%	Modifie	ed-t U	•	ohnso	on-1978)	3036
202																		
203									Gamma	GOF Test								
204						A-D	Test	Statisti	0.319	Anderson-Darling Gamma GOF Test								
205					5	% A-D	Critic	al Valu	e 0.722	Detected data appear Gamma Distributed at 5% Significance Leve								nce Level
206						K-S	Test	Statisti	c 0.191		Kolmo	ogrov-S	mirnof	f Gar	nma (	GOF	Test	
207					5	% K-S	Critic	al Valu	e 0.28	Detecte	ed data appe	ear Gam	nma Di	stribu	ited at	5% S	Significa	nce Level
208					۵	Detecte	ed dat	ta appe	ar Gamma D	istributed at	5% Significa	ance Le	evel					
209																		
210									Gamma	Statistics								
211							k h	at (MLE	) 6.383				k s	star (b	oias co	orrect	ed MLE)	4.329
212						Th	eta h	at (MLE	) 384.1			-	Theta s	star (b	oias co	orrect	ed MLE)	566.4
213							nu h	at (MLE	) 114.9					nu s	star (b	ias co	prrected)	77.93
214				М	LE M	lean (bi	ias co	orrected	) 2452					MLE	Sd (b	ias co	orrected)	1178
215												Appro	ximate	Chi S	Square	e Valu	ue (0.05)	58.59
216				Adjus	sted I	Level o	of Sigr	nificance	e 0.0231				Ad	ljuste	d Chi	Squa	re Value	55.07
217																		
218								A	ssuming Gar	nma Distribu	ition							
219	g	5% Approx	kimate	Gamma	a UCI	L (use v	when	n>=50)	) 3261		95% A	djusted	l Gamn	na UC	CL (us	e whe	en n<50)	3470
220																		
221									Lognorma	I GOF Test								
222				S	Shapi	ro Wilk	Test	Statisti	0.894		Sha	apiro W	ilk Log	norm	al GO	)F Te	st	
223				5% S	hapir	o Wilk	Critic	al Valu	e 0.829		Data appe	ar Logr	normal	at 5%	Sign	ifican	ce Level	
224					Li	lliefors	Test	Statisti	0.227		Li	illiefors	Logno	ormal	GOF	Test		
225				5	5% Li	lliefors	Critic	al Valu	e 0.295		Data appe	ar Logr	normal	at 5%	Sign	ifican	ce Leve	
226							Dat	a appea	ar Lognorma	at 5% Signi	ficance Lev	el						
227																		
228									Lognorma	al Statistics								
229					Minir	num of	f Logo	ged Data	a 6.718					Ν	lean o	of logg	ged Data	7.724
230				ſ	Maxir	num of	f Logg	ged Data	a 8.276						SD o	of logg	ged Data	0.457
231																		
232								As	suming Logn	ormal Distrit	oution							
233							95%	6 H-UCI	3577				90% (	Cheb	yshev	(MVL	JE) UCL	3627
234				95%	Cheb	oyshev	(MVI	JE) UCI	4146			ç	97.5% (	Cheb	yshev	(MVL	JE) UCL	4867
235				99%	Cheb	oyshev	(MVI	JE) UCI	6283									
236																		
237							No	nparam	etric Distrib	ution Free U	CL Statistics	s						
238					Dat	a appe	ar to	follow a	Discernible	Distribution	at 5% Signi	ificance	e Level					
239																		
240								Nonpa	arametric Dis	stribution Fre	e UCLs							
241						9	95% C	CLT UCI	2968					9	95% J	lackkr	nife UCL	3035
242				95%	Star	ndard B	Bootst	rap UCI	2932					95	5% Bo	otstra	ap-t UCL	3118
243				ç	95% I	Hall's B	Bootst	rap UCI	3131				95% F	Perce	ntile B	Bootst	rap UCL	2955
244					95%	BCA B	Bootst	rap UCI	2938									
245				90% Cł	nebys	shev(M	ean,	Sd) UCI	3393			9	5% Ch	ebysł	hev(M	ean, S	Sd) UCL	3819
246			9	7.5% Cł	nebys	shev(M	ean,	Sd) UCI	_ 4411			9	9% Ch	ebysł	nev(M	ean, S	Sd) UCL	5573
247									1	1								1
248									Suggested	UCL to Use	•							
249					ę	95% St	uden	t's-t UCI	3035									
250									1									
200										1	1			1				<u> </u>

	A	В	С		D		E	F		G		Н		I		J		K	T	L
251		Note: Sugges							•		•					••	•			
252		These reco				•												aci (2002)	l	
253			and Sin	ngh and				ver, simula							Vorld	data se	ts.			
254					For a	dditiona	al insig	ht the use	er ma	ay want t	o con	sult a st	tatisti	ician.						
255																				
256																				
257	Nickel																			
258																				
259						<u></u>			ral 3	Statistics						(				•
260			IC	otal Nu	mber of	Observ	ations	; 9										servation		9
261								E 400						Num	iber c	ot iviissir	ng Ob	servation		0
262							nimum											Mea		17972
263						IVIa.	iximum									<u></u>	al <b>F</b> aaa	Media or of Mea		18250
264						-+ -f \//	SD		<b>`</b>							50				
265				Ĺ	Coefficier	It of Va	irlation	0.439	9									Skewnes	s	0.47
266			Note: S	ampla		mall /		10), if data			dual			aaab		hould				
267				=			-	g Guide o				-			-					
268			-	-				to use Che		•		•	-				631.			
269								using the							-		5.0			
270							puteu	using the		iparamet				puona			0.0			
271								Norma	al G	OF Test										
272				Shar	oiro Wilk	Test S	tatistic						s	haniro	Wilk	GOF T	est			
273			5%		oiro Wilk							Data ar		-				ce Level		
274					Lilliefors								pour					20101		
275					Lilliefors							Data ar	opear					ce Level		
276								ar Norma	l at	5% Sian			-			J				
277																				
278							A	ssuming N	lorn	nal Distril	butio	า								
279 280			95%	Norm	al UCL			•				95	5% U	CLs (A	\djus	ted for \$	Skewi	ness)		
281					95% Stu	udent's	-t UCL	22861					95	i% Adjı	usted	-CLT U	CL (C	hen-1995	5) 2	22737
282													9	5% Mo	dified	I-t UCL	(John	son-1978	3) 2	22930
283																				
284								Gamm	na G	GOF Test	:									
285					A-D	Test S	tatistic	0.248	3			And	derso	n-Darl	ling G	amma	GOF	Test		
286					5% A-D	Critical	l Value	0.723	3	Detec	cted c	ata app	bear (	Gamma	a Dis	tributed	at 5%	Significa	anc	e Level
287					K-S	Test S	tatistic	0.162	2			Kolm	nogra	ov-Smi	rnoff	Gamma	a GOF	- Test		
288					5% K-S	Critical	l Value	0.28		Deteo	cted c	ata app	bear (	Gamma	a Dis	tributed	at 5%	Significa	anc	e Level
289					Detecte	d data	appea	r Gamma	Dis	stributed	at 5%	Signifi	canc	e Leve	əl					
290																				
291								Gamn	na S	Statistics										
292						k hat	(MLE)	5.086	6						k st	ar (bias	corre	cted MLE	=)	3.465
293					The	eta hat	(MLE)	3534						The	eta st	ar (bias	corre	cted MLE	E)	5187
294						nu hat	(MLE)	91.55								nu star	(bias	corrected	(t	62.37
295				MLE I	Mean (bi	as corr	rected)	17972										corrected	<i>`</i>	9655
296													Ap	proxim	nate (	Chi Squ	are Va	alue (0.05	5)	45.2
297			Ac	djusted	Level of	f Signif	icance	0.0231	1						Adj	usted C	hi Squ	uare Valu	е	42.14
298																				
299							As	suming G	iam	ma Distri	butio	n								
300		95% Approxin	nate Gam	nma UC	CL (use v	when n	>=50))	24797				95%	Adju	sted Ga	amma	a UCL (	use w	hen n<50	)) 2	26601
						-														

	А	В	С	D	E	F	G	Н	1	J	К	L
301												
302						Lognorma	GOF Test					
303			S	hapiro Wilk	Fest Statistic	0.924		Shap	oiro Wilk Log	normal GOF	Test	
304			5% S	hapiro Wilk C	Critical Value	0.829		Data appea	r Lognormal	at 5% Signifi	cance Level	
305				Lilliefors	Fest Statistic	0.199			-	ormal GOF T		
306			5		Critical Value	0.295			-	at 5% Signifi	cance Level	
307					Data appear	r Lognormal	at 5% Signif	icance Leve	I			
308												
309						-	I Statistics					
310				Minimum of I		8.594					logged Data	9.695
311			Ν	laximum of I	_ogged Data	10.4				SD of	logged Data	0.512
312												
313							ormal Distrib	ution				
314					95% H-UCL	27805				Chebyshev (		27691
315				Chebyshev (	-	31981			97.5%	Chebyshev (	MVUE) UCL	37935
316			99%	Chebyshev (	MVUE) UCL	49630						
317												
318					•		tion Free UC					
319				Data appea	r to follow a	Discernible	Distribution a	at 5% Signifi	cance Level			
320												
321					=		tribution Free	e UCLs				
322					% CLT UCL	22297					ckknife UCL	22861
323				Standard Bo	•	22094					tstrap-t UCL	
324				5% Hall's Bo	•	24997			95% F	Percentile Bo	otstrap UCL	22300
325					otstrap UCL	22172						
326				ebyshev(Me	-	25860				ebyshev(Me		29433
327			97.5% Ch	ebyshev(Me	an, Sd) UCL	34392			99% Ch	ebyshev(Me	an, Sd) UCL	44133
328												
329							UCL to Use					
330				95% Stu	dent's-t UCL	22861			1	1		ļ
331								-		_		
332	1		stions regard	-								
333		I hese rec	ommendatio							-	laci (2002)	
334			and Singh				ons results wi			d data sets.		
335				For ad	ditional insig	ht the user m	hay want to c	onsult a stati	stician.			
336												

	A B C D E	F	G H I J K	<u>L</u>							
1	UCL Statist	tics for Unce	ensored Full Data Sets								
2											
3	User Selected Options										
4	Date/Time of Computation 8/19/2014 4:22:00 PM										
5	From File worse-case UCLM_d.xls										
6	Full Precision OFF										
7	Confidence Coefficient 95%										
8	Number of Bootstrap Operations 2000										
9											
10											
11	Arsenic										
12											
13		General	Statistics								
14	Total Number of Observations	15	Number of Distinct Observations	12							
15			Number of Missing Observations	1							
16	Minimum	3.2	Mean	16.28							
17	Maximum	28.5	Median	20.2							
18	SD	8.072	Std. Error of Mean	2.084							
19	Coefficient of Variation	0.496	Skewness	-0.298							
20											
21		Normal G	iOF Test								
22	Shapiro Wilk Test Statistic	0.919	Shapiro Wilk GOF Test								
23	5% Shapiro Wilk Critical Value	0.881	Data appear Normal at 5% Significance Level								
24	Lilliefors Test Statistic	0.22	Lilliefors GOF Test								
25	5% Lilliefors Critical Value	0.229	Data appear Normal at 5% Significance Level								
26	Data appea	r Normal at	5% Significance Level								
27											
28	Ass	uming Norn	nal Distribution								
29	95% Normal UCL		95% UCLs (Adjusted for Skewness)								
30	95% Student's-t UCL	19.95	95% Adjusted-CLT UCL (Chen-1995)	19.54							
31			95% Modified-t UCL (Johnson-1978)	19.92							
32											
33		Gamma C	GOF Test								
34	A-D Test Statistic	0.823	Anderson-Darling Gamma GOF Test								
35	5% A-D Critical Value	0.744	Data Not Gamma Distributed at 5% Significance Leve	el							
36	K-S Test Statistic	0.253	Kolmogrov-Smirnoff Gamma GOF Test								
37	5% K-S Critical Value	0.223	Data Not Gamma Distributed at 5% Significance Leve	el							
38	Data Not Gamm	na Distribute	ed at 5% Significance Level								
39											
40		Gamma	Statistics								
41	k hat (MLE)	3.091	k star (bias corrected MLE)	2.518							
41	Theta hat (MLE)	5.266	Theta star (bias corrected MLE)	6.467							
43	nu hat (MLE)	92.74	nu star (bias corrected)	75.53							
44	MLE Mean (bias corrected)	16.28	MLE Sd (bias corrected)	10.26							
44			Approximate Chi Square Value (0.05)	56.51							
46	Adjusted Level of Significance	0.0324	Adjusted Chi Square Value	54.49							
40											
47	Ass	uming Gam	ma Distribution								
48 49	95% Approximate Gamma UCL (use when n>=50))	21.76	95% Adjusted Gamma UCL (use when n<50)	22.57							
	··· · · · · · · //		- ` ` '								
50											

	А	1	В		С			D	Т	E		F	G	Т	Н		1			J		<u> </u>	К		<u> </u>	L
51			_		-								GOF Test				-								<u> </u>	_
52						S	hapi	ro Wil	k Tes	st Sta	tistic	0.855			SI	napir	o Wil	k Lo	gno	rmal	GOF	Те	st			
53					5	i% Sł	hapir	o Will	k Criti	ical V	/alue	0.881		[	Data N	ot Lo	gnori	mal	at 5	% Sig	nifica	ance	e Le	vel		
54							Li	illiefor	s Tes	st Sta	tistic	0.25				Lillie	fors	Logr	norn	nal Go	OF T	est				
55						59	% Lil	lliefors				0.229			Data N		gnori	mal	at 5	% Sig	nifica	ance	e Le	vel		
56									0	Data I	Not L	ognormal at	5% Signific	cano	e Lev	el										
57																										
58												Lognorma	I Statistics													
59								num c	-			1.163											-	Data		2.62
60						Ν	<i>l</i> laxir	num c	of Log	jged l	Data	3.35								S	D of	logg	ged I	Data	(	).675
61																										
62												iming Logno	rmal Distrib	outic	on											
63										5% H-		25.98								ebysł			,			6.24
64								oyshe	•			30.45					97	7.5%	5 Ch	ebysł	iev (	ΜV	JE)	UCL	3	6.3
65					ç	<u>}9% (</u>	Chet	oyshe	v (MV	/UE)	UCL	47.79														
66																										
67										-		tric Distribu														
68							Data	a app	ear to	o follo	ow a l	Discernible	Distribution	at 5	5% Sig	nifica	ance	Lev	el							
69																										
70									050/		-	ametric Dis	ribution Fre	e U	CLS					0.50	<u> </u>		.,			0.05
71		95% CL1 95% Standard Bootstrap										19.71												UCL		9.95
72										-		19.59						050/	De	95%			•			9.74
73		95% Hall's Bootstrap UCL     19.45     95% Percentile Bootstrap UCL       95% BCA Bootstrap UCL     19.44										9.55														
74					000							19.44					05	0/ 0					<u> </u>			E 20
75								shev(N shev(N				22.53 29.3	95% Chebyshev(Mean, Sd) UCL							5.36						
76					97.5		ebys		/iean,	, Su)	UCL	29.5	3 99% Chebyshev(Mean, Sd) UCL						3	7.02						
77												Suggested	UCL to Lise	<u> </u>												
78								95% S	Studer	nt's_t		19.95													<u> </u>	
79											UUL	10.00													<u> </u>	
80		Note	: Suac	restio	ons re	aard	lina t	he se	lectio	on of a	95%	UCL are pr	ovided to he	elp th	ne use	r to s	elect	the	mos	t appi	ropri	ate 9	95%		 L.	
81						-	-					ults of the si		-												
82												er, simulatio								•			<b>\</b>			
83 84								-				nt the user m														
85													-													
86		No	ote: Fo	or hig	ihly r	negat	ively	/-skev	ved d	lata, (	confic	lence limits	(e.g., Chen	, Jo	hnson	, Log	norm	al, a	and	Gamr	na) I	may	not	be		
87				I	reliat	ole. (	Cher	n's an	d Joh	nnson	n's me	thods provi	de adjustme	ents	for po	sitve	ly sk	ewe	d da	ata se	ts.					
88																										
89																										
	Cobalt																									
91																										
92												General	Statistics													
93					-	Fotal	Num	nber o	fObs	servat	tions	15					Νι	umb	er of	Disti	nct C	bse	ervat	tions	1	3
94																	Nu	imbe	er of	Missi	ing C	bse	ervat	tions		1
95						-				Minir	mum	12											Ν	<i>l</i> lean	3	4.07
96										Maxir	mum	77											Me	edian	3	4
97											SD	19.78							!	5.108						
98							Сс	pefficie	ent of	f Varia	ation	0.581										Sł	kewi	ness	<u> </u>	1.095
99																										
100												Normal (	GOF Test					_					_			

	A B C D E	F	G H I J K	1
101	Shapiro Wilk Test Statistic	0.877	Shapiro Wilk GOF Test	
102	5% Shapiro Wilk Critical Value	0.881	Data Not Normal at 5% Significance Level	
102	Lilliefors Test Statistic	0.182	Lilliefors GOF Test	
104	5% Lilliefors Critical Value	0.229	Data appear Normal at 5% Significance Level	
105	Data appear Approx	kimate No	rmal at 5% Significance Level	
106				
107	Assu	ming Norr	nal Distribution	
107	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
109	95% Student's-t UCL	43.06	95% Adjusted-CLT UCL (Chen-1995)	44.01
110			95% Modified-t UCL (Johnson-1978)	43.3
111				
112		Gamma	GOF Test	
	A-D Test Statistic	0.353	Anderson-Darling Gamma GOF Test	
113	5% A-D Critical Value	0.743	Detected data appear Gamma Distributed at 5% Significance	e Level
114	K-S Test Statistic	0.118	Kolmogrov-Smirnoff Gamma GOF Test	
115	5% K-S Critical Value	0.223	Detected data appear Gamma Distributed at 5% Significance	e Level
116			stributed at 5% Significance Level	
117				
118		Gamma	Statistics	
119	k hat (MLE)	3.383	k star (bias corrected MLE)	2.751
120	Theta hat (MLE)	10.07	Theta star (bias corrected MLE)	12.38
121	· · · · ·	101.5	nu star (bias corrected)	82.54
122	MLE Mean (bias corrected)	34.07	MLE Sd (bias corrected)	20.54
123		01.07	Approximate Chi Square Value (0.05)	62.6
124	Adjusted Level of Significance	0.0324	Adjusted Chi Square Value	60.47
125		0.0024		00.47
126	Assu	ming Gam	ma Distribution	
127	95% Approximate Gamma UCL (use when n>=50))	44.92	95% Adjusted Gamma UCL (use when n<50)	46.5
128		11.02		40.0
129	1	ognormal	GOF Test	
130	Shapiro Wilk Test Statistic	0.94	Shapiro Wilk Lognormal GOF Test	
131	5% Shapiro Wilk Critical Value	0.881	Data appear Lognormal at 5% Significance Level	
132	Lilliefors Test Statistic	0.137	Lilliefors Lognormal GOF Test	
133	5% Lilliefors Critical Value	0.229	Data appear Lognormal at 5% Significance Level	
134			at 5% Significance Level	
135		- 9.1011101		
136		Lognorma	I Statistics	
137	Minimum of Logged Data	2.485	Mean of logged Data	3.373
138	Maximum of Logged Data Maximum of Logged Data	4.344	SD of logged Data	0.585
139				0.000
140	Δεειιπ	ing Logno	rmal Distribution	
141	95% H-UCL	48.56	90% Chebyshev (MVUE) UCL	50.28
142	95% Chebyshev (MVUE) UCL	57.57	97.5% Chebyshev (MVUE) UCL	67.69
143	99% Chebyshev (MVUE) UCL	87.58		07.00
144		07.00		
145	Napparamatri	o Dietribut	tion Free UCL Statistics	
146	-		Distribution at 5% Significance Level	
147			Sisuisauon at 5 /0 Significance Leven	
148	Norrere	notria Dia	rribution Free UCLs	
149	95% CLT UCL	42.47	95% Jackknife UCL	43.06
150	95% CLT UCL	42.4/	95% Jackkniie UCL	43.00

	A	B C D E	F	G H I J K	1
151		95% Standard Bootstrap UCL	42.19	95% Bootstrap-t UCL	46.52
152		95% Hall's Bootstrap UCL	52.64	95% Percentile Bootstrap UCL	42.67
152		95% BCA Bootstrap UCL	43.93		
154		90% Chebyshev(Mean, Sd) UCL	49.39	95% Chebyshev(Mean, Sd) UCL	56.33
154		97.5% Chebyshev(Mean, Sd) UCL	65.97	99% Chebyshev(Mean, Sd) UCL	84.89
156					
			Suggested	UCL to Use	
157		95% Student's-t UCL	43.06		
158 159					
160		Note: Suggestions regarding the selection of a 95%	UCL are pro	ovided to help the user to select the most appropriate 95% UCL.	
161		These recommendations are based upon the res	ults of the si	mulation studies summarized in Singh, Singh, and Iaci (2002)	
162		-		ns results will not cover all Real World data sets.	
163				ay want to consult a statistician.	
164					
165	Copper				
100					
167			General	Statistics	
168		Total Number of Observations	15	Number of Distinct Observations	14
169				Number of Missing Observations	1
170		Minimum	58	Mean	305.3
171		Maximum	577	Median	333
172		SD	162.6	Std. Error of Mean	41.98
173		Coefficient of Variation	0.533	Skewness	-0.0505
174					
175			Normal C	GOF Test	
176		Shapiro Wilk Test Statistic	0.93	Shapiro Wilk GOF Test	
177		5% Shapiro Wilk Critical Value	0.881	Data appear Normal at 5% Significance Level	
178 179		Lilliefors Test Statistic	0.154	Lilliefors GOF Test	
		5% Lilliefors Critical Value	0.229	Data appear Normal at 5% Significance Level	
180		Data appe	ar Normal at	5% Significance Level	
181		· · ·		•	
182		As	suming Norr	nal Distribution	
183		95% Normal UCL	•	95% UCLs (Adjusted for Skewness)	
184 185		95% Student's-t UCL	379.2	95% Adjusted-CLT UCL (Chen-1995)	373.7
186				95% Modified-t UCL (Johnson-1978)	379.1
187					
188			Gamma	GOF Test	
189		A-D Test Statistic	0.886	Anderson-Darling Gamma GOF Test	
190		5% A-D Critical Value	0.745	Data Not Gamma Distributed at 5% Significance Leve	əl
190		K-S Test Statistic	0.239	Kolmogrov-Smirnoff Gamma GOF Test	
191		5% K-S Critical Value	0.224	Data Not Gamma Distributed at 5% Significance Leve	əl
192		Data Not Gam	na Distribute	ed at 5% Significance Level	
193					
194 195			Gamma	Statistics	
195		k hat (MLE)		k star (bias corrected MLE)	2.112
		Theta hat (MLE)	118.1	Theta star (bias corrected MLE)	144.5
197 108		nu hat (MLE)	77.53	nu star (bias corrected)	63.36
198		MLE Mean (bias corrected)	305.3	MLE Sd (bias corrected)	210.1
199				Approximate Chi Square Value (0.05)	46.05
200					-

	A B C D E	F	0		I J K	
201	A B C D E Adjusted Level of Significance	г 0.0324	G	Н	Adjusted Chi Square Value	44.24
201						
202	Ass	uming Gam	ma Distribu	tion		
203	95% Approximate Gamma UCL (use when n>=50))	420		95% Adj	justed Gamma UCL (use when n<50)	437.2
204						
205		Lognormal	GOF Test			
207	Shapiro Wilk Test Statistic	0.823		Shap	iro Wilk Lognormal GOF Test	
208	5% Shapiro Wilk Critical Value	0.881		Data Not L	ognormal at 5% Significance Level	
209	Lilliefors Test Statistic	0.265		Lill	iefors Lognormal GOF Test	
210	5% Lilliefors Critical Value	0.229		Data Not L	ognormal at 5% Significance Level	
211	Data Not Lo	ognormal at	5% Signific	ance Level		
212						
213		Lognorma	I Statistics			
214	Minimum of Logged Data	4.06			Mean of logged Data	5.515
215	Maximum of Logged Data	6.358			SD of logged Data	0.757
216			I			
217	Assu	ming Logno	ormal Distrib	ution		
218	95% H-UCL	536.2			90% Chebyshev (MVUE) UCL	524.6
219	95% Chebyshev (MVUE) UCL	615.8			97.5% Chebyshev (MVUE) UCL	742.4
220	99% Chebyshev (MVUE) UCL	990.9				
221	·		I			
222	Nonparame	tric Distribu	tion Free UC	CL Statistics		
223	Data appear to follow a D	Discernible I	Distribution	at 5% Signifi	cance Level	
224						
225	Nonpar	ametric Dist	tribution Fre	e UCLs		
226	95% CLT UCL	374.3			95% Jackknife UCL	379.2
227	95% Standard Bootstrap UCL	371.1			379.9	
228	95% Hall's Bootstrap UCL	379			95% Percentile Bootstrap UCL	371.6
229	95% BCA Bootstrap UCL	373.7				
230	90% Chebyshev(Mean, Sd) UCL	431.2			95% Chebyshev(Mean, Sd) UCL	488.2
231	97.5% Chebyshev(Mean, Sd) UCL	567.4			99% Chebyshev(Mean, Sd) UCL	722.9
232						
233			UCL to Use			
234	95% Student's-t UCL	379.2				
235						
236	Note: Suggestions regarding the selection of a 95%	•		•		
237	These recommendations are based upon the resu					
238	and Singh and Singh (2003). Howeve					
239	For additional insigh	nt the user m	ay want to c	onsult a stati	stician.	
240						
241	Note: For highly negatively-skewed data, confid					
242	reliable. Chen's and Johnson's me	thods provi	de adjustme	ents for positv	vely skewed data sets.	
243						
244						
245	Nickel					
246						
247			Statistics			
	Total Number of Observations	15			Number of Distinct Observations	13
248					Number of Missing Observations	1
248 249	Minimum	355			Mean	1872

B C D E Maximum SD Coefficient of Variation	4310 1170	G H I J K Median Std. Error of Mean	1860 302.1
		Std. Error of Mean	302.1
Coefficient of Variation			
	0.625	Skewness	0.623
	Normal C	GOF Test	
Shapiro Wilk Test Statistic	0.931	Shapiro Wilk GOF Test	
5% Shapiro Wilk Critical Value	0.881	Data appear Normal at 5% Significance Level	
Lilliefors Test Statistic	0.19	Lilliefors GOF Test	
5% Lilliefors Critical Value	0.229	Data appear Normal at 5% Significance Level	
Data appea	ar Normal at	5% Significance Level	
As:	suming Norr	nal Distribution	
	2404		2421
			2412
			22
	Gamma (	SOF Test	
A-D Test Statistic			
			e Level
		_	
			e Levei
Detected data appear	Gamma Dis	stributed at 5% Significance Level	
			1.816
· · ·			1031
			54.48
MLE Mean (bias corrected)	1872		1389
			38.52
Adjusted Level of Significance	0.0324	Adjusted Chi Square Value	36.87
Ass	suming Gam	ma Distribution	
95% Approximate Gamma UCL (use when n>=50))	2648	95% Adjusted Gamma UCL (use when n<50)	2766
	Lognormal	GOF Test	
Shapiro Wilk Test Statistic	0.881	Shapiro Wilk Lognormal GOF Test	
5% Shapiro Wilk Critical Value	0.881	Data appear Lognormal at 5% Significance Level	
Lilliefors Test Statistic	0.193	Lilliefors Lognormal GOF Test	
5% Lilliefors Critical Value	0.229	Data appear Lognormal at 5% Significance Level	
Data appear	Lognormal	at 5% Significance Level	
	Lognorma	I Statistics	
Minimum of Logged Data	5.872	Mean of logged Data	7.292
Maximum of Logged Data	8.369	SD of logged Data	0.801
Assu	iming Logno	rmal Distribution	
95% H-UCL	3417	90% Chebyshev (MVUE) UCL	3277
95% Chebyshev (MVUE) UCL	3868	97.5% Chebyshev (MVUE) UCL	4688
99% Chebyshev (MVUE) UCL	6300		
	5% Shapiro Wilk Critical Value Lilliefors Test Statistic 5% Lilliefors Critical Value Data appea 95% Normal UCL 95% Student's-t UCL 35% A-D Test Statistic 55% A-D Critical Value K-S Test Statistic 5% K-S Critical Value Detected data appear k hat (MLE) Theta hat (MLE) Theta hat (MLE) MLE Mean (bias corrected) Adjusted Level of Significance Adjusted Level of Significance Shapiro Wilk Test Statistic 5% Approximate Gamma UCL (use when n>=50)) Shapiro Wilk Test Statistic 5% Shapiro Wilk Critical Value Lilliefors Test Statistic 5% Lilliefors Critical Value Data appear	5% Shapiro Wilk Critical Value         0.881           Lilliefors Test Statistic         0.19           5% Lilliefors Critical Value         0.229           Data appear Normal at           Student's-t Value           95% Normal UCL         2404           95% Student's-t UCL         2404           0.504         5%           A-D Test Statistic         0.504           5% A-D Critical Value         0.746           K-S Test Statistic         0.157           5% K-S Critical Value         0.224           Detected data appear Gamma Dit           Camma           K hat (MLE)           2.215         3% K-S Critical Value         0.224           Detected data appear Gamma Dit           Camma           K hat (MLE)         2.215           Theta hat (MLE)         845.5           nu hat (MLE)         845.5           nu hat (MLE)         66.44           MLE Mean (bias corrected)         1872           Adjusted Level of Significance         0.0324           Shapiro Wilk Test Statistic         0.881           Shapiro Wilk Critical Value         0.881           Shapiro Wilk Critical Va	5% Shapiro Wilk Critical Value     0.881     Data appear Normal at 5% Significance Level       118/efors Test Statistic     0.19     Ulliefors COF Test       5% Lilliefors Critical Value     0.29     Data appear Normal at 5% Significance Level       Data appear Normal at 5% Significance Level       Assuming Normal Distribution       95% Normal UCL     2404     95% Adjusted-CLT UCL (Johnson-1978)       95% Student's-t UCL     2404     95% Modified-t UCL (Johnson-1978)       Statistic     0.504     Anderson-Darling Gamma GOF Test       A-D Test Statistic     0.576     Kohmogrov-Smirhoff Gamma GOF Test       Statistic     0.577     Kohmogrov-Smirhoff Gamma GOF Test       Statistic     0.577     Kohmogrov-Smirhoff Gamma GOF Test       Statistic     0.577     Kohmogrov-Smirhoff Gamma GOF Test       Detected data appear Gamma Distributed at 5% Significance       Detected data appear Camma Distributed at 5% Significance       Adjusted Level of Significance

	А	В	С	D	E	F	G	Н	I	J	K	L
301					Nonparame	etric Distribu	tion Free UC	L Statistics				
302				Data appea	ar to follow a	Discernible	Distribution a	at 5% Signifi	icance Leve			
303												
304					Nonpa	rametric Dis	tribution Fre	e UCLs				
305				95	5% CLT UCL	2369				95% Ja	ackknife UCL	2404
306			95%	Standard Bo	ootstrap UCL	2352				95% Boo	otstrap-t UCL	2446
307			9	5% Hall's Bo	ootstrap UCL	2513			95% I	Percentile B	ootstrap UCL	2347
308			:	95% BCA Bo	ootstrap UCL	2407						
309		90% Chebyshev(Mean, Sd) UCL 2779 95% Chebyshev(Mean, Sd) UCL 318										3189
310			97.5% Ch	ebyshev(Me	an, Sd) UCL	3759			99% Ch	ebyshev(Me	ean, Sd) UCL	4878
311												
312						Suggested	UCL to Use					
313				95% Stu	ident's-t UCL	2404						
314												
315	I	Note: Sugge	stions regard	ing the seled	ction of a 95%	6 UCL are pr	ovided to hel	p the user to	select the m	nost appropr	iate 95% UCL	
316		These rec	commendation	ns are based	l upon the res	ults of the si	imulation stud	dies summar	ized in Singl	n, Singh, and	d laci (2002)	
317		and Singh and Singh (2003). However, simulations results will not cover all Real World data sets.										
318				For ac	lditional insig	ht the user n	nay want to c	onsult a stati	istician.			
319												

	A B C	DE	F	GHIJK	L
1		UCL Statist	ics for Unc	ensored Full Data Sets	
2					
3	User Selected Options				
4	Date/Time of Computation	9/18/2014 11:39:44 AM			
5	From File	Sediment and Surface Wa	ater Summa	ry_a.xls	
6	Full Precision	OFF			
7	Confidence Coefficient	95%			
8	Number of Bootstrap Operations	2000			
9					
10					
11	Arsenic				
12			-		
13			General		
14	Total	Number of Observations	12	Number of Distinct Observations	8
15				Number of Missing Observations	0
16		Minimum	2.3	Mean	5.217
17		Maximum	12.4	Median	4
18		SD	3.311	Std. Error of Mean	0.956
19		Coefficient of Variation	0.635	Skewness	1.861
20			Normal		
21		haning Wills Tast Otatistic		OF Test	
22		hapiro Wilk Test Statistic	0.666	Shapiro Wilk GOF Test Data Not Normal at 5% Significance Level	
23	5% 5	Lilliefors Test Statistic	0.859	Lilliefors GOF Test	
24	5	% Lilliefors Critical Value	0.395	Data Not Normal at 5% Significance Level	
25				% Significance Level	
26					
27		Ass	umina Norr	nal Distribution	
28	95% N	ormal UCL		95% UCLs (Adjusted for Skewness)	
29		95% Student's-t UCL	6.933	95% Adjusted-CLT UCL (Chen-1995)	7.337
30				95% Modified-t UCL (Johnson-1978)	7.018
31 32					
32			Gamma	GOF Test	
34		A-D Test Statistic	1.385	Anderson-Darling Gamma GOF Test	
34 35		5% A-D Critical Value	0.736	Data Not Gamma Distributed at 5% Significance Level	
36		K-S Test Statistic	0.346	Kolmogrov-Smirnoff Gamma GOF Test	
37		5% K-S Critical Value	0.246	Data Not Gamma Distributed at 5% Significance Level	
38		Data Not Gamm	a Distribute	ed at 5% Significance Level	
39					
40			Gamma	Statistics	
41		k hat (MLE)	3.911	k star (bias corrected MLE)	2.989
42		Theta hat (MLE)	1.334	Theta star (bias corrected MLE)	1.745
43		nu hat (MLE)	93.87	nu star (bias corrected)	71.73
44	М	LE Mean (bias corrected)	5.217	MLE Sd (bias corrected)	3.017
45					53.23
46	Adjus	sted Level of Significance	0.029	Adjusted Chi Square Value	50.81
47					
48			uming Gam	ma Distribution	
49	95% Approximate Gamma	UCL (use when n>=50))	7.03	95% Adjusted Gamma UCL (use when n<50)	7.365
50		<u>.</u>			

	A	В		С		D		E	F	G	н		1		J			К	Т	
51										GOF Test					-					
52					Shapi	iro Will	k Test	Statistic	0.818		S	hapiro	Wilk	Logn	ormal C	GOF	Test			
53				5%	Shapi	ro Wilk	Critic	al Value	0.859		Data N	lot Lo	gnorma	al at 5	% Sigr	nifica	nce L	_evel		
54					L	illiefors	s Test	Statistic	0.31			Lillie	ors Lo	gnori	nal GC	)F Te	est			
55					5% Li	lliefors	S Critic	al Value	0.256		Data N	lot Lo	gnorma	al at 5	% Sigr	nifica	nce l	_evel		
56							Da	ata Not I	ognormal at	5% Signific	ance Lev	el								
57																				
58									Lognorma	I Statistics										
59					Mini	mum o	of Logg	ged Data	0.833						Mear	n of lo	ogge	d Data	a '	1.519
60					Maxi	mum o	of Logg	ged Data	2.518						SE	D of lo	ogge	d Data	a (	0.498
61																				
62								Ass	uming Logno	rmal Distrib	ution									
63							95%	6 H-UCL	7.128				90	)% Cł	ebysh	ev (N	1VUE	E) UCI	-	7.369
64				95%	% Che	byshev	V (MVL	JE) UCL	8.391				97.5	5% Cł	ebysh	ev (N	1VUE	E) UCI	!	9.81
65				99%	% Che	byshev	shev (MVUE) UCL 12.6													
66																				
67							No	nparam	etric Distribu	tion Free UC	CL Statisti	ics								
68							Data	i do not '	follow a Disc	ernible Dist	ribution (0	.05)								
69																				
70								Nonpa	rametric Dis	ribution Fre	e UCLs									
71						!	95% C	CLT UCL	6.789						95%	6 Jac	kknif	fe UCI	(	6.933
72				95	% Star	ndard F	Bootst	rap UCL	6.729						95%	Boots	strap	-t UCI	_ 1	2.04
73					95%	Hall's F	Bootst	rap UCL	19.29		95% Percentile Bootstrap UCL						_ (	6.8		
74					95%	BCA	Bootst	rap UCL	7.233											
75				90% (	Cheby	shev(N	/lean, \$	Sd) UCL	8.084	95% Chebyshev(Mean, Sd) UCL						!	9.382			
76			ę	<del>)</del> 7.5% (	Cheby	shev(N	lean, s	Sd) UCL	11.18	99% Chebyshev(Mean, Sd) UCL						_ 1	4.73			
77																				
78									Suggested	UCL to Use										
79					9	95% S	tudent	t's-t UCL	6.933						or 95%	Mod	lified	-t UCI	-	7.018
80																				
81		Note: Sug	ggestio	ns rega	arding t	the sel	ection	of a 95%	6 UCL are pr	ovided to he	lp the use	r to se	elect th	e mo	st appro	opria	te 95	5% UC	L.	
82		These	recomm	nendati	ions ar	re base	ed upo	on the res	sults of the si	mulation stu	dies sumr	narize	ed in Si	ngh,	Singh,	and I	aci (	2002)		
83			a	nd Sing	jh and	Singh	(2003	). Howe	ver, simulatio	ns results w	ill not cov	er all I	Real W	/orld (	lata se	ts.				
84						For a	additio	nal insig	ht the user m	ay want to c	onsult a s	tatisti	cian.							
85																				
86																				
<sub>87</sub> C	Cobalt																			
88																				
89									General	Statistics										
90				Tot	al Nun	nber of	ł Obse	ervations	12						f Distin					8
91										Number of Missing Observations								0		
92								Minimum		Mean							3.31			
93							Μ	laximum										Mediar		1
94								SD							Ste	d. Eri		f Mear		1.639
95					Co	cefficie	ent of \	Variation	0.427								Ske	wness	3	1.07
96									-											
97										GOF Test										
98					-			Statistic					-		GOF T					
99				5%				al Value			Data a	ppear					nce l	_evel		
					L	illiefors	s Test	Statistic	0.241				Lilliefo	ors G	OF Tes	st				

	A B C D E	F	G H I J K	L
101	5% Lilliefors Critical Value	0.256	Data appear Normal at 5% Significance Level	
102	Data appea	ar Normal at	5% Significance Level	
103				
104	Ass	suming Norr	nal Distribution	
105	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
106	95% Student's-t UCL	16.26	95% Adjusted-CLT UCL (Chen-1995)	16.55
107			95% Modified-t UCL (Johnson-1978)	16.34
108				
109			GOF Test	
110	A-D Test Statistic	0.509	Anderson-Darling Gamma GOF Test	
111	5% A-D Critical Value	0.731	Detected data appear Gamma Distributed at 5% Significand	ce Level
112	K-S Test Statistic	0.217	Kolmogrov-Smirnoff Gamma GOF Test	
113	5% K-S Critical Value	0.246	Detected data appear Gamma Distributed at 5% Significance	ce Level
114	Detected data appear	Gamma Di	stributed at 5% Significance Level	
115				
116			Statistics	
117	k hat (MLE)	6.551	k star (bias corrected MLE)	4.969
118	Theta hat (MLE)	2.032	Theta star (bias corrected MLE)	2.679
119	nu hat (MLE)	157.2	nu star (bias corrected)	119.3
120	MLE Mean (bias corrected)	13.31	MLE Sd (bias corrected)	5.972 95.04
121		0.029	Approximate Chi Square Value (0.05)	
122	Adjusted Level of Significance	0.029	Adjusted Chi Square Value	91.74
123			ma Distribution	
124	95% Approximate Gamma UCL (use when n>=50)	16.7	95% Adjusted Gamma UCL (use when n<50)	17.3
125		10.7	35 % Aujusteu Ganina OCL (use when 11<50)	17.5
126		Lognorma	GOF Test	
127	Shapiro Wilk Test Statistic	0.934	Shapiro Wilk Lognormal GOF Test	
128	5% Shapiro Wilk Critical Value	0.859	Data appear Lognormal at 5% Significance Level	
129	Lilliefors Test Statistic	0.191	Lilliefors Lognormal GOF Test	
130	5% Lilliefors Critical Value	0.256	Data appear Lognormal at 5% Significance Level	
131 132		Lognormal	at 5% Significance Level	
133		-		
134		Lognorma	I Statistics	
135	Minimum of Logged Data	1.705	Mean of logged Data	2.51
136	Maximum of Logged Data	3.178	SD of logged Data	0.412
137				
138	Assu	iming Logno	rmal Distribution	
139	95% H-UCL	17.27	90% Chebyshev (MVUE) UCL	18.13
140	95% Chebyshev (MVUE) UCL	20.32	97.5% Chebyshev (MVUE) UCL	23.35
141	99% Chebyshev (MVUE) UCL	29.32		
142				
143	Nonparame	tric Distribu	tion Free UCL Statistics	
144	Data appear to follow a [	Discernible	Distribution at 5% Significance Level	
145				
146	Nonpar	ametric Dis	tribution Free UCLs	
147	95% CLT UCL	16.01	95% Jackknife UCL	16.26
148	95% Standard Bootstrap UCL	15.95	95% Bootstrap-t UCL	17.94
149	95% Hall's Bootstrap UCL	21.91	95% Percentile Bootstrap UCL	16.08
143	95% BCA Bootstrap UCL	16.42		

	A B C D E	F	G H I J K	L
151	90% Chebyshev(Mean, Sd) UCL	18.23	95% Chebyshev(Mean, Sd) UCL	20.46
152	97.5% Chebyshev(Mean, Sd) UCL	23.55	99% Chebyshev(Mean, Sd) UCL	29.62
153				
154		Suggested	UCL to Use	
155	95% Student's-t UCL	16.26		
156				
157	Note: Suggestions regarding the selection of a 95%	UCL are pr	ovided to help the user to select the most appropriate 95% UCL.	
158	These recommendations are based upon the res	ults of the si	mulation studies summarized in Singh, Singh, and laci (2002)	
159	and Singh and Singh (2003). Howev	er, simulatio	ons results will not cover all Real World data sets.	
160	For additional insight	nt the user m	nay want to consult a statistician.	
161				
162				
163	Copper			
164				
165		General	Statistics	
166	Total Number of Observations	12	Number of Distinct Observations	12
167			Number of Missing Observations	0
168	Minimum	25	Mean	68.85
169	Maximum	171	Median	56.63
170	SD	50.71	Std. Error of Mean	14.64
171	Coefficient of Variation	0.737	Skewness	1.531
172				
173			GOF Test	
174	Shapiro Wilk Test Statistic	0.761	Shapiro Wilk GOF Test	
175	5% Shapiro Wilk Critical Value	0.859	Data Not Normal at 5% Significance Level	
176	Lilliefors Test Statistic	0.272	Lilliefors GOF Test	
177	5% Lilliefors Critical Value	0.256	Data Not Normal at 5% Significance Level	
178	Data Not	Normal at 5	5% Significance Level	
179			n - I Distribution	
180		suming Non	mal Distribution	
181	95% Normal UCL	05.15	95% UCLs (Adjusted for Skewness)	00.05
182	95% Student's-t UCL	95.15	95% Adjusted-CLT UCL (Chen-1995) 95% Modified-t UCL (Johnson-1978)	99.85 96.22
183			95% Modified-t OCE (Johnson-1978)	90.22
184		Gamma	GOF Test	
185	A-D Test Statistic	0.626	Anderson-Darling Gamma GOF Test	
186	5% A-D Critical Value	0.020	Detected data appear Gamma Distributed at 5% Significance	
187	K-S Test Statistic	0.194	Kolmogrov-Smirnoff Gamma GOF Test	e Level
188	5% K-S Critical Value	0.194	Detected data appear Gamma Distributed at 5% Significance	e   evel
189			stributed at 5% Significance Level	
190				
191		Gamma	Statistics	
192	k hat (MLE)	2.607	k star (bias corrected MLE)	2.011
193	Theta hat (MLE)	26.41	Theta star (bias corrected MLE)	34.25
194 105	nu hat (MLE)	62.56	nu star (bias corrected)	48.26
195	MLE Mean (bias corrected)	68.85	MLE Sd (bias corrected)	48.56
196 107			Approximate Chi Square Value (0.05)	33.31
197	Adjusted Level of Significance	0.029	Adjusted Chi Square Value	31.42
198 199	<b>·</b>			
	Ase	suming Garr	nma Distribution	
200		•		

201 202 203 204	A B C D E 95% Approximate Gamma UCL (use when n>=50)	F 99.75	G         H         I         J         K         L           95% Adjusted Gamma UCL (use when n<50)         105.7								
202 203											
203											
		Lognormal	al GOF Test								
LU41	Shapiro Wilk Test Statistic	0.913	Shapiro Wilk Lognormal GOF Test								
205	5% Shapiro Wilk Critical Value	0.859	Data appear Lognormal at 5% Significance Level								
206	Lilliefors Test Statistic	0.15	Lilliefors Lognormal GOF Test								
207	5% Lilliefors Critical Value	0.256	Data appear Lognormal at 5% Significance Level								
208	Data appear Lognormal at 5% Significance Level										
209											
210		Lognorma	al Statistics								
211	Minimum of Logged Data	3.219	Mean of logged Data 4.028								
212	Maximum of Logged Data	5.142	SD of logged Data 0.64								
213											
214		ming Logno	90% Chebyshev (MVUE) UCL 106.4								
215	95% H-UCL 108 90% Chebyshev (MVUE) UCL 95% Chebyshev (MVUE) UCL 97.5% Chebyshev (MVUE) UCL										
216	95% Chebyshev (MVUE) UCL	124	97.5% Chebyshev (MVUE) UCL 148.4								
217	99% Chebyshev (MVUE) UCL	99% Chebyshev (MVUE) UCL 196.4									
218											
219	-		ution Free UCL Statistics								
220	Data appear to follow a L	Discernible I	e Distribution at 5% Significance Level								
221	M										
222	Nonparametric Distribution Free UCLs 95% CLT UCL 92.93 95% Jackknife UCL 92.93										
223			95% Jackknife UCL 95.15 95% Bootstrap-t UCL 131.5								
224	95% Standard Bootstrap UCL	91.93 241.7	· ·								
225	95% Hall's Bootstrap UCL 95% BCA Bootstrap UCL	97.52	95% Percentile Bootstrap UCL 93.6								
226	90% Chebyshev(Mean, Sd) UCL	112.8	95% Chebyshev(Mean, Sd) UCL 132.7								
227	97.5% Chebyshev(Mean, Sd) UCL	160.3	99% Chebyshev (Mean, Sd) UCL 214.5								
228	37.5% Chebysnev(Weah, Su) OCL	100.5									
229		Suggested	d UCL to Use								
230	95% Adjusted Gamma UCL	105.7									
231											
232 233	Note: Suggestions regarding the selection of a 95%	UCL are pro	provided to help the user to select the most appropriate 95% UCL.								
233	These recommendations are based upon the resu	ults of the si	simulation studies summarized in Singh, Singh, and Iaci (2002)								
235	and Singh and Singh (2003). Howeve	er, simulatio	ions results will not cover all Real World data sets.								
236	For additional insigh	it the user m	may want to consult a statistician.								
237											
238											
	ckel										
240											
241		General	I Statistics								
242	Total Number of Observations	12	Number of Distinct Observations 12								
243			Number of Missing Observations 0								
244	Minimum	25	Mean 305.7								
245	Maximum	1050	Median 194								
246	SD	364.3	Std. Error of Mean 105.2								
247	Coefficient of Variation	1.192	Skewness 1.636								
248											
249			GOF Test								
250	Shapiro Wilk Test Statistic	0.721	Shapiro Wilk GOF Test								

	A B C D E	F	G H I J K	L							
251	5% Shapiro Wilk Critical Value	0.859	Data Not Normal at 5% Significance Level								
252	Lilliefors Test Statistic	0.309	Lilliefors GOF Test								
253	5% Lilliefors Critical Value	0.256									
254	Data Not	Normal at 5	% Significance Level								
255											
256		suming Nori	mal Distribution								
257	95% Normal UCL		95% UCLs (Adjusted for Skewness)								
258	95% Student's-t UCL	494.6	95% Adjusted-CLT UCL (Chen-1995)	531.8							
259			95% Modified-t UCL (Johnson-1978)	502.9							
260											
261			GOF Test								
262	A-D Test Statistic	0.473	Anderson-Darling Gamma GOF Test								
263	5% A-D Critical Value	0.76	Detected data appear Gamma Distributed at 5% Significance	e Level							
264	EV/ K. C. Critical Value 0.252 Detected data appear Comma Distributed at EV/ Signifi										
265	Detected data appear Commo Distributed at 5% Cignificance Loyal										
266	Detected data appear	Gamma Di	stributed at 5% Significance Level								
267		-									
268				0.741							
269	k hat (MLE)	0.914	k star (bias corrected MLE)								
270	Theta hat (MLE)	334.5 21.93	Theta star (bias corrected MLE)	412.6							
271	nu hat (MLE)	305.7	nu star (bias corrected)	355.2							
272	MLE Mean (bias corrected)	305.7	MLE Sd (bias corrected) Approximate Chi Square Value (0.05)	9.235							
273	Adjusted Level of Significance	0.029	Approximate Ciri Square Value (0.05) Adjusted Chi Square Value	8.31							
274		0.029		0.51							
275	۵۵۵	uming Gar	nma Distribution								
276	95% Approximate Gamma UCL (use when n>=50)	588.7	95% Adjusted Gamma UCL (use when n<50)	654.3							
277		000.7		004.0							
278		Lognorma	I GOF Test								
279	Shapiro Wilk Test Statistic	0.95	Shapiro Wilk Lognormal GOF Test								
280 281	5% Shapiro Wilk Critical Value	0.859	Data appear Lognormal at 5% Significance Level								
282	Lilliefors Test Statistic	0.142	Lilliefors Lognormal GOF Test								
283	5% Lilliefors Critical Value	0.256	Data appear Lognormal at 5% Significance Level								
284	Data appear	Lognormal	at 5% Significance Level								
285											
286		Lognorma	I Statistics								
287	Minimum of Logged Data	3.219	Mean of logged Data	5.084							
288	Maximum of Logged Data	6.957	SD of logged Data	1.217							
289											
290	Assu	iming Logno	ormal Distribution								
291	95% H-UCL	1147	90% Chebyshev (MVUE) UCL	661							
292	95% Chebyshev (MVUE) UCL	820.7	97.5% Chebyshev (MVUE) UCL	1042							
293	99% Chebyshev (MVUE) UCL	1478									
294			· I								
295	Nonparame	tric Distribu	tion Free UCL Statistics								
296	Data appear to follow a I	Discernible	Distribution at 5% Significance Level								
297											
<u> </u>	Nonpar	ametric Dis	tribution Free UCLs								
298											
298 299	95% CLT UCL 95% Standard Bootstrap UCL	478.7	95% Jackknife UCL 95% Bootstrap-t UCL	494.6 767.5							

	А	В	С	D	E	F	G	Н		J	K	L
301			ç	95% Hall's Bo	otstrap UCL	1472		ootstrap UCL	487.3			
302				95% BCA Bo	otstrap UCL	527.3						
303			90% Cł	nebyshev(Me	an, Sd) UCL	621.2		764.2				
304		90% Chebyshev(Mean, Sd) U( 97.5% Chebyshev(Mean, Sd) U( 95% Adjusted Gamma U(						1352				
305												
306		Suggested UCL to Use										
307			95	% Adjusted C	amma UCL	654.3						
308												
309		Note: Sugges	stions regard	ling the selec	tion of a 95%	UCL are pr	ovided to hel	p the user to	select the m	nost appropr	iate 95% UCL	
310		These recommendations are based upon the results of the simulation studies summarized in Singh, Singh, and laci (2002)										
311		and Singh and Singh (2003). However, simulations results will not cover all Real World data sets.										
312				For ad	ditional insig	ht the user m	nay want to c	onsult a stati	stician.			
313												

10         Maximum         0.038         Median         5.000           17         Maximum         0.038         Median         5.000         0.0112         Std. Error of Mean         0.0           19         Coefficient of Variation         2.524         Skewness         3.           20         Std. Error of Mean         0.0         0.0         19         Std. Error of Mean         0.0           21         Normal GOF Test         Std. Error of Mean         0.0         3.         3.         2.           22         Shapiro Wilk Test Statistic         0.408         Shapiro Wilk GOF Test         2.         3.         5.% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level         2.         2.         2.         3.         1.         0.267         Data Not Normal at 5% Significance Level         2. </th <th></th> <th>A B C D E</th> <th>F</th> <th>G H I J K</th> <th>L</th>		A B C D E	F	G H I J K	L								
1         User Selected Options Date/Time of Computations From File         Sediment and Surface Water Summay_c.xls           6         Full Precision OFF         OFF           7         Confinence Carefficient 8 off         Sediment and Surface Water Summay_c.xls           7         Number of Bootstrap Operations         2000           8         Full Precision         DFF           8         Number of Bootstrap Operations         2000           9         Sediment and Surface Water Summay_c.xls         Summary	_1		stics for Unc	ensored Full Data Sets	-								
1         User Selected Options Date/Time of Computations From File         Sediment and Surface Water Summay_c.xls           6         Full Precision OFF         OFF           7         Confinence Carefficient 8 off         Sediment and Surface Water Summay_c.xls           7         Number of Bootstrap Operations         2000           8         Full Precision         DFF           8         Number of Bootstrap Operations         2000           9         Sediment and Surface Water Summay_c.xls         Summary	2												
Image: sediment and Surface Water Summary_c.xls           6         Full Precision         OFF           7         Confidence Coefficient 95%,           8         Number of Bootstrap Operations         2000           9         Image: sediment and surface Water Summary_c.xls           10         Number of Bootstrap Operations         2000           11         Number of Bootstrap Operations         2000           12         Image: sediment and surface Water Summary_c.xls         6           13         Confidence Coefficient of Variation         11         Number of Distinct Observations         6           15         Image: sediment and surface Water Summary_c.xls         11         Number of Distinct Observations         6           16         Minimum, 5000E4         Number of Distinct Observations         5.000         18         0.0112         Std Error of Mean         0.0           18         Coefficient of Variation         2.524         Std Error of Mean         0.0           19         Coefficient of Variation         2.524         Steppiro Wilk GOF Test           21         Normal GOF Test         Normal GOF Test         Lillifors GR Test         2.0           22         Shapiro Wilk Critical Value         0.455         Data Not Normal at 5% Significance Level <td>3</td> <td>User Selected Options</td> <td></td> <td></td> <td></td>	3	User Selected Options											
S         Full Practision         OFF           2         Confidence Coefficient         55%           8         Number of Bootsrap Operations         2000           10	4	Date/Time of Computation 9/18/2014 12:41:55 PM											
Canitalence Coefficient         95%           Number of Bootstrap Operations         2000           1         Arsenic (mg/L)           12	5		Vater Summa	ry_c.xls									
Number of Bootstrap Operations         2000           0         0           10         Intering (ng/L)           12         0           13         General Statistics           14         Total Number of Observations         11           15         0         Number of Missing Observations         0           16         Minimum \$0.000E4         Mean         0.0           17         Maximum 0.033         Median \$500         0.112         Std. Error of Mean         0.0           18         SbD         0.0112         Std. Error of Mean         0.0         18         0.0         18         0.0         18         0.0         12         Std. Error of Mean         0.0         19         Coefficient of Variation         2.524         Std. Error of Mean         0.0         19         2.524         Std. Error of Mean         0.0         10         12         12         Std. Error of Mean         0.0         12 <td>6</td> <td></td> <td></td> <td></td> <td></td>	6												
a         Image: Complexity           10         Ansenic (mg/L)           12         Image: Complexity           13         General Statistics           14         Total Number of Observations         11           15         Image: Complexity         6           16         Minimum 5.0000E-4         Mealan 50.000           17         Maximum 0.038         Median 50.000           18         SD 0.0112         Std. Error of Mean 0.0           19         Coefficient of Variation 2.524         Skewness 3.           20         Skewness         3.           21         Shapiro Wilk Coff Test         Skewness           22         Shapiro Wilk Critical Value         0.424         Lillefors GOF Test           23         Sky Shapiro Wilk Critical Value         0.424         Lillefors GOF Test           24         Lillefors Critical Value         0.424         Lillefors GOF Test           25         Sky Shapiro Wilk Coff Test Statistic         0.424         Lillefors GOF Test           28         Obst Not Normal at Sky Significance Level         10           29         Sky Student-st UCL         0.015         Sky Anged: GCL UCL (Chen-1995)         0.0           30         General Statistic	7												
In         Arsenic (mg/L)           11         Arsenic (mg/L)           12         General Statistics           13         Total Number of Observations         1           14         Total Number of Observations         1           15         Number of Missing Observations         0           16         Minimum         0.038         Median           17         Maximum         0.038         Median           18         Coefficient of Variation         2.524         Stet. Error of Mean         0.0           19         Coefficient of Variation         2.524         Stet. Error of Mean         0.0           20         Normal GOF Test         Stet. Error of Mean         0.0         10         Stet. Error of Mean         0.0           21         Shapiro Wilk Test Statistic         0.408         Shapiro Wilk GOF Test         2.524         Stet. Normal at 5% Significance Level           23         5% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level         2.6           24         Lilliefors Critical Value         0.424         Lilliefors GOF Test         2.6           25         5% Normal UCL         0.0105         95% Modified-1 UCL (Johnson-1978)         0.0           <	8	Number of Bootstrap Operations 2000											
Arsenic (mg/L)           12           13           Ceneral Statistics           14         Total Number of Observations           15         Number of Missing Observations           16         Minimum 5.0000E-4           17         Maximum           18         SD           19         Coefficient of Variation           20         Std. Error of Mean           21         Std. Error of Mean           22         Shapiro Wilk Test Statistic           23         Sty Shapiro Wilk Critical Value         0.48           24         Lilliefors Test Statistic         0.408           25         Sty Shapiro Wilk Critical Value         0.267           26         Data Not Normal at 5% Significance Level           27         Assuming Normal Distribution           28         95% Normal UCL         0.267           29         95% Normal UCL         0.0105           29         95% Normal UCL         0.201           20         Statistic         2.149           31         Gamma GOF Test           32         Statistic         2.149           33         Gamma GOF Test           34         A-D Test Statistic	9												
Image: Control of the second	-												
Image: Control of Con	11 '	Arsenic (mg/L)											
13         Control Number of Observations         11         Number of Distinct Observations         6           15         Number of Missing Observations         0         0         0         0           16         Minimum         5.000E-4         Mean         0.00         0           17         Maximum         0.038         Median         5.00         0         0           18         Ocofficient of Variation         2.524         Skewness         3.           20         Normal GOF Test         3         3         3           21         Normal IdeoF Test         0.0424         Uilliefors GOF Test         3           22         Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level         4           23         5% Shapiro Scritical Value         0.267         Data Not Normal at 5% Significance Level         4           26         Data Not Normal at 5% Significance Level         2         5         3         0           28         Assuming Normal Distribution         95% UCLs (Adjusted for Skewness)         0.0         0           30         95% Normal UCL         0.0105         95% Modified+ UCL (Johnson-1978)         0.0           31         Camma GOF Test	12												
14	13				-								
10         Minimum         5.000E-4         Mean         0.0           17         Maximum         0.038         Median         5.00           18         Coefficient of Variation         2.524         Std. Error of Mean         0.0           19         Coefficient of Variation         2.524         Stewness         3.           20         .         Stewness         3.         3.           21         Normal GOF Test         .         .         .         .           23         Shapiro Wilk Critical Value         0.485         Data Not Normal at 5% Significance Level         .           24         Lillefors Test Statistic         0.424         Lillefors GOF Test         .         .           25         5% Lillefors Critical Value         0.267         Data Not Normal at 5% Significance Level         .           28         Data Not Normal at 5% Significance Level         .         .         .         .           29         95% Normal UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         .         .         .         .         0.67           32         .         .         .         .         .         . <td< td=""><td>14</td><td>Total Number of Observations</td><td>11</td><td></td><td></td></td<>	14	Total Number of Observations	11										
Ind         Maximum         0.038         Median         5.000           18         Coefficient of Variation         2.524         Std. Error of Mean         0.0           19         Coefficient of Variation         2.524         Skewness         3.           20	15		5 00005 4		-								
Image: style	16				0.00443								
Io         Coefficient of Variation         2.524         Skewness         3.           20	17												
19         Normal GOF Test           20         Shapiro Wilk Test Statistic         0.403         Shapiro Wilk GOF Test           23         5% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level           24         Lilliefors GOF Test         25         5% Lilliefors GOF Test         26           24         Significance Level         0.267         Data Not Normal at 5% Significance Level         26           26         Data Not Normal at 5% Significance Level         27         28         Assuming Normal Distribution           29         95% Normal UCL         95% UCLs (Adjusted for Skewness)         0.0           30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Adjusted-CLT UCL (Johnson-1978)         0.0         0.0         0.0         0.0           32         33         Gamma GOF Test         33         0.0         0.787         Data Not Gamma GOF Test           33         Gamma GOF Test         34         A-D Test Statistic         0.346         Kolmogrov-Smimoff Gamma GOF Test           34         Gamma GOF Test Statistic         0.346         Kolmogrov-Smimoff Gamma GOF Test         33           35         5% K-S Critical Value         0.27<	18	-			0.00337								
Normal GOF Test           22         Shapiro Wilk Test Statistic         0.408         Shapiro Wilk GOF Test           23         5% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level           24         Lilliefors Test Statistic         0.424         Lilliefors GOF Test           25         5% Lilliefors Critical Value         0.267         Data Not Normal at 5% Significance Level           26         Data Not Normal at 5% Significance Level         26           27	19	Coefficient of Variation	2.524	Skewness	3.263								
21         Shapiro Wilk Test Statistic         0.408         Shapiro Wilk GOF Test           23         5% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level           24         Lilliefors Test Statistic         0.424         Lilliefors GOF Test           25         5% Lilliefors Critical Value         0.267         Data Not Normal at 5% Significance Level           26         Data Not Normal at 5% Significance Level         26           27	20		Normal (										
22         5% Shapiro Wilk Critical Value         0.85         Data Not Normal at 5% Significance Level           24         Lilliefors Test Statistic         0.424         Lilliefors GOF Test           25         5% Lilliefors Critical Value         0.267         Data Not Normal at 5% Significance Level           26         Data Not Normal at 5% Significance Level         26           27	21												
23         Lilliefors Test Statistic         0.424         Lilliefors GOF Test           26         5% Lilliefors Critical Value         0.267         Data Not Normal at 5% Significance Level           26         Data Not Normal at 5% Significance Level         26           27	22												
24         5% Lilliefors Critical Value         0.267         Data Not Normal at 5% Significance Level           26         Data Not Normal at 5% Significance Level         26           27	23												
26         Data Not Normal at 5% Significance Level           26         Assuming Normal Distribution           29         95% Normal UCL         95% UCLs (Adjusted for Skewness)           30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Modified-t UCL (Johnson-1978)         0.0         0.0         0.0           32         95% Modified-t UCL (Johnson-1978)         0.0         0.0           34         A-D Test Statistic         2.149         Anderson-Darling Gamma GOF Test           35         5% A-D Critical Value         0.787         Data Not Gamma Distributed at 5% Significance Level           36         K-S Test Statistic         0.346         Kolmogrov-Smimoff Gamma GOF Test           37         5% K-S Critical Value         0.27         Data Not Gamma Distributed at 5% Significance Level           38         Data Not Gamma Statistics         40         Gamma Statistics           41         k hat (MLE)         0.467         k star (bias corrected MLE)         0.0           43         nu hat (MLE)         10.28         nu star (bias corrected MLE)         0.0           44         MLE Mean (bias corrected)         0.00443         MLE Sd (bias corrected)         0.0           45													
Column         Assuming Normal Distribution           28         Assuming Normal Distribution           29         95% Normal UCL         95% UCLs (Adjusted for Skewness)           30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Modified-t UCL (Johnson-1978)         0.0         0.0           32         95% Modified-t UCL (Johnson-1978)         0.0           34         A-D Test Statistic         2.149         Anderson-Darling Gamma GOF Test           34         A-D Test Statistic         0.787         Data Not Gamma GOF Test           36         K-S Test Statistic         0.346         Kolmogrov-Smirnoff Gamma GOF Test           37         5% K-S Critical Value         0.27         Data Not Gamma Distributed at 5% Significance Level           38         Data Not Gamma Distributed at 5% Significance Level         38           40         Gamma Statistics         41         K hat (MLE)         0.467         k star (bias corrected MLE)         0.0           42         Theta hat (MLE)         0.0043         Theta star (bias corrected MLE)         0.0         43           44         MLE Mean (bias corrected)         0.00443         MLE Sd (bias corrected)         0.0         44				_									
Assuming Normal Distribution           29         95% Normal UCL         95% UCLs (Adjusted for Skewness)           30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Modified-t UCL (Johnson-1978)         0.0         0.0           32         95% Modified-t UCL (Johnson-1978)         0.0           34         A-D Test Statistic         2.149         Anderson-Darling Gamma GOF Test           35         5% A-D Critical Value         0.787         Data Not Gamma Distributed at 5% Significance Level           36         K-S Test Statistic         0.346         Kolmogrov-Smirnoff Gamma GOF Test           37         5% K-S Critical Value         0.27         Data Not Gamma Distributed at 5% Significance Level           38         Data Not Gamma Distributed at 5% Significance Level         0.467           40         Gamma Statistics         0.471           41         K hat (MLE)         0.467         k star (bias corrected MLE)         0.0           42         Theta hat (MLE)         0.00443         MLE Sd (bias corrected MLE)         0.0           43         nu hat (MLE)         10.28         nu star (bias corrected MLE)         0.0           44         MLE Mean (bias corrected)         0.00443													
28         95% Normal UCL         95% UCLs (Adjusted for Skewness)           30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Modified-t UCL (Johnson-1978)         0.0         0.0           32         95% Modified-t UCL (Johnson-1978)         0.0           32         95% Modified-t UCL (Johnson-1978)         0.0           34         A-D Test Statistic         2.149         Anderson-Darling Gamma GOF Test           35         5% A-D Critical Value         0.787         Data Not Gamma Distributed at 5% Significance Level           36         K-S Test Statistic         0.346         Kolmogrov-Smirnoff Gamma GOF Test           37         5% K-S Critical Value         0.27         Data Not Gamma Distributed at 5% Significance Level           38         Data Not Gamma Distributed at 5% Significance Level         0.27           39         0.467         k star (bias corrected MLE)         0.0           41         K hat (MLE)         0.0948         Theta star (bias corrected MLE)         0.0           42         Theta hat (MLE)         10.28         nu star (bias corrected MLE)         0.0           43         MLE Mean (bias corrected)         0.00443         MLE Sd (bias corrected)         0.0		As	suming Norr	nal Distribution									
29         30         95% Student's-t UCL         0.0105         95% Adjusted-CLT UCL (Chen-1995)         0.0           31         95% Modified-t UCL (Johnson-1978)         0.0         0.0         0.0           32         33         Gamma GOF Test         0.0         0.0         0.0           34         A-D Test Statistic         2.149         Anderson-Darling Gamma GOF Test         0.0           35         5% A-D Critical Value         0.787         Data Not Gamma Distributed at 5% Significance Level         0.346           36         K-S Test Statistic         0.346         Kolmogrov-Smirnoff Gamma GOF Test         0.27           38         Data Not Gamma Distributed at 5% Significance Level         0.27         Data Not Gamma Distributed at 5% Significance Level         0.27           39			Journing Horr										
31       95% Modified-t UCL (Johnson-1978)       0.0         32       33       Gamma GOF Test         34       A-D Test Statistic       2.149       Anderson-Darling Gamma GOF Test         35       5% A-D Critical Value       0.787       Data Not Gamma Distributed at 5% Significance Level         36       K-S Test Statistic       0.346       Kolmogrov-Smirnoff Gamma GOF Test         37       5% K-S Critical Value       0.27       Data Not Gamma Distributed at 5% Significance Level         38       Data Not Gamma Statistics       0.27         40       Gamma Statistics       0.467         41       k hat (MLE)       0.467         42       Theta hat (MLE)       0.00948         43       nu hat (MLE)       10.28         44       MLE Mean (bias corrected)       0.00443         45       0.00278       Adjusted Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value (2.05)       3.			0.0105		0.0135								
31       Gamma GOF Test         33       A-D Test Statistic       2.149       Anderson-Darling Gamma GOF Test         34       A-D Test Statistic       2.149       Anderson-Darling Gamma GOF Test         35       5% A-D Critical Value       0.787       Data Not Gamma Distributed at 5% Significance Level         36       K-S Test Statistic       0.346       Kolmogrov-Smirnoff Gamma GOF Test         37       5% K-S Critical Value       0.27       Data Not Gamma Distributed at 5% Significance Level         38       Data Not Gamma Distributed at 5% Significance Level       39         40       Gamma Statistics         41       k hat (MLE)       0.467       k star (bias corrected MLE)       0.0         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value (2.					0.0111								
Gamma GOF Test         33       A-D Test Statistic       2.149       Anderson-Darling Gamma GOF Test         35       5% A-D Critical Value       0.787       Data Not Gamma Distributed at 5% Significance Level         36       K-S Test Statistic       0.346       Kolmogrov-Smirnoff Gamma GOF Test         37       5% K-S Critical Value       0.27       Data Not Gamma Distributed at 5% Significance Level         38       Data Not Gamma Distributed at 5% Significance Level       39         40       Gamma Statistics       0.467       k star (bias corrected MLE)       0.0         42       Theta hat (MLE)       0.467       k star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected MLE)       0.0         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.													
34       A-D Test Statistic       2.149       Anderson-Darling Gamma GOF Test         35       5% A-D Critical Value       0.787       Data Not Gamma Distributed at 5% Significance Level         36       K-S Test Statistic       0.346       Kolmogrov-Smirnoff Gamma GOF Test         37       5% K-S Critical Value       0.27       Data Not Gamma Distributed at 5% Significance Level         38       Data Not Gamma Distributed at 5% Significance Level       39         40       Gamma Statistics       0.467       k star (bias corrected MLE)       0.0         41       k hat (MLE)       0.467       k star (bias corrected MLE)       0.0         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.         47       Accumping Commo Distribution       Adjusted Chi Square Value       2.			Gamma	GOF Test									
34     5% A-D Critical Value     0.787     Data Not Gamma Distributed at 5% Significance Level       36     K-S Test Statistic     0.346     Kolmogrov-Smirnoff Gamma GOF Test       37     5% K-S Critical Value     0.27     Data Not Gamma Distributed at 5% Significance Level       38     Data Not Gamma Distributed at 5% Significance Level       39		A-D Test Statistic	2.149	Anderson-Darling Gamma GOF Test									
36       K-S Test Statistic       0.346       Kolmogrov-Smirnoff Gamma GOF Test         37       5% K-S Critical Value       0.27       Data Not Gamma Distributed at 5% Significance Level         38       Data Not Gamma Distributed at 5% Significance Level         39		5% A-D Critical Value	0.787	_	/el								
30     5% K-S Critical Value     0.27     Data Not Gamma Distributed at 5% Significance Level       38     Data Not Gamma Distributed at 5% Significance Level       39       40       41     K hat (MLE)     0.467       42     Theta hat (MLE)     0.00948       43     nu hat (MLE)     10.28       44     MLE Mean (bias corrected)     0.00443       45     Approximate Chi Square Value (0.05)     3.       46     Adjusted Level of Significance     0.0278     Adjusted Chi Square Value (2.		K-S Test Statistic	0.346	Kolmogrov-Smirnoff Gamma GOF Test									
38       Data Not Gamma Distributed at 5% Significance Level         39       40         40       Gamma Statistics         41       k hat (MLE)       0.467       k star (bias corrected MLE)       0.0         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Approximate Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.		5% K-S Critical Value	0.27	Data Not Gamma Distributed at 5% Significance Lev	/el								
39       Gamma Statistics         40       K hat (MLE)       0.467       k star (bias corrected MLE)       0.         41       K hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Approximate Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.		Data Not Gam	ma Distribute	ed at 5% Significance Level									
40       Gamma Statistics         41       k hat (MLE)       0.467       k star (bias corrected MLE)       0.47         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.01         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.1         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Approximate Chi Square Value (0.05)       3.1         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.1         47       Accuming Commo Distribution       Adjusted Chi Square Value       2.1													
41       k hat (MLE)       0.467       k star (bias corrected MLE)       0.41         42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.01         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.41         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.00         45       Approximate Chi Square Value (0.05)       3.41         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.41			Gamma	Statistics									
42       Theta hat (MLE)       0.00948       Theta star (bias corrected MLE)       0.0         43       nu hat (MLE)       10.28       nu star (bias corrected)       8.         44       MLE Mean (bias corrected)       0.00443       MLE Sd (bias corrected)       0.0         45       Approximate Chi Square Value (0.05)       3.         46       Adjusted Level of Significance       0.0278       Adjusted Chi Square Value       2.         47       Accuming Commo Distribution       Adjusted Chi Square Value       2.		k hat (MLE)	0.467	k star (bias corrected MLE)	0.401								
43     nu hat (MLE)     10.28     nu star (bias corrected)     8.       44     MLE Mean (bias corrected)     0.00443     MLE Sd (bias corrected)     0.0       45     Approximate Chi Square Value (0.05)     3.       46     Adjusted Level of Significance     0.0278     Adjusted Chi Square Value     2.       47     Accuming Commo Distribution		Theta hat (MLE)	0.00948	Theta star (bias corrected MLE)	0.0111								
44     MLE Mean (bias corrected)     0.00443     MLE Sd (bias corrected)     0.0       45     Approximate Chi Square Value (0.05)     3.1       46     Adjusted Level of Significance     0.0278     Adjusted Chi Square Value     2.1       47     Adjusted Chi Square Value     4.1		nu hat (MLE)	10.28	nu star (bias corrected)	8.812								
45     Approximate Chi Square Value (0.05)     3.       46     Adjusted Level of Significance     0.0278     Adjusted Chi Square Value     2.       47     Accuming Commo Distribution		MLE Mean (bias corrected)	0.00443	MLE Sd (bias corrected)	0.007								
46     Adjusted Level of Significance     0.0278     Adjusted Chi Square Value     2.       47     Accuming Commo Distribution			1	Approximate Chi Square Value (0.05)	3.214								
47		Adjusted Level of Significance	0.0278	Adjusted Chi Square Value	2.687								
Accuming Commo Distribution			1										
		As	suming Gam	ma Distribution									
		95% Approximate Gamma UCL (use when n>=50))	0.0122	95% Adjusted Gamma UCL (use when n<50)	0.0145								
50													

	A	В		С		D		E	F	G	Н		1		J		К		L
51									Lognorma	GOF Test	•	•							
52					Shapi	ro Will	k Test	Statistic	0.685	Shapiro Wilk Lognormal GOF Test									
53				5%	Shapi	ro Wilk	Critic	cal Value	0.85	Data Not Lognormal at 5% Significance Level									
54	Lilliefors Test Statistic										Lilliefors Lognormal GOF Test								
55	5% Lilliefors Critical Value										Data Not	Lognoi	rmal a	at 5%	Signif	ficano	ce Lev	/el	
56 Data Not Lognormal at 5% Significance Level																			
57																			
58									Lognorma	I Statistics									
59					Mini	mum o	of Logg	ged Data	-7.601						Mean	of log	gged D	Data	-6.792
60					Maxi	mum o	of Logg	-3.27						SD	of log	gged D	Data	1.358	
61									1	I									
62								Ass	uming Logno	ormal Distrib	ution								
63							95%	% H-UCL	. 0.014				90%	Che	byshev	v (M\	/UE) l	JCL	0.00573
64				95%	% Che	byshev	. 0.00721			9	7.5%	Che	byshev	v (M\	/UE) l	JCL	0.00926		
65				99%	% Che	byshev	√ (MVI	UE) UCL	. 0.0133										
66																			
67							No	nparam	etric Distribu	tion Free UC	CL Statistics	5							
68							Data	a do not	follow a Disc	ernible Distr	ibution (0.0	)5)							
69																			
70								Nonpa	rametric Dis	tribution Fre	e UCLs								
71	95% CLT UCL								. 0.00998						95%	Jack	knife l	JCL	0.0105
72	95% Standard Bootstrap UCL								0.00963					9	95% B	ootst	rap-t l	JCL	0.0965
73	95% Hall's Bootstrap UCL									95% Percentile Bootstrap UCL						0.011			
74	95% BCA Bootstrap UCL																		
75	90% Chebyshev(Mean, Sd) UCL													-	shev(N		-		0.0191
76				97.5% (	Cheby	shev(N	/lean, s	Sd) UCL	. 0.0255	99% Chebyshev(Mean, Sd) UCL						0.038			
77																			
78										UCL to Use									
79				95% C	hebys	hev (N	/lean, S	Sd) UCL	. 0.0191			1							
80																			
81									% UCL are pr		-								•
82		These					•		sults of the si						-		ci (200	02)	
83			a	ind Sing	jh and				ver, simulatio					rld da	ta sets	6.			
84						For a	additio	nal insig	pht the user m	hay want to c	onsult a sta	tistician	1.						
85																			
86		<u></u>																	
87	Cobalt (mg/	L)																	
88									Conorol	Statiation									
89				T+	tal Nur	nhor of	fOhor	anyations		Statistics Number of Distinct Observation							iona	11	
90	Total Number of Observations								Number of Missing Observation								0		
91	Minimum														ions ean	0.00682			
92	Maximum															6.0000E-4			
93	SD													6+4	Erro	or of M		0.000E-4	
94	Coefficient of Variation														3.0.		Skewn		2.161
95						Jenicie		variatiOf	1.731								SVEMU	1005	2.101
96									Normal (	GOF Test									
97					Shan	iro \//iII	k Tect	Statistic				Shan	iro \A		OF Te	et			
98					-			cal Value			Data N	-						1	
99				370				Statistic			Data Not Normal at 5% Significance Level								
100					L	meiors	31081	JiauSuC	0.555			LIII		3 00	1851				

	A B C D E	F	G H I J K	L
101	5% Lilliefors Critical Value	0.267	Data Not Normal at 5% Significance Level	
102	Data Not	Normal at 5	5% Significance Level	
103				
104	Ass	suming Norr	mal Distribution	
105	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
106	95% Student's-t UCL	0.0133	95% Adjusted-CLT UCL (Chen-1995)	0.0151
107			95% Modified-t UCL (Johnson-1978)	0.0136
107				
109		Gamma	GOF Test	
110	A-D Test Statistic	0.681	Anderson-Darling Gamma GOF Test	
111	5% A-D Critical Value	0.805	Detected data appear Gamma Distributed at 5% Significance	e Level
112	K-S Test Statistic	0.301	Kolmogrov-Smirnoff Gamma GOF Test	
113	5% K-S Critical Value	0.273	Data Not Gamma Distributed at 5% Significance Leve	el
114	Detected data follow App	or. Gamma	Distribution at 5% Significance Level	
115				
116		Gamma	Statistics	
117	k hat (MLE)	0.377	k star (bias corrected MLE)	0.335
118	Theta hat (MLE)	0.0181	Theta star (bias corrected MLE)	0.0204
119	nu hat (MLE)	8.295	nu star (bias corrected)	7.366
120	MLE Mean (bias corrected)	0.00682	MLE Sd (bias corrected)	0.0118
120			Approximate Chi Square Value (0.05)	2.374
121	Adjusted Level of Significance	0.0278	Adjusted Chi Square Value	1.938
122				
123	Ass	uming Gam	nma Distribution	
124	95% Approximate Gamma UCL (use when n>=50)	0.0212	95% Adjusted Gamma UCL (use when n<50)	0.0259
125				
120		Lognorma	I GOF Test	
127	Shapiro Wilk Test Statistic	0.936	Shapiro Wilk Lognormal GOF Test	
120	5% Shapiro Wilk Critical Value	0.85	Data appear Lognormal at 5% Significance Level	
129	Lilliefors Test Statistic	0.218	Lilliefors Lognormal GOF Test	
131	5% Lilliefors Critical Value	0.267	Data appear Lognormal at 5% Significance Level	
132	Data appear	Lognormal	at 5% Significance Level	
132		•		
		Lognorma	I Statistics	
134	Minimum of Logged Data	-9.903	Mean of logged Data	-6.75
135	Maximum of Logged Data	-3.278	SD of logged Data	2.172
136 137				
	Assu	ming Logno	ormal Distribution	
138 130	95% H-UCL	0.559	90% Chebyshev (MVUE) UCL	0.023
139	95% Chebyshev (MVUE) UCL	0.03	97.5% Chebyshev (MVUE) UCL	0.0398
140	99% Chebyshev (MVUE) UCL	0.0589		
141		-		
142	Nonparame	tric Distribu	tion Free UCL Statistics	
143 144	-		Distribution at 5% Significance Level	
144			-	
145	Nonbar	ametric Dis	tribution Free UCLs	
146	95% CLT UCL	0.0127	95% Jackknife UCL	0.0133
147	95% Standard Bootstrap UCL	0.0125	95% Bootstrap-t UCL	0.0233
148	95% Hall's Bootstrap UCL	0.0311	95% Percentile Bootstrap UCL	0.0126
149	95% BCA Bootstrap UCL	0.0156		
150				

	A B C D E	F	G H I J K	1							
151	90% Chebyshev(Mean, Sd) UCL	0.0175	95% Chebyshev(Mean, Sd) UCL	0.0223							
152	97.5% Chebyshev(Mean, Sd) UCL	0.029	99% Chebyshev(Mean, Sd) UCL	0.0422							
152											
153		Suggested	UCL to Use								
155	95% Adjusted Gamma UCL	0.0259									
156											
157	Note: Suggestions regarding the selection of a 95%	UCL are pr	ovided to help the user to select the most appropriate 95% UCL.								
157			mulation studies summarized in Singh, Singh, and Iaci (2002)								
158			ns results will not cover all Real World data sets.								
160			ay want to consult a statistician.								
161			·								
162											
	opper (mg/L)										
164											
		General	Statistics								
165 166	Total Number of Observations	11	Number of Distinct Observations	11							
			Number of Missing Observations	0							
167	Minimum	3.0000E-4	Mean	0.0176							
168	Maximum	0.082	Median	0.00365							
169	SD	0.0296	Std. Error of Mean	0.00894							
170	Coefficient of Variation	1.683	Skewness	1.892							
171											
172		Normal (	GOF Test								
173	Shapiro Wilk Test Statistic     0.594     Shapiro Wilk GOF Test										
174	Shapiro Wilk Test Statistic     0.594     Shapiro Wilk GOF Test       5% Shapiro Wilk Critical Value     0.85     Data Not Normal at 5% Significance Level										
175	Lilliefors Test Statistic	0.387	Lilliefors GOF Test								
176	5% Lilliefors Critical Value	0.267	Data Not Normal at 5% Significance Level								
177	Data Not	Normal at 5	% Significance Level								
178 179											
180	As	suming Nori	nal Distribution								
181	95% Normal UCL		95% UCLs (Adjusted for Skewness)								
182	95% Student's-t UCL	0.0338	95% Adjusted-CLT UCL (Chen-1995)	0.0378							
183			95% Modified-t UCL (Johnson-1978)	0.0347							
184											
185		Gamma	GOF Test								
186	A-D Test Statistic	0.909	Anderson-Darling Gamma GOF Test								
187	5% A-D Critical Value	0.779	Data Not Gamma Distributed at 5% Significance Leve	el							
188	K-S Test Statistic	0.242	Kolmogrov-Smirnoff Gamma GOF Test								
189	5% K-S Critical Value	0.269	Detected data appear Gamma Distributed at 5% Significance	e Level							
190	Detected data follow Ap	pr. Gamma	Distribution at 5% Significance Level								
191	-										
192		Gamma	Statistics								
193	k hat (MLE)	0.531	k star (bias corrected MLE)	0.447							
194	Theta hat (MLE)	0.0332	Theta star (bias corrected MLE)	0.0394							
195	nu hat (MLE)	11.69	nu star (bias corrected)	9.833							
196	MLE Mean (bias corrected)	0.0176	MLE Sd (bias corrected)	0.0264							
197		I	Approximate Chi Square Value (0.05)	3.838							
198	Adjusted Level of Significance	0.0278	Adjusted Chi Square Value	3.251							
199		<u> </u>									
200	As	suming Garr	ma Distribution								
200		-									

<b>—</b> ——	ABCDE	F	GHIJK	
201	A B C D E 95% Approximate Gamma UCL (use when n>=50)	г 0.0451	95% Adjusted Gamma UCL (use when n<50)	0.0533
201				
202		Lognorma	GOF Test	
203	Shapiro Wilk Test Statistic	0.938	Shapiro Wilk Lognormal GOF Test	
	5% Shapiro Wilk Critical Value	0.85	Data appear Lognormal at 5% Significance Level	
205	Lilliefors Test Statistic	0.146	Lilliefors Lognormal GOF Test	
206	5% Lilliefors Critical Value	0.267	Data appear Lognormal at 5% Significance Level	
207		Lognormal	at 5% Significance Level	
208	······		<u> </u>	
209		Lognorma	Statistics	
210	Minimum of Logged Data	-8.112		-5.223
211	Maximum of Logged Data	-2.502	SD of logged Data	1.631
212			02 01 09900 2000	
213	Assu	mina Loanc	rmal Distribution	
214	95% H-UCL	0.19	90% Chebyshev (MVUE) UCL	0.0423
215	95% Chebyshev (MVUE) UCL	0.054	97.5% Chebyshev (MVUE) UCL	0.0703
216	99% Chebyshev (MVUE) UCL	0.102		0.0700
217		0.102		
218	Nonporomo	trio Distribu	tion Free UCL Statistics	
219	-		Distribution at 5% Significance Level	
220		Jiscemible	Distribution at 5% Significance Level	
221	News			
222			ribution Free UCLs	0.0000
223	95% CLT UCL	0.0323	95% Jackknife UCL	0.0338
224	95% Standard Bootstrap UCL	0.0315	95% Bootstrap-t UCL	0.134
225	95% Hall's Bootstrap UCL	0.125	95% Percentile Bootstrap UCL	0.032
226	95% BCA Bootstrap UCL	0.0381		
227	90% Chebyshev(Mean, Sd) UCL	0.0444	95% Chebyshev(Mean, Sd) UCL	0.0566
228	97.5% Chebyshev(Mean, Sd) UCL	0.0734	99% Chebyshev(Mean, Sd) UCL	0.107
229				
230			UCL to Use	
231	95% Adjusted Gamma UCL	0.0533		
232				
233			ovided to help the user to select the most appropriate 95% UCL.	
234			mulation studies summarized in Singh, Singh, and laci (2002)	
235			ns results will not cover all Real World data sets.	
236	For additional insigh	it the user m	ay want to consult a statistician.	
237				
238				
239 N	Nickel (mg/L)			
240				
241		General	Statistics	
242	Total Number of Observations	11	Number of Distinct Observations	10
243			Number of Missing Observations	0
244	Minimum	0.004	Mean	0.159
245	Maximum	0.884	Median	0.019
246	SD	0.302	Std. Error of Mean	0.0909
247	Coefficient of Variation	1.901	Skewness	2.051
248	I			
249		Normal C	GOF Test	
250	Shapiro Wilk Test Statistic	0.571	Shapiro Wilk GOF Test	
200				

	A B C D E	F	G H I J K	L					
251	5% Shapiro Wilk Critical Value	0.85	Data Not Normal at 5% Significance Level						
252	Lilliefors Test Statistic	0.394	Lilliefors GOF Test						
253	5% Lilliefors Critical Value	0.267	Data Not Normal at 5% Significance Level						
254	Data Not	Normal at 5	% Significance Level						
255									
256	Ass	suming Norr	nal Distribution						
257	95% Normal UCL		95% UCLs (Adjusted for Skewness)						
258	95% Student's-t UCL	0.323	95% Adjusted-CLT UCL (Chen-1995)	0.368					
259			95% Modified-t UCL (Johnson-1978)	0.333					
260									
261		Gamma	GOF Test						
262	A-D Test Statistic	1.262	Anderson-Darling Gamma GOF Test						
263	5% A-D Critical Value	0.797	Data Not Gamma Distributed at 5% Significance Leve						
264	K-S Test Statistic	0.352	Kolmogrov-Smirnoff Gamma GOF Test						
265	5% K-S Critical Value	0.272	Data Not Gamma Distributed at 5% Significance Leve	l					
266	Data Not Gamm	na Distribute	ed at 5% Significance Level						
267									
268		Gamma	Statistics						
269	k hat (MLE)	0.421	k star (bias corrected MLE)	0.367					
270	Theta hat (MLE)	0.377	Theta star (bias corrected MLE)	0.433					
271	nu hat (MLE)	9.26	nu star (bias corrected)	8.068					
272	MLE Mean (bias corrected)	0.159	MLE Sd (bias corrected)	0.262					
273			Approximate Chi Square Value (0.05)	2.774					
274	Adjusted Level of Significance	0.0278	Adjusted Chi Square Value	2.294					
275									
276			ma Distribution						
277	95% Approximate Gamma UCL (use when n>=50))	0.461	95% Adjusted Gamma UCL (use when n<50)	0.558					
278									
279		-	GOF Test						
280	Shapiro Wilk Test Statistic	0.873	Shapiro Wilk Lognormal GOF Test						
281	5% Shapiro Wilk Critical Value	0.85	Data appear Lognormal at 5% Significance Level						
282	Lilliefors Test Statistic	0.261	Lilliefors Lognormal GOF Test						
283	5% Lilliefors Critical Value	0.267	Data appear Lognormal at 5% Significance Level						
284	Data appear	Lognormal	at 5% Significance Level						
285									
286		Lognorma							
287	Minimum of Logged Data	-5.521	Mean of logged Data	-3.392					
288	Maximum of Logged Data	-0.123	SD of logged Data	1.772					
289									
290			rmal Distribution						
291	95% H-UCL	2.177	90% Chebyshev (MVUE) UCL	0.333					
292	95% Chebyshev (MVUE) UCL	0.428	97.5% Chebyshev (MVUE) UCL	0.56					
293	99% Chebyshev (MVUE) UCL	0.82							
294									
295	-		tion Free UCL Statistics						
296	Data appear to follow a D	Discernible	Distribution at 5% Significance Level						
297									
298	-		tribution Free UCLs						
299	95% CLT UCL	0.308	95% Jackknife UCL	0.323					
300	95% Standard Bootstrap UCL	0.299	0.299 95% Bootstrap-t UCL						

	А	В	С	D	E	F	G	Н		J	К	L
301			9	5% Hall's Bo	otstrap UCL	1.981			95%	Percentile B	ootstrap UCL	0.313
302			9	95% BCA Bo	otstrap UCL	0.344						
303			90% Ch	ebyshev(Me	an, Sd) UCL	0.431			95% Cł	nebyshev(Me	ean, Sd) UCL	0.555
304			97.5% Ch	ebyshev(Me	an, Sd) UCL	0.727			99% Cł	nebyshev(Me	ean, Sd) UCL	1.063
305												
306						Suggested	UCL to Use					
307			99% Che	ebyshev (Me	an, Sd) UCL	1.063						
308												
309				Re	commended	UCL exceed	ts the maxim	num observa	tion			
310												
311		Note: Sugge	stions regard	ling the seled	tion of a 95%	UCL are pr	ovided to hel	p the user to	select the n	nost appropr	iate 95% UCL	
312		These rec	ommendatior	ns are based	upon the res	ults of the si	mulation stud	dies summar	ized in Sing	h, Singh, and	d laci (2002)	
313			and Singh	and Singh (2	2003). Howev	er, simulatio	ons results wi	ll not cover a	all Real Worl	ld data sets.		
314				For ad	ditional insig	nt the user m	nay want to co	onsult a stati	stician.			
315												

	A B C	DE	F	G H I J K	L
1		UCL Statis	tics for Unc	ensored Full Data Sets	
2					
3	User Selected Options				
4	Date/Time of Computation	9/18/2014 12:43:46 PM			
5	From File	Sediment and Surface Wa	ater Summa	ry_d.xls	
6	Full Precision	OFF			
7	Confidence Coefficient	95%			
8	Number of Bootstrap Operations	2000			
9					
10					
11	Arsenic (mg/L)				
12			-		
13				Statistics	-
14	Total	Number of Observations	13	Number of Distinct Observations	3
15				Number of Missing Observations	0
16		Minimum			7.6923E-4
17		Maximum	0.002		5.0000E-4
18			5.6330E-4	Std. Error of Mean	
19		Coefficient of Variation	0.732	Skewness	1.954
20					
21				GOF Test	
22		hapiro Wilk Test Statistic hapiro Wilk Critical Value	0.532	Shapiro Wilk GOF Test Data Not Normal at 5% Significance Level	
23	5%3	Lilliefors Test Statistic	0.860	Lilliefors GOF Test	
24		% Lilliefors Critical Value	0.433	Data Not Normal at 5% Significance Level	
25				% Significance Level	
26					
27		Ass	umina Norr	nal Distribution	
28	95% N	ormal UCL	, anning i terr	95% UCLs (Adjusted for Skewness)	
29		95% Student's-t UCL	0.00105	95% Adjusted-CLT UCL (Chen-1995)	0.00112
30				95% Modified-t UCL (Johnson-1978)	0.00106
31 32				, , , , , , , , , , , , , , , , , , ,	
33			Gamma	GOF Test	
34		A-D Test Statistic	3.022	Anderson-Darling Gamma GOF Test	
35		5% A-D Critical Value	0.739	Data Not Gamma Distributed at 5% Significance Lev	vel
36		K-S Test Statistic	0.47	Kolmogrov-Smirnoff Gamma GOF Test	
37		5% K-S Critical Value	0.238	Data Not Gamma Distributed at 5% Significance Lev	vel
38		Data Not Gamm	na Distribute	ed at 5% Significance Level	
39					
40			Gamma	Statistics	
41		k hat (MLE)	3.202	k star (bias corrected MLE)	2.515
42		Theta hat (MLE)	2.4021E-4	Theta star (bias corrected MLE)	
43		nu hat (MLE)	83.26	nu star (bias corrected)	65.38
44	M	LE Mean (bias corrected)	7.6923E-4	MLE Sd (bias corrected)	
45				Approximate Chi Square Value (0.05)	47.77
46	Adjus	sted Level of Significance	0.0301	Adjusted Chi Square Value	45.64
47					
48				ma Distribution	
49	95% Approximate Gamma	a UCL (use when n>=50))	0.00105	95% Adjusted Gamma UCL (use when n<50)	0.0011
50					

	A	В	<b>—</b>	С	<b>—</b>	D	—	E	F	Т	G	<u> </u>	Н	T	1			J		K			
51			_		_					mal	GOF Test				-			-			<u> </u>		
52				÷	Shapir	ro Will	k Test	t Statistic	0.553	}			Shap	piro '	Wilk	Logn	orm	al GC	OF T	est			
53				5% 5	Shapir	o Wilk	Critic	cal Value	e 0.866	6		Da	ata Not	Logr	norma	al at !	5% 5	Signif	ican	ce Le	evel		
54					Li	lliefors	s Test	t Statistic	0.461				Lil	liefo	rs Lo	gnor	mal	GOF	Tes	st			
55				!	5% Lil	lliefors	s Critic	cal Value	e 0.246	6		Da	ata Not	Logr	norma	al at !	5% 5	Signif	ican	ce Le	evel		
56							D	ata Not	Lognorma	l at	5% Signific	cance	Level										
57							-													-			
58									Lognor	mal	Statistics												
59					Minir	num o	of Log	ged Data	-7.601								Μ	lean	of log	gged	Data	-7.3	34
60					Maxir	num o	of Log	ged Data	-6.215									SD	of log	gged	Data	0.	532
61																					I		
62								Ase	suming Log	gno	rmal Distrib	oution											
63							95	% H-UCL	0.0010	)5					90	)% C	heby	/shev	/ (M\	VUE)	UCL	0.0	0108
64				95%	Cheb	yshev	v (MV	UE) UCL	0.0012	24					97.5	5% C	heby	/shev	/ (M\	VUE)	UCL	0.0	0145
65				99%	Cheb	yshev	v (MV	UE) UCL	0.0018	37													
66																					1		
67							No	onparam	etric Distr	ibut	ion Free U	CL St	atistics										
68							Data	a do not	follow a D	isce	ernible Dist	ributi	on (0.0	5)									
69																							
70								Nonpa	arametric I	Dist	ribution Fre	e UC	Ls										
71								CLT UCL		)3							ç	95% 、	Jack	knife	UCL	0.0	0105
72				95%	6 Stan	idard E	Boots	trap UCL	N/A								95	5% Bo	ootst	trap-t	UCL	N/A	
73								trap UCL				95% Percentile Bootstrap UCL								N/A			
74					95%	BCAE	Boots	trap UCL	N/A														
75					-			Sd) UCL									-				UCL		0145
76			97	′.5% C	hebys	shev(N	/lean,	Sd) UCL	0.0017	/4					99%	Che	bysł	nev(N	lean	ı, Sd)	UCL	0.0	0232
77																							
78											UCL to Use	)											
79			ç	}5% Cł	nebysl	hev (N	lean,	Sd) UCL	0.0014	15		1		1									
80																							
81				-						•	ovided to he	•										•	
82	Th	iese rec									nulation stu					-				ıci (2	002)		
83			and	d Singl	n and						ns results w					/orld	data	sets					
84						⊢or a	additio	onal insig	ght the use	er ma	ay want to c	consu	lt a stat	istici	an.								
85																							
86	Coholt (mg/l)																						
07	Cobalt (mg/L)																						
88									Gana	rol	Statistics												
89				Tata	al Nur~	hor of	fOha	ervations			Statistics				Num	bor	of Di	etinet	h Ohr		ations	12	
90									, 13												ations	0	
91								Minimur	n 2.0000E-	1					INUIN	inel (	וועו וכ	sang			Mean	-	0183
92								Maximum													edian	0.0	
93								SE										6+4	Erro		Mean		
94					<u> </u>	officia	ant of	Variatior										Siu.			vness		667
95						ienicie		variatiOf	0.732	-										OKen	1655	0.0	107
96									Norm	al C	OF Test												
97					Shani	ro \//ill	k Tool	t Statistic			ICF TESL			Ch.	apiro	W/iII	<u>, CO</u>		et				
98								cal Value				<i>ب</i> ח	ata appe		-						امريد		
99				5703				t Statistic				Da	ira ahhe		.illiefo			-					
100						meiore	5 169	. ວເລແວແ	0.213	,						013 0		1031					

	A B C D E	F	G H I J K	L
101	5% Lilliefors Critical Value	0.246	Data appear Normal at 5% Significance Level	
102	Data appea	ar Normal at	5% Significance Level	
103				
104	Ass	suming Norr	nal Distribution	
105	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
106	95% Student's-t UCL	0.00249	95% Adjusted-CLT UCL (Chen-1995)	0.00251
107			95% Modified-t UCL (Johnson-1978)	0.0025
108				
109		Gamma (	GOF Test	
110	A-D Test Statistic	0.216	Anderson-Darling Gamma GOF Test	
111	5% A-D Critical Value	0.747	Detected data appear Gamma Distributed at 5% Significance	ce Level
112	K-S Test Statistic	0.137	Kolmogrov-Smirnoff Gamma GOF Test	
113	5% K-S Critical Value	0.24	Detected data appear Gamma Distributed at 5% Significance	ce Level
114	Detected data appear	Gamma Dis	stributed at 5% Significance Level	
115				
116		Gamma		
117	k hat (MLE)	1.715	k star (bias corrected MLE)	1.371
118	Theta hat (MLE)	0.00107	Theta star (bias corrected MLE)	0.00133
119	nu hat (MLE)	44.59	nu star (bias corrected)	35.63
120	MLE Mean (bias corrected)	0.00183	MLE Sd (bias corrected)	0.00156
121	· · · · · · · · · · · · · · · · · · ·		Approximate Chi Square Value (0.05)	22.97
122	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	21.53
123				
124		-	ma Distribution	
125	95% Approximate Gamma UCL (use when n>=50))	0.00283	95% Adjusted Gamma UCL (use when n<50)	0.00302
126				
127		Lognormal		
128	Shapiro Wilk Test Statistic	0.942	Shapiro Wilk Lognormal GOF Test	
129	5% Shapiro Wilk Critical Value Lilliefors Test Statistic	0.866	Data appear Lognormal at 5% Significance Level Lilliefors Lognormal GOF Test	
130	5% Lilliefors Critical Value	0.113	Data appear Lognormal at 5% Significance Level	
131			at 5% Significance Level	
132		Lognorman		
133		Lognorma	I Statistics	
134	Minimum of Logged Data	-8.517	Mean of logged Data	-6.624
135	Maximum of Logged Data	-5.473	SD of logged Data	0.92
136		0.470		0.02
137	ussA	mina Loana	rmal Distribution	
138	95% H-UCL	0.00416	90% Chebyshev (MVUE) UCL	0.00353
139	95% Chebyshev (MVUE) UCL	0.00425	97.5% Chebyshev (MVUE) UCL	0.00525
140	99% Chebyshev (MVUE) UCL	0.00721		
141				
142	Nonparame	tric Distribut	tion Free UCL Statistics	
143	-		Distribution at 5% Significance Level	
144			-	
145	Nonpar	ametric Dist	ribution Free UCLs	
146	95% CLT UCL	0.00244	95% Jackknife UCL	0.00249
147	95% Standard Bootstrap UCL	0.00241	95% Bootstrap-t UCL	0.00259
148	95% Hall's Bootstrap UCL	0.00248	95% Percentile Bootstrap UCL	0.00244
149	95% BCA Bootstrap UCL	0.00248		
150		-		

	A B C D E	F	G H I J K	
151	90% Chebyshev(Mean, Sd) UCL	0.00294	95% Chebyshev(Mean, Sd) UCL	0.00344
152	97.5% Chebyshev(Mean, Sd) UCL	0.00414	99% Chebyshev(Mean, Sd) UCL	0.00552
153				
154		Suggested	UCL to Use	
155	95% Student's-t UCL	0.00249		
156				
157	Note: Suggestions regarding the selection of a 95%	UCL are pro	ovided to help the user to select the most appropriate 95% UCL	
158	These recommendations are based upon the res	ults of the si	mulation studies summarized in Singh, Singh, and Iaci (2002)	
159	and Singh and Singh (2003). However	er, simulatio	ns results will not cover all Real World data sets.	
160	For additional insigh	nt the user m	ay want to consult a statistician.	
161				
162				
163 C	Copper (mg/L)			
164				
165		General		
166	Total Number of Observations	13	Number of Distinct Observations	11
167			Number of Missing Observations	0
168	Minimum	0.0014	Mean	0.00625
169	Maximum	0.0124	Median	0.0048
170	SD	0.0035	Std. Error of Mean	
171	Coefficient of Variation	0.559	Skewness	0.561
172				
173			GOF Test	
174	Shapiro Wilk Test Statistic 5% Shapiro Wilk Critical Value	0.896	Shapiro Wilk GOF Test	
175	5% Snapiro Wilk Critical Value	0.866	Data appear Normal at 5% Significance Level Lilliefors GOF Test	
176	5% Lilliefors Critical Value	0.235	Data Not Normal at 5% Significance Level	
177			rmal at 5% Significance Level	
178				
179	Ass	sumina Norr	nal Distribution	
180	95% Normal UCL	<b>-</b>	95% UCLs (Adjusted for Skewness)	
181	95% Student's-t UCL	0.00798	95% Adjusted-CLT UCL (Chen-1995)	0.00801
182			95% Modified-t UCL (Johnson-1978)	0.00801
183 184				
185		Gamma	GOF Test	
186	A-D Test Statistic	0.475	Anderson-Darling Gamma GOF Test	
187	5% A-D Critical Value	0.739	Detected data appear Gamma Distributed at 5% Significan	ce Level
188	K-S Test Statistic	0.193	Kolmogrov-Smirnoff Gamma GOF Test	
189	5% K-S Critical Value	0.238	Detected data appear Gamma Distributed at 5% Significan	ce Level
190	Detected data appear	Gamma Dis	stributed at 5% Significance Level	
191				
192		Gamma	Statistics	
193	k hat (MLE)	3.217	k star (bias corrected MLE)	2.526
194	Theta hat (MLE)	0.00194	Theta star (bias corrected MLE)	0.00248
195	nu hat (MLE)	83.65	nu star (bias corrected)	65.68
196	MLE Mean (bias corrected)	0.00625	MLE Sd (bias corrected)	0.00393
197			Approximate Chi Square Value (0.05)	48.03
198	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	45.89
199				
200	Ass	uming Gam	ma Distribution	

	A B C D E	F	G H I J K I	
201	95% Approximate Gamma UCL (use when n>=50))	0.00855	95% Adjusted Gamma UCL (use when n<50)	0.00895
202				
203		Lognorma	GOF Test	
204	Shapiro Wilk Test Statistic	0.926	Shapiro Wilk Lognormal GOF Test	
205	5% Shapiro Wilk Critical Value	0.866	Data appear Lognormal at 5% Significance Level	
206	Lilliefors Test Statistic	0.172	Lilliefors Lognormal GOF Test	
207	5% Lilliefors Critical Value	0.246	Data appear Lognormal at 5% Significance Level	
208	Data appear	Lognormal	at 5% Significance Level	
209				
210		Lognorma	I Statistics	
211	Minimum of Logged Data	-6.571	Mean of logged Data	-5.238
212	Maximum of Logged Data	-4.39	SD of logged Data	0.628
213			I	
214	Assu	ming Logno	rmal Distribution	
215	95% H-UCL	0.00976	90% Chebyshev (MVUE) UCL	0.0098
216	95% Chebyshev (MVUE) UCL	0.0114	97.5% Chebyshev (MVUE) UCL	0.0135
217	99% Chebyshev (MVUE) UCL	0.0178		
218	· · · · · ·			
219	Nonparamet	tric Distribu	tion Free UCL Statistics	
220	Data appear to follow a D	Discernible	Distribution at 5% Significance Level	
221				
222	Nonpara	ametric Dist	ribution Free UCLs	
223	95% CLT UCL	0.00785	95% Jackknife UCL	0.00798
224	95% Standard Bootstrap UCL	0.00777	95% Bootstrap-t UCL	0.00823
225	95% Hall's Bootstrap UCL	0.00783	95% Percentile Bootstrap UCL	0.00783
226	95% BCA Bootstrap UCL	0.00791		
227	90% Chebyshev(Mean, Sd) UCL	0.00916	95% Chebyshev(Mean, Sd) UCL	0.0105
228	97.5% Chebyshev(Mean, Sd) UCL	0.0123	99% Chebyshev(Mean, Sd) UCL	0.0159
229				
230		Suggested	UCL to Use	
231	95% Student's-t UCL	0.00798		
232				
233			ovided to help the user to select the most appropriate 95% UCL.	
234			mulation studies summarized in Singh, Singh, and laci (2002)	
235			ns results will not cover all Real World data sets.	
236	For additional insigh	it the user m	ay want to consult a statistician.	
237				
238				
239 <sup>N</sup>	lickel (mg/L)			
240		0	Chattation	
241			Statistics	
242	Total Number of Observations	13	Number of Distinct Observations	12
243		0.000	Number of Missing Observations	0
244	Minimum	0.003	Mean	0.0404
245	Maximum	0.092	Median	0.038
246	SD Coefficient of Variation	0.0278	Std. Error of Mean	0.0077
247		0.688	Skewness	0.401
248		Normal (	GOF Test	
249	Chapting Mills Tage Original			
250	Shapiro Wilk Test Statistic	0.952	Shapiro Wilk GOF Test	

	A B C D E	F	G H I J K	
251	5% Shapiro Wilk Critical Value	0.866	Data appear Normal at 5% Significance Level	
252	Lilliefors Test Statistic	0.121	Lilliefors GOF Test	
253	5% Lilliefors Critical Value	0.246	Data appear Normal at 5% Significance Level	
254	Data appea	r Normal at	5% Significance Level	
255				
256	Ass	suming Norr	nal Distribution	
257	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
258	95% Student's-t UCL	0.0541	95% Adjusted-CLT UCL (Chen-1995)	0.054
259			95% Modified-t UCL (Johnson-1978)	0.0543
260	· · · · · · · · · · · · · · · · · · ·			
261		Gamma (	GOF Test	
262	A-D Test Statistic	0.437	Anderson-Darling Gamma GOF Test	
263	5% A-D Critical Value	0.75	Detected data appear Gamma Distributed at 5% Significanc	e Level
264	K-S Test Statistic	0.212	Kolmogrov-Smirnoff Gamma GOF Test	
265	5% K-S Critical Value	0.241	Detected data appear Gamma Distributed at 5% Significanc	e Level
266	Detected data appear	Gamma Dis	stributed at 5% Significance Level	
267				
268		Gamma	Statistics	
269	k hat (MLE)	1.514	k star (bias corrected MLE)	1.216
270	Theta hat (MLE)	0.0267	Theta star (bias corrected MLE)	0.0332
271	nu hat (MLE)	39.37	nu star (bias corrected)	31.62
272	MLE Mean (bias corrected)	0.0404	MLE Sd (bias corrected)	0.0366
273			Approximate Chi Square Value (0.05)	19.77
274	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	18.44
275				
276		uming Gam	ma Distribution	
277	95% Approximate Gamma UCL (use when n>=50))	0.0646	95% Adjusted Gamma UCL (use when n<50)	0.0692
278				
279		Lognormal		
280	Shapiro Wilk Test Statistic	0.869	Shapiro Wilk Lognormal GOF Test	
281	5% Shapiro Wilk Critical Value	0.866	Data appear Lognormal at 5% Significance Level	
282	Lilliefors Test Statistic	0.269	Lilliefors Lognormal GOF Test	
283	5% Lilliefors Critical Value	0.246	Data Not Lognormal at 5% Significance Level	
284	Data appear Approx	kimate Logn	ormal at 5% Significance Level	
285				
286		Lognorma		
287	Minimum of Logged Data	-5.809	Mean of logged Data	-3.574
288	Maximum of Logged Data	-2.386	SD of logged Data	1.062
289				
290			rmal Distribution	
291	95% H-UCL	0.122	90% Chebyshev (MVUE) UCL	0.0907
292	95% Chebyshev (MVUE) UCL	0.111	97.5% Chebyshev (MVUE) UCL	0.139
293	99% Chebyshev (MVUE) UCL	0.194		
294				
295	-		tion Free UCL Statistics	
296	Data appear to follow a D	Discernible I	Distribution at 5% Significance Level	
297				
298	-		ribution Free UCLs	
299	95% CLT UCL 95% Standard Bootstrap UCL	0.0531	95% Jackknife UCL	0.0541
	Ub% Standard Bootstran UCI	0.0523	95% Bootstrap-t UCL	0.0557

	А	В	С	D	E	F	G	Н			J	K	L
301			ç	5% Hall's Bo	otstrap UCL	0.0555			ç	95% F	Percentile Bo	ootstrap UCL	0.0528
302				95% BCA Bo	otstrap UCL	0.0532							
303			90% Cł	ebyshev(Me	an, Sd) UCL	0.0635			959	% Ch	ebyshev(Me	ean, Sd) UCL	0.074
304			97.5% Cł	ebyshev(Me	an, Sd) UCL	0.0885			99	% Ch	ebyshev(Me	ean, Sd) UCL	0.117
305													
306						Suggested	UCL to Use						
307				95% Stu	dent's-t UCL	0.0541					-		
308													
309		Note: Sugge	stions regard	ling the selec	tion of a 95%	UCL are pr	ovided to hel	p the user to	select	the m	lost appropri	iate 95% UCL.	
310		These rec	ommendatio	ns are based	upon the res	ults of the si	mulation stud	dies summar	ized in	Singh	n, Singh, and	d laci (2002)	
311			and Singh	and Singh (2	2003). Howev	er, simulatio	ons results wi	ill not cover a	all Real	Worle	d data sets.		
312				For ad	ditional insigl	ht the user m	nay want to c	onsult a stati	istician.				
313													

	A B C D E	F	G H I J K	L
1	UCL Statist	tics for Unce	ensored Full Data Sets	
2				
3	User Selected Options			
4	Date/Time of Computation 9/18/2014 12:44:37 PM			
5	From File Sediment and Surface Wa	ater Summa	ry_e.xls	
6	Full Precision OFF			
7	Confidence Coefficient 95%			
8	Number of Bootstrap Operations 2000			
9				
10				
11	Arsenic (mg/L)			
12				
13		General S		
14	Total Number of Observations	13	Number of Distinct Observations	5
15			Number of Missing Observations	0
16	Minimum :		Mean	0.00158
17	Maximum SD	0.006	Median Std. Error of Mean	5.0000E-4
18		1.074		
19	Coefficient of Variation	1.074	Skewness	1.866
20		Normal G		
21	Shapiro Wilk Test Statistic	0.703	Shapiro Wilk GOF Test	
22	5% Shapiro Wilk Critical Value	0.703	Data Not Normal at 5% Significance Level	
23	Lilliefors Test Statistic	0.800	Lilliefors GOF Test	
24	5% Lilliefors Critical Value	0.246	Data Not Normal at 5% Significance Level	
25			% Significance Level	
26				
27	Ass	sumina Norn	nal Distribution	
28 29	95% Normal UCL	<b>.</b>	95% UCLs (Adjusted for Skewness)	
	95% Student's-t UCL	0.00241	95% Adjusted-CLT UCL (Chen-1995)	0.00261
30 31			95% Modified-t UCL (Johnson-1978)	0.00245
32				
33		Gamma G	GOF Test	
34	A-D Test Statistic	1.345	Anderson-Darling Gamma GOF Test	
35	5% A-D Critical Value	0.753	Data Not Gamma Distributed at 5% Significance Leve	el
36	K-S Test Statistic	0.326	Kolmogrov-Smirnoff Gamma GOF Test	
37	5% K-S Critical Value	0.242	Data Not Gamma Distributed at 5% Significance Leve	el
38	Data Not Gamm	na Distribute	d at 5% Significance Level	
39				
40		Gamma S	Statistics	
41	k hat (MLE)	1.32	k star (bias corrected MLE)	1.067
42	Theta hat (MLE)	0.00119	Theta star (bias corrected MLE)	0.00148
43	nu hat (MLE)	34.33	nu star (bias corrected)	27.74
44	MLE Mean (bias corrected)	0.00158	MLE Sd (bias corrected)	0.00153
45			Approximate Chi Square Value (0.05)	16.72
46	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	15.52
47				
48	Ass	uming Gam	ma Distribution	
		0.00262		0.00000
49	95% Approximate Gamma UCL (use when n>=50))	0.00262	95% Adjusted Gamma UCL (use when n<50)	0.00282

	Α		В		С	T	D	Т	Е		F	G	Т	Н		I			J		K		L
51										- L	ognorma	GOF Test											
52						Shap	iro Wil	k Tes	st Statis	tic	0.781			Sł	napiro	o Will	k Log	gnori	nal G	OF 1	fest		
53					5%	Shap	ro Will	k Criti	ical Val	ue	0.866			Data N	ot Lo	gnorn	nal a	t 5%	Signi	fican	ice Le	vel	
54						L	lliefor	s Tes	st Statis	tic	0.326				Lillie	fors L	ogn	orma	I GOI	= Te	st		
55						5% L	illiefors		ical Val		0.246			Data N		gnorn	nal a	t 5%	Signi	fican	ice Le	vel	
56								0	Data No	ot Log	gnormal at	5% Signific	cano	e Leve	el								
57																							
58											-	I Statistics											
59								-	gged Da		-7.601								Mean				-6.877
60						Maxi	mum c	of Log	gged Da	ata	-5.116								SD	of lo	gged	Data	0.909
61																							
62												rmal Distrib	butio	on									
63									5% H-U(		0.00316								byshe	•			0.002
64								•	/UE) U(		0.00325					97	.5%	Che	byshe	v (M)	VUE)	UCL	0.0040
65					999	% Che	byshev	v (MV	/UE) U(	CL	0.00551												
66																							
67									-			tion Free U											
68								Dat	ta do no	ot foll	ow a Disc	ernible Dist	tribu	tion (0	.05)								
69												<u> </u>											
70								050/		-		tribution Fre	ee L	CLS					050/				
71		95% Cl									0.00235										knife		0.0024
72		95% Standard Bootstr									0.0023		95% Bootstrap-t UCL									0.003	
73		95% Hall's Bootstra 95% BCA Bootstra									0.00585			95% Percentile Bootstrap UCL								0.002	
74					000/						0.00262					050			- k / l	4			0.003
75				0					, Sd) U( , Sd) U(		0.00299							-	shev(l shev(l		-		0.003
76				9	7.5%			nean,	, 30) 00		0.00431					33	/0 CI	leby	SIIEV(I	vieai	i, Su)	UCL	0.0002
77										s	uaaested	UCL to Use	<u>,</u>										
78					95% (	Cheby	shev (N	Vean	, Sd) U(		0.00362		-										
79																							
80 81		Note:	Sugg	estior	is rega	arding	the sel	lectio	n of a 9	5% U	JCL are pro	ovided to he	elp ti	ne usei	r to se	elect t	the n	nost	appro	priate	e 95%	UCL	
82												mulation stu	•							-			
83				ar	nd Sing	gh anc	I Singh	ı (200	)3). Hov	vever	, simulatio	ns results w	vill n	ot cove	er all	Real	Worl	d da	ta sets	5.			
84							For	additi	ional in:	sight	the user m	ay want to c	cons	sult a s	tatisti	cian.							
85																							
86																							
	obalt (mg	ı/L)																					
88					-	-	-		-														
89											General	Statistics											
90					To	tal Nur	mber o	f Obs	servatio	ns	13					Nu	mbe	r of [	Distinc	t Ob	serva	tions	11
91																Nu	mbe	r of N	lissin	g Ob	serva	tions	0
92					-	-		-	Minimu	ım 1.	0000E-4										Ν	<i>l</i> lean	0.002
93									Maximu	ım	0.007										Me	edian	0.0013
94											0.00248								Std	. Erro	or of N	/lean	6.8891E
95						С	oefficie	ent of	f Variati	on	1.071										Skew	ness	1.06
96																							
97											Normal C	GOF Test											
98									st Statis		0.82								OF Te				
99					5%				ical Val		0.866			Data	Not N				Signific		e Leve	əl	
						L	illiefor	s Tes	st Statis	tic	0.204					Lillie	fors	GO	- Test	t			

A	BCDE	F	G H I J K	L
101	5% Lilliefors Critical Value	0.246	Data appear Normal at 5% Significance Level	
102	Data appear App	oximate No	rmal at 5% Significance Level	
103				
104	As	suming Norr	nal Distribution	
105	95% Normal UCL		95% UCLs (Adjusted for Skewness)	
106	95% Student's-t UCL	0.00355	95% Adjusted-CLT UCL (Chen-1995)	0.00367
107			95% Modified-t UCL (Johnson-1978)	0.00358
108				
109		Gamma	GOF Test	
110	A-D Test Statistic	0.331	Anderson-Darling Gamma GOF Test	
111	5% A-D Critical Value	0.768	Detected data appear Gamma Distributed at 5% Significand	ce Level
112	K-S Test Statistic	0.151	Kolmogrov-Smirnoff Gamma GOF Test	
112	5% K-S Critical Value	0.245	Detected data appear Gamma Distributed at 5% Significance	ce Level
114	Detected data appear	Gamma Dis	stributed at 5% Significance Level	
115				
116		Gamma	Statistics	
117	k hat (MLE)	0.799	k star (bias corrected MLE)	0.666
118	Theta hat (MLE)	0.0029	Theta star (bias corrected MLE)	0.00348
119	nu hat (MLE)	20.76	nu star (bias corrected)	17.31
120	MLE Mean (bias corrected)	0.00232	MLE Sd (bias corrected)	0.00284
			Approximate Chi Square Value (0.05)	8.891
121 122	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	8.045
	, ,		, , ,	
123	Ass	suming Gam	ma Distribution	
124	95% Approximate Gamma UCL (use when n>=50))	0.00451	95% Adjusted Gamma UCL (use when n<50)	0.00499
125				
126		Lognorma	GOF Test	
127	Shapiro Wilk Test Statistic	0.939	Shapiro Wilk Lognormal GOF Test	
128	5% Shapiro Wilk Critical Value	0.866	Data appear Lognormal at 5% Significance Level	
129	Lilliefors Test Statistic	0.129	Lilliefors Lognormal GOF Test	
130	5% Lilliefors Critical Value	0.246	Data appear Lognormal at 5% Significance Level	
131			at 5% Significance Level	
132				
133		Lognorma	I Statistics	
134	Minimum of Logged Data	-9.21	Mean of logged Data	-6.81
135	Maximum of Logged Data	-4.962	SD of logged Data	1.429
136				
137	Assi	iming Loand	rmal Distribution	
138	95% H-UCL	0.0138	90% Chebyshev (MVUE) UCL	0.00621
139	95% Chebyshev (MVUE) UCL	0.00781	97.5% Chebyshev (MVUE) UCL	0.01
140	99% Chebyshev (MVUE) UCL	0.0144		
141	, · · · · · · · · · · · · · · · · ·			
142	Nonparame	tric Distribu	tion Free UCL Statistics	
143	•		Distribution at 5% Significance Level	
144			•	
145	Nonpar	ametric Dist	ribution Free UCLs	
146	95% CLT UCL	0.00345	95% Jackknife UCL	0.00355
147	95% Standard Bootstrap UCL	0.00344	95% Bootstrap-t UCL	0.00394
148	95% Hall's Bootstrap UCL	0.00344	95% Percentile Bootstrap UCL	0.00345
149	95% BCA Bootstrap UCL	0.0036		0.00010
150		0.0000		

A           151           152           153           154           155           156           157           158           159           160           161           162           163           164           165           166           167           168           169           170	90% Chebyshev(Mean, Sd) UCL 97.5% Chebyshev(Mean, Sd) UCL 95% Student's-t UCL Note: Suggestions regarding the selection of a 95% These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum 5	0.00355 UCL are pro ults of the sin	G       H       I       J       K         95% Chebyshev(Mean, Sd) UCL       99% Chebyshev(Mean, Sd) UCL         99% Chebyshev(Mean, Sd) UCL         UCL to Use         UCL to help the user to select the most appropriate 95% UCL.         mulation studies summarized in Singh, Singh, and Iaci (2002)         ns results will not cover all Real World data sets.         ay want to consult a statistician.         Statistics         Number of Distinct Observations	0.00532		
152       153       154       155       156       157       158       159       160       161       162       163       164       165       166       167       168       169	95% Student's-t UCL Note: Suggestions regarding the selection of a 95% These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations	Suggested 0.00355 UCL are pro ults of the sin er, simulatio t the user m	UCL to Use UCL to Use Divided to help the user to select the most appropriate 95% UCL. Imulation studies summarized in Singh, Singh, and Iaci (2002) Ins results will not cover all Real World data sets. Inay want to consult a statistician. Statistics			
153       154       155       156       157       158       159       160       161       162       163       164       165       166       167       168       169	95% Student's-t UCL Note: Suggestions regarding the selection of a 95% These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum 5	0.00355 UCL are pro ults of the sin er, simulatio t the user m General	ovided to help the user to select the most appropriate 95% UCL. mulation studies summarized in Singh, Singh, and Iaci (2002) ns results will not cover all Real World data sets. ay want to consult a statistician.			
154       155       156       157       158       159       160       161       162       163       164       165       166       167       168       169	95% Student's-t UCL Note: Suggestions regarding the selection of a 95% These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum 5	0.00355 UCL are pro ults of the sin er, simulatio t the user m General	ovided to help the user to select the most appropriate 95% UCL. mulation studies summarized in Singh, Singh, and Iaci (2002) ns results will not cover all Real World data sets. ay want to consult a statistician.			
155       156       157       158       159       160       161       162       163       164       165       166       167       168       169	Note: Suggestions regarding the selection of a 95% These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations	UCL are pro ults of the sin er, simulatio It the user m General s	mulation studies summarized in Singh, Singh, and Iaci (2002) ns results will not cover all Real World data sets. ay want to consult a statistician.			
156       157       158       159       160       161       162       163       164       165       166       167       168       169	These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum	ults of the sin er, simulatio It the user m General s	mulation studies summarized in Singh, Singh, and Iaci (2002) ns results will not cover all Real World data sets. ay want to consult a statistician.			
157       158       159       160       161       162       163       164       165       166       167       168       169	These recommendations are based upon the resu and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum	ults of the sin er, simulatio It the user m General s	mulation studies summarized in Singh, Singh, and Iaci (2002) ns results will not cover all Real World data sets. ay want to consult a statistician.			
158       159       160       161       162       163       164       165       166       167       168       169	and Singh and Singh (2003). Howeve For additional insigh or (mg/L) Total Number of Observations Minimum 5	er, simulatio t the user m General s	ns results will not cover all Real World data sets. ay want to consult a statistician.			
159       160       161       162       163       164       165       166       167       168       169	For additional insigh or (mg/L) Total Number of Observations Minimum 5	t the user m	ay want to consult a statistician.			
160           161           162           163           Coppe           164           165           166           167           168           169	r (mg/L) Total Number of Observations Minimum 5	General	Statistics			
161           162           163           164           165           166           167           168           169	Total Number of Observations Minimum 5					
162         Coppe           164	Total Number of Observations Minimum 5					
163         Coppe           164	Total Number of Observations Minimum 5					
164       165       166       167       168       169	Minimum {					
165 166 167 168 169	Minimum {					
166 167 168 169	Minimum {	13	Number of Distinct Observations			
167 168 169				13		
168 169			Number of Missing Observations	0		
169		5.1000E-4	Mean	0.00642		
	Maximum	0.0179	Median	0.0043		
170	SD	0.00599	Std. Error of Mean	0.00166		
171	Coefficient of Variation	0.932	Skewness	0.89		
172						
172		Normal C	GOF Test			
174	Shapiro Wilk Test Statistic	0.864	Shapiro Wilk GOF Test			
175	5% Shapiro Wilk Critical Value 0.866 Data Not Normal at 5% Significance Level					
176	Lilliefors Test Statistic 0.19 Lilliefors GOF Test					
177	5% Lilliefors Critical Value 0.246 Data appear Normal at 5% Significance Level					
178	Data appear Appro	oximate No	rmal at 5% Significance Level			
179						
180	Ass	suming Norr	nal Distribution			
181	95% Normal UCL		95% UCLs (Adjusted for Skewness)			
182	95% Student's-t UCL	0.00938	95% Adjusted-CLT UCL (Chen-1995)	0.00959		
183			95% Modified-t UCL (Johnson-1978)	0.00945		
184						
185		Gamma (	GOF Test			
186	A-D Test Statistic	0.273	Anderson-Darling Gamma GOF Test			
187	5% A-D Critical Value	0.756	Detected data appear Gamma Distributed at 5% Significance	e Level		
188	K-S Test Statistic	0.148	Kolmogrov-Smirnoff Gamma GOF Test			
189	5% K-S Critical Value	0.243	Detected data appear Gamma Distributed at 5% Significance	e Level		
190	Detected data appear	Gamma Dis	stributed at 5% Significance Level			
191						
192		Gamma	Statistics			
193	k hat (MLE)	1.096	k star (bias corrected MLE)	0.894		
194	Theta hat (MLE)	0.00586	Theta star (bias corrected MLE)	0.00718		
195	nu hat (MLE)	28.49	nu star (bias corrected)	23.25		
196	MLE Mean (bias corrected)	0.00642	MLE Sd (bias corrected)	0.00679		
197	1		Approximate Chi Square Value (0.05)	13.28		
198	Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	12.21		
199						
200	Ass	uming Gam	ma Distribution			

	A B C D E	F	G H I J K	1				
201	95% Approximate Gamma UCL (use when n>=50))	0.0112	95% Adjusted Gamma UCL (use when n<50)	0.0122				
202								
203	Lognormal GOF Test							
204	Shapiro Wilk Test Statistic	0.948	Shapiro Wilk Lognormal GOF Test					
205	5% Shapiro Wilk Critical Value	0.866	Data appear Lognormal at 5% Significance Level					
206	Lilliefors Test Statistic	0.129	Lilliefors Lognormal GOF Test					
207	5% Lilliefors Critical Value 0.246 Data appear Lognormal at 5% Significance Level							
208	Data appear	Lognormal	at 5% Significance Level					
209								
210		Lognorma	I Statistics					
211	Minimum of Logged Data	-7.581	Mean of logged Data	-5.569				
212	Maximum of Logged Data	-4.023	SD of logged Data	1.168				
213								
214	Assu	ming Logno	rmal Distribution					
215	95% H-UCL	0.0218	90% Chebyshev (MVUE) UCL	0.0144				
216	95% Chebyshev (MVUE) UCL	0.0177	97.5% Chebyshev (MVUE) UCL	0.0224				
217	99% Chebyshev (MVUE) UCL	0.0315						
218								
219	Nonparame	tric Distribu	tion Free UCL Statistics					
220	Data appear to follow a [	Discernible	Distribution at 5% Significance Level					
221								
222	Nonpara	ametric Dist	tribution Free UCLs					
223	95% CLT UCL	0.00915	95% Jackknife UCL	0.00938				
224	95% Standard Bootstrap UCL	0.00912	95% Bootstrap-t UCL	0.0103				
225	95% Hall's Bootstrap UCL	0.00917	95% Percentile Bootstrap UCL	0.00917				
226	95% BCA Bootstrap UCL	0.00957						
227	90% Chebyshev(Mean, Sd) UCL	0.0114	95% Chebyshev(Mean, Sd) UCL	0.0137				
228	97.5% Chebyshev(Mean, Sd) UCL	0.0168	99% Chebyshev(Mean, Sd) UCL	0.0229				
229								
230			UCL to Use					
231	95% Student's-t UCL	0.00938						
232								
233			ovided to help the user to select the most appropriate 95% UCL.					
234			mulation studies summarized in Singh, Singh, and laci (2002)					
235			ns results will not cover all Real World data sets.					
236	For additional insigh	nt the user m	ay want to consult a statistician.					
237								
238								
239 <b>N</b>	lickel (mg/L)							
240		0	Chatlation					
241		General		4.4				
242	Total Number of Observations	13	Number of Distinct Observations	11				
243			Number of Missing Observations	0				
244	Minimum : Maximum		Mean	0.0244				
245	Maximum	0.103	Median	0.0105				
246	SD Coofficient of Veriation	0.0361	Std. Error of Mean	0.01				
247	Coefficient of Variation	1.48	Skewness	1.668				
248		Naw14						
249								
250	Shapiro Wilk Test Statistic	0.683	Shapiro Wilk GOF Test					

25         5% Shapiro Wilk Critical Value         0.365         Data Nd Normal at 5% Significance Level           222         Lillefors GOF Test         0.329         Lillefors GOF Test           233         5% Lillefors Critical Value         0.246         Data Nd Normal at 5% Significance Level           256         Assuming Normal Distribution         95% VICLa (Agusted for Skewness)         0.0423           256         Assuming Normal Distribution         95% VICLa (Agusted for Skewness)         0.0           257         95% Normal UCL         95% Modified 1UCL (Clone-1998)         0.0           259         95% Sludent's-LUCL         0.423         95% Modified 1UCL (Clone-1998)         0.0           250         Since Level         95% Modified 1UCL (Clone-1998)         0.0         0.0           260         Since Level         95% Modified 1UCL (Clone-1998)         0.0         0		A B C D E	F	G H I J K	1				
250         Ullifetors Test Statistic         0.230         Ullifetors CoC Fract           253         5% Lillefors Crited Value         0.246         Data Not Normal at 5% Significance Level           256         Assuming Normal Distribution         5% Vicia (Adjusted for Skewness)         0.000           257         95% Normal UCL         95% Adjusted-CLT UCL (Chen-1995)         0.0           259         95% Normal UCL         0.422         95% Adjusted-CLT UCL (Chen-1995)         0.0           259         95% Student's-t UCL         0.423         95% Adjusted-CLT UCL (Chen-1995)         0.0           260         95% Adjusted-CLT UCL (Chen-1995)         0.0         0.000         95% Modified-T UCL (Chen-1995)         0.0           261         A-D Test Statistic         0.465         Anderson-Darling Garma GOF Test         266         267         268         268         268         267         268         268         267         268		-		-					
253         Significance Level         Data Not Normal at 5% Significance Level           226         Assuming Normal Distribution         5%           286         Assuming Normal Distribution         5%           287         95% Normal UCL         95% KUCLs (Adjusted CLT UCL (Chen-1995)         0.0           288         95% Student%-LUCL         0.0423         95% Modified-LUCL (Johnson-1978)         0.0           289		Lilliefors Test Statistic	0.329	Lilliefors GOF Test					
256         Date Not Normel at 5% Significance Level           256         Assuming Normel Distribution           257         95% Normel VCL         0.9423         95% VCLa (Adjusted for Skewnese)         0.0           258         95%, Student's-t UCL         0.0423         95%, Adjusted-CL TUCL (Chen-1996)         0.0           259         95%, Modified-4 UCL (Johnson - 1978)         0.0         0.0           260         95%, Modified-4 UCL (Johnson - 1978)         0.0           261         Camma GOF Test         95%, Modified-4 UCL (Johnson - 1978)         0.0           262         A-D Test Statistic         0.465         Anderson-Darling Gamma GOF Test         100           263         5%, A-D Critical Value         0.25         Detected data appear Gamma Distributed at 5%, Significance Level         26           264         Camma Statistics         10.2         Kaing on-Siminof Gamma GOF Test         10.0           270         Theta hit (MLE)         0.31         k star (bias corrected)         10.0           271         m hat (MLE)         0.31         K star (bias corrected)         10.0           272         MLE Mean (bias corrected)         0.024         MLE S data corrected)         0.0           273         MLE Mean (bias corrected)         0.027		5% Lilliefors Critical Value	0.246	Data Not Normal at 5% Significance Level					
Assumal Distribution           256         95% Normal UCL         0.0423         95% Adjusted-CLT UCL (Chen-1985)         0.0           259         95% Adjusted-CLT UCL (Chen-1985)         0.0         95% Adjusted-CLT UCL (Chen-1985)         0.0           250         95% Adjusted-CLT UCL (Chen-1985)         0.0         95% Adjusted-CLT UCL (Chen-1985)         0.0           250         Camma COF Test         Camma COF Test         0.10         95% Adjusted-CLT UCL (Chen-1985)         0.0           261         Camma COF Test         Camma COF Test         0.10         Nonportability of the test of test ormed test % significance. Level           263         Checked data appear Camma Distributed at 5% significance. Level         0.01         Nonportability of test test of test ormed test % significance. Level           264         Checked data appear Camma Distributed at 5% significance. Level         0.021         Nonportability of test test of test ormed test % significance. Level           275         Camma Coff Test         Camma Coff Test         Camma Coff Test         Camma Coff Test </td <td></td> <td>Data Not</td> <td>Normal at 5</td> <td>% Significance Level</td> <td></td>		Data Not	Normal at 5	% Significance Level					
Bio									
95% VCLs (Adjusted: for Skewnese)         UCLs (Adjusted: for Skewnese)           258         95% Student's-UCL         0.0423         95% Adjusted: CLT UCL (Chen-1995)         0.0           269         95% Modified: UCL (Johnson-1978)         0.0         0.0           260         95% Modified: UCL (Johnson-1978)         0.0           261		Ass	suming Norr	nal Distribution					
95% Student's-LUCL         0.0423         95% Adjusted-CLT UCL (Chen-1995)         0.0           269         95% Modified+UCL (Johnson-1978)         0.0           260         Gamma GOF Test         0.0           261         A-D Test Statistic         0.165         Anderson-Darling Gamma GOF Test         0.0           263         5% AD Critical Value         0.162         Kolmogrov-Smirnoff Gamma GOF Test         0.0           264         K-S Test Statistic         0.162         Kolmogrov-Smirnoff Gamma GOF Test         0.0           266         Detected data appear Gamma Distributed at 5% Significance Level         0.25         Detected data appear Gamma Distributed at 5% Significance Level           267         Camma Statistics         0.0476         Theta star (bias corrected MLE)         0.47           270         Theta hat (MLE)         0.0476         Theta star (bias corrected MLE)         0.0244           271         mu hat (MLE)         0.321         Adjusted Chi Square Value         4.3           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value         4.3           275         Camma Statistics         Camma Statistics         0.23         27         28         27         28         28         27         28         28		95% Normal UCL 95% UCLs (Adjusted for Skewness)							
259         95% Modified-t UCL (Johnson-1978)         0.0           260         Camma GOF Test         261           262         A-D Test Statistic         0.465         Anderson-Darling Gamma GOF Test           263         5% A-D Critical Value         0.789         Detected data appear Gamma Distributed at 5% Significance Level           264         K-S Test Statistic         0.162         Kolmogrov-Smirnoff Gamma GOF Test           265         Detected data appear Gamma Distributed at 5% Significance Level         266           266         Detected data appear Gamma Distributed at 5% Significance Level         267           267         Camma Statistics         0.0270           270         Theta hat (MLE)         0.513         K star (bias corrected)         0.11           271         nu hat (MLE)         0.0274         MLE 53 (bias corrected)         0.0274           273         MLE Maan (bias corrected)         0.0244         MLE 53 (bias corrected)         0.42           273         Approximate Gamma UCL (use when n>=50)         0.0571         Approximate Gamma UCL (use when n=50)         0.0271           274         Adjusted Level of Significance         0.0431         Shapiro Wilk Lognormal GOF Test         228           275         Cagnormal GOF Test         232         242		95% Student's-t UCL	0.0423	95% Adjusted-CLT UCL (Chen-1995)	0.0459				
260         Gamma GOF Test           261         A-D Test Statistic         0.465         Anderson-Darling Gamma GOF Test           263         5% A-D Critical Value         0.783         Detected data appear Gamma Distributed at 5% Significance Level           264         K-S Test Statistic         0.162         Kolmogrov-Smirof Gamma GOF Test           265         5% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           266         Detected data appear Gamma Distributed at 5% Significance Level         0.45         0.45           268         Gamma Statistics         0.476         Theta star (bias corrected MLE)         0.47           270         Theta hat (MLE)         0.513         K star (bias corrected MLE)         0.024           271         nu hat (MLE)         13.34         nu star (bias corrected)         0.0244           273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0371         95% Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma GOF Test         4.5           273         Lognormal GOF Test         1.23         Lillifeors Critical Value         0.246         Data appear Lognormal at 5% Significance Level<				95% Modified-t UCL (Johnson-1978)	0.0431				
Camme GOF Test           262         A-D test Statistic         0.466         Anderson-Darting Gamma GOF Test           263         5% A-D Critical Value         0.789         Detected data appear Gamma Distributed at 5% Significance Level           264         K-S Test Statistic         0.162         Kolmogrov-Smimoff Gamma GOF Test           265         5% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           266         Detected data appear Gamma Distributed at 5% Significance Level         0.27           267									
And Test Statistic         0.465         Anderson-Darling Gamma GOF Test           263         S% A-D. Critical Value         0.789         Detected data appear Gamma Distributed at 5% Significance Leve           264         K-S Test Statistic         0.152         Kohmogov-Sminnef Gamma GOF Test           265         5% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           267			Gamma	GOF Test					
283         5% AD Critical Value         Detected data appear Gamma Distributed at 5% Significance Lev           284         K-S Test Statistic         0.162         Kolmogrov-Sminoff Gamma GOF Test           285         5% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           286         Detected data appear Gamma Distributed at 5% Significance Level         0.0           287         Gamma Statistics         0.0           288         Matter MILE         0.513         k star (bias corrected)         0.0           270         Theta hat (MLE)         0.344         mu star (bias corrected)         0.0           271         nu hat (MLE)         0.344         MLE Sd (bias corrected)         0.0           273         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.00)         4.3           275         Assuming Gamma Distribution         276         Assuming Gor Test         0.0           278         Lognormal GOF Test         0.057         95% Adjusted Gamma UCL (use when n<50)		A-D Test Statistic	0.465	Anderson-Darling Gamma GOF Test					
264         K-S Test Statistic         0.162         Kolmogrov-Smimoff Gamma GOF Test           265         5% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           266         Detected data appear Gamma Distributed at 5% Significance Level         0           267         Camma Statistics         0           268         Camma Statistics         0           269         K hat (MLE)         0.513         k star (bias corrected MLE)         0           270         Theta hat (MLE)         0.513         k star (bias corrected MLE)         0           271         nu hat (MLE)         0.324         Au star (bias corrected)         0.0244           272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0571           273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0371         95% Adjusted Gamma UCL (use when n=50)         0.0571           276         Camma Statistics         0.943         Shapiro Wilk Critical Value         0.866         Data appear Lognormal at S% Significance Level           281         Shapiro Wilk Critical Value         0.246         Data appear Lognormal at S		5% A-D Critical Value	0.789	Detected data appear Gamma Distributed at 5% Significanc	e Level				
S% K-S Critical Value         0.25         Detected data appear Gamma Distributed at 5% Significance Level           266         Detected data appear Gamma Distributed at 5% Significance Level         266           268         Gamma Statistics         267           269         K hat (MLE)         0.513         K star (bias corrected MLE)         0.4           270         Theta hat (MLE)         0.376         Theta star (bias corrected)         0.0           271         nu hat (MLE)         0.344         nu star (bias corrected)         0.0           272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.6)         4.5           275         Corpormal GOF Test         Significance Level         0.0571         95% Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<=50)		K-S Test Statistic	0.162	Kolmogrov-Smirnoff Gamma GOF Test					
Detected data appear Gamma Distributed at 5% Significance Level           266         Gamma Statistics           268         Camma Statistics           269         k hat (MLE)         0.513         k star (bias corrected MLE)         0.0           270         Theta hat (MLE)         0.0476         Theta star (bias corrected MLE)         0.0           271         mu hat (MLE)         13.34         mu star (bias corrected)         0.0           273         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.3           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.3           275		5% K-S Critical Value	0.25	Detected data appear Gamma Distributed at 5% Significanc	e Level				
267           268         Gamma Statistics           269         K hat (MLE)         0.513         K star (bias corrected MLE)         0.4           270         Theta hat (MLE)         0.347         Theta star (bias corrected MLE)         0.0           271         mu hat (MLE)         13.34         mu star (bias corrected)         0.0           273         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Adjusted Level of Significance         0.001         Adjusted Chi Square Value (0.05)         4.5           276         Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<50)		Detected data appear	Gamma Dis	stributed at 5% Significance Level					
268         Gamma Statistics           269         k hat (MLE)         0.513         k star (bias corrected MLE)         0.0           270         Theta hat (MLE)         0.3476         Theta star (bias corrected MLE)         0.0           271         mu hat (MLE)         0.334         mu star (bias corrected)         0.0           272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Approximate Chi Square Value (0.05)         4.5         4.3           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (4.3         4.3           275         Assuming Gamma Distribution         276         95% Approximate Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<50)									
269         k hat (MLE)         0.513         k star (bias corrected MLE)         0.4           270         Theta hat (MLE)         0.0476         Theta star (bias corrected MLE)         0.0           271         nu hat (MLE)         13.34         nu star (bias corrected)         0.0           271         MLE Mean (bias corrected)         0.0244         MLE Star (bias corrected)         0.0           272         MLE Mean (bias corrected)         0.0244         Approximate Chi Square Value (0.05)         4.5           273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n>=50)         0.0           278         Cagnormal GOF Test         279         279         270         272         273         0.00         273         0.00         273         0.00         273         0.00         274         283         5% Shapiro Wilk Tritical Value         0.246         Data appear Lognormal at 5% Significance Level         284         284         284         284         284         285         287         350 of logged Data         7.601         Mean of logged Data         1.6 <td></td> <td></td> <td>Gamma</td> <td>Statistics</td> <td></td>			Gamma	Statistics					
270         Theta hat (MLE)         0.0476         Theta star (bias corrected)         0.0           271         nu hat (MLE)         13.34         nu star (bias corrected)         11.           272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.02           273         Approximate Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.5           275         Adjusted Chi Square Value (0.05)         0.0571         95% Adjusted Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n>50)         0.0           278         Cognormal GOF Test         279         Cognormal GOF Test         279         0         0.0           278         Shapiro Wilk Test Statistic         0.943         Shapiro Wilk Lognormal GOF Test         0.0         0.0           281         5% Shapiro Wilk Critical Value         0.866         Data appear Lognormal at 5% Significance Level         284         0         285           282         Lilliefors Test Statistic         0.123         Lilliefors Cognormal at 5% Significance Level         1.8           283         Shapiro Milk Cognormal Advinum of Logged Data         -7.601         Mean of logged Data		k hat (MLE)	0.513	k star (bias corrected MLE)	0.446				
271         nu hat (MLE)         13.34         nu star (bias corrected)         11.           272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Approximate Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (4.3           275         Adjusted Chi Square Value (0.05)         4.5           276         Assuming Gamma Distribution         0.0278           277         95% Approximate Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<50)		Theta hat (MLE)	0.0476	Theta star (bias corrected MLE)	0.0548				
272         MLE Mean (bias corrected)         0.0244         MLE Sd (bias corrected)         0.0           273         Approximate Chi Square Value (0.05)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.45)         4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (4.5)         4.5           275		nu hat (MLE)	13.34	nu star (bias corrected)	11.59				
273         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value (0.05)         4.4.5           274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value         4.3           275		MLE Mean (bias corrected)	0.0244	MLE Sd (bias corrected)	0.0366				
274         Adjusted Level of Significance         0.0301         Adjusted Chi Square Value         4.3           275         Assuming Gamma Distribution         277         95% Approximate Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<50)				Approximate Chi Square Value (0.05)	4.96				
275       Assuming Gamma Distribution         276       Assuming Gamma Distribution         277       95% Approximate Gamma UCL (use when n>=50)       0.0571       95% Adjusted Gamma UCL (use when n<50)		Adjusted Level of Significance	0.0301	Adjusted Chi Square Value	4.357				
Assuming Gamma Distribution         277       95% Approximate Gamma UCL (use when n>=50)       0.0571       95% Adjusted Gamma UCL (use when n<50)									
277         95% Approximate Gamma UCL (use when n>=50)         0.0571         95% Adjusted Gamma UCL (use when n<50)         0.0           278		Ass	uming Gam	ma Distribution					
278       Lognormal GOF Test         279       Shapiro Wilk Test Statistic       0.943       Shapiro Wilk Lognormal GOF Test         281       5% Shapiro Wilk Critical Value       0.866       Data appear Lognormal at 5% Significance Level         282       Lilliefors Test Statistic       0.123       Lilliefors Lognormal GOF Test         283       5% Lilliefors Critical Value       0.246       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level       285         285       Lognormal Statistics         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601         288       Maximum of Logged Data       -2.273       SD of logged Data       -4.9         289		95% Approximate Gamma UCL (use when n>=50)	0.0571	95% Adjusted Gamma UCL (use when n<50)	0.065				
Z79       Lognormal GOF Test         280       Shapiro Wilk Test Statistic       0.943       Shapiro Wilk Lognormal GOF Test         281       5% Shapiro Wilk Critical Value       0.866       Data appear Lognormal at 5% Significance Level         282       Lilliefors Test Statistic       0.123       Lilliefors Lognormal GOF Test         283       5% Lilliefors Critical Value       0.246       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level       285         285       Lognormal Statistics         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289        290       Assuming Lognormal Distribution       -2.273       90% Chebyshev (MVUE) UCL       0.0         291       95% Chebyshev (MVUE) UCL       0.375       90% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       294       -2.273       200       201         294       Lognormateric Distribution Free UCL Statistics       296       295       295       295         296       Data appear to f									
280       5% Shapiro Wilk Critical Value       0.866       Data appear Lognormal at 5% Significance Level         282       Lilliefors Test Statistic       0.123       Lilliefors Lognormal GOF Test         283       5% Lilliefors Critical Value       0.246       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level       285         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       -4.9         290       Assuming Lognormal Distribution       292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.0         293       99% Chebyshev (MVUE) UCL       0.19       294       294       295       295         296       Data appear to follow a Discernible Distribution at 5% Significance Level       296       297       296       297			Lognormal	GOF Test					
Zasi       Lilliefors Test Statistic       0.123       Lilliefors Lognormal GOF Test         283       5% Lilliefors Critical Value       0.246       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level         285       Lognormal Statistics         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289       Assuming Lognormal Distribution         291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       2       2       2         294       Lognormal to Significance Level         295       Nonparametric Distribution Free UCL Statistics         296       Data appear to follow a Discernible Distribution at 5% Significance Level         297       Nonparametric Distribution at 5% Significance Level	280	Shapiro Wilk Test Statistic	0.943	Shapiro Wilk Lognormal GOF Test					
282       Lilliefors Test Statistic       0.123       Lilliefors Lognormal GOF Test         283       5% Lilliefors Critical Value       0.246       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level         285       Lognormal Statistics         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289       Assuming Lognormal Distribution         291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.19         293       99% Chebyshev (MVUE) UCL       0.19       0.19       0.1         294       Data appear to follow a Discernible Distribution at 5% Significance Level         296       Data appear to follow a Discernible Distribution at 5% Significance Level         296       Data appear to follow a Discernible Distribution at 5% Significance Level	281	5% Shapiro Wilk Critical Value	0.866	Data appear Lognormal at 5% Significance Level					
283       Data appear Lognormal at 5% Significance Level         284       Data appear Lognormal at 5% Significance Level         285       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.6         289	282	Lilliefors Test Statistic	0.123	Lilliefors Lognormal GOF Test					
284       Lognormal Statistics         286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289       -2200       Assuming Lognormal Distribution       1.8         291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.19         293       99% Chebyshev (MVUE) UCL       0.19       1       1         294	283	5% Lilliefors Critical Value	0.246	Data appear Lognormal at 5% Significance Level					
286       Lognormal Statistics         287       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         288       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289	284	Data appear	Lognormal	at 5% Significance Level					
280       Minimum of Logged Data       -7.601       Mean of logged Data       -4.9         287       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289	285								
287       Maximum of Logged Data       -2.273       SD of logged Data       1.8         289       290       Assuming Lognormal Distribution         291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       1       1         294       295       Nonparametric Distribution Free UCL Statistics       2         295       Data appear to follow a Discernible Distribution at 5% Significance Level       2         297         1	286		Lognorma	I Statistics					
289         290         291       95% H-UCL         0.375       90% Chebyshev (MVUE) UCL         0.0         292       95% Chebyshev (MVUE) UCL         0.19         293         294         295         Nonparametric Distribution Free UCL Statistics         296         Data appear to follow a Discernible Distribution at 5% Significance Level	287				-4.946				
290       Assuming Lognormal Distribution         291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       0.19       0         294       294       294       294       295       296       297         296       Data appear to follow a Discernible Distribution at 5% Significance Level       297       297	288	Maximum of Logged Data	-2.273	SD of logged Data	1.822				
291       95% H-UCL       0.375       90% Chebyshev (MVUE) UCL       0.0         292       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       0       0         294       294       295       Nonparametric Distribution Free UCL Statistics       296         296       Data appear to follow a Discernible Distribution at 5% Significance Level       297	289								
291       95% Chebyshev (MVUE) UCL       0.0993       97.5% Chebyshev (MVUE) UCL       0.1         293       99% Chebyshev (MVUE) UCL       0.19       0.19       0.19         294       295       Nonparametric Distribution Free UCL Statistics       296       Data appear to follow a Discernible Distribution at 5% Significance Level       297	290								
293     99% Chebyshev (MVUE) UCL     0.19       294       295       Nonparametric Distribution Free UCL Statistics       296       297	291				0.0773				
293     294       295     Nonparametric Distribution Free UCL Statistics       296     Data appear to follow a Discernible Distribution at 5% Significance Level       297     Nonparametric Distribution Error UCL statistics	292			97.5% Chebyshev (MVUE) UCL	0.13				
295       Nonparametric Distribution Free UCL Statistics         296       Data appear to follow a Discernible Distribution at 5% Significance Level         297       Nonparametric Distribution Error UCL statistics	293	99% Chebyshev (MVUE) UCL	0.19						
296       Data appear to follow a Discernible Distribution at 5% Significance Level         297	294								
297 Nemeremetrie Distribution Free UCLe	295	-							
Nonnorametria Distribution Free U.O. a	296	Data appear to follow a D	Discernible I	Distribution at 5% Significance Level					
Nonparametric Dietribution Free LICLe	297								
230	298	-		ribution Free UCLs					
299 95% CLT UCL 0.0409 95% Jackknife UCL 0.0					0.0423				
300 95% Standard Bootstrap UCL 0.0401 95% Bootstrap-t UCL 0.0	300	95% Standard Bootstrap UCL	0.0401	95% Bootstrap-t UCL	0.0614				

	А	В	С	D	E	F	G	Н			J	K	L
301		95% Hall's Bootstrap UCL				0.0454		95% Percentile Bootstrap UCL					0.0411
302				95% BCA Bo	otstrap UCL	0.0447							
303		90% Chebyshev(Mean, Sd) UCL			an, Sd) UCL	0.0545	95% Chebyshev(Mean, Sd) UCL				ean, Sd) UCL	0.0681	
304			97.5% Cł	ebyshev(Me	an, Sd) UCL	0.087			999	% Ch	ebyshev(Me	ean, Sd) UCL	0.124
305													
306						Suggested	UCL to Use						
307			95	% Adjusted C	amma UCL	0.065		-			-		
308													
309		Note: Suggestions regarding the selection of a 95% UCL are provided to help the user to select the most appropriate 95% UCL											
310		These rec	ommendatio	ns are based	upon the res	ults of the si	mulation stud	dies summar	rized in	Singł	n, Singh, and	d laci (2002)	
311	and Singh and Singh (2003). However, simulations results will not cover all Real World data sets.												
312				For ad	ditional insigl	ht the user m	nay want to c	onsult a stati	istician.				
313													

Appendix C

EcoRam Mode



Appendix C Example Calculations and Input Data for Ecological Risk Assessment October 10, 2014

### **INTRODUCTION**

The first part of this appendix serves to assist the reader in understanding how the quantitative ERA was conducted by providing example calculations using data from the Site. The worked example will progress from the exposure assessment (environmental concentrations that a VEC is expected to encounter) through to the ecological risk characterization stage (estimation of risk from all environmental concentrations).

This example focuses on meadow vole exposure to the 95% Upper Confidence Limit of the Mean (95 UCLM) concentration for nickel.

### MEADOW VOLE EXPOSURE TO NICKEL IN SOIL

To quantify the potential risk to the meadow vole as a result of nickel concentrations in soil, an estimated average daily dose (ADD) from each applicable exposure pathway was first estimated as defined below:

$$ADD_j = IF_j x AF_j x EPC_j$$

For exposure pathway 'j',

Where:

$ADD_j$	Average Daily Dose of COPC from media j (mg COPC/kg body weight - day)
$IF_j$	Intake Factor for media j (kg contaminated medium/kg body weight - day)
$AF_j$	Absorption Factor of media j (default value of 1), and
$EPC_j$	Exposure Point Concentration of media j (mg chemical/kg medium)

And:

$$IF_j = (IR_j x f_{site})/BW$$

Where:

$IF_j$	Intake Factor for media j (kg contaminated medium/kg body weight - day)
$IR_j$	Ingestion Rate of media j (kg/day)
$f_{site}$	Fraction of time spent on site (dimensionless, assumed 100%), and
BW	Body Weight of ecological receptor (in kg)

Intake factors (IF) for all ecological receptors for all applicable exposure pathways are presented in this Appendix. Life history traits for the meadow vole are summarized in the table below:



Appendix C Example Calculations and Input Data for Ecological Risk Assessment October 10, 2014

General Parameters						
BW	Body weight	0.044	kg			
IR	Food intake rate	0.005	kg wet-wt/day			
Ingestion of Soil						
	Ingestion rate	1.8E-05	kg dry-wt/day			
IFing- sl	Intake factor	4.1E-03	kg/kg-day			
Ingestion of Terrestrial Plants						
NA	Fraction of food intake rate	1.0E+00	unitless			
IR	Ingestion rate	5.0E-03	kg wet-wt/day			
IFing- tpIntake factor1.1E-01kg/kg-day						
Ingestio	Ingestion of Terrestrial Invertebrates – pathway not applicable					
Ingestio	n of Terrestrial Mammals/B	irds – pathway not	applicable			

#### Site EPCs are as follows:

Exposure Pathway	EPC
Soil	2.3E+04 mg nickel / kg dry weight soil (Woodlot #3)
Terrestrial Plant	2.1E+01 mg nickel / kg wet weight terrestrial plant material (calculated for Woodlot #3 using site-specific BAF)

Estimation of nickel ADDs for all exposure pathways applicable to the meadow vole are outlined below:

 $\begin{aligned} ADD_{soil} &= IF_{soil} \ x \ AF_{soil} \ x \ EPC_{soil} \\ ADD_{soil} &= (4.1E-03) \ x \ (0.22) \ x \ (2.3E+04) \\ ADD_{soil} &= 2.1E+00 \ mg/kg-bw-day \\ \end{aligned}$   $\begin{aligned} ADD_{terrestrial \ plant} &= IF_{terrestrial \ plant} \ x \ AF_{terrestrial \ plant} \ x \ EPC_{terrestrial \ plant} \\ ADD_{terrestrial \ plant} &= (1.1E-01) \ x \ (1) \ x \ (2.1E+01) \\ ADD_{terrestrial \ plant} &= 2.4E+00 \ mg/kg-bw-day \end{aligned}$ 

To estimate the total nickel ADD from all exposure pathways i.e., the total daily amount of nickel the meadow vole would be expected to ingest as a result of all sources (dietary items plus associated nickel in soil):

 $ADD_{total} = ADD_{soil} + ADD_{terrestrial plant}$ 

$$ADD_{total} = (2.1E+00) + (2.4E+00)$$



Appendix C Example Calculations and Input Data for Ecological Risk Assessment October 10, 2014  $ADD_{total} = 4.5E + 00 \text{ mg/kg-bw-day}$ 

In the final step of risk characterization, the total ADD is compared against the Toxicity Reference Values (TRV) for nickel exposure to mammalian receptors in order to estimate a Hazard Quotient (HQ). In this assessment TRV for nickel sourced from the MOE was utilized (80 mg/kg-day).

Estimation of an HQ for the meadow vole exposed to nickel is thus:

 $HQ_{nickel} = (ADD_{nickel} / TRV_{nickel})$  $HQ_{nickel} = (4.5E + 00 / 8.0E + 01)$  $HQ_{nickel} = 5.6E - 02$ 

Alternatively, each pathway specific ADD may be compared against the TRV to derive a pathway specific HQ. Each individual HQ may then be summed to arrive at a final HQ, which would be identical to that derived via the methods described above.

The following tables list the intake parameters for all of the VECs.



xample Site 1 aseline Case No 0.01 0.0706 0.01 0.0706 0.017 0.017 0.25 1.487 1 2 2 2 2 2 1 2 2 1 2 2 1 0 0 2 2 2 1 2 2 1 1 2 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 2 1 2 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 1 2 1 1 1 2 2 1 1 1 2 2 1 1 1 2 1 1 1 2 1 2 1 1 1 2 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 1 2 1 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 2 1 1 1 1 1 1 2 1	(unitless)         (unitless, usual range is 0.003 to 0.03)         (unitless, usual range is 0.012 to 0.025)         (cm <sup>3</sup> /cm <sup>3</sup> )         (1-top 5% most sensitive species, 2-Rainbow Trout, 3-Daphnia magna)         (1-Freshwater Sediment, 2-Surface Water)         Default value should be 1         (1-Freshwater Sediment, 2-Surface Water)         Default value should be 2         (1-Freshwater Sediment, 2-Surface Water)         Default value should be 2         (1-Marine Sediment, 2-Seawater)         Default value should be 2         (1-Marine Sediment, 2-Seawater)         Default value should be 1         kg         kg         kg dry-wt/day         kg dry-wt/day         kg wet-wt/day
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2 2 1 0.015 9.0E-03 0.0E+00 1 0.0E+00 0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	(1-Freshwater Sediment, 2-Surface Water)         Default value should be 2         (1-Marine Sediment, 2-Seawater)         Default value should be 2         (1-Marine Sediment, 2-Seawater)         Default value should be 1         kg         kg wet-wt/day         L/day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         L/day
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1 0.015 9.0E-03 0.0E+00 1 0.0E+00 0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	Default value should be 2           (1-Marine Sediment, 2-Seawater)           Default value should be 1           kg           kg wet-wt/day           L/day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           L/day
0.015 9.0E-03 0.0E+00 1 0.0E+00 1.9E-04 1 1.2E-02 0 0 0.0E+00 0 0.0E+00 0 0.0E+00 1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	Default value should be 1           kg           kg wet-wt/day           L/day           (0 = no, 1 = yes)           kg dry-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg wet-wt/day           kg/kg-day           (0 = no, 1 = yes)           kg/kg-day           (0 = no, 1 = yes)           kg/kg-day           (0 = no, 1 = yes)           L/day
9.0E-03 0.0E+00 1 0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0 0.0E+00 9.0E-03 1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg wet-wt/day L/day (0 = no, 1 = yes) kg dry-wt/day (0 = no, 1 = yes) kg wet-wt/day (0 = no, 1 = yes) kg wet-wt/day
9.0E-03 0.0E+00 1 0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0 0.0E+00 9.0E-03 1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg wet-wt/day L/day (0 = no, 1 = yes) kg dry-wt/day (0 = no, 1 = yes) kg wet-wt/day (0 = no, 1 = yes) kg wet-wt/day
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0.0E+00 0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0 0.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg dry-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         L/day
0.0E+00 1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0 0.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         L/day
1.9E-04 1 1.2E-02 0 0.0E+00 0.0E+00 0 0.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg wet-wt/day         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         kg/kg-day         (0 = no, 1 = yes)         L/day
1.2E-02 0 0.0E+00 0.0E+00 0 1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	(0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) kg wet-wt/day (0 = no, 1 = yes) kg/kg-day (0 = no, 1 = yes) L/day
0.0E+00 0.0E+00 0 0.0E+00 1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	kg wet-wt/day kg/kg-day (0 = no, 1 = yes) kg wet-wt/day (0 = no, 1 = yes) kg wet-wt/day (0 = no, 1 = yes) kg/kg-day (0 = no, 1 = yes) L/day
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1 1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0.0E+00 0 0 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0	(0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) L/day
1.0E+00 9.0E-03 1 6.0E-01 0 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0	kg wet-wt/day kg/kg-day (0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) L/day
1 6.0E-01 0 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0	kg/kg-day (0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) L/day
6.0E-01 0 0.0E+00 0.0E+00 0 0.0E+00 0 0.0E+00 0	(0 = no, 1 = yes) kg wet-wt/day kg/kg-day (0 = no, 1 = yes) L/day
0.0E+00 0.0E+00 0.0E+00 0 0.0E+00 0	kg wet-wt/day kg/kg-day (0 = no, 1 = yes) L/day
0.0E+00 0 0.0E+00 0 0.0E+00 0	kg/kg-day (0 = no, 1 = yes) L/day
0.0E+00 0 0.0E+00 0	kg/kg-day (0 = no, 1 = yes) L/day
0 0.0E+00 0	(0 = no, 1 = yes) L/day
0.0E+00 0	L/day
-	L/kg-day
0.02.00	
<u> </u>	
0 0.0E+00	(0 = no, 1 = yes)
0.0E+00 0.0E+00	kg dry-wt/day
0 0.0E+00	kg/kg-day
0.02.00	ng ng aay
0	(0 = no, 1 = yes)
0.0E+00 0.0E+00	kg wet-wt/day
0 0.0E+00	
	kg/kg-day
0 0.0E+00	(0 = no, 1 = yes)
0.0E+00 0	kg wet-wt/day
0.0E+00	kg/kg-day
0	(0 = no, 1 = yes)
0.0E+00 0.0E+00	kg wet-wt/day
0 0.0E+00	ka/ka-day
0.0E+00	(0 = no, 1 = yes) L/day
0 0.0E+00	L/kg-day
	(0 = no, 1 = yes)
0.0E+00	
0.0E+00	kg dry-wt/day
0 0.0E+00	kg/kg-day
	(0 = no, 1 = yes)
0.0E+00	
0.0E+00 0	kg wet-wt/day
0.0E+00	kg/kg-day
0	(0 = no, 1 = yes)
0.0E+00 0.0E+00	kg wet-wt/day
0 0.0E+00	kg/kg-day
0 0.0E+00	(0 = no, 1 = yes)
0.0E+00	kg wet-wt/day
	0 0.0E+00 0.0E+00 0 0 0 0 0 0 0 0 0 0 0 0



Receptor Name Name of Study Area	Example Site 1	
Entire Local Study Area or Project Alone	Baseline Case	
Does the OMOE 511/09 regulation apply to this site? Fraction of organic carbon in the soil	No 0.01	(unitless)
Fraction organic carbon in freshwater (dry)		
ædiment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Soil Moisture Content	0.25	(cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	<u>1.487</u> 1	(g/cm³) (1-top 5% most sensitive species, 2-Rainbov
Receptor Type	2	Trout, 3-Daphnia magna) (1-Bird, 2-Mammal)
s Receptor Sensitive Species for the Project?	0	(1-Yes, 0-No)
Small Mammal Type	2	(1-General, 2-Herbivore, 3-Insectivore) Default value should be 1
Fish board on Sadimant on Sunface Water Unter	2	(1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake Aquatic Plants based on Sediment or Surface	1	Default value should be 1 (1-Freshwater Sediment, 2-Surface Water)
Water Uptake	2	Default value should be 2
Fish based on Sediment or Seawater Uptake	2	(1-Marine Sediment, 2-Seawater) Default value should be 2
Marine Benthic Invertebrates based on Sediment or	1	(1-Marine Sediment, 2-Seawater)
Seawater Uptake	I	Default value should be 1
Beneral Parameters Body weight	0.044	kg
Food intake rate	5.0E-03	kg wet-wt/day
Water intake rate           ngestion of Soil	0.0E+00	L/day
Applicable pathway? Fraction diet that is dry solid	1 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	1.8E-05 1	kg dry-wt/day
Intake factor (IFing-sI)	4.1E-04	kg/kg-day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction of food intake rate	1.0E+00 5.0E-03	kg wet-wt/day
Fraction from site	1	
Intake factor (IFing-tp) ngestion of Terrestrial Invertebrates	1.1E-01	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ti)	0 0.0E+00	kg/kg-day
Ingestion of Terrestrial Mammals/Birds		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-tm)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0	L/day
Intake factor (IFing-sw)	0.0E+00	L/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction diet that is dry solid	0.0E+00	
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg dry-wt/day
Fraction from site Intake factor (IFing-sed)	0 0.0E+00	kg/kg-day
	0.02.00	
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-ap)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
ngestion of Freshwater Fish		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-fsh)	0.0E+00	kg/kg-day
ngestion of Seawater Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	L/day
Fraction from site Intake factor (IFing-sw)	0 0.0E+00	L/kg-day
ngestion of Marine Sediment Applicable pathway?	0	(0 = no, 1 = yes)
Fraction diet that is dry solid	0.0E+00	······································
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg dry-wt/day
Fraction from site Intake factor (IFing-sed)	0 0.0E+00	kg/kg-day
ngestion of Marine Plants		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	0 0.0E+00	kg/kg-day
ngestion of Marine Benthic Invertebrates Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ai)	0.0E+00	kg/kg-day
Ingestion of Marine Fish           Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate	0.0E+00	kg wet-wt/day



Receptor Name Name of Study Area	Domestic Sheep (OMOE) Example Site 1	
Entire Local Study Area or Project Alone	Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
sediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
	0.017	
Fraction lipid in marine invertebrates (wet weight) Soil Moisture Content	0.017 0.25	(unitless, usual range is 0.012 to 0.025) (cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	1.487	(g/cm³) (1-top 5% most sensitive species, 2-Rainbov
Calculate TU based on	1	Trout, 3-Daphnia magna)
Receptor Type Is Receptor Sensitive Species for the Project?	2 0	(1-Bird, 2-Mammal) (1-Yes, 0-No)
Small Mammal Type	2	(1-General, 2-Herbivore, 3-Insectivore) Default value should be 1
	2	(1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake	1	Default value should be 1
Aquatic Plants based on Sediment or Surface Nater Uptake	2	(1-Freshwater Sediment, 2-Surface Water) Default value should be 2
·		(1-Marine Sediment, 2-Seawater)
Fish based on Sediment or Seawater Uptake Marine Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters		
Body weight Food intake rate	52 1.0E+01	kg kg wet-wt/day
Water intake rate	0.0E+00	L/day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction diet that is dry solid	0.0E+00	· · · · · · · · · · · · · · · · · · ·
Fraction of food intake rate Ingestion rate	0.0E+00 6.5E-02	kg dry-wt/day
Fraction from site	1 1.3E-03	
Intake factor (IFing-sI) ngestion of Terrestrial Plants		kg/kg-day
Applicable pathway? Fraction of food intake rate	1 1.0E+00	(0 = no, 1 = yes)
Ingestion rate	1.0E+01	kg wet-wt/day
Fraction from site Intake factor (IFing-tp)	1 2.0E-01	kg/kg-day
ngestion of Terrestrial Invertebrates		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ti)	0 0.0E+00	kg/kg-day
ngestion of Terrestrial Mammals/Birds Applicable pathway?	0	
Fraction of food intake rate	0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-tm)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0	L/day
Fraction from site Intake factor (IFing-sw)	0.0E+00	L/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction diet that is dry solid	0.0E+00	(0 - 110, 1 - 903)
Fraction of food intake rate	0.0E+00 0.0E+00	kg dry-wt/day
Fraction from site	0	
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Freshwater Aquatic Plants Applicable pathway?	0	$(0 - n_0, 1 - y_{00})$
Fraction of food intake rate	0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ap)	0.0E+00	kg/kg-day
ngestion of Freshwater Benthic Invertebrates Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ai) ngestion of Freshwater Fish	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-fsh) ngestion of Seawater	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	L/day
Intake factor (IFing-sw) ngestion of Marine Sediment	0.0E+00	L/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction diet that is dry solid Fraction of food intake rate	0.0E+00 0.0E+00	
Ingestion rate	0.0E+00	kg dry-wt/day
Fraction from site Intake factor (IFing-sed)	0 0.0E+00	kg/kg-day
ngestion of Marine Plants		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	0 0.0E+00	kg/kg-day
ngestion of Marine Benthic Invertebrates		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
ngestion of Marine Fish Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
	U	kg/kg-day



Receptor Name Name of Study Area	White-Tailed Deer Example Site 1	
Entire Local Study Area or Project Alone	Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
sediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight) Soil Moisture Content	0.017 0.25	(unitless, usual range is 0.012 to 0.025) (cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	1.487	(g/cm <sup>3</sup> ) (1-top 5% most sensitive species, 2-Rainboy
Calculate TU based on	1	Trout, 3-Daphnia magna)
Receptor Type s Receptor Sensitive Species for the Project?	2	(1-Bird, 2-Mammal) (1-Yes, 0-No)
	-	(1-General, 2-Herbivore, 3-Insectivore)
Small Mammal Type	1	Default value should be 1 (1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake	1	Default value should be 1
Aquatic Plants based on Sediment or Surface Nater Uptake	2	(1-Freshwater Sediment, 2-Surface Water) Default value should be 2
		(1-Marine Sediment, 2-Seawater)
Fish based on Sediment or Seawater Uptake Marine Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters		
Body weight	60 4.65+00	kg ka wat ut/day
Food intake rate Water intake rate	4.6E+00 3.9E+00	kg wet-wt/day L/day
ngestion of Soil		
Applicable pathway? Fraction diet that is dry solid	1 3.7E-01	(0 = no, 1 = yes)
Fraction of food intake rate	2.2E-02 3.8E-02	kg dry-wt/day
Fraction from site	1	
Intake factor (IFing-sI) ngestion of Terrestrial Plants	6.3E-04	kg/kg-day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	1.0E+00 4.6E+00	kg wet-wt/day
Fraction from site	1	
Intake factor (IFing-tp) ngestion of Terrestrial Invertebrates	7.7E-02	kg/kg-day
Applicable pathway? Fraction of food intake rate	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ti)	1 0.0E+00	kg/kg-day
ngestion of Terrestrial Mammals/Birds	0.0E+00	
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-tm)	1 0.0E+00	kg/kg-day
Ingestion of Surface Water		
Applicable pathway? Ingestion rate	1 3.9E+00	(0 = no, 1 = yes) L/day
Fraction from site Intake factor (IFing-sw)	1 6.6E-02	L/kg-day
ngestion of Freshwater Sediment		
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 1	kg dry-wt/day
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Freshwater Aquatic Plants		
Applicable pathway?	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	1 0.0E+00	kg/kg-day
ngestion of Freshwater Benthic Invertebrates		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	1 0.0E+00	kg/kg-day
ngestion of Freshwater Fish		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Intake factor (IFing-fsh)	1 0.0E+00	kg/kg-day
ngestion of Seawater Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	(U = no, 1 = yes) L/day
Fraction from site Intake factor (IFing-sw)	1 0.0E+00	L/kg-day
ngestion of Marine Sediment		
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	ka day ut/day
Ingestion rate Fraction from site	0.0E+00 1	kg dry-wt/day
Intake factor (IFing-sed) ngestion of Marine Plants	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	1	
Intake factor (IFing-ap) ngestion of Marine Benthic Invertebrates	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	1	
Intake factor (IFing-ai) ngestion of Marine Fish	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	1	



Receptor Name Name of Study Area	Red Fox (OMOE) Example Site 1	
Entire Local Study Area or Project Alone	Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	(
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
sediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight) Soil Moisture Content	0.017	(unitless, usual range is 0.012 to 0.025) (cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	1.487	(g/cm <sup>3</sup> ) (1-top 5% most sensitive species, 2-Rainbox
Calculate TU based on	1	Trout, 3-Daphnia magna)
Receptor Type Is Receptor Sensitive Species for the Project?	2 0	(1-Bird, 2-Mammal) (1-Yes, 0-No)
		(1-General, 2-Herbivore, 3-Insectivore)
Small Mammal Type	2	Default value should be 1 (1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake	1	Default value should be 1
Aquatic Plants based on Sediment or Surface Water Uptake	2	(1-Freshwater Sediment, 2-Surface Water) Default value should be 2
•		(1-Marine Sediment, 2-Seawater)
Fish based on Sediment or Seawater Uptake Marine Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters		
Body weight Food intake rate	4.5 4.3E-01	kg kg wet-wt/day
Water intake rate	4.3E-01 0.0E+00	kg wet-wt/day L/day
ngestion of Soil Applicable pathway?	1	(0 = no, 1 = yes)
Fraction diet that is dry solid	0.0E+00	
Fraction of food intake rate Ingestion rate	0.0E+00 3.9E-03	kg dry-wt/day
Fraction from site	1	
Intake factor (IFing-sI)	8.6E-04	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-tp) ngestion of Terrestrial Invertebrates	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ti)	0 0.0E+00	kg/kg-day
Ingestion of Terrestrial Mammals/Birds	0.0E+00	
Applicable pathway? Fraction of food intake rate	1 1.0E+00	(0 = no, 1 = yes)
Ingestion rate	4.3E-01	kg wet-wt/day
Fraction from site Intake factor (IFing-tm)	1 9.6E-02	kg/kg-day
Ingestion of Surface Water		
Applicable pathway?	0 0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site	0	
Intake factor (IFing-sw) Ingestion of Freshwater Sediment	0.0E+00	L/kg-day
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Freshwater Aquatic Plants		
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-ap) ngestion of Freshwater Benthic Invertebrates	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
ngestion of Freshwater Fish		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-fsh)	0 0.0E+00	kg/kg-day
ngestion of Seawater	0	(0 = no, 1 = yes)
Applicable pathway? Ingestion rate	0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site Intake factor (IFing-sw)	0 0.0E+00	L/kg-day
ngestion of Marine Sediment		
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Marine Plants Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ap)	0.0E+00	kg/kg-day
ngestion of Marine Benthic Invertebrates           Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-ai)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00 0.0E+00	kg wet-wt/day
Ingestion rate		



Receptor Name Name of Study Area Entire Local Study Area or Project Alone	Dr the Redwinged Blackbird           Redwinged Blackbird (OMOE)           Example Site 1           Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
sediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight) Soil Moisture Content	0.017 0.25	(unitless, usual range is 0.012 to 0.025) (cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	1.487	(g/cm <sup>3</sup> ) (1-top 5% most sensitive species, 2-Rainbov
Calculate TU based on	1	Trout, 3-Daphnia magna)
Receptor Type Is Receptor Sensitive Species for the Project?	<u> </u>	(1-Bird, 2-Mammal) (1-Yes, 0-No)
Small Mammal Type	2	(1-General, 2-Herbivore, 3-Insectivore) Default value should be 1
		(1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake Aquatic Plants based on Sediment or Surface	1	Default value should be 1 (1-Freshwater Sediment, 2-Surface Water)
Water Uptake	2	Default value should be 2
Fish based on Sediment or Seawater Uptake	2	(1-Marine Sediment, 2-Seawater) Default value should be 2
Marine Benthic Invertebrates based on Sediment or		(1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters Body weight	0.064	kg
Food intake rate	9.1E-02	kg wet-wt/day
Water intake rate ngestion of Soil	0.0E+00	L/day
Applicable pathway? Fraction diet that is dry solid	1 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	1 m alm
Ingestion rate Fraction from site	1.1E-03 1	kg dry-wt/day
Intake factor (IFing-sI) ngestion of Terrestrial Plants	1.7E-02	kg/kg-day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	1.0E+00 9.1E-02	kg wet-wt/day
Fraction from site Intake factor (IFing-tp)	1 1.4E+00	kalka day
ngestion of Terrestrial Invertebrates		kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ti)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-tm) Ingestion of Surface Water	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	L/day
Intake factor (IFing-sw) Ingestion of Freshwater Sediment	0.0E+00	L/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction diet that is dry solid Fraction of food intake rate	0.0E+00 0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Freshwater Aquatic Plants		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	0 0.0E+00	kg/kg-day
ngestion of Freshwater Benthic Invertebrates		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ai)	0.0E+00	kg/kg-day
ngestion of Freshwater Fish Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-fsh) ngestion of Seawater	0.0E+00	kg/kg-day
Applicable pathway? Ingestion rate	0 0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site	0	
Intake factor (IFing-sw) ngestion of Marine Sediment	0.0E+00	L/kg-day
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed) ngestion of Marine Plants	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-ap) Ingestion of Marine Benthic Invertebrates	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
Angestion of Marine Fish Applicable pathway?	0	
Fraction of food intake rate	0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
	0.0E+00	kg/kg-day



Intake Parameters fo	American Woodcock (OMOE	
Name of Study Area Entire Local Study Area or Project Alone	Example Site 1 Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
sediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Soil Moisture Content	0.25	(cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density Calculate TU based on	1.487	(g/cm <sup>3</sup> ) (1-top 5% most sensitive species, 2-Rainbov
Receptor Type	1	Trout, 3-Daphnia magna) (1-Bird, 2-Mammal)
s Receptor Sensitive Species for the Project?	0	(1-Yes, 0-No) (1-General, 2-Herbivore, 3-Insectivore)
Small Mammal Type	2	Default value should be 1
Fish based on Sediment or Surface Water Uptake	2	(1-Freshwater Sediment, 2-Surface Water) Default value should be 2
Benthic Invertebrates based on Sediment or Surface Water Uptake	1	(1-Freshwater Sediment, 2-Surface Water) Default value should be 1
Aquatic Plants based on Sediment or Surface		(1-Freshwater Sediment, 2-Surface Water)
Water Uptake	2	Default value should be 2 (1-Marine Sediment, 2-Seawater)
Fish based on Sediment or Seawater Uptake Marine Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters		
Body weight Food intake rate	0.198 1.5E-01	kg kg wet-wt/day
Water intake rate ngestion of Soil	0.0E+00	L/day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction diet that is dry solid Fraction of food intake rate	0.0E+00 0.0E+00	
Ingestion rate Fraction from site	2.5E-03 1	kg dry-wt/day
Intake factor (IFing-sI)	1.3E-02	kg/kg-day
ngestion of Terrestrial Plants Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-tp) ngestion of Terrestrial Invertebrates	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	1 1.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	1.5E-01 1	kg wet-wt/day
Intake factor (IFing-ti)	7.6E-01	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-tm) ngestion of Surface Water	0.0E+00	kg/kg-day
Applicable pathway? Ingestion rate	0 0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site Intake factor (IFing-sw)	0 0.0E+00	L/kg-day
Ingestion of Freshwater Sediment		
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg dry-wt/day
Fraction from site	0	
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00 0.0E+00	kg wet-wt/day
Ingestion rate Fraction from site	0	
Intake factor (IFing-ap) ngestion of Freshwater Benthic Invertebrates	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
ngestion of Freshwater Fish Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	, , , , , , , , , , , , , , , , , , ,
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-fsh) ngestion of Seawater	0.0E+00	kg/kg-day
Applicable pathway? Ingestion rate	0 0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site	0	
Intake factor (IFing-sw) ngestion of Marine Sediment	0.0E+00	L/kg-day
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	الم ماهد بينا بات.
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed) ngestion of Marine Plants	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	0 0.0E+00	kg/kg-day
ngestion of Marine Benthic Invertebrates Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ai) ngestion of Marine Fish	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	



Receptor Name Name of Study Area	Red-tailed Hawk (OMOE) Example Site 1	
Entire Local Study Area or Project Alone	Baseline Case	
Does the OMOE 511/09 regulation apply to this site?	No	(unidade)
Fraction of organic carbon in the soil Fraction organic carbon in freshwater (dry)	0.01	(unitless)
ediment	0.0706	(unitless, usual range is 0.003 to 0.03)
Fraction organic carbon in marine (dry) sediment	0.01	(unitless, usual range is 0.003 to 0.03)
Fraction lipid in freshwater invertebrates (wet veight)	0.017	(unitless, usual range is 0.012 to 0.025)
Fraction lipid in marine invertebrates (wet weight)	0.017	(unitless, usual range is 0.012 to 0.025)
Soil Moisture Content	0.25	(cm <sup>3</sup> /cm <sup>3</sup> ) or (ml/cm <sup>3</sup> )
Soil Bulk Density	<u>1.487</u> 1	(g/cm³) (1-top 5% most sensitive species, 2-Rainbov
Receptor Type	1	Trout, 3-Daphnia magna) (1-Bird, 2-Mammal)
s Receptor Sensitive Species for the Project?	0	(1-Yes, 0-No)
Small Mammal Type	2	(1-General, 2-Herbivore, 3-Insectivore) Default value should be 1
		(1-Freshwater Sediment, 2-Surface Water)
Fish based on Sediment or Surface Water Uptake Benthic Invertebrates based on Sediment or	2	Default value should be 2 (1-Freshwater Sediment, 2-Surface Water)
Surface Water Uptake Aquatic Plants based on Sediment or Surface	1	Default value should be 1 (1-Freshwater Sediment, 2-Surface Water)
Nater Uptake	2	Default value should be 2
Fish based on Sediment or Seawater Uptake	2	(1-Marine Sediment, 2-Seawater) Default value should be 2
Marine Benthic Invertebrates based on Sediment or		(1-Marine Sediment, 2-Seawater)
Seawater Uptake	1	Default value should be 1
General Parameters Body weight	1.13	kg
Food intake rate	9.9E-02	kg wet-wt/day
Water intake rate ngestion of Soil	0.0E+00	L/day
Applicable pathway?	1	(0 = no, 1 = yes)
Fraction diet that is dry solid Fraction of food intake rate	0.0E+00 0.0E+00	
Ingestion rate	1.8E-03 1	kg dry-wt/day
Intake factor (IFing-sI)	1.6E-03	kg/kg-day
ngestion of Terrestrial Plants Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0.02+00	
Intake factor (IFing-tp) ngestion of Terrestrial Invertebrates	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ti)	0 0.0E+00	kg/kg-day
Ingestion of Terrestrial Mammals/Birds		
Applicable pathway? Fraction of food intake rate	1 1.0E+00	(0 = no, 1 = yes)
Ingestion rate	9.9E-02	kg wet-wt/day
Fraction from site Intake factor (IFing-tm)	1 8.7E-02	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	L/day
Fraction from site Intake factor (IFing-sw)	0 0.0E+00	L/kg-day
Ingestion of Freshwater Sediment	0	
Applicable pathway? Fraction diet that is dry solid	0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg dry-wt/day
Fraction from site	0	
Intake factor (IFing-sed)	0.0E+00	kg/kg-day
ngestion of Freshwater Aquatic Plants Applicable pathway?	0	$(0 - n_0, 1 - y_{00})$
Fraction of food intake rate	0.0E+00	(0 = no, 1 = yes)
Ingestion rate Fraction from site	0.0E+00 0	kg wet-wt/day
Intake factor (IFing-ap)	0.0E+00	kg/kg-day
Ingestion of Freshwater Benthic Invertebrates           Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site	0	
Intake factor (IFing-ai) ngestion of Freshwater Fish	0.0E+00	kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-fsh)	0 0.0E+00	kg/kg-day
ngestion of Seawater		
Applicable pathway? Ingestion rate	0 0.0E+00	(0 = no, 1 = yes) L/day
Fraction from site Intake factor (IFing-sw)	0 0.0E+00	L/kg-day
ngestion of Marine Sediment		
Applicable pathway? Fraction diet that is dry solid	0 0.0E+00	(0 = no, 1 = yes)
Fraction of food intake rate	0.0E+00	ka day w#/day
Ingestion rate Fraction from site	0.0E+00 0	kg dry-wt/day
Intake factor (IFing-sed) ngestion of Marine Plants	0.0E+00	kg/kg-day
Applicable pathway?	0	(0 = no, 1 = yes)
Fraction of food intake rate Ingestion rate	0.0E+00 0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ap)	0 0.0E+00	
ngestion of Marine Benthic Invertebrates		kg/kg-day
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00	kg wet-wt/day
Fraction from site Intake factor (IFing-ai)	0 0.0E+00	kg/kg-day
ngestion of Marine Fish		
Applicable pathway? Fraction of food intake rate	0 0.0E+00	(0 = no, 1 = yes)
Ingestion rate	0.0E+00 0	kg wet-wt/day
r raotion nom alto	0.0E+00	kg/kg-day



													Short-taile	ed Shrew				
										Intake Factor (kg	g/kg-day): 1.2E-02	Intake Factor	(kg/kg-day):	Intake Factor (kg	g/kg-day): 6.0E-01	Intake Factor	(kg/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	1.3E+00	6.8E-01	5.2E-01			6.8E-01	5.2E-01			1.0E+00
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	8.8E+00	1.4E+00	1.6E-01			1.3E+00	1.5E-01			3.1E-01
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	1.5E+01	1.4E+01	9.1E-01			1.8E+01	1.2E+00			2.1E+00
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	8.0E+01	6.3E+01	7.8E-01			2.7E+01	3.4E-01			1.1E+00

													Meadow Vole					
				-				-		Intake Factor (kg/kg-day):	4.1E-04	Intake Factor (kg/kg-day)	: 1.1E-01	Intake Factor (kg/kg-	day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	1.3E+00	2.2E-02	1.7E-02	5.2E-01	4.0E-01					4.1E-01
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	8.8E+00	4.6E-02	5.2E-03	1.3E+00	1.5E-01					1.5E-01
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	1.5E+01	4.5E-01	3.0E-02	1.9E+00	1.2E-01					1.5E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	8.0E+01	2.1E+00	2.6E-02	2.4E+00	3.1E-02					5.6E-02

													Domestic Sheep	0				
			-							Intake Factor (kg/kg-day):	1.3E-03	Intake Factor (kg/kg-day)	2.0E-01	Intake Factor (kg/kg-	day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics				1	•													
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	1.3E+00	6.8E-02	5.2E-02	9.0E-01	6.9E-01					7.4E-01
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	8.8E+00	1.4E-01	1.6E-02	2.3E+00	2.6E-01					2.8E-01
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	8.9E-01	1.4E+00	1.5E+00	3.2E+00	3.6E+00					5.2E+00
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	8.0E+01	6.3E+00	7.9E-02	4.3E+00	5.3E-02					1.3E-01

													White-Taile	d Deer				
										Intake Factor (kg	g/kg-day): 7.4E-03	Intake Factor (kg	/kg-day): 1.1E-01	Intake Factor	(kg/kg-day):	Intake Factor	(kg/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	1.3E+00	4.0E-01	3.1E-01	4.9E-01	3.8E-01					6.9E-01
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	8.8E+00	8.2E-01	9.4E-02	1.2E+00	1.4E-01					2.4E-01
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	1.5E+01	8.0E+00	5.4E-01	1.8E+00	1.2E-01					6.5E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	8.0E+01	3.7E+01	4.6E-01	2.3E+00	2.9E-02					4.9E-01

													Red Fox					
		-	1		-			•		Intake Factor (kg/kg-day):	8.6E-04	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg-da	y): 9.6E-02	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Invertebrate Ingestion	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HC	Indestion	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	1.3E+00	4.7E-02	3.6E-02					1.1E-01	8.3E-02	1.2E-01
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	8.8E+00	9.6E-02	1.1E-02			<del></del>		3.1E-01	3.5E-02	4.6E-02
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	1.5E+01	9.3E-01	6.2E-02					5.8E+00	3.9E-01	4.5E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	8.0E+01	4.3E+00	5.4E-02					8.7E+00	1.1E-01	1.6E-01

													Redwinged Blackbir	d				
										Intake Factor (kg/kg-day):	1.7E-02	Intake Factor (kg/kg-day):	1.4E+00	Intake Factor (kg/kg	-day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	7.4E+00	9.3E-01	1.3E-01	6.5E+00	8.7E-01					1.0E+00
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	7.8E+00	1.9E+00	2.4E-01	1.6E+01	2.1E+00					2.3E+00
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	6.2E+01	1.9E+01	3.0E-01	2.3E+01	3.8E-01					6.8E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	1.1E+02	8.6E+01	8.0E-01	3.1E+01	2.9E-01					1.1E+00

													American Wood	cock				
										Intake Factor (kg/kg-day):	1.3E-02	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg-day)	: 7.6E-01	Intake Factor (kg/	/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Ingestion	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ		Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics				1														
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	7.4E+00	6.9E-01	9.3E-02			8.6E-01	1.2E-01			2.1E-01
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	7.8E+00	1.4E+00	1.8E-01			1.7E+00	2.2E-01			4.0E-01
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	6.2E+01	1.4E+01	2.2E-01			2.3E+01	3.7E-01			5.9E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	1.1E+02	6.4E+01	5.9E-01			3.5E+01	3.2E-01			9.2E-01

													Red-tailed H	awk				
		-	1	1	-					Intake Factor (kg/kg-day):	I.6E-03	Intake Factor (kg/kg-c	day):	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg-d	ay): 8.7E-02	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Invertebrate Ingestion	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Indestion	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	1.1E+02	4.5E+00	1.1E+00	1.1E+00		1	1	1	7.4E+00	8.7E-02	1.2E-02					9.9E-02	1.3E-02	2.5E-02
Cobalt	3.2E+02	1.2E+01	2.2E+00	3.2E+00		1	1	1	7.8E+00	1.8E-01	2.3E-02					2.8E-01	3.6E-02	5.9E-02
Copper	3.0E+03	1.6E+01	3.0E+01	6.1E+01		1	1	1	6.2E+01	1.7E+00	2.8E-02					5.3E+00	8.6E-02	1.1E-01
Nickel	2.3E+04	2.1E+01	4.6E+01	9.1E+01		1	1	1	1.1E+02	8.0E+00	7.5E-02					8.0E+00	7.5E-02	1.5E-01

													Short-taile	ed Shrew				
										Intake Factor (k	g/kg-day): 1.2E-02	Intake Factor	(kg/kg-day):	Intake Factor (kg	g/kg-day): 6.0E-01	Intake Factor	(kg/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	1.3E+00	1.2E-01	9.2E-02			6.3E+00	4.9E+00			5.0E+00
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	8.8E+00	1.9E-01	2.1E-02			1.4E+01	1.6E+00			1.6E+00
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	1.5E+01	1.7E+00	1.1E-01			6.6E+01	4.4E+00			4.5E+00
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	8.0E+01	6.6E+00	8.2E-02			1.6E+02	2.0E+00			2.1E+00

													Meadow Vole					
				-			-	-		Intake Factor (kg/kg-day):	4.1E-04	Intake Factor (kg/kg-day)	: 1.1E-01	Intake Factor (kg/kg-	day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	1.3E+00	3.9E-03	3.0E-03	2.3E-02	1.7E-02					2.0E-02
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	8.8E+00	6.2E-03	7.0E-04	9.8E-02	1.1E-02					1.2E-02
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	1.5E+01	5.6E-02	3.7E-03	4.3E-01	2.9E-02					3.2E-02
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	8.0E+01	2.2E-01	2.7E-03	8.2E-01	1.0E-02					1.3E-02

													Domestic Sheep	)				
										Intake Factor (kg/kg-day):	1.3E-03	Intake Factor (kg/kg-day)	2.0E-01	Intake Factor (kg/kg-o	day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	1.3E+00	1.2E-02	9.2E-03	4.0E-02	3.0E-02					4.0E-02
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	8.8E+00	1.9E-02	2.1E-03	1.7E-01	1.9E-02					2.2E-02
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	8.9E-01	1.7E-01	1.9E-01	7.5E-01	8.4E-01					1.0E+00
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	8.0E+01	6.6E-01	8.3E-03	1.4E+00	1.8E-02					2.6E-02

													White-Taile	d Deer				
										Intake Factor (kg	/kg-day): 7.4E-03	Intake Factor (kg	/kg-day): 1.1E-01	Intake Factor	(kg/kg-day):	Intake Factor	(kg/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	1.3E+00	7.0E-02	5.4E-02	2.2E-02	1.7E-02					7.1E-02
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	8.8E+00	1.1E-01	1.3E-02	9.3E-02	1.1E-02					2.3E-02
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	1.5E+01	1.0E+00	6.7E-02	4.1E-01	2.7E-02					9.4E-02
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	8.0E+01	3.9E+00	4.9E-02	7.8E-01	9.7E-03					5.8E-02

													Red Fo	x				
		-	-	-		-		-		Intake Factor (kg/kg-day):	8.6E-04	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg-	-day):	Intake Factor (kg/kg-	lay): 9.6E-02	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HC		Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	1.3E+00	8.2E-03	6.3E-03					1.9E-02	1.5E-02	2.1E-02
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	8.8E+00	1.3E-02	1.5E-03					4.1E-02	4.7E-03	6.1E-03
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	1.5E+01	1.2E-01	7.8E-03					7.2E-01	4.8E-02	5.6E-02
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	8.0E+01	4.5E-01	5.7E-03					9.2E-01	1.1E-02	1.7E-02

													Redwinged Blackbirg	1				
		-	1			-	-	-		Intake Factor (kg/kg-day):	1.7E-02	Intake Factor (kg/kg-day	: 1.4E+00	Intake Factor (kg/kg-	day):	Intake Factor (kg/	kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	7.4E+00	1.6E-01	2.2E-02	2.8E-01	3.8E-02					6.0E-02
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	7.8E+00	2.6E-01	3.3E-02	1.2E+00	1.6E-01					1.9E-01
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	6.2E+01	2.3E+00	3.7E-02	5.4E+00	8.7E-02					1.2E-01
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	1.1E+02	9.0E+00	8.4E-02	1.0E+01	9.6E-02					1.8E-01

													American Woodc	ock				
					-			-		Intake Factor (kg/kg-day): '	.3E-02	Intake Factor (kg/kg-c	ay):	Intake Factor (kg/kg-day	): 7.6E-01	Intake Factor (kg	/kg-day):	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ	Average Daily Dose from Plant Ingestion (mg/kg-day)	Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics				<u> </u>														
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	7.4E+00	1.2E-01	1.6E-02			8.0E+00	1.1E+00			1.1E+00
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	7.8E+00	1.9E-01	2.4E-02			1.7E+01	2.2E+00			2.2E+00
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	6.2E+01	1.7E+00	2.8E-02			8.3E+01	1.3E+00			1.4E+00
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	1.1E+02	6.7E+00	6.2E-02			2.0E+02	1.9E+00			1.9E+00

													Red-tailed I	ławk				
r			1			-	1			Intake Factor (kg/kg-day):	1.6E-03	Intake Factor (kg/kg-	day):	Intake Factor (kg/kg·	-day):	Intake Factor (kg/kg	-day): 8.7E-02	
Constituent	Surface Soil Conc. (mg/kg dw)	Terrestrial Plant Conc. (mg/kg ww)	Terrestrial Invertebrate Conc. (mg/kg ww)	Terrestrial Mammals Conc. (mg/kg ww)	Soil Ingestion Absorption Factor	Plant Ingestion Absorption Factor	Terrestrial Invertebrate Ingestion Absorption Factor	Terrestrial Mammals Ingestion Absorption Factor	Reference Toxicity Dose (mg/kg-day)	Average Daily Dose from Soil Ingestion (mg/kg-day)	Surface Soil Ingestion HQ		Terrestrial Plant Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Invertebrate Ingestion HQ	Average Daily Dose (mg/kg-day)	Terrestrial Mammal Ingestion HQ	Total Hazard Quotient
Inorganics																		
Arsenic	2.0E+01	2.0E-01	1.1E+01	2.0E-01		1	1	1	7.4E+00	1.5E-02	2.1E-03					1.7E-02	2.4E-03	4.4E-03
Cobalt	4.3E+01	8.6E-01	2.3E+01	4.3E-01		1	1	1	7.8E+00	2.4E-02	3.1E-03					3.8E-02	4.8E-03	7.9E-03
Copper	3.8E+02	3.8E+00	1.1E+02	7.6E+00		1	1	1	6.2E+01	2.2E-01	3.5E-03					6.6E-01	1.1E-02	1.4E-02
Nickel	2.4E+03	7.2E+00	2.6E+02	9.6E+00		1	1	1	1.1E+02	8.4E-01	7.9E-03					8.4E-01	7.8E-03	1.6E-02

Port Colborne Community-Based Risk Assessment 2014 Update Report Chapter 5 - Ecological Risk Assessment - Crops



Prepared for:

Vale Canada Limited

Prepared by:

#### Stantec Consulting Ltd.

70 Southgate Dr., Suite 1 Guelph, ON N1G 4P5

File No. 122210662 September 12, 2014

#### **Sign-off Sheet**

This document entitled Port Colborne Community-Based Risk Assessment 2014 Update Report Chapter 5 - Ecological Risk Assessment - Crops was prepared by Stantec Consulting Ltd. for Vale Canada Limited. The material in it reflects Stantec's best judgment in light of the information available to it at the time of preparation. Any use which a third party makes of this report, or any reliance on or decisions made based on it, are the responsibilities of such third parties. Stantec Consulting Ltd. accepts no responsibility for damages, if any, suffered by any third party as a result of decisions made or actions based on this report.

Prepared by (signature)

Wai Ma

Prepared by

(signature)

Tereza Dan

Reviewed by

**Gladys Stephenson** 



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### 5.0 Crops Assessment

#### 5.1 BACKGROUND

Vale Canada Limited (Vale - formerly Inco) commissioned a Community Based Risk Assessment (CBRA) in 2000. The risk assessment component that addressed risk to agricultural crops included field and greenhouse studies conducted in 2000 and 2001 and were completed by Jacques Whitford Ltd. in 2004 (Jacques Whitford, 2004a). The Crops risk assessment was intended to determine "the concentrations of historically deposited CoC in Port Colborne soil that present an unacceptable risk (phytotoxicity) to agricultural crops". The design approach for the Ecological Risk Assessment - Crop Studies (i.e. the Crops risk assessment) is presented in Figure 5-0.

An Addendum Report was released in 2006 (Jacques Whitford, 2006)<sup>1</sup> to address issues raised and concerns expressed by the external reviewers, the public, and the Consultant to the PLC. In 2008, after the release of the Addendum Report (Jacques Whitford, 2006), the Consultant to the PLC (Watters Environmental Group Inc. (WEGI)), on behalf of the Public Liaison Committee and City of Port Colborne, provided a peer review of the Crops Assessment studies and reports (WEGI, 2008)<sup>2</sup> raising additional concerns and issues primarily related to the uncertainties associated with the process and data used to derive the site-specific threshold limits (SSTLs) for nickel (Ni) and the degree to which the SSTLs would be protective of crop species grown in the soils of Port Colborne. These concerns and issues were addressed by Jacques Whitford Ltd. in 2009 (Jacques Whitford, 2009) with detailed responses provided regarding uncertainties and other issues raised; a sensitivity analysis summarized Jacques Whitford's resolution of these uncertainties. Jacques Whitford Ltd. became Stantec Consulting Ltd. (Stantec) in 2010.

Based on the multiple rounds of review and response, there were areas of disagreement between reviewers and the authors of the report. To this discussion, the MOE review is added, and this chapter of the 2014 Update Report is primarily a response to the MOE's review comments. It is hoped that the discussion below provides the necessary clarity to finalize the Crops risk assessment fourteen years after its initiation.

For background, the details of the Crops risk assessment, the review documents, and addendum reports are found in full in Appendices 1J, 1K, and 1L of this Port Colborne Community-Based Risk Assessment 2014 Update Report.

<sup>&</sup>lt;sup>2</sup> Watters Environmental Group Inc. (WEGI). 2008. Independent consultant peer review report for the community based risk assessment (CBRA): Ecological risk assessment on agricultural crops in Port Colborne, Ontario. Report prepared for Public liaison committee & City of Port Colborne.

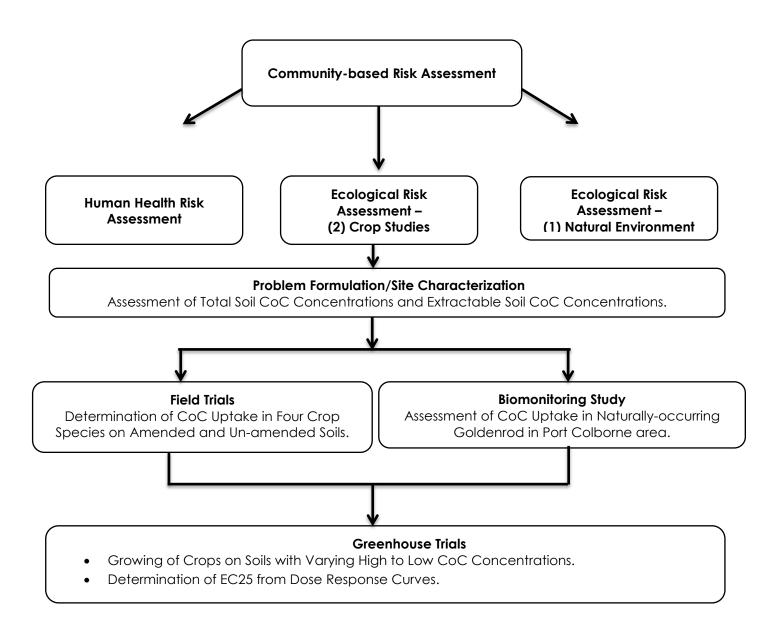


<sup>&</sup>lt;sup>1</sup> Jacques Whitford Ltd. 2006. Port Colborne Community Based Risk Assessment: Ecological risk assessment – Crops. Addendum report prepared September, 2006 for Inco Ltd.

#### 5.2 DESIGN APPROACH FOR THE ECOLOGICAL RISK ASSESSMENT – CROPS

Figure 5-0 presents the design approach for the Crops Risk Assessment graphically. The Problem Formulation is discussed in detail in (Jacques Whitford, 2004a).

Figure 5-0 Design Approach to Ecological Risk Assessment - Crop Studies





The Crops Risk Assessment evaluated the distribution of CoCs within the main agricultural soil types present in Port Colborne, (Heavy Clay (Welland soil series), Shallow Till Clay (Alluvial soils series), Organic Muck (Quarry soil series), and Sand (Beach – Scarp soil series)) (Jacques Whitford, 2004). The potential bioavailability of the CoCs for uptake by plants was assessed by using a series of leaching solutions [water, strontium nitrate, DTPA (diethylenetriamine pentaacetic acid), and acid ammonium oxalate)] (Jacques Whitford, 2004a). These studies showed that, while the strong extractants DTPA and ammonium oxalate are certainly able to extract significant quantities of Ni from soil, the gentler extractants likely reflect the conditions within the soil more accurately, with very low extraction of Ni achieved by water and strontium nitrate. Field and greenhouse studies were undertaken in 2000 and 2001 to evaluate the uptake of CoCs and any potential resulting impairment of growth. To provide linkage between the Crops and Natural Environment Risk Assessments, a biomonitoring study of CoCs in goldenrod plants was completed in 2001. These studies are presented in detail in Jacques Whitford (2004a).

#### 5.3 CROPS STUDIES

#### 5.3.1 Year 2000 Studies

The field work for the Crops Risk Assessment began in 2000, with a soil sampling program to identify the types of soils present in the agricultural areas of Port Colborne, the CoC concentrations in these soils, and the characteristics of these soils, including pH, cation exchange capacity (CEC), organic content, and nickel speciation.<sup>3,4</sup> Preliminary field and greenhouse trials were also conducted in 2000. The field trials were undertaken on organic and clay soils. For the preliminary greenhouse trials, organic, clay, and sand soils were selected. Corn, soybean and oat were the crop species studied in year 2000.

Greenhouse and field trials carried out in Port Colborne by other groups (e.g., Kukier and Chaney, 2000), identified dolomitic limestone (a mixture of calcium and magnesium carbonates) as an appropriate soil amendment to mitigate phytotoxicity of CoCs. The use of limestone is a common agricultural practice that increases the low soil pH values that develop over time from agricultural fertilizer use.

Due to the low solubility of limestone, there is a lag phase between application and measurable effect in the field, which ranges from months to years, depending on limestone particle size, among other factors. For this reason, soils used in the Greenhouse Trials (with the exception of sand) were amended with reagent grade, amorphous calcium carbonate (CaCO<sub>3</sub>) and magnesium carbonate (MgCO<sub>3</sub>) at the same ratio as found in dolomitic limestone; this is the fastest-reacting of the various forms available.

The year 2000 studies evaluated the potential for limestone addition to reduce uptake and toxicity of CoCs in agricultural settings at Port Colborne.

<sup>&</sup>lt;sup>4</sup> Vol. IV of Jacques Whitford (2004). Soils Characterization Report. Found in Appendix 1J of this report.



<sup>&</sup>lt;sup>3</sup> Vol. I Part 2 of Jacques Whitford (2004). Soil Selection and Characterization for the Year 2000/2001 Greenhouse, Field Phytotoxicity Trials and Biomonitoring Studies. Found in Appendix 1J of this report.

The year 2000 field and greenhouse studies were preliminary in nature. With hindsight, the study design in year 2000 was not optimal. The year 2000 data were not relied-upon in the final Crops Risk Assessment report, as the year 2001 studies (which developed out of the year 2000 experience) were more robust. Nevertheless, several important findings came from the year 2000 field and greenhouse studies.

Greenhouse and field trials in 2000 with three agronomic plant species (corn (Zea mays) and soybean (Glycine max), and oat (Avena sativa)) and with soils (clay, organic, and sand) from the Port Colborne study area amended with calcium carbonate and fertilizer were conducted to evaluate the dose-response relationship between Ni-soil concentrations and phytotoxicity. The results indicated that: 1) the dose-response relationship can be used to assess phytotoxic effects on agricultural crops using a range of increasing CoC exposure concentrations in un-amended natural soils from the Port Colborne area; 2) crops grown in site soils from the Port Colborne area with Ni concentrations higher than the then current MOE generic effects-based guideline values exhibited little phytotoxicity; 3) based on the concentrations of individual CoCs present in plant tissues, phytotoxic effects in Port Colborne soils were attributed primarily to nickel as opposed to copper or cobalt; 4) oat is sensitive to Ni and a good candidate (relative to the other species examined) for subsequent studies; and, 5) amendment of clay soil with calcium and magnesium carbonates resulted in increased crop yields (biomass). Data generated from the 2000 Greenhouse Trials proved unsuitable for derivation of phytotoxicity thresholds due to confounding soil variables (e.g., soil pH and others), analytical difficulties and (in some cases) an inappropriate range in soil CoC exposure concentrations.

The result of the field trials conducted in 2000 were equivocal; however, they generally supported the tenet that crops could successfully be grown in soils greatly exceeding the MOE generic soil criterion for Ni. The field crop trials also clearly showed that increasing soil pH with the addition of soil amendments most often resulted in a significant reduction in tissue Ni and Cu concentrations with all crop species but was not consistent among soil types or among amendment levels tested for all crop species.

#### 5.3.2 Year 2001 Studies

As a result of year 2000 studies, in 2001, a distinction was made between the lacustrine-derived Heavy Clay soils (containing >40% clay) and other clayey soils of till origin containing <40% clay (which were arbitrarily categorized together under the term: "Till Clay" soils). Consequently four soil types were used in the Year 2001 Greenhouse Trials: Organic, Sand, Till Clay and Heavy Clay. Following from the preliminary Year 2000 Field Trial phytotoxicity results, the Year 2001 trials focused on soils impacted with greater than 500 mg Ni/kg. Clay Loam soils were not considered in the Year 2001 Trials because only 8% of the Port Colborne land area which exceeds 500 mg Ni/kg contains Clay Loam soil.

In the 2000 Preliminary Field Trials, no phytotoxicity symptoms were observed on impacted Organic soils and moderately impacted Clay soils; therefore no further trials were conducted on



these sites in 2001. In 2001, a second field test site (e.g., Clay Site 3) located in an area of Heavy (Welland Series) Clay soils was included in the study; the Clay 3 site was impacted with soil nickel concentrations intermediate to those of the Clay 1 and Clay 2 sites.

For the 2001 Greenhouse Studies, soil blending was introduced to reduce heterogeneity of soil properties (other than CoC concentrations) that influenced plant growth. The crop species included radish and oat and the Greenhouse Trials involved exposing these species to different concentrations of CoCs formulated by blending four soil types (Organic, Sand, Welland clay and Till clay) collected from the Port Colborne area. Focus was placed on the calculation of EC25 values based upon soil and tissue Ni levels; metal levels were co-correlated. The calculated values differed among soil types (Sand = 1350 mg Ni/kg; Organic > 2400 mg Ni/kg (3490 mg Ni/kg from meta-analysis); Welland Clay = 1880 mg Ni/kg; Till Clay = 1950 mg Ni/kg), but all greatly exceeded the MOE's generic guideline of 200 mg/kg at the time the work was completed in 2004.

In addition to Greenhouse and Field Trials, a Biomonitoring Study was carried out during Year 2001<sup>5</sup>. The Biomonitoring Study involved assessment of CoC impacts at various non-agricultural field locations containing Sand soils, Organic soils, and Heavy Clay soils. Soils and plants from these locations were collected to assess CoC impacts on naturally-occurring vegetation. Results from the Biomonitoring Study indicated that, for native plant species growing naturally in contaminated areas, the relationship between plant tissue concentrations of CoCs and soil concentrations of CoCs was comparable to that for crop species grown in the greenhouse which greatly reduced the uncertainty regarding the legitimacy of the toxicity thresholds as calculated.

#### 5.4 MOE REVIEW

As discussed in Chapter 1, review comments, issues of concern, and requests for clarification from the MOE were received by Vale in a letter dated May 2011. The complete comments are provided in **Appendix 1A**. The comments were divided into two types: 1) Global Comments (Table 5-1), which were not specific to any one section; and 2) Specific Comments, which were identified by volume, section, and page number (Comments specific to the Crops Risk Assessment are provided in Appendix 5A). Some of the comments had been addressed previously in the Addendum Reports (Jacques Whitford Ltd., 2006) based on preliminary discussions with the MOE. Responses were presented to the MOE on August 25, 2012 and the remaining outstanding issues that could not be resolved by consensus required additional analyses of the existing data to address unresolved/outstanding issues.

Vale and Stantec developed and implemented a strategy to address and resolve these outstanding issues. It is important to recognize the limitations inherent in conducting a review of the studies more than a decade after they were undertaken. This Update Report, prepared late in 2013 and early 2014, attempts to resolve technical issues from greenhouse and field studies that were completed 12 or 13 years earlier. In addition, the MOE review comments

<sup>&</sup>lt;sup>5</sup> Vol. I Part 5 of Jacques Whitford (2004). Biomonitoring Study. Found in Appendix 1J of this report.



recommended that earlier field studies, conducted a further 20 years before the CBRA studies, (when Ni emissions were still occurring from the Port Colborne refinery) be re-considered for inclusion in this 2014 Update Report.

Table 5-1Global Issues of Concern Raised by MOE after reviewing the CBRA for Port Colborne (MOE, 2011)			
Issue No.	MOE Comment		
Calculation of assessment endpoints from the 2000 Greenhouse Study data	Assessment endpoints, such as EC <sub>25</sub> or PNEC values, were not calculated from the 2000 Greenhouse Study data. As stated in the report "analysis of the [2000 Study] data revealed significant limitations in experimental design and execution that prevented development of dose-response relationships, and calculation of toxicity thresholds." However, data from the 2000 Greenhouse study were presented and limited statistical analyses were conducted, including the use of some of the data in the meta-analysis of oats. Therefore, EC <sub>25</sub> and PNEC values should be calculated from the available 2000 Greenhouse data and included in the report.		
Were the objectives of the Crop Studies met?	Valuable information was gained by these studies, but there are many studies in the scientific literature on the effects of nickel in soil on the growth of plants and on the effects of liming in ameliorating these effects (refer to Volume 1 Part 3 Page 3-3). Several of these referenced studies were conducted on Port Colborne area soils (Freedman and Hutchinson (1980), Temple and Bisessar (1981), (Bisessar (1982), Frank et. al., (1982), Bisessar et. al. (1983), Bisessar (1989), McIlveen and Negusanti (1994), Kukier and Chaney (2000)). It is recommended that the determination of soil quality criteria for soils in the Port Colborne area not be based solely on the results of the CBRA Crop Studies but include the results from all crop studies in the scientific literature that were conducted in the Port Colborne area where soil nickel concentrations are reported.		
Use of soils from the Port Colborne area rather than standard soils spiked with metal salts	Using Port Colborne area soils and crops typically grown in this area was an appropriate approach to determine the concentration of historically deposited CoC in soil that present an unacceptable risk to crops grown in the Port Colborne area. It is understood that the soils in the Port Colborne area are variable in terms of physico-chemical parameters, such as pH, texture, organic matter content, nutrient status, cation exchange capacity and concentrations of chemicals of concern. Also, it is understood that when conducting crop studies with these soils that it is not practical to match soil exactly or to find soils that		



Table 5-1Global Issues of Concern Raised by MOE after reviewing the CBRA for Port Colborne (MOE, 2011)			
Issue No.	MOE Comment		
	are identical in all ways except CoC concentration. Finally, it is acknowledged that it would have been easier to have spiked a standard soil with metal salts to create a range of soil CoC treatments but the use of spiked soils would not have met the study's objectives.		
Appropriateness of the soils used in the studies.	It is recognized that the researchers took considerable effort to assemble information on Port Colborne soils from several sources and to properly analyze the soils before starting the studies. The soils selected were representative of the major soil groupings of the Port Colborne area. However, very limited data was available from the 2000 Field Study and the 2001 Field Study plots were restricted to heavy clay soil. Many of the soils used in the 2001 Greenhouse Study, upon which the EC <sub>25</sub> and PNEC values are based, were not from agricultural land, as can be seen in Table 1. The use of woodlot or railway right-of-way soil does not negate the value of this study but the use of agricultural soils would have been preferable.		
Use of blended soils in the 2001 Greenhouse Study	The mixing of a control soil with a highly contaminated soil in various ratios in order to create a range of CoC concentrations in the study soils is acceptable. It is understood that the blended soil will not represent a particular soil that can be found in the field and it is acknowledged that drying, sieving, and mixing of the soil will alter the soil structure and severely affect the microfauna in the soil. However, there are limited options when conducting this type of research study. The alternative of selecting soils with different CoC concentrations was attempted in 2000 but the problems of confounding factors made the interpretation of the data problematic. This latter approach can be successful but it would have required more soils and much higher replication.		
Statistical analysis of the data	Appropriate statistical tests were used to analyse the data in the report, although there are a few points that require clarification, as outlined in the Specific Comments section.		
Assessment endpoints	Although it is recognized that various assessment endpoints could have been used (NOEC, LOEC, PNEC, ECx), the EC25 and PNEC assessment		



Table 5-1Global Issues of Concern Raised by MOE after reviewing the CBRA for Port Colborne (MOE, 2011)		
Issue No.	MOE Comment	
	endpoint are acceptable to the Ministry.	
Structure of the Report	The Crop Studies component of the Port Colborne CBRA consists of six main studies, as given in Comment 2. In the main report, these studies are grouped according to study type (Greenhouse versus Field Studies), rather than in chronological order. This makes it difficult to follow the experimental approach, especially since the 2001 studies were designed in response to the 2000 results. It would be much easier to follow the studies in chronological order, which would follow the thought processes of the researchers. If a summary document is created, it is recommended that the chronological approach to presenting the studies be used.	

The focus of this chapter of the 2014 Update Report is the resolution of the outstanding issues related to the Crops Risk Assessment that required additional evaluation following from the MOE review. The aim is to determine whether the SSTLs that were derived for four types of site soils in the original Crops Risk Assessment<sup>6</sup> are scientifically defensible and protective of the crop species likely to be grown in the region, or whether these SSTLs should be revised in light of the resolution of these outstanding technical issues.

#### 5.4.1 Strategy for Resolving Issues and Concerns identified in the MOE review

The eight "global" issues raised or commented upon by MOE (Appendix 5A) are summarized in Table 5-1. Specific comments from MOE are also summarized in Appendix 5A, along with the corresponding specific responses. These concerns were discussed by Vale, Stantec and the MOE. A consensus was reached that the information and data for the mineral soils were sufficient to support the derived SSTLs for Ni; however, the MOE remained concerned with the Ni SSTL for the organic muck (highly organic) soil. Vale and Stantec agreed to re-evaluate all of the studies that had been conducted on soils from Port Colborne, including published scientific literature and unpublished reports provided by the MOE, as well as the Jacques Whitford Studies conducted in 2000 and 2001, with the purpose of extracting data (e.g., EC25) that could contribute, in a scientifically reasonable way, to the derivation of SSTLs. This re-evaluation would:

1. Develop a scoring system that would enable the relevant data from each study to be assigned a score (based on professional judgment).

<sup>&</sup>lt;sup>6</sup> Jacques Whitford Ltd. 2004. Port Colborne CBRA – Ecological Risk Assessment: Crop Studies Studies Volume 1 – Main Report, Binder 1 of 3, pp iv (Executive Summary). Found in Appendix 1J of this report.



- 2. Develop acceptance criteria for the scores;
- 3. Implement a process that could use these weighted values (scores) for derivation of a SSTL for Ni in organic muck soil; and,
- 4. Consider any new information relevant to the crops assessment developed after the completion of the Crops Risk Assessment in 2004.

The re-evaluation considered the incorporation of agricultural phytotoxicity data from the past forty years into the development of an SSTL for nickel in organic muck soil. The original CBRA Crops Risk Assessment (Jacques Whitford, 2004a) had not incorporated some of the earlier data. Data as recent as 2012 were also considered (Cioccio, 2009).

#### 5.5 THE HISTORICAL CONTEXT OF PHYTOTOXICITY IN PORT COLBORNE

The MOE conducted several agricultural phytotoxicity investigations in Port Colborne since the 1950s. A large amount of phytotoxicity information is present within those studies. The MOE's review of the Crops Risk Assessment (Appendix 5A) and MOE personnel themselves have been persistent in ensuring that the valuable information from the earlier studies was not lost to the CBRA. This re-evaluation of the literature relevant to Port Colborne is intended to demonstrate that all relevant data from studies were considered in the derivation of the SSTLs. The review considered earlier studies (from the 1950s to the early 1990s) right up to the time of the preliminary Greenhouse and Field Studies in the year 2000. These studies spanned the period during which the Refinery went from operating at its highest output with no emission controls, to the period when the Refinery stopped producing Ni (1984) and onward to 2001.

The soil contamination at Port Colborne was a result of airborne refinery emissions. While the refinery was in operation, Ni was being added to the soil incrementally due to the emissions from the main stack, the secondary stacks, and from fugitive sources such as roof vents. During the period of active emissions, toxicity to vegetation (phytotoxicity) would have occurred as a result of foliar deposition of metal-enriched dustfall as well as from the uptake of Ni and the other CoCs from the soil. Once emissions from the refinery ceased, metals in the soil became the primary source of plant exposure. This is the main distinction between phytotoxicological studies that took place while refinery emissions were occurring and those that have taken place since the refinery ceased emitting Ni. In 1958, the Air Pollution Control Branch studied stack solids and found them to contain considerable proportions of water soluble Ni and Cu (Air Pollution Control Branch, 1959). Studies were initiated during this time that saw the application of anode furnace dust and nickel chloride solutions to barley and oat crops (Air Pollution Control Branch, 1959). The studies were not well-documented, but demonstrated that foliar application of anode furnace dust could cause phytoxicity and accumulation of Ni in oats.

In Port Colborne during six decades of operation of the Ni refinery, reports of phytotoxicity were common on farms near the refinery. Phytotoxicity would have included a foliar uptake component and a root uptake component. The importance of the foliar component of phytotoxicity in Port Colborne is evidenced from several MOE studies. In 1981, the MOE concluded that 70% of the Ni present in vegetation (silver maple leaves) was from active

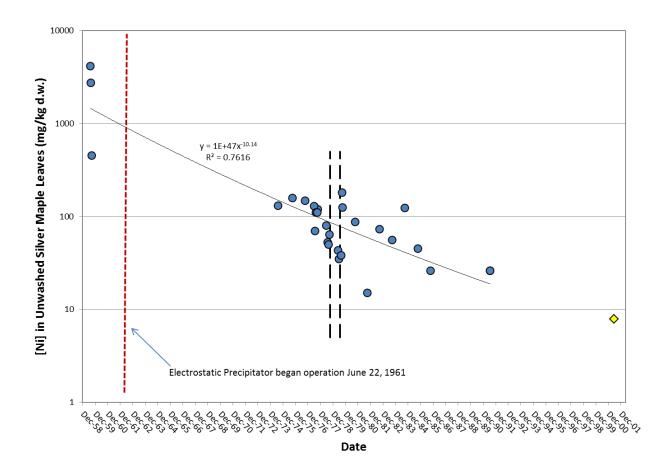


emissions (MOE, 1981). Agricultural phytotoxicity complaints occurred beyond the refinery closure, and in 1991 phytotoxicity investigations were conducted by the MOE on the Davison property (MOE, 1991). A review of the historical phytotoxicity data from Port Colborne must consider the temporal aspects associated with the refinery metal emissions, their subsequent deposition onto forest, agricultural, and field ecosystems, and their ultimate disposition in terms of ageing and weathering phenomena of the metal contamination in the soils.

The Ministry of the Environment and Ministry of Agriculture and Food conducted many phytotoxicity studies during the period between1958 and 2000. Silver maple trees were studied across much of this period, and trends in metal contamination of these trees provided valuable information. Differences between metal concentrations in leaves on opposite sides of individual trees provided one indication that active emissions from the refinery was the primary source of Ni in the maple leaves (and, therefore, also agricultural plants) during the period of active emission. Differences were observed between Ni concentrations in leaves on the sides of trees facing the refinery and those facing away from the refinery, particularly for trees nearest to the refinery during the earlier periods of study. In periods of refinery shut-down due to strikes or for general maintenance, Ni concentrations in leaves were found to decrease. In Figure 5-1, Ni in unwashed silver maple leaves at the MOE's "Station 11" is plotted over time from 1958 to 1991<sup>7</sup>. In addition, Ni in sugar maple leaves in 2001 (from the CBRA; Jacques Whitford, 2004a) is also indicated in the figure.

<sup>&</sup>lt;sup>7</sup> Station 11 was station 2 in 1972 and 1973. From 1974 to 1991, Station 11 was on the Snider farm near Snider Road. Station 11 did not exist in 1958, but samples were taken from the Snider farm that year. The station moved up to 300 m closer to the refinery as of 1985. MOE (1975; 1976; 1977; 1981; 1989; 1994).





#### Figure 5-1 Nickel in unwashed Silver Maple leaves (mg/kg dry wt.) at MOE's Station 11. Sugar Maple was sampled for the CBRA in 2001. The effect of the refinery shutdown on the Ni content of leaves is evident.

There are several features of interest on this figure. First, the emissions decreased substantially between 1958 and 1974, with the commissioning of an electrostatic precipitator to remove particulates from stack gases in 1961.

The Ni in unwashed silver maple leaves continued to drop after the Ni refinery ceased operations in 1984. In 2001, the Ni concentration in sugar maple leaves in areas east of the Vale property (samples L-H-2 to L-H-5 from Volume V Tab 41 of the ERA report (Jacques Whitford, 2004b) ranged between 3 and 12.4 mg/kg, with an arithmetic average of 7 mg/kg (dry weight). The trend observed for Ni in maple leaves over time points to the importance of active emissions to Ni accumulation and toxicity in silver maple trees. The same trend would apply to agricultural plants.



Deposition also varied within years (Figure 5-1). The effect of a strike (between Sept. 1978 and June 1979) which caused production to cease at the refinery resulted in reduced Ni in maple leaves over that period. An additional reduction in Ni in maple leaves at MOE Station 11 is seen in September 1981 following a summer shut-down at the refinery (Figure 5-1).

In Figure 5-2, trends in Ni content in unwashed silver maple foliage can be seen from 1975 to 1991. For each year, data for leaves from the sides of trees facing the refinery and for leaves on the opposite sides of the tree facing away from the refinery are plotted. Generally, the Ni concentrations were highest on the sides of trees facing the refinery. The magnitude of the differences decreased as the distance from the refinery increased (i.e., as soil Ni concentration decreased on the x-axis). In 1991, the last year for which data were available from the MOE, the Ni concentrations in leaves had been reduced close to background levels in the absence of active emissions. Although slight, further reductions were evident from 1991 to 2000 (Figure 5-1).

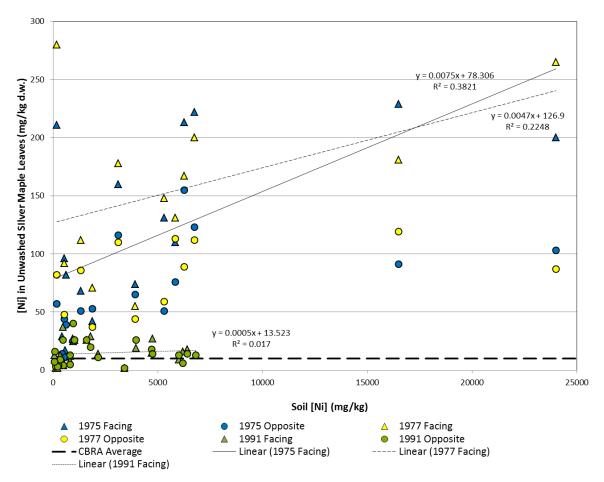
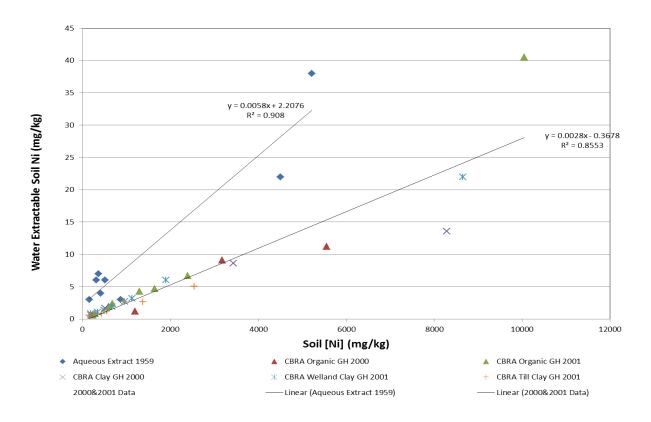


Figure 5-2 Nickel in unwashed Silver Maple leaves from the sides of trees facing the refinery and from the opposite sides.





#### Figure 5-3 Water-extractable Ni in Port Colborne soils measured in 1959, 2000, and 2001.

Ni in the Ni-contaminated Port Colborne soils is largely present as oxidic Ni particles (NiO, bunsenite) containing metallic Ni cores (see Chapter 2 of this report). In Port Colborne soils, Ni oxide is also associated with two types of slag, a ferrite slag and an alkaline slag. Finally, Ni is present in the form of the mineral nickel nontronite (often called Ni clay) on the surface of NiO particles. The presence of the Ni nontronite is evidence for the slow weathering of Ni to essentially a very inert "lateritic" Ni species in the Port Colborne area. Figure 5-3 presents aqueous soil leachate data collected in 1959 and again in 2000. For perspective, in 1959, the refinery was in its peak production period, whereas in year 2000, the refinery had been closed for sixteen years during which the Ni in the Port Colborne soils had weathered. Therefore, in 1959, emissions containing 10-20% soluble Ni (Air Pollution Control Branch, 1959) were being added to the soil. This is reflected by the steeper curve of the water-leached Ni in soil (Figure 5-3). In contrast, in 2000, with deposition having ceased 16 years earlier, Ni in soil was less leachable. It is highly probable that as Ni in soil weathers, the bioavailability of this Ni decreases over time, so some caution is required when comparing the toxicity of Ni in Port Colborne soils from the period before 1984 with the toxicity of the Ni in soil today.

These three figures provide context for the review of the phytotoxicity literature from Port Colborne. It is important to distinguish phytotoxicity that occurred during the period of active emissions from the refinery with those existing today, thirty years after the Ni emissions ceased. This in no way negates the fact that there is historical soil contamination of agricultural lands



near the refinery, but merely considers that the nature of the Ni contamination is slowly changing as it ages and weathers to a less bioavailable Ni species. As a result, the thresholds for phytotoxicity appear to be higher than they once were. The CBRA Crops Risk Assessment assessed risk associated with current conditions.

#### 5.5.1 **Re-analysis of Earlier Phytotoxicity Studies in Port Colborne**

In the original CBRA Crops Report (Jacques Whitford, 2004a), the earlier studies from the literature, including published reports from the 1980s, were not relied-upon in the risk assessment because they were unsuitable for deriving EC25s due to experimental design constraints. In addition, the earlier (1970s-1980s) Port Colborne phytotoxicity studies took place when atmospheric deposition was still occurring, and foliar exposure would have been an important factor. Nevertheless, in its review of the Crops Risk Assessment, the MOE identified that the methodology by which the various papers were rejected was not transparent. In order to address MOE comments on the original CBRA Crops Risk Assessment, this earlier literature has been re-evaluated.

All studies provided or recommended by the MOE were evaluated, with the intent of extracting toxicological data that could be used to derive an SSTL for Ni in organic muck soil. However, the majority of the studies were not originally designed as exposure (dose) -concentration-response experiments to determine an effect concentration for Ni in soil based on crop growth or yield reduction. Rather, these studies were designed to establish the effect and magnitude of the effect on the yields. Control treatments with un-impacted soil were rarely included in the experimental designs, so effect levels (e.g., EC25s) could not be determined without including control data from sources outside of the original studies. In such cases, response values (yield or weight of the plant in question) were estimated using surrogate data. Further confounding this is the fact that the metals in the soils were often not uniformly distributed within fields. Nevertheless, it was possible to estimate "effects-based concentrations" from several independent studies. A total of 56 crop endpoints were evaluated and eighteen (18) of these endpoints were eliminated from further consideration (see subsection 1.6; Appendix 5B). The remaining 32 endpoints were used in a meta-analysis of the data to derive a site-specific threshold limit that would be protective of agronomic crop species grown in the on-site organic muck soils.

Briefly, the process involved the following steps:

- 1. Deriving effects-based endpoints for phytotoxicity (e.g., actual or predicted emergence, growth, yield or biomass) from eligible studies;
- 2. Formulating a key comprising the scoring criteria to objectively assign a numerical value (score) to each endpoint based on the scientific quality of its source study;
- 3. Endpoints above a certain score (e.g., greater than 55%) were included for calculation of an overall EC25 for organic soil;
- 4. The scores were used as "weights" to weight the value of each EC25; and,



5. Calculate the SSTL as the weighted average of the individual EC25s from all studies.

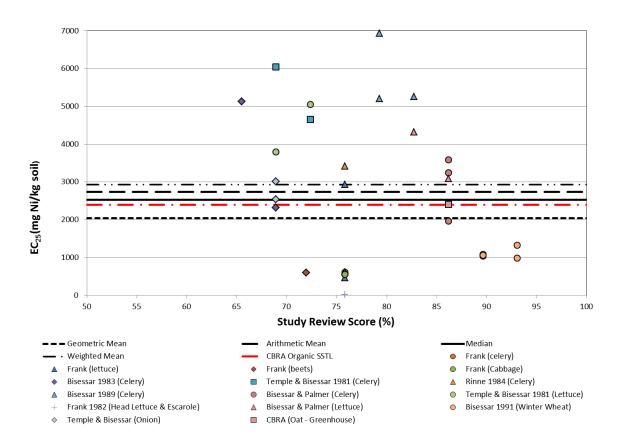
The meta-analysis is described in detail in Appendix 5B, approaches to deriving EC25 values from effects-based endpoints from available studies are demonstrated in Appendix 5B-1, and the MOE-approved scoring key for assigning confidence to the EC25 values from eligible studies is presented in Appendix 5B-2. The effect level of interest was that concentration of nickel in soil that would result in either an effect to  $\leq 25$  % of the individuals in the population (e.g., EC25) or an effect that was  $\leq 25$  % of that observed for the control organisms (e.g., IC25). The methods used to derive effects endpoints are described in detail in Subsection 1.2 (Appendix 5B). Briefly, dose-response relationships were developed using linear or non-linear curve-fitting procedures. For a number of endpoints, either no control treatments were included in the original study design, or the control treatment was inappropriate for the purpose of deriving SSTLs. In such cases, data sources from outside the original study were used, as appropriate (see Subsection 1.3.3.1; Appendix 5B). Where control responses were derived from data sources outside of the original study, it was assumed that "normal" growth occurs in soil containing Ni at 50 mg/kg, the Ontario Typical Range (OTR98) value for Ni. Ni is present naturally in soils that develop from the weathering of parent rocks over geological time, and the OTR data reflects this fact.

Each endpoint was multiplied by its score (%) to produce a weighted EC25 value for that particular endpoint (as described in Section 1.5). The weighted EC25 value of a crop species was calculated by dividing the sum of the scores of the crop's endpoints (e.g., root weight, % yield) by the sum of the crop's weighted EC25 values. The weighted EC25 value for nine (9) crop species in this meta-analysis derived in this manner is presented in Table 5B.13.

#### 5.5.2 Meta-analysis of Applicable Data

The process developed to evaluate the scientific quality of the studies and their resulting effects data used a systematic scoring and weighting approach that would give greater "weight" to the most reliable data. This is discussed in detail in Appendix 5B. The result of the meta-analysis provided a distribution of weighted endpoints from which different estimates of central tendency included the weighted mean calculated as above, the arithmetic mean, geometric mean, and median for the reviewed studies. For perspective, the SSTL derived for organic soils in the original Crops risk assessment (Jacques Whitford, 2004a) was also included in Figure 5-4. The weighted mean, arithmetic mean, and median are all similar in value to the SSTL for organic soil derived in the CRBA in 2004. The weighted mean value is the highest of these estimates (2,935 mg Ni/kg). The arithmetic mean (2,041 mg Ni/kg) is less than the CBRA SSTL of >2,400 mg Ni/kg. The proposed SSTL for organic soils from the CBRA (Jacques Whitford, 2004a) is not dissimilar to that derived in consideration of the historical literature.





## Figure 5-4 Compilation of reviewed EC25s for crops grown on organic soil in Port Colborne with estimates of central tendency.

# 5.6 RE-EVALUATION OF THE 2000 AND 2001 STUDIES AND CONSIDERATION OF STUDY DATA SINCE 2004

#### 5.6.1 Greenhouse and Field Trials (2000, 2001)

The greenhouse and field studies conducted for the CBRA are discussed in Appendix 5B.

#### 5.6.2 Consideration of Studies since 2004

Professor Beverly Hale of the School of Environmental Science at the University of Guelph, completed an NSERC Collaborative Research and Development (CRD) grant entitled "*Plant* Accumulation of Mn and Ni: Interaction among soil Mn, Ni and pH". A Master of Science thesis "*Field Trial of Dolomitic Limestone as an In Situ Technique to Reduce Nickel Toxicity in Soybean* and Oat" (Cioccio, 2012) was produced from this research. These new data were used as a lens through which to view the acceptability of the derived SSTL for organic muck soil. There were no new data applicable to organic muck soils in this thesis, as the research was undertaken with clay soils with 10-16% organic content. The research did provide some valuable insights into the current conditions for crops in the Port Colborne area. The former Hruska and Snider farms were



the sites for the field trials. The fields had been unused for several years prior to these studies being undertaken, and the organic matter content was higher than in the reference plots from Point Abino (4.6%). The study took place over a three year period from 2005-2007. Oats were planted in 2005 and 2007, with soybeans being planted in all three years. Yields of soybean in 2005 were poor at all sites (treatment and reference), so no crop data were reported for 2005. In 2006, all plots were planted with soybean, and in 2007, oats and soybean were again planted.

For oats, the Ontario average yield was 2.2 T/ha in 2005<sup>8</sup>. The yield at the reference site that year was 0.89 T/ha. At the three test sites (Hruska west (limed at 50 T/ha), Hruska east (limed at 10 T/ha), and Snider (un-limed)), the yields were 0.69, 1, and 1.74 T/ha, respectively. The soil Ni concentrations in these plots were, 2420, 2860, and 2490 mg/kg, respectively. In 2007, the average oat yield from Ontario farms was 2.4 T/ha. At the reference site at Port Abino, the oat yield that year was 2.88 T/ha. At the Port Colborne sites, the yields were 1.69, 2.07, and 0 T/ha. The oats planted on the Snider plots in 2007 did not germinate. The Snider plots had no manipulation of soil chemistry (i.e. no liming or Mn supplementation) and reflect the soil conditions in these plots after lying fallow for several years. In 2005, the oat yield in the Snider plots was approximately 76% of the Ontario average, but at the reference site containing no Ni contamination, the yield was only 0.89 T/ha. Oat yields on the Hruska plots were similar to those at the reference site. It is difficult to make specific conclusions as to the impact of the soil metal contamination on oat growth and yield on the test plots in 2005 and 2007. Liming did cause pH to be higher in the Hruska test plots relative to the Snider plots, and both foliar and soilextractable Ni concentrations were reduced as soil pH increased (Cioccio, 2009). The Valeowned agricultural lands in Port Colborne are leased and are currently being farmed. While Vale is not specifically studying the yields on these lands, communications with the farmer leasing and farming the lands indicate that the yields of soybean, corn, and wheat on these lands have been comparable to the Niagara regional average yields since 2008, using modern agricultural methods (Mike Dutton, pers. comm.)<sup>9</sup>.

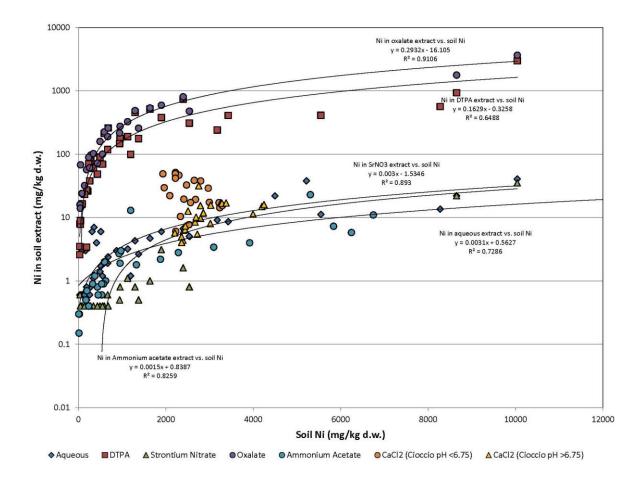
Soybean yields on the reference plot was 51% of the Ontario average yield (3.1 T/ha) in 2006 and 99% of the Ontario average yield (2.2 T/ha) in 2007 (Cioccio, 2009). In 2006, the yields on the limed Hruska plots and un-limed Snider plots were poor, but in 2007, the yields were 5, 11, and 19% below the Ontario average on the plots that were limed with 50, 0, and 10 T/ha, respectively. In conjunction with the information obtained from the farming of the leased Vale lands since 2008, it appears that soybean farming is viable on the Ni-contaminated agricultural lands in Port Colborne.

One aspect of significance regarding Cioccio's work is the chemical extraction of Ni from soils and the relationship between soil Ni, extractable soil Ni, bioavailable Ni, and toxicity. Several soil extraction methods are used interchangeably for metals in soil and sediments (Selim, 2011; Dean, 2007; Allen, 2002). At Port Colborne, neutral ammonium acetate was used to extract Ni

<sup>&</sup>lt;sup>8</sup> The average Ontario yields were obtained from the OMAF website (<u>http://omafra.gov.on.ca/english/stats/welcome.html</u>)
<sup>9</sup> Mike ...

**Stantec** 

from soils by the Ministry of the Environment and its predecessor, the Air Pollution Control Branch of the Ministry of Health (Air Pollution Control Branch, 1959).

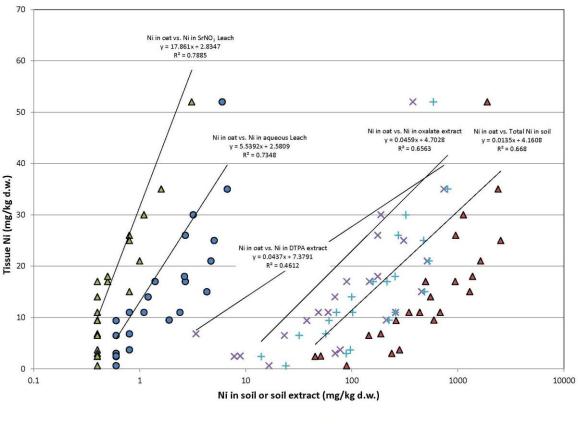


## Figure 5-5 Ni in soil extracts from the CBRA 2001 Greenhouse Studies, MOE Studies, and Cioccio (2009).

In Figure 5-5, soil extraction data have been compiled from three sources. First, ammonium acetate extracts from MOE's historical phytotoxicity studies (MOE, 1975, 1991). Aqueous extractions were from Air Pollution Control Branch (1959) and the CBRA (Jacques Whitford, 2004a). Strontium nitrate extractions from the CBRA 2001 greenhouse studies track together with the aqueous, ammonium acetate, and calcium chloride extractions from Cioccio (2009) on the bottom group of curves in Figure 5-5. The top group of curves consists of diethylene triamine penta-acetic acid (DTPA) and ammonium oxalate extraction data from the CBRA 2001 greenhouse studies. The calcium chloride extraction data from Cioccio (2009) have been



separated into those from limed soil plots (pH > 6.75) and those with soil pH < 6.75. Some of the un-limed soils had pH as low as 4.6. The CaCl<sub>2</sub>-extracted Ni was clearly related to soil pH in the plots studied by Cioccio.



Oats - Aqueous ▲ Oats - total Ni ▲ Oats - SrNO3 × Oats - DTPA + Oats - Oxalate

## Figure 5-6 Ni in oat tissue as a function of soil extracts or total Ni (from the CBRA 2001 Greenhouse Studies).

In Figure 5-6, Ni in oat tissues (only from the CBRA 2001 greenhouse studies) are plotted as functions of the various extractants (water, DTPA, oxalate, and strontium nitrate) as well as total Ni in soil.

There are two aspects to these curves. First, all of the linear relationships between variables are reasonably good. A strong relationship (high  $R^2$  (coefficient of determination)) is useful for the purposes of prediction of Ni in oat tissue from soil or extracts. The second aspect is the slope of the curves. In Figure 5-6, all the curves are linear relationships and the equations are included on



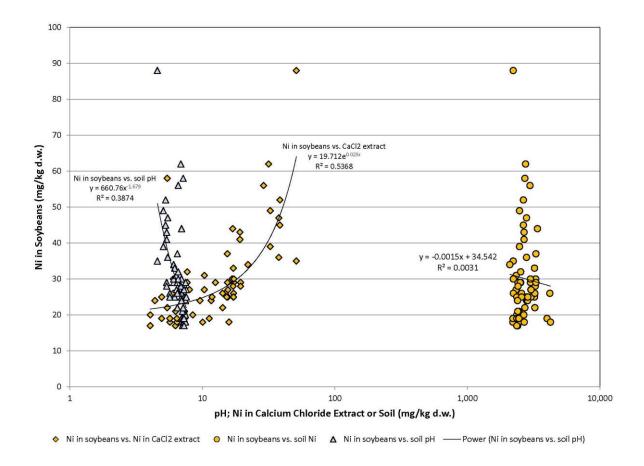
the graph. The data relating Ni in oat tissue and Ni in soil (red triangles in Figure 5-6) show a good relationship ( $R^2$  of 0.668), but the slope of the curve (0.0135) is very small. Ni in oat tissue can be predicted well from soil Ni<sup>10</sup>, but it is difficult to give physical meaning to the relationship, other than to say that only a small proportion (around 1.35%) of the soil Ni makes its way into oat tissue (i.e. is bioavailable). The remaining curves on Figure 5-6 relate the Ni accumulated in oat tissue to the Ni extracted by the four extractants. A slope of 1 would indicate a direct relationship between Ni in oat tissue and Ni in the extract – the extract would reflect, perfectly, the Ni taken up by the oat plants. Among the extractants, DTPA and ammonium oxalate have slopes of roughly 0.04. These two chemicals leach quite a large proportion of soil Ni relative to what is accumulated in oat tissue. The slopes of the aqueous and strontium nitrate curves were 5.5 and 17.9, respectively. The Ni in oat tissue was roughly 5 and 18 times higher than in the extracts. These extracts under-predict the Ni in oat tissue, but the aqueous leach provides the closest approximation of Ni in oat tissue. One final point regarding Figure 5-6 is that all curves relating Ni in oat tissue to either soil Ni or Ni in extracts from soil is that the y-axis intercepts of the linear curves are all between 2 and 5 mg Ni/kg oat tissue. This can be interpreted that background levels of Ni in oat tissues are between 2 and 5 mg/kg in soils not contaminated with Ni. This is normal and to be expected. For future risk management efforts at Port Colborne or elsewhere, extracted soil Ni offers potential for risk management purposes. Strontium nitrate, calcium chloride, or aqueous extractants offer the most meaningful information. Ammonium oxalate and DTPA, while certainly good extractants, do not reflect bioavailability accurately. A solution such as that used in the US EPA synthetic precipitation leachate procedure (SPLP) (US EPA Method 1312) could be used, adjusted to local rainwater pH conditions.

Figure 5-7 identifies the relationships between Ni in soybeans, Ni in CaCl<sub>2</sub> soil extracts, and Ni in soil. Ni in soybeans was inversely related to soil pH (data from limed and un-limed plots are included) and proportional to Ni in the extract. In other words, the extracted Ni integrates the effect of liming (i.e. elevated pH) on Ni bioavailability from soil. There is no statistical relationship between total Ni in soil and Ni in soybeans. For the purposes of risk management, it will be important to use a combination of soil extractions and tissue analysis (plant vegetative tissue as well as the relevant crop, if seeds or grains).

The long-term management of the agricultural lands affected by Ni contamination at Port Colborne will need to balance production and Ni translocation into the crops.

<sup>&</sup>lt;sup>10</sup> A power curve (y=0.0813x<sup>0.7819</sup>; R<sup>2</sup>=0.7681) provides a better fit than the linear curve, but for clarity, the linear relationship was used for reasons of comparison in all curves in Figure 5.6.





## Figure 5-7 Relationship between Ni in soybeans and total Ni in soil (circles), Ni in calcium chloride soil extracts (diamonds), and pH (triangles) (from Cioccio(2009)).

#### 5.7 SUMMARY OF CROPS UPDATE REPORT FINDINGS

Of the MOE's eight "global" comments on the 2004 Crops risk assessment (Table 5-1) Comments 3, 4, 5, 6, and 7 generally support the approaches used by Jacques Whitford. These comments are full of nuance, which reflect the difficulties that were faced in conducting the Crops risk assessment. For example, global comment #3 observed that using Port Colborne area soils and crops typically grown in this area was an appropriate approach to evaluate risk to crops grown in the Port Colborne area. The comment noted that there is considerable variability among the three general soil types in the area, not the least of which is the soil CoC content, and that when conducting crop studies with these soils that it is not practical to match soil exactly or to find soils that are identical in all ways except CoC concentration. Finally, the comment acknowledged that it would have been easier to have spiked a standard soil with



#### PORT COLBORNE COMMUNITY-BASED RISK ASSESSMENT 2014 UPDATE REPORT CHAPTER 5 - ECOLOGICAL RISK ASSESSMENT - CROPS

metal salts to create a range of soil CoC treatments but the use of spiked soils would not have met the study's objectives. This comment is particularly important, as the chemical form of the CoCs in the soil is a critical aspect of the risk assessment. A risk assessment needs to address the contamination that is present, not other forms of CoCs that are not actually present.

Comment #4 noted that the decisions for the design of the 2001 greenhouse studies (and only conducting field studies on clay soils in 2001) were made with limited data, with the unstated implication that better decisions might have been made with additional data. The crop studies were discussed in some detail at the time with all relevant parties (the PLC, its consultant, the MOE, Inco, and Jacques Whitford) and the path forward was developed for better or for worse. The use of non-agricultural soils as source soils for blending in 2001 was a certainly a constraint on the study. It is likely, however, that the selection of till clay soil from a railway right-of-way did not impact the findings or possibly even led to more protective EC25 generation, as the tilth of the highly contaminated till clay soil would have been poor.

Comment #5 supported the decision to use blended soils in the 2001 greenhouse studies, while acknowledging that the blending process itself affected the soil characteristics. Comments #6 and #7 acknowledged the general acceptability of the statistical analysis conducted and the toxicological endpoints derived to denote risk to crops.

Comment #8 identified the unwieldiness of the six main studies comprising the Crops risk assessment. The review comment identified the desirability of presenting these studies chronologically rather than as discrete studies. This 2014 Update Report is intended to address comment #8 by providing a more unified presentation of the Crops risk assessment.

MOE comment #1 identified that the decision to exclude year 2000 greenhouse data from specific calculation of EC25s or PNECs had not been clearly justified. It was later discovered in 2012 in subsequent meetings with the MOE that the MOE did not have for their review copies of the 2006 and 2009 Jacques Whitford Addendum Reports which would have provided rationale for this justification. The year 2000 data actually did not show clear dose-response behavior, which made it difficult to calculate representative EC25 values. Instead, it was decided to incorporate the year 2000 non-numerically by using the knowledge gained in year 2000 to guide in the proper design of the year 2001 studies. Nevertheless, it is possible with caution to manipulate the year 2000 data to approximate EC25 values in some cases. The fact still remains that the year 2000 studies were preliminary in nature and any derivation of approximated EC25s may not be representative because of the large associated uncertainties. Approximated EC25 values are found in Appendix 5B for transparency, but these values were not considered in the numerical development of SSTLs for the main soil types of Port Colborne. The year 2000 soils were selected from various site locations to provide a gradient in CoC concentration. Differences were found in soil tilth, soil pH, and soil nutrient status (Mn, Fe, organic carbon). Only after the fact was it clear that these factors in the 2000 study design were found to act as confounders. The study design of the year 2001 studies corrected for the inaccuracies of the year 2000 studies by adopting a blended soil approach to achieve uniformity in soil texture and soil composition and enabling a study to gather representative data to better understand the effect of CoCs on



#### PORT COLBORNE COMMUNITY-BASED RISK ASSESSMENT 2014 UPDATE REPORT CHAPTER 5 - ECOLOGICAL RISK ASSESSMENT - CROPS

agricultural crops. As stated above, the year 2000 results can provide insight, but should not be considered definitive.

The Ministry's eight global review comments have captured the essence of the Crops Risk Assessment challenges, in that the refinery's location was in an area that had four different soil types affected by the refinery emissions: the risk assessment had to address, for four soil types, the risk to agricultural crops that remains in the soils forty years after emissions ceased. The preliminary (year 2000) crop studies did not adequately address the confounding influences of soil texture, soil chemistry, soil pH and soil COC concentrations within the study area. The 2001 studies subsequently adequately addressed many of the confounders, but did so only by blending contaminated and uncontaminated soils to obtain common contaminated soils for each of the four soil types. In addition, though some of the soils used were not agricultural soils and less than ideal, it nonetheless provided adequate site coverage.

This Crops Risk Assessment Update Report is intended to provide closure on a process that has now been open for fourteen years and was in planning stages for several years before that. Some challenges still exist because it is not possible to travel back in time to alter decisions that were made 13 or 14 years ago in this pioneering wide-area or community-based risk assessment in Ontario. In spite of these deficiencies, site-specific target levels (SSTLs) have been derived for the four main soil types in the Port Colborne area (Jacques Whitford, 2004a) (Table 5-2). Inclusion of additional information – earlier data from Port Colborne that had not been used in the earlier CBRA as well as more recent research findings – provide further context for these SSTLs. The review of the earlier literature generally supports the SSTL for organic muck soils (Figure 5-4). The newer research (Cioccio, 2009) has confirmed soil liming as a tool to manage soil pH, the master variable that influences plant health as well as Ni accumulation in agricultural crops grown on the lands affected by the historical contamination of soil with Ni, Cu, Co, and As due to historical emissions from the nickel refinery in Port Colborne.

Table 5-2         Site-specific threshold levels (SSTLs) derived for four soil types representative of the study area.	
Soil Type	SSTL for Ni (mg/kg)
Sandy Soil	7501
Organic Muck Soil	2,3351 (>2,400)2
Welland (Heavy) Clay	1,650 <sup>1</sup>
Till (Shallow) Clay	1,4001
<sup>1</sup> Determined using the PNEC approach (EU, 1996 <sup>2</sup> Determined using regression analyses of the Gre	) enhouse Trial site-specific data (Jacques Whitford Ltd., 2004)



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# Appendix 5A

# Comments from OMOE (May 2011) and Responses



Ministry Ministère of the de Environment l'Environnement Standards Development Branch Direction de l élaboration des normes 40 St. Clair Ave. West 40. avenue St. Clair ouest 7<sup>th</sup> Floor 7<sup>e</sup> étage Toronto ON M4V 1M2 Toronto ON M4V 1M2 www.ene.gov.on.ca www.ene.gov.on.ca Tel.: 416 327-5519 Tél.: 416 327-5519 416 327-2936 Téléc.: 416 327-2936 Fax:

May 11, 2011

Mrs. Maria Bellantino Perco, Senior Specialist, Environment Vale, Port Colborne Refinery 187 Davis Street, Box 250 Port Colborne, ON L3K 5V2

Dear Mrs. Bellantino:

# **RE:** Ministry Comments on Vale Port Colborne Community Based Risk Assessment (CBRA)

The ministry has completed the review of the following Vale Port Colborne CBRA reports submitted to us on August 2010:

 Port Colborne Community Based Risk Assessment - Crops Studies, prepared by Jacques Whitford Limited, dated December 2004.

*P*Ontario

- Community Based Risk Assessment, Port Colborne, Ontario Ecological Risk Assessment Natural Environment, prepared by Jacques Whitford Limited, dated September 2004.
- Port Colborne Community Based Risk Assessment Human Health, prepared by Jacques Whitford Limited, dated December, 2007.

Prior to reviewing the above noted documents, the Ministry review team met with representatives of Vale and Jacques Whitford Environmental Ltd. (JWEL) and received a detailed technical briefing of the CBRA studies. In addition, the Ministry has considered comments on the documents prepared by Watters Environmental Group (WEG) and the Public Liaison Committee, and JWEL's response to those comments. The review team also participated in a two day field trip to Port Colborne to obtain a first hand understanding of the study area, which included a tour of the Vale refinery and Vale owned land.

The Ministry comments are presented in the attached document in three main sections: Ecological Risk Assessment -Crops, Ecological Risk Assessment - Natural Environment, and Human Health Risk Assessment. Please note that at this point the Ministry is not providing comments on the Integration Report (June 2008). The comments that follow are comprehensive and detailed. There are numerous comments, some of which are considered major because they may affect the report's conclusions. Other comments are provided to improve the transparency, organization, and clarity of the CBRA reports. After Vale and your consultants have reviewed the comments, the Ministry is willing to meet with you to provide further context to our comments. It would be an opportunity for Vale to identify specific issues that wishes to discuss with the Ministry's reviewers. In addition, the Ministry is committed to work with you and your consultants to resolve the issues identified by our reviewers with the ultimate goal of endorsing the CBRA, the risk-based soil concentrations, and risk management measures.

If you have any questions about our review please feel free to contact me at (416) 327 8220.

Yours truly,

Camilo Martinez Coordinator, Community Based Risk Assessment MOE – Standards Development Branch

# Comments by the Ministry of the Environment On Community Based Risk Assessment For Port Colborne Community

The following are Ministry comments on the following reports:

- I. Port Colborne Community Based Risk Assessment Crops Studies, prepared by Jacques Whitford Limited, dated December 2004.
- II. Community Based Risk Assessment, Port Colborne, Ontario Ecological Risk Assessment Natural Environment, prepared by Jacques Whitford Limited, dated September 2004. (see page 17)
- III. Port Colborne Community Based Risk Assessment Human Health, prepared by Jacques Whitford Limited, dated December, 2007. (see page 67)

# I. MOE Review Comments on CBRA ERA- Crops Studies

The following comments are related to the Port Colborne Community Based Risk Assessment - Crops Studies prepared by Jacques Whitford Limited, dated December 2004. The report consists of the following volumes:

Volume I – Main Report Volume I – Appendices Volumes II – VI

There are major sections to this set of comments: global comments and specific comments. Global comments generally reflect overarching aspects of this risk assessment report and are usually not specific to any one section or specific part of the report. Specific comments are identified by volume, section and page number and typically reflect comments specific to the subject matter presented in these sections.

#### **Global Comments**

#### 1. Calculation of assessment endpoints from the 2000 Greenhouse Study data

Assessment endpoints, such as EC25 or PNEC values, were not calculated from the 2000 Greenhouse Study data. As stated in the report "analysis of the [2000 Study] data revealed significant limitations in experimental design and execution that prevented development of dose-response relationships, and calculation of toxicity thresholds." However, data from the 2000 Greenhouse study was presented and limited statistical analyses were conducted, including the use of some of the data in the meta-analysis of

oats. Therefore, EC25 and PNEC values should be calculated from the available 2000 Greenhouse data and included in the report.

#### 2. Were the objectives of the Crop Studies met?

The main purpose of these studies, as stated in the report, was to determine the concentration of historically deposited [Chemicals of Concern] CoCs in soil that present an unacceptable risk to crops grown in the Port Colborne area. Although six main studies (2000 Greenhouse Study, 2000 Field Study, 2001 Greenhouse Study, 2001 Field Study, 2001 Engineered Plot Study and the Biomonitoring Study) were conducted as part of the CBRA, none of these studies provided assessment endpoints for field crops grown under field conditions in Port Colborne soils with a range of CoC concentrations. The following bullets provide the main deficiencies of each study.

- 2000 Greenhouse Study
  - high variability in soil parameters with confounding factors that made data interpretation difficult
  - missing data for biomass in clay soils and lack of germination in the organic control soil
  - o no yield data or calculated assessment endpoints
- 2000 Field Study
  - Started too late in the season (late July)
  - o Poor growth due to wet weather conditions and short growing time
  - o No yield data, root data or calculated assessment endpoints
  - High variability in soil parameters in the organic soil
  - No replication of field plots
  - 2001 Greenhouse Study
    - No yield data that could be related to yield of field crops in the Port Colborne area
    - No data on root growth
    - Soils used were often not agricultural soils (refer to Table 1)

Soil Type	Treatment	Present Land Use
Organic	Background	Rural farm, border between open field and woodlot
Organic	Contaminated	Abandon rural farm, woodlot
Heavy Clay	Background	Woodlot
Heavy Clay	Contaminated	Industrial – abandoned farmland
Sand	Background	Re-vegetation area
Sand	Contaminated	Wooded area
Till Clay	Background	Wooded area
Till Clay	Contaminated	Railway right of way, abandoned

 Table 1: Soil collected for 2001 Greenhouse Study

- 2001 Field Study
  - No replication of field plots
  - o No control field plots
  - No range of CoC concentrations within a plot
  - o No yield data, root data or calculated assessment endpoints
- 2001 Engineered Field Plot
  - Pots bottoms were removed and so plants were exposed to soil within the pot and field soil below the pots, making interpretation of the results difficult
  - Pots started in the greenhouse and then moved to the field, with the reported potential of transplant stress
  - No yield data or root data
  - Planted in the field too late
  - o Assessment endpoints only for heavy clay soil
- Biomonitoring Study
  - Only one species sampled
  - Plant parts were not separated before chemical analysis and age of the tissue and stage of development of the Goldenrod was not taken into consideration
  - No assessment of roots

Valuable information was gained by these studies, but there are many studies in the scientific literature on the effects of nickel in soil on the growth of plants and on the effects of liming in ameliorating these effects (refer to Volume 1 Part 3 Page 3-3). Several of these referenced studies were conducted on Port Colborne area soils (Freedman and Hutchinson (1980), Temple and Bisessar (1981), (Bisessar (1982), Frank et. al., (1982), Bisessar et. al. (1983), Bisessar (1989), McIlveen and Negusanti (1994), Kukier and Chaney (2000)). It is recommended that the determination of soil quality criteria for soils in the Port Colborne area not be based solely on the results of the CBRA Crop Studies but include the results all crop studies in the scientific literature that were conducted in the Port Colborne area where soil nickel concentrations are reported.

# **3.** Use of soils from the Port Colborne area rather than standard soils spiked with metal salts

Using Port Colborne area soils and crops typically grown in this area was an appropriate approach to determine the concentration of historically deposited CoCs in soil that present an unacceptable risk to crops grown in the Port Colborne area. It is understood that the soils in the Port Colborne area are variable in terms of physico-chemical parameters, such as pH, texture, organic matter content, nutrient status, cation exchange capacity and concentrations of chemicals of concern. Also, it is understood that when conducting crop studies with these soils that it is not practical to match soil exactly or to find soils that are identical in all ways except CoC concentration. Finally, it is acknowledged that it would have been easier to have spiked a standard soil with metal

salts to create a range of soil CoC treatments but the use of spiked soils would not have met the study's objectives.

#### 4. Appropriateness of the soils used in the studies

It is recognized that the researchers took considerable effort to assemble information on Port Colborne soils from several sources and to properly analyze the soils before starting the studies. The soils selected were representative of the major soil groupings of the Port Colborne area. However, very limited data was available from the 2000 Field Study and the 2001 Field Study plots were restricted to heavy clay soil.

Many of the soils used in the 2001 Greenhouse Study, upon which the EC25 and PNEC values are based, were not from agricultural land, as can be seen in Table 1. The use of woodlot or railway right-of-way soil does not negate the value of this study but the use of agricultural soils would have been preferable.

#### 5. Use of blended soils in the 2001 Greenhouse Study

The mixing of a control soil with a highly contaminated soil in various ratios in order to create a range of CoC concentrations in the study soils is acceptable. It is understood that the blended soil will not represent a particular soil that can be found in the field and it is acknowledged that drying, sieving, and mixing of the soil will alter the soil structure and severely affect the microfauna in the soil. However, there are limited options when conducting this type of research. The alternative of selecting soils with different CoC concentrations was attempted in 2000 but the problems of confounding factors made the interpretation of the data problematic. This latter approach can be successful but it would have required more soils and much higher replication.

#### 6. Statistical analysis of the data

Appropriate statistical tests were used to analyse the data in the report, although there are a few points that require clarification, as outlined in the Specific Comments section.

#### 7. Assessment endpoints

Although it is recognized that various assessment endpoints could have been used (NOEC, LOEC, PNEC, ECx), the EC25 and PNEC assessment endpoint are acceptable to the Ministry.

#### 8. Structure of the Report

The Crop Studies component of the Port Colborne CBRA consists of six main studies, as given in Comment 2. In the main report, these studies are grouped according to study type (Greenhouse versus Field Studies), rather than in chronological order. This makes it difficult to follow the experimental approach, especially since the 2001 studies were designed in response to the 2000 results. It would be much easier to follow the studies in

chronological order, which would follow the thought processes of the researchers. If a summary document is created, it is recommended that the chronological approach to presenting the studies be used.

#### **Specific Comments**

#### 9. Volume I – vi

Part 6 - General Study Conclusions - General is spelt incorrectly

#### 10. Volume I – Page 1-1

The third paragraph needs a graph showing emissions over time or at least a reference.

#### 11. Volume I – Page 1-3

Section 1.2 is labelled Study Purpose but it is really how the crop study component of the CBRA fits into the CBRA. A statement of the purpose of the Crop Studies is required.

#### 12. Volume I – Page 1-4

In the first paragraph the term "safe concentrations of chemicals is used. Consider revising to acceptable concentrations of chemicals or concentrations of chemicals at a low risk.

#### **13.** Volume I – Page 1-12

Only three components of the CBRA process are shown in Figure 1-1, yet on Volume I – Page 1-3, five components are identified.

It is not clear why the arrows point away from the overall CBRA process, when the various components feed into the CBRA process. Finally, it is not clear why there is not an arrow between the Field Studies and Biomonitoring Study since both are assessing the impact of CoCs in the soil under field conditions. Consider revising the diagram.

#### 14. Volume I – Page 1-14

In the paragraph under Section 3.2, it is not clear why the authors mention that the organic soil are more permeable than the clays in the context of CoC concentration. Either expand on this idea or remove the statement.

#### **15.** Volume I – Page 1-15

In the first paragraph, the number of soil pits should be given. Also, it is not clear whether CoCs are evenly distributed in the top 20 cm of only clay and organic soils that

have been historically ploughed or whether some soils that have not been ploughed also show this pattern.

In the final paragraph it would be helpful if the percentage area of woodlots were given.

# **16.** Volume I – Page 1-16

In the second paragraph, there is mention of a visual survey of crops growing in the Port Colborne area that was conducted in 2001. It is not clear why this survey was only conducted in 2001. Also, why was the crop harvest data given in Table 1-2 not related to the percent of Niagara Region harvested land rather than Southern Ontario harvested land.

# 17. Volume I – Page 1-17

It would be helpful if the Study Objectives were stated earlier in the report in the Purpose section.

# 18. Volume I – Page 1-18

Reference is made to the MOE generic criteria. MOE criteria Tables A through E are effects-based and are set to protect against the potential for adverse effects to human health, ecological health, and the natural environment, whichever is the most sensitive. By protecting the most sensitive parameter the rest of the environment is protected by default. Criteria were developed only if there were sufficient, defensible, effects-based data on the potential to cause an adverse effect. These criteria are conservative and protective of the environment.

Throughout the Crop Studies report the authors use language that infers the MOE criteria for nickel in soil is unrealistic; such as "MOE generic guidelines were conducted using experimental designs that are likely to maximize nickel solubility and availability in plants" (Volume I – Page 1-18), the listing of factors that may result in overestimating phytotoxicity "(Volume I – Page 1-18), stating that "the existing guideline is based on total nickel concentrations in soils, and not on its bioavailable fraction, a more meaningful indicator or phytotoxicity (Volume II – Page 5-12) and referring to one of the studies the Ministry used to develop the guidelines as a "contentious study" (Volume II, Section 8, Page 1).

It is understood that the MOE site specific risk assessment approach allows the incorporation of considerations, which are specific to the site, in the development of soil and groundwater criteria. However, it is expected that those conducting research for the development of site-specific criteria (or community specific) will approach the research in a scientifically detached manner and not assume, a priori, that a soil nickel concentration of 200 mg/kg could not be toxic to plants under field conditions.

# **19. Volume I – Page 1-19**

The last sentence of the first paragraph under Section 4.3 begins by stating "To counter this [meaning that greenhouse studies are not reflective of natural growing conditions] field experiments were conducted .... It is my understanding that the field studies were conducted as a check on or to verify the greenhouse results rather than to counter a perception that greenhouse studies are artificial or not reflective of field conditions. Consider rewording.

#### 20. Volume I – Page 2-1

In the forth paragraph, the last sentence reads "Because of the consistent correlation found between nickel and CoCs .... It is not clear why a consistent correlation is of importance. Should this read either consistent ratio or high correlation?

#### 21. Volume I – Page 2-2

With regard to the first bullet, was the objective of the Year 2000 Greenhouse and Field Trials really "to select and characterise soil types typical of the Port Colborne area containing varying concentrations of CoCs for use in Greenhouse and parallel Field Trials"?

#### 22. Volume I – Page 2-10

The report says that sand soils were not being included in the 2000 Field Trials because they make up only a small portion of the impacted lands in Port Colborne. However, since the focus of this study is on growing crops on contaminated land, the reason to include or exclude sand soil from the study should be based on the portion of the impacted lands that are both sand and potentially used for agricultural purposes.

#### 23. Volume I – Page 2-15

The second to last paragraph states that "Soils were collected mostly from farmed (or formerly farmed) agricultural fields and a variety of other sources (agricultural fields, woodlots, and beaches) [It is assumed that agricultural fields were mistakenly included in the other sources category].

Tables similar to Table GH-16 (Volume I – Part 3 – Page GH-1B-2) should be included in the main report for both the 2000 and 2001 studies. For the 2000 studies, the Table should also include a column for pH and a column identifying where the soil was collected (e.g., agricultural field, woodlot, sand dune or from one of the field plots). This type of table in the main report would make it much easier to interpret the results.

In addition, it would be helpful to know the status of the agricultural field that were sampled (i.e., were the fields fallow, abandoned, actively farmed and if so, with what crops). This type of information would help identify confounding variables such as

levels of soil pathogens (e.g., nematodes) or levels of rhizobium in the soil or the likelihood of herbicide residues being in the soil.

## 24. Volume I – Page 2-16

Following the list of five soil-metal concentrations, the MOE Table F value of 43 mg/kg nickel is referenced with Ontario Typical Range in brackets. The Ontario Typical Range is the range of concentrations for the element or compound of interest in Ontario soils for a specified land-use category. The OTR98 is a value that represents the 97.5 percentile of the sample population. The Table F background-based guidelines are based on the OTR98 and reflect the upper limit of typical background concentrations. Therefore, 43 mg/kg nickel in soil is not a typical background soil nickel concentration in Ontario, but the upper limit of background nickel concentrations in Ontario. A control soil should be well below this value.

# 25. Volume I – Page 2-17

The first sentence reads, "Field Trials in year 2000 paralleled the Preliminary Greenhouse Trials ...". It is not clear what is meant by the term "paralleled" as usually, in a parallel trial, a subject is randomly assigned to a treatment group, such as potted plants being randomly assigned either to the field or to the greenhouse. In the Crop Studies it appears that the only thing that might have been paralleled between the field and greenhouse studies is the seed used.

In paragraph four, it is mentioned that the three test sites chosen had been used by other researchers in previous studies. These studies should be referenced.

#### 26. Volume I – Page 2-19

The second paragraph in Section 2.4.2 reads "In order to establish a possible link between greenhouse and field trials, a set of pots with blended Heavy Clay (Welland Clay) soils identical to those used in the 2001 Greenhouse trials was prepared". While it may be true the soil was identical, the volume of the pots and the type of pot used were different (6.5 L Treepots versus Classic 1200 pots).

#### 27. Volume I – Page 2-21

It is understood that it is not easy to match soils for a study of this type and that it is difficult to obtain soil CoC (or nickel) concentrations at the desired levels. However, it is not clear how the Soil CoC levels were chosen and why such a wide range of concentrations was considered reasonable for a set Soil CoC level. For example, the nickel concentrations in the three soils at the Medium Soil CoC level are 1200, 517 and 307 mg/kg.

#### 28. Volume I – Page 2-22

In Table 2-4, the average given is the average of the numbers not the average of the pH values. Correct.

## **29.** Volume I – Page 2-33

Table 2-18 give P, K, and Mg concentrations in the soils used to make the blends for the 2001 Greenhouse experiment. Although the concentrations given may be adequate for the growth of crops, this does not mean that crop growth will not be greater in soils with higher nutrient levels. Although it may not be practical to get an exact match in nutrient levels between the control and very high CoC level, differences in nutrient levels of up five times are likely to influence plant growth.

#### **30.** Volume I – Page 2-36

In Table 2-19, the nickel concentration in Plot #3 unamended soil is 7360 mg/kg and in Plot #3 1X soil it is 2800 mg/kg. With this difference in nickel concentrations, it is not clear how the effect of liming can be assessed.

# **31. Volume I – Page 2-23**

In the notes below Table 2-23, when using acronyms like EQL it would be more helpful to the reader to explain the term such as "lowest concentration that can be reliably achieved within specified limits of precision and accuracy during routine laboratory operating conditions" rather than "estimated quantification limit for analytical method".

#### 32. Volume I – Page 2-45

In section 6.4, a greater explanation of why Plot 2A has such a high CEC is required.

#### **33.** Volume I – Page 2-51

The fourth paragraph reads "Jacques Whitford and staff of the University of Guelph Greenhouse measured soil pH and some other physical properties (e.g., density). The other physical properties should be listed.

#### **34.** Volume I – Page 2-53

In the fourth bullet, it is not clear why pH is the most crucial soil characteristic.

#### 35. Volume I – Page 3-3

A review of pertinent studies is appropriate, but it is not clear why more studies were not included and why no reference was made to review papers on nickel phytotoxicity.

#### **36.** Volume I – Page 3-11

In Section 2.2, it is stated that the 2000 testing used soybean and corn, which are agricultural crops in the Port Colborne area. This statement could be strengthened considerably by including crop statistics from the Port Colborne area.

The final sentence reads "Continuity in the plant species selected for use in both Greenhouse and Field Trials in Years 2000 and 2001...". This statement is correct in that oats were used in both years, but the variety was different. At some point in the report the reason for changing varieties and the implications of this change on the results should be discussed.

#### **37.** Volume I – Page 3-15

In Volume I – Page 2-16, the concentration of the control is given as approximately 43 mg/kg nickel yet in the table on page 3-15 the control is given as < 100 mg/kg nickel. Why was the value for the control changed?

#### **38.** Volume I – Page 3-22

It is understood that there were problems with the 2000 Greenhouse study, but in spite of these problems, the soybean data shows drastic declines in biomass, particularly in the clay soil, which can be attributed to soil nickel concentrations. Although EC25 values were not given for soybean in this study, the data suggests that growth effects are occurring well below the EC25 values of 1888 mg/kg Ni for clay and 1350 mg/kg Ni for sand, which were determined in the 2001 Greenhouse study. Unfortunately, the oat biomass data for clay was not available, since the nickel uptake data shows a similar trend to that of the soybeans.

#### **39.** Volume I – Page 3-28

The second conclusion states, "there are environmentally safe (non-phytotoxic) CoC concentration levels that are higher than the current MOE generic effects-based guideline values". While it may be true that no measurable effects were documented on plants growing in some of the soils with nickel concentrations above the MOE generic effects-based guideline value, the primary objective of the Crop Studies was to determine the concentration of historically deposited CoCs in soil that present an unacceptable risk to crops grown in the Port Colborne area. The soybean data from the Greenhouse 2000 sand soil suggests that reductions in biomass may occur at soil nickel concentrations as low as the MOE effects-based guideline value. A similar trend can be seen in the soybean in clay soil data, although due to the lack of clay control data it is not possible to determine at what soil nickel concentration effects start to occur. Although it is acknowledged that there were problems with the 2000 Greenhouse Study, nevertheless EC25 and PNEC values should be calculated from the available data.

#### 40. Volume I – Page 3-29

The focus on oats for the 2001 studies is reasonable; although the 2000 soybean data also showed sensitivity to nickel uptake and soybean may be a more economically important crop in the Port Colborne area.

#### 41. Volume I – Page 3-31

In the fourth paragraph, it is not clear where the data analysis is that identifies which soil variable are confounded with total soil nickel concentrations.

# 42. Volume I – Page 3-33

In Section 4.3.1, it was noted that the plants were harvested after 28 days due to severe toxicity symptoms. It is understood that this was an extreme case but typically, oats take 90 to 100 days to reach maturity. In Table 5 on page 11 (Volume II, Section 4) the maximum growth duration was 77 days. It is possible that the oats matured more rapidly under greenhouse conditions. However, oats is a cool weather crop and it is known that the higher air temperature adversely affect yield. There should be some discussion of how the greenhouse conditions (temperature, humidity and natural light levels) may have affected crop maturation and yield.

#### 43. Volume I – Page 3-40

In the report, decreases in biomass are often attributed in part to manganese deficiency. Although it is understood that a deficiency of manganese can affect plant growth, perhaps more emphasis is put on manganese than is warranted. For example, Figure 3-7 shows growth in most pots in the 1081 mg/kg nickel treatment to be comparable to the control, yet the tissue manganese concentrations are below the tissue manganese threshold value. In contrast, growth is poor in the 188 mg/kg nickel treatment, yet tissue manganese concentrations appear to be adequate. It would appear that other factors are more important in affecting growth than manganese concentrations.

Manganese deficiency is not necessarily a separate issue from CoC concentrations in the soil, since metals such as nickel and copper are known to displace manganese in soils.

# 44. Volume I – Page 3-42

It was worthwhile to investigate whether DTPA-extractable and Water-extractable nickel were better predictors of toxicity than total soil nickel. It is interesting that they were not.

#### 45. Volume I – Page 3-46

In the 2000 Greenhouse study, the biomass of oats grown in clay soil was comparable to the biomass of oats grown in organic soil (with the exception of higher growth in the organic soil from the Grotelaar farm, which was attributed to higher nutrient (phosphorus) levels). In the 2001 Greenhouse study, oat biomass in the organic soil (Table GH-25) was much less than oat biomass in the clay soil (Table GH-30).

Discussion would be helpful regarding the relatively poor growth of oats on the 2001 organic soil and may shed some light on why the limestone amendments decreased growth of oats in this soil.

#### 46. Volume I – Page 3-47

It is not clear why there was an apparent increase in growth at the highest soil nickel concentrations relative to oat growth around 1000 mg/kg nickel.

## 47. Volume I – Page 3-50

The idea of conducting a parallel experiment (Engineered Field Plot (EFP)) with pots in the greenhouse and field is sound. However, there were several aspects in the experimental design that precluded making a direct comparison between the field and greenhouse results. The pot size differed between the field and greenhouse, the field pots were started in the greenhouse and then moved to the field rather than being seeded in the field, and the bottoms of the EFP pots were cut off in the field so the plant roots were contacting two soil types.

According to the report, the plants in the EFP were more sensitive to soil nickel concentrations, which was attributed to greater stress under field conditions or transplant shock. However, oat biomass in the Greenhouse grown plants ranged from 22.93 to 31.42 g DW/pot and the oat biomass in the Engineered Field plot ranged from 26.8 to 43.6 g DW/pot. These data suggest the plants in the field plot had better growth than the plants in the Greenhouse, which would suggest they are not more stressed.

#### 48. Volume I – Page 3-51

The lack of manganese deficiency in the Engineered Field plot may be because the roots of these plants penetrated the underlying soil and took up nutrients including manganese. Further discussion is required.

#### **49.** Volume I – Page 3-57

In Figure 3-24, it is not clear why tissue nickel concentrations were not also in a log scale.

#### 50. Volume I – Page 3-62

It is not clear what is meant by the statement that variation in soil parameters that were confounded with soil Ni, do not have a large influence on plant accumulation of Ni, thus are not likely to have a large influence on the determination of EC25. How is this known?

#### 51. Volume I – Page 4-3

In the second paragraph, the land use for the OTR98 value quoted should be included.

## 52. Volume I – Page 4-4 to 4-6

OTR98 values should be included.

## 53. Volume I – Page 4-19

In is understood that the 2000 field trials did not get underway until late July and the "data were too sparse to provide for a comprehensive analysis". According to OMAFRA, the target date for planting spring cereals is April 10, and for corn and soybeans is about May 7. As planting date has a great effect on yield, it is questionable how the growth and yield of the 2000 field crops can be related to the normal growth of field crops in the Port Colborne area.

# 54. Volume I – Page 4-27

It is not clear why agronomic tissue samples are being used to look at CoC uptake, since in Volume II Section 5 - Page 8, it states that agronomic sampling best describes the relationship between the concentration of essential nutrients and final grain yield, whereas toxicologic sampling best describes the relationship between the concentration of CoCs in the soil and the aboveground yield. Should the toxicologic data have been used?

#### 55. Volume I – Page 4-34

In the fourth paragraph, the report states, "In no tissue did concentrations of cobalt or arsenic even approach levels thought to cause phytotoxic effects in plants". However, the greatest effect of arsenic is on the roots of plants. Why were the crop roots not examined?

#### 56. Volume I – Page 4-37

The conclusions start by saying, "Within the field trials, there were few cases where plant nickel or copper concentrations approached or exceeded tissue concentrations reported in the literature to cause phytotoxic effects". However, on Page 4-32 we are told that in the C3 plot, symptoms of phytotoxicity are evident. Also, germination was affected and approximately 50% of the leaves [of oats] were necrotic and plants were stunted and slender with less foliage. In Figures 4-3 and 4-4 on Page 4-30, nickel concentrations in tissues of oat and soybean are very high in the C3 unamended treatment. Clearly, there is evidence of phytotoxicity due to nickel under field conditions where soil nickel concentrations in the number of field plots and soil nickel concentrations, the soil nickel concentration at which significant phytotoxic effects and reductions in crop yield occur could not be determined.

#### 57. Volume I – Page 4-36

It is not clear why nickel induced iron deficiency is mentioned in the field report yet it is not mentioned in the Greenhouse studies and is not mentioned in the overall conclusions.

#### 58. Volume I – Page 5-4

There are better reasons for using Goldenrod as the species of choice than because it was the conspicuous floral element common to the chosen sites.

In any uptake study, it is important to separate the various plant parts before chemical analysis, as uptake can be, and usually is, quite different among plant parts. Why this was not done is unknown. Also, the age of the tissue and stage of development are important factors when conducting any biomonitoring study. Again, why these factors were not taken into consideration while conducting this study is unknown.

Since many of the biomonitoring plots were adjacent to the Year 2000 sampling locations, it is not clear why the natural vegetation samples were not taken from all the Year 2000 sites so the uptake data could be compared to the 2000 Greenhouse data?

Since the Spearman Rank Correlation was used, which does not require normality in the data, it is not clear why the data was trimmed. The trimming of the data could affect the correlations.

#### **59.** Volume I – Page 5-7

Why was the arcsine-square root transformation used?

Stating "glm" was used is not sufficient; the actual model should be given.

#### 60. Volume I – Page 5-10

Table 5-3 shows data for two sand sites (reference and medium), yet the Biomonitoring study table in Appendix B-1 shows three sand sites (reference, medium and high). Why is the high sand site not included in the table? Also, the mean and standard deviations given in the organic high treatment in Table 5-3 does not match the mean and standard deviations given in Appendix B-1.

#### 61. Volume I – Page 5-17

Reporting correlations for two data points is of questionable value.

62. Volume I – Page 5-24

The second paragraph reads, "generally nickel is readily and rapidly taken up by plants and is mobile in plants; therefore, the nickel content in plants ..." This should read nickel concentration in plants not nickel content in plants.

#### 63. Volume I – Appendix Page 7-4

CEC levels in the organic soil are surprisingly low, as well as in clay soil (given on the following page).

# 64. Volume I – Appendix F-5

The layouts shown are strip plot designs rather than the conventional split plot designs. Presumably, this design was chosen because liming the soil in strips is easier than liming sub-plots in a split plot design. Discussion is required regarding the effect this design has on the precision of the main effects and interaction and the implications in interpreting the experimental results.

#### 65. Volume II – Section 1 Page 4

In Table 1, for the sandy soils the nickel values for the medium and low CoC levels are both technically at the "low" level. It is understood that due to analytical challenges that the medium value is slightly lower than the low value. Nevertheless, there should have been a larger difference in nickel concentrations between the medium and low levels.

#### 66. Volume II – Section 1 Page 5

In 2000, the variety of oats was <u>Avena sativa</u> L. cv. Stewart but in 2001 the oats variety was <u>Avena sativa</u> L. cv. Rigadoon)(Section 4 Page 4). Why was the variety of oats changed?

Is the 2001 oat variety Rigadoon or Rigodon? Also, why was the oat variety "Ogle" used in the 2001 organic soil?

# 67. Volume II– Section 1 Page 10

Each pot had two plastic liners closed at the bottom to prevent leachate from escaping. This means that the soil would not drain and it is likely that the soil at the bottom of the pot became anaerobic. Was there evidence (reduced sulphur smell) that the soil had become anaerobic? Was the redox potential of the soil measured? The redox potential of the soil will have an effect on arsenic speciation (and other metals) and could affect arsenic availability and phytotoxicity.

# 68. Volume II– Section 1 Page 11

In the first paragraph it is stated that "intact root systems of plants removed from each pot experiment were initially separated by shaking soil from them. Broken roots were

removed from the loose soil using a combination of tweezers and dry sieving. Roots were discarded". With all this work done to remove the roots, it is not clear why the condition of the roots was not noted and why the roots were not washed, weighed and chemically analyzed.

#### 69. Volume II – Section 4 Page 6

A greenhouse temperature of 27 degrees Celsius is high for oats.

#### 70. Volume II – Section 4 Page 10

Insect and pathogen problems are commonly encountered in greenhouse and field experiments and it was appropriate to apply common agricultural pesticides in order to control the thrip and other insects. However, the percentage crop loss due to insect or other pathogen damage should have been calculated and the results included in the Main Report.

## **II. MOE Comments of Vale CBRA ERA-Natural Environment**

The following comments pertain to the Community Based Risk Assessment, Port Colborne, Ontario – Ecological Risk Assessment Natural Environment dated September 2004 and which was prepared by Jacques Whitford Ltd. on behalf of INCO Ltd. The ERA report consists of the following volumes:

Volume I:	Main Report (including Appendices A to D)
Volume II:	Field Data Collection and Analysis Protocols
Volume III:	Supporting Data
Volume IV:	Consultants Report
Volume V:	Bio-Physical Data

Additional reports have also been provided and were reviewed along with the ERA report. These reports are:

- Addendum Report March 2005
- Community-Based Risk Assessment Integration Report June 1, 2008

#### **Summary of Review Comments**

Overall, potential risks to the natural environment have been underestimated for this site, particularly at locations close to the refinery. Below we provide extensive comments for the proponent to consider. The vast majority of our review comments address scientific or transparency issues or requests for further clarification. Pending satisfactory resolution of these comments, this ERA appears to provide sufficient information to characterize most ecological risks at this site and support the majority of the reports conclusions. However, there remain some limitations with this ERA. There are some concluding statements that will need to be revised due to a recommended reanalysis of the data. In addition, due to limitations in sampling data and time constraints with this study, some revisions are warranted for a number of concluding statements to more appropriately characterize the results of this ERA.

The ERA concludes that ecological impacts from Ni, Cu, Co and As are not significant in the Study Area. This conclusion is based on inappropriately averaging data and biological response information across the entire study area. Data are presented in these reports that suggest adverse impacts to vegetation, soil organisms and wildlife (e.g. amphibians) in close proximity to the refinery boundaries. Using Ni as an example, this risk assessment found that Ni is elevated in environmental media (soil, surface water, sediments) and exposure is occurring to aquatic and terrestrial biota (as demonstrated by elevated concentrations in exposed organisms such as grasses, maple leaves, insects, tadpoles, frogs, earthworms and voles). Evidence of toxicity in areas with high COCs (i.e., the primary study area) include: earthworm toxicity measured in laboratory toxicity tests, visible Ni damage observed to terrestrial vegetation (maple leaves), potential toxicity to amphibians (e.g., American Toad), evidence of impaired leaf litter decomposition, and toxicity observed in maple seedlings (from reference areas that were grown on contaminated soils). Some evidence is presented in the report of limited or no adverse

effects as well but it is difficult to assess the significance of this information due to concerns with the overall report. Based on the experience at similar sites, distance from the refinery is a major factor that needs to be considered. However, there was only a limited attempt in this report to evaluate the potential relationship that might exist between potential adverse effects and distance from the refinery. Reference or control samples collected west and generally upwind of the refinery appear to be appropriate (based on chemistry – COC levels in soil, water, sediment). However, "Control" samples collected downwind may not be as it appears COC concentrations are elevated in these samples but at lower concentrations than those found in the primary and secondary study areas. Hence, the downwind "controls" were exposed to COCs and may not be suitable reference sites. Overall, it appears that adverse impacts are occurring as a result of exposure to COCs in soil but that the scope of these impacts is limited with respect to the entire study area.

#### MAJOR COMMENTS

- 1. The overall sampling design and site characterization is not well described in this report. It took a lot of effort by the reviewers to determine what data was collected and used in this Risk Assessment report. The sampling design is often uneven between the primary and secondary study areas (with respect to soil and biological samples). For example, a total of 127 soil samples were collected from the Primary Study Area, 112 from the control area but only 36 soil samples from Secondary Study Area. Twice as many soil samples were collected from woodlots in the Primary Area (34) than from woodlots in Secondary Study Area (17). The opposite was often observed for some of the biological data where more samples were collected from the secondary area (e.g., earthworm data, frog survey data). Site characterization and specific sample sites need to be more clearly presented in this report and where unequal sampling occurs, a rationale should be provided to justify that site characterization is adequate and that subsequent statistical analysis is not biased.
- 2. The soil sampling conducted for the woodlots was highly variable. In numerous cases, only one soil sample was collected and chemically characterized for COC levels. For Woodlots where additional soil samples were collected, the number of soil samples was usually low (i.e., 4 or 5 samples from Woodlots 4, 5, 11, and 14). In fact, only two woodlots appear to have been adequately characterized: woodlot 3 (11 samples) and woodlot 7 (9 soil samples). It is difficult to interpret the COC concentrations for those woodlots with only one soil sample given the relationship identified in the report between soil COC levels within Woodlots (and elevated concentrations on the windward site). Additional information should be provided to identify where within the woodlot these soil samples were collected and how representative they may be of expected conditions across the woodlot.

3. At present, there is no serious attempt to relate COC levels in soils (and potential for adverse effects) with distance from the refinery. Often the entire study area is lumped together resulting in an inappropriate averaging of areas with extremely elevated COC concentrations with areas with lower levels of COCs. For demonstration purposes, we have selected woodlots 2, 3, 7, 8, 11, and 12 as they fall more or less along an easterly transect downwind of the refinery out to approximately 4 km. The average (or typically the only soil Ni) concentrations for these woodlots are: 22,700 ppm, 15,257 ppm, 2,498 ppm, 2,025 ppm, 642 ppm, and 288 ppm. Even with the low sample sizes (number of soil samples are 1, 11, 9, 1, 4, and 1 respectively), a clear relationship between decreasing Ni concentration and increasing distance from the refinery is apparent (see Figure 1 below).

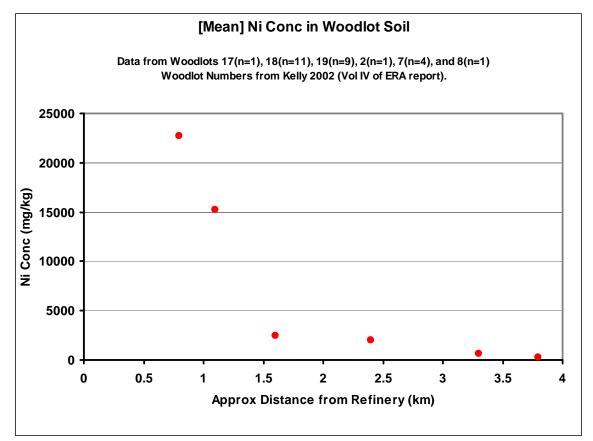


Figure 1.

4. No or very limited biological samples were collected from the main plume area north east of the refinery. A concentration gradient downwind of the refinery was observed with soils collected along the main plume area (see Comment #26; Figure 2 below). The lack of biological samples from these areas limits the ability to conduct a proper analysis of distance to the refinery along the concentration gradient in the soil. Please provide a rationale supporting why biological samples were not collected from this area and include a discussion on the limitations of not having this data on interpreting the conclusions of the report.

- 5. Potential for adverse effects to Amphibians. Amphibian calling sites are unequal between the primary (n=10) and the secondary study area (n=20). Two sites within the primary study area are located in the Rodney Street community that should not be flagged based on poor habitat suitability (since urban environment). Hence, frog calling sites within the Primary study area are limited to Sites 17 to 22 and 26 (n=8). Based on the information provided in the amphibian survey field data, chorus frogs, spring peepers, and the American toad appear to be common across the entire study area. However, it is stated in the report that the expected high densities of spring peeper and chorus frog at quality breeding sites were not encountered. It is also stated that there may be some suppression in population numbers but not at levels that affect long term persistence of frog and toad populations in Study Area. In addition, the American Toad was not found at sites 17 or 26 on any of the 4 visits. Since the American Toad was found at every other site from across the study area, the absence of the toad at these sites within the primary study area should be noted and discussed. The authors conclude that the potential risk of soil COCs to the maintenance of frog and toad populations in the Study Area are low despite a hazard quotient (HQ) of 18 for Ni (based on toxicity data for tadpoles from the literature). The low densities observed at the breeding sites may suggest that an adverse impact is in fact occurring resulting in reduced peeper and chorus frog numbers. Based on the observations in the breeding call survey, the conclusion that potential risk to frog and toad populations are not at risk is not fully supported.
- 6. Overall, the authors conclude that they are highly confident that the ERA has shown potential risks to VECs in the Study Area are not underestimated. The rational given for this conclusion is that it is based on the use of site specific data (scientifically credible sampling) as well as scientifically defensible data from the literature. Generally, we agree that site-specific data is very useful in determining actual risks at a site. However, the author's conclusions rely heavily on site-specific data sets which are relatively small considering the size of the Study Area being assessed. Overall, this report does not provide enough information (as currently written) to support the authors claim that they are "highly confident" in the ERA results. Additional rationale is required to support these concluding statements (as discussed below in our specific comments). In addition, there should be a discussion of the uncertainty associated with such small data sets in the uncertainty analysis.
- 7. The goal of a risk assessment report is to evaluate the potential risk to the natural environment; not to determine if there is an immediate need to mitigate or manage risk to the natural environment. If the results of the risk assessment identifies that adverse impacts are occurring, then potential risk management measures may be considered. This should be clearly noted in the report. In addition, the executive summary should clearly note that adverse effects were identified for some soils

that have Ni concentrations in excess of the soil intervention levels and these specific adverse effects should be noted.

- 8. The report should provide additional information on the generalized linear model procedure and how to interpret these results. How do these models account for unequal sampling between Primary and Secondary study areas? What are the underlying assumptions for these models?
- 9. Presentation of data is often limited to means or tables of simple summary statistics. Often Figures are more effective for interpreting these statistics. In general, the use of Box plots or other graphical plots with data grouped by primary, secondary and reference areas (and by soil or habitat type as appropriate) should be provided when summarizing chemical and biological data. In addition, full data summary statistics and information on the underlying data distribution are often not provided or summary statistics are missing or incomplete. This information should be provided.
- 10. The application of the earthworm Ni TRV is troubling as it appears estimated Ni bioavailability is being double counted; once in developing the Ni TRV (where a high TRV is selected based on minimal bioavailability of Ni oxides) and again where the total Ni concentration in the soil is modified to estimate the bioavailable fraction based on a water extract or acid ammonium oxalate extraction (see Section 8.3.3.1). Total Ni in soil should be compared to the Ni oxide TRV and a bioavailable estimate of Ni (water and acid ammonium oxalate extract) should be compared to a bioavailable Ni TRV (e.g. 100-200 mg/kg as soluble Ni salt). It is not appropriate to compare Ni oxide effects (based on total Ni) to exposures modified to estimate a bioavailable fraction.
- 11. Additional clarification is required to support the statement that the 20% effect level should be considered a No Observable Effect Concentration (NOEC). Clearly, if 20% of the test species are affected, then an effect has been detected. A No Observed Adverse Effect Level (NOAEL) would be the highest concentration tested that was not statistically different from the control. In a properly conducted toxicity test, a NOAEL is often found at concentrations less than 20%. Please note that the use of the 20% effect level in this risk assessment is generally acceptable. The only concern would be for species of special concern where a lower effect level may be required. Overall, the 20% effect level should not be referred to as a no-effect level; rather it represents an acceptable effect level for most VEC species.
- 12. Greenhouse and field bioassays were conducted with Pt. Colborne soils and crops (oat, soybean, radish, corn). A field program was also conducted using golden rod (the reviewer assumes it is the common *Solidago canadensis*, an old field colonizer). This one field herb species is used to represent over a hundred herbaceous species, many of which are woodlot plants. No rationale is provided as to why one or two woodlot species were not included in the study. It is not

clear how these bioassays results are applicable to herbaceous plants expected in the under-story of woodlots; some of which may be more sensitive to Ni and/or other COCs. For example, there is no information on the relative toxicity of Ni (and other COCs) to various natural herb plants in the Study Area with respect to the test plants from the ERA Crop Study report. At a minimum, the relative toxicity of goldenrod to other herbaceous plants needs to be provided to put the bioassay results into context. These species may be more (or less) sensitive than the test species used in the Crop Study bioassays. The conclusions of the ERA-Crop Study report and their applicability to the natural environment should be summarized in this report. A rationale should be provided to support using the bioassay results from the Crops Study to predict potential adverse impacts to herbaceous plants.

- 13. The Niagara Region has 38 tree species and 46 shrub specie but this ERA only addressed one tree species (a soft maple) in any detail. The report notes that there are four provincially rare species in the Pt. Colborne area (i.e. Hop tree, Pignut Hickory, Pin Oak, Swamp White Oak). However, there is no discussion concerning potential impacts to these provincially rare tree and shrub species. Additional rationale is required that compares the relative toxicity of COCs to maples, and demonstrates that these rare and/or sensitive species are not being adversely impacted.
- 14. This ERA looked at flora and fauna in all fields and woodlots (a total of 21) in the Study Area as a single population and concluded that there are no adverse effects to these populations. We do not agree with this approach as it inappropriately averages the COC concentrations over too large an area and reduces the likelihood of observing adverse impacts to VEC species. For example, a meadow vole in a woodlot is exposed to the COCs in the woodlot. It is not exposed to the average COCs from a "population of woodlots". This approach can also potentially mask real impacts on a local scale. Measurable impacts were observed in a small number of woodlots but may not appear significant when the data is included in a data set for a much larger group of woodlots. For instance, trends that may exist with increased distance from the refinery can become obscured when averaged over a large distance. This issue needs to be addressed in this ERA.
- 15. Specific objectives were proposed by the authors in this ERA with the intention of determining if there is a relationship between effects and soil type/habitat type. One obvious objective that appears to be missing is determining whether a relationship exists between effects vs. distance from the refinery. This relationship needs to be evaluated in this ERA.
- 16. The overall study design is never clearly presented in this report. It is evident that the study design was grouped based primary on COC levels in soil (primary and secondary study area), but also by soil type (clay vs. organic) and by habitat type (field vs. woodlot). The location of actual sampling sites within these categories is

not clear. For example, the information presented in Table 1 of Volume II, Section 18 needs to be grouped by these major categories and illustrated in a series of Figures. It is also very difficult to determine what data was used in this report. Additional maps, figures, and tables are required that clearly summarize sample locations, data sources, and data results. If this information is available in other reports, then the specific locations in these reports should be identified. The large inset maps (map #1 and #2) have too many different types of data/samples included on them to be useful. Instead they are simply confusing and very difficult to interpret. Please provide Figures grouped by different types of sample data so it can be readily understood.

- 17. It is stated in the report that risk characterization was done for the entire Study Area including both the Primary and Secondary Study Areas. Populations representative of either the Primary or Secondary Areas were not assessed independently of each other. Therefore, it is not possible to determine if risks to populations in the Primary Study Area were higher than in the Secondary Study Area. This analysis needs to be conducted. Also, there is no mention of any evaluation (or discussion) of special areas considered significant (ANSIs, ESAs, PSWs).
- 18. Section 2.1.1. Overall, very little information is provided in this section to provide an historical overview of contamination. Instead, some information is provided to illustrate metal particulate emissions from the refinery over time.
- 19. Section 2.1.2. This section states that the list of selected contaminants of concern (Ni, Cu, Co, As) resulted from meeting three conditions. No information is provided concerning the COC selection process; the section just refers to three independent JWEL reports that addressed these three conditions. A short summary of the COC selection process needs to be added to this section as the risk assessment should be a stand alone report (i.e., it should not be necessary to review other reports to understand what was done in this ERA).
- 20. Page 2-5. 1st paragraph. The text indicates that the soil data used to generate the isolines in Figures 2-2 to 2-5 is provided in Tab 9 of Volume III. However, only the location of the soil samples is provided; no information is provided on the actual measured soil concentrations for the 4 COCs or information on soil type (or the relative distance and direction from the refinery) in this section. This raw data should be provided as an Appendix to this report and electronically as an excel spreadsheet or Access database on a CD. The text should also include a discussion on the number of soil samples used to develop these isolines and where they were located. In addition, the actual soil sampling locations can be superimposed on these Figures to allow for comparison of soil sample locations and COC concentration isolines.
- 21. There appears to be a number of discrepancies between the concentrations of Ni in soil and the isoline plots. For instance:

- a. Concentrations of Ni in soil were measured at concentrations much greater than the 4000 ppm isoline (e.g., In woodlot #3 located east of Reuters Road, the maximum Ni concentration was 33,000 ppm; mean was 15,300 ppm). Why are these elevated Ni concentrations not identified in Figure 2-2? Given these extremely elevated Ni concentrations, it is not acceptable to simply use the 4000 ppm isoline to indicate Ni concentrations greater than 4000 ppm fall within this area. Additional isolines should be added (e.g., 8000 ppm and 16,000 ppm).
- b. Woodlot 7 had a maximum Ni concentration of 4,745 ppm (mean of 2,498 ppm) but appears to be located between the 1000 and 2000 ppm isoline.
- c. Woodlot 8 has a Ni concentration of 2000 ppm based on a single soil sample but appears to be located between the 500 and 1000 ppm isolines.
- d. No data was collected from Woodlots #1 and #2 west of Reuters Road (a few samples were collected from open spaces along the north-east corner of Reuters Road). The single soil samples collected from each of these woodlots east of Reuters Road indicate very high Ni levels (12,900 and 22,700 ppm respectively). Given these elevated concentrations east of Reuters Road based on limited soil sampling, the lack of data west of the road is troubling and raises significant concerns regarding the accuracy of the 4000 ppm isoline.
- 22. Tab 9, Volume III. What was the sampling design used to collect these soil samples. It is not apparent from this Figure how soil samples locations were determined or who collected them (JW, AMEC, or MOE).
- 23. Page 2-5 2nd paragraph. The statement is made that "for both clay and organic soils the zone of potential adverse effects of soil COCs on area's biota and ecological processes is from the soil surface to a lower depth of approximately 20cm" and that "the soil depth 0-5cm interval represents a zone where COC values are considered to be representative of higher concentrations". However, Table 2-2 indicates that the highest metal levels were often observed in the 5-10 and 10-15 cm depth, yet sampling throughout the study area was taken at the 0-5cm depth only. This raises concerns that the COC concentrations in surface soil in the Study Area may not have been properly characterized because the 5-10 and 10-15cm depth was not sampled throughout the Study Area (especially in heavy clay soil). This needs to be addressed in the ERA report.
- 24. This ERA concentrates on woody species (i.e. trees and shrubs) but the vegetation that may be most impacted by contaminants in surface soil (0-5cm depth) would be shallow-rooted herbaceous plants established on the forest floor as well as in old fields. Tree seedlings would also fall into this category. The "woodlot health study" targeted mature trees only. No "field health study" was conducted to assess field herbs and grasses. Justification should be provided for limiting the 'health studies' to only mature trees in woodlots. The lack of this information should be discussed in the uncertainty section.

- 25. Figure 2-6. Please note that that the numbering of these woodlots is inconsistent in the ERA report and the appendixes: these woodlots are numbered 2, 3, 7, 8, 11, and 12 in Figure 2-6 of this main report (Vol I) but are also numbered 17, 18, 19, 2, 7, and 8 in the Kelly 2002 report [see Figure 4 of Volume IV of the ERA report]). A clear Figure/Table is required to delineate Woodlots, soil characterization (including COC concentrations), and terrestrial data collected so information in the Kitty 2002 report can be properly compared to information in the main ERA report.
- 26. Page 2-13. Tables 2-5 and 2-6. Similarly, additional information on metal levels in soil in relation to the distance to the refinery should be provided in a Figure. For example, Figure 4 from Volume IV of the ERA-Crops Studies provides the location of the test pit locations. From this Figure, we have selected several test pits that fall along a NE transect at various locations downwind of the refinery (e.g., Test pits Tp5, Tp6, Tp7, Tp3, J, J1, J2, K, X2, L, and M). We plotted Ni concentration in soil at three soil depth profiles (0-5, 5-10, and 10-15 cm) with distance to the refinery along this "NE transect". This figure clearly illustrates that Ni levels decrease significantly with distance from the refinery and that Ni levels are not always highest in the 0-5 cm soil profile (as suggested by the authors on page 2-5). (see Figure 2 below)

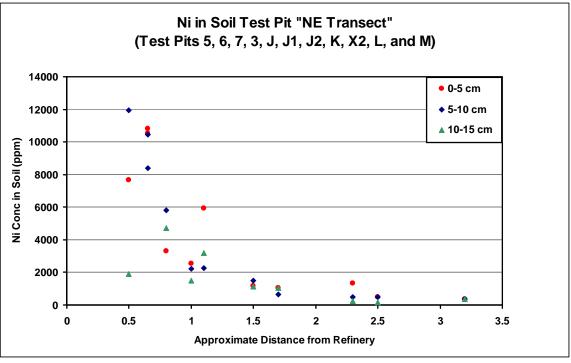


Figure 2

27. Page 2-15. Tables 2-8 and 2-9 illustrate that the % leaching of Ni and Cu was 100 fold higher in DTPA extracts than aqueous extractions in organic soil and clay

soils. The authors state that when considering conditions in the Study Area, aqueous extraction are the closest representation of potential conditions (e.g. rain and snow). We disagree. DTPA is a better representation as it is likely closer to the extraction of COCs by root exudates in the rhizosphere. Thus, Ni and Cu availability to plants may actually be much higher than suggested in this Section. The section should be revised to reflect this fact.

- 28. Table 2-10 illustrates that COC concentrations (Ni, Cu, Co) in sediment decrease with increased distance from refinery (primary versus secondary areas); however, As is the exception whereby sediments in the reference area were found to have higher As than sediments in the Primary Area. Some explanation as to why this might be occurring should be added to the report.
- 29. Page 2-16. The maximum and mean Ni concentrations measured in pond sediment exceed the Provincial Sediment Quality Guideline (PSQG) Severe Effect Level (SEL) in the primary and secondary study areas (the SEL is 75 mg/kg for Ni, 110 mg/kg for Cu, and 33 mg/kg for As; there is no PSQG for Co). In addition, the PSQG Lowest Effect Level (LEL) is exceeded for Cu in the primary and secondary study areas and the reference areas (LEL = 16 mg/kg). This should be addressed in the report.
- 30. Page 2-23. Concentrating on data from the Wignell and Beaverdam Drains, the higher Ni concentrations were observed in surface water in areas closer to the refinery and surface water Ni concentrations were greater in woodlots than in fields. The predation of aquatic invertebrates by terrestrial receptors is a potential ingestion pathway but aquatic invertebrates were not sampled from these drains. The authors should provide a rationale for excluding this exposure pathway from the ERA. Also, it appears that the units in Table 2-11 should be mg/L instead of mg/kg. The mean concentrations of Ni, Cu, and Co in the primary and secondary study areas exceed the Provincial Water Quality Objectives (PWQOs) to protect aquatic life. The PWQOs are 25 ug/L for Ni, 5 ug/L for Cu, and 0.9 ug/L for Co. The PWQO for As is 100 ug/L and was not exceeded in these surface water samples. This should be addressed in the report.
- 31. Overall, the TRV selection is incomplete. In many cases, insufficient information is provided to summarize the critical studies or how the TRVs were selected.
- 32. Page 6-40. The report states that a bioavailability study in rats is described in the HHRA. The information reported in this ERA is vague and only notes that rats were fed organic and clay soil from the Pt. Colborne study area with known COC concentrations. No information is provided on the details of this study (e.g., number of soils tested, COC concentrations, study design, etc.). Ni concentration in blood was measured and Ni concentrations in blood, urine and tissue were calculated. Soil Ni concentrations were compared to blood Ni concentration and % bioavailability was estimated. This study concluded that the % bioavailability of Ni is 3.2% for organic soils and 3.9% for clay soils and these results were

applied to many of the receptors assessed in this ERA. For transparency reasons this study, including the data and the corresponding calculations, need to be summarized in the ERA report (rather than simply referring to the HHRA which is in a separate report). In addition, while we agree that an assumption of 100% bioavailability would likely overestimate the true fraction that is bioavailable, we have some concerns with relying solely on the in-vivo bioavailability data presented in the HHRA report. We have not reviewed the entire bioaccessibility report at this time. However, we understand that only 3 soil samples were tested (clay soil, organic soil, and fill from the Rodney Street area) and each had a Ni concentration of about 10,000 ppm. Rats were exposed to a single dose of contaminated soil and blood was collected over 72 hours. Since only the tests done with the clay and organic soil are appropriate for estimating Ni bioavailability for this ERA, the sample size is quite limited (n=2). In addition, there is no dose-response information on percent bioavailability at different soil Ni concentrations (e.g., does Ni bioavailability vary at different total Ni levels in soil?). There is also some uncertainty with regard to interpreting a single dose exposure with expected chronic exposures and if that would influence expected bioavailability estimates. Pending addition information, it may be acceptable to use this information in the ERA but not by itself. We understand that in-vitro information is also available that estimated the bioaccessible fraction. Both should be reported and used in subsequent data analysis; not just the in-vivo estimate.

#### SPECIFIC COMMENTS

#### **VOLUME I – MAIN REPORT (including Appendices A to D)**

#### **EXECUTIVE SUMMARY**

33. The concentration of soil Ni is highest in woodlots located nearest to the refinery with the highest soil Ni levels being observed on the windward edge of these woodlots. The Executive summary does not indicate whether similar comparisons were carried out in other woodlots sampled throughout the Study Area. Also, woodlot soil was shown to accumulate significantly more COCs than in adjacent fields near the refinery (e.g. the Ni ratio for woodlot soil to field soil is stated to be 7.7 at a distance of 1 km). Was this scenario evident across the Study Area? Given this relationship, the uncertainty associated with characterizing individual woodlots where only 1 soil sample was collected would be expected to be quite high. These single data points may (or may not) be reflective of the actual conditions found within the woodlot. The Executive Summary or main report should explain why such a difference in soil concentrations might occur (e.g. one possible explanation is that during the growing season, a much higher surface area of foliage up in the forest canopy may intercepts more particulates than grasses and shrubs growing at ground level in adjacent fields).

- 34. Four environmentally sensitive areas are recognized in the Niagara Region that fall within the Study area but no information is provided as to whether or not there were any adverse impacts observed or predicted for these specific significant areas:
  - Nickel Beach Wetland (58ha) PSW (in Primary Area)
  - Nickel Beach Woodlot (47ha) ESA (in Primary Area)
  - Weaver Road Woodlot (82ha) ESA (in Secondary Area
  - Humberstone Swamp/Forest (82ha) PSW, ESA, ANSI
- 35. The report concludes that based on the ERA results and data analyses; there is no unacceptable risk to the natural environment in the Study Area as a whole and that there is no immediate need to mitigate or manage risk to the natural environment. It is premature to make this concluding statement given the number of uncertainties with this ERA. For example, there are several caveats to consider which may add significant uncertainty to the ERA study results and conclusions:
  - a. decomposers (i.e. earthworms) were shown to be adversely impacted in woodlots with organic soil near the refinery
  - b. the leaf litter study did not use standard methods to determine decomposition rates; a proxy method was used which severely reduces the usefulness of this line of evidence,
  - c. risks to 36 tree species and 48 shrub species were only partially determined from toxicity tests based on one tree species,
  - d. due to time and resources limitations imposed early in the study, no data is available from a quantitative or a qualitative terrestrial survey to determine the health of herbaceous species in fields or woodlots.
  - e. The data characterizing the site is highly variable and limited given the size of the study area. This introduces considerable uncertainty as results are averaged across the entire area (apparently without considering the influence of uneven sampling).
  - f. The data was collected in the early 2000s. While it is unlikely that conditions have changed very much over the last 8+ years, the lack of current data should be identified as a limitation.
  - g. No analysis was conducted to examine the relationship with potential adverse impacts and distance from the refinery. Instead results are averaged for the whole study area; severely limiting the ability to identify adverse impacts in areas with elevated COC levels in the vicinity of the refinery.
- 36. Table ES-4 summarizes COC concentrations is surface water. However, the data is reported in mg/kg; not ug/L. Is this a typo? All aquatic concentrations should be reported as mass per unit volume; not mass per mass.

## **1.0 INTRODUCTION**

### 1.2 Purpose of CBRA

37. Herbaceous plants were not covered under this ERA because the authors claim they are addressed in the Quantitative crop studies (phytotoxicity testing) ERA – Crop Studies. However, only one herbaceous plant was examined in the ERA Crops Study report: goldenrod. As mentioned previously, the conclusions of the ERA-Crop Study report and their applicability to native vegetation should be summarized in this report with additional detail provided on how the conclusions from that ERA can be extrapolated to the natural field and woodlot plant species which are not addressed in this ERA.

### 1.4.8 General Study Design and Approach

- 38. The study area does not represent all lands in Pt. Colborne where soil Ni concentrations exceed the 200 ppm MOE standard for Ni. The authors explain that for the ERA to be completed on schedule, the collection of biological data began before all soil data collected was analyzed. It is possible that this may have introduced bias or error in the results. It is unfortunate that the initial project schedule took precedence over ensuring that adequate, high quality scientific data was collected, especially given the extensive time period that has elapsed since the data was collected back in 2001-2003.
- 39. Page 1-8 how are these earlier MOE reports used? Data clearly indicate injury was observed in maple trees closest to the refinery and that tissue levels dropped off 30 km away (Smith 1975). How does the data collected for this study compare to this historical data?
- 40. For this ERA, a sustainable level of ecological functioning was selected as the most appropriate level of environmental protection desired. Measuring sustainability, such as determining a decline in VEC population numbers over time (e.g. changes in birth rate and/or mortality rate, emigration and immigration), generally requires measurements and observations to be taken over a number of growing seasons/years. In this ERA, sampling was all done within a single season. The authors should clarify how population(s) 'sustainability' was determined, based on a single year's data.

### 2.0 PROBLEM FORMATION

#### 2.1.1 Historical Overview of Contamination

41. Page 2-1. This section should clearly state that "particulate emissions" included metals since this risk assessment is focused on elevated metals in soils; not elevated "particulates".

- 42. Page 2-1 last paragraph. It is stated that the downwind area (to the northeast) has been exposed to the greatest deposition (of metals released from the refinery) from 1918-1960. Sampling for this ERA occurred 40 yrs after this period. This section should also discuss chemical speciation of the various COCs and any potential changes resulting from weathering processes and/or natural attenuation which may have occurred over this lengthy period.
- 43. Page 2-1. For completeness, please add information on non-particulate emissions from the refinery.
- 44. Page 2-1. 2nd last sentence. What is the basis for the statement that "potentially harmful environmental effects on local biota ... are considered to have been greatly reduced compared to past elevated soils". Is this simply that emissions have been reduced or is there data available on adverse environmental effects when emission levels were higher? If so, please summarize this information.
- 45. Page 2-1. Last sentence. Add summary details from McLaughlin and Bisessar (1994) of how levels have remained unchanged.

### 2.1.3 Drainage Characteristics and General Soil Types

- 46. Page 2-4. Please identify where in this risk assessment report the "COC plume" identified by JW is located. If not, please add this information to the report.
- 47. Page 2-4 last sentence: "For simplicity, field data collection efforts focus on three general soil types; clay, organic and sand." Additional rationale is required to justify lumping clay loam, heavy clay and shallow clay into one group as these clay soils can differ in drainage and aeration properties.
- 48. Page 2-5 2nd paragraph. Please provide summary details of the test-pitting program (how many test pits (n=44?), where collected, etc.) and specifically where this information can be found in the ERA-Crops Studies report.
- 49. Page 2-10. Table 2-2. The range of metal concentrations should be provided from low to high; not high to low. Add sample size for each soil type to this table.
- 50. Page 2-11. Table 2-4 only provides information for 3 soil samples at various distances from the refinery. A figure with data from additional sites would aid in identifying this relationship and providing context on the geographical area of elevated metal levels. For example, as noted in our major comments, we developed a transect due East of the refinery that crosses several woodlots to more fully examine this relationship (Figure 1 above). This Figure supports the relationship that Ni soil concentrations decrease significantly with distance from the refinery.

- 51. Table 2-5 shows soil COC concentrations for field sites. The maximum soil Ni was observed in the Primary Study Area (10,525ppm); the mean for fields in the Primary Area was 1,354ppm Ni. There is no information provided concerning the location of this field but it appears that it was not the field adjacent to the woodlot with the highest soil Ni concentration (33,000 ppm in woodlot; 1,860 ppm in the adjacent field). Locations of field sample sites need to be clearly illustrated. In addition, was there a field inventory carried out of the plant species established at this (and other) field sites to determine if there were any observable adverse effects (e.g., reduced species diversity)?
- 52. Table 2-6 shows soil COC concentrations in the woodlots. The maximum soil Ni concentration was much higher in the Primary Area (33,000 ppm soil Ni) than in the Secondary Area (2,110 ppm soil Ni). The woodlots in the Primary Area are in closer proximity to the refinery, and based on the soil data, appear to have higher soil Ni concentration (as shown in Table 2-10). However, data from the woodlots were not assessed as a function of distance from the refinery, which may identify significant trends (as noted in previous comments).
- 53. The maximum Ni concentration in surface water is 1,045 ug/L; not 429 ug/L as shown in this Table. For some reason, not all of the surface water data was used in the summary statistics. This is troubling as the report does not make any mention of why this data point was removed. If there are concerns with the data quality of any of the sample results and they were not used in subsequent analysis, then this needs to be clearly discussed in the report. In general, unless there is overwhelming evidence to the contrary, all data should be used in the subsequent analysis including apparent outlier values since that may in fact represent actual elevated concentrations in the environmental media.

### 2.1.3 Hydrological Parameters

- 54. Note: under Reg 153/04 as amended, the Ministry developed aquatic protection values for the groundwater to surface water pathway. These APVs are 39 ug/L for Ni, 6.9 ug/L for Cu, 5.2 ug/L for Co, and 150 ug/L for As. Groundwater results could be compared to these APV values. Note: Table 2-10. The maximum Ni concentration in surface water is 1,045; not 429 as shown in this Table.
- 55. Page 2-25. 1st sentence. Revise "historical dust deposition" to more accurately reflect RA is examining particulate metal emissions from the refinery.

## 3.0 ECOLOGICAL SITE CHARACTERIZATION

56. Please add a rationale supporting why no effort was made to conduct a semiquantitative or quantitative assessment of the ecological risks of COCs within these urban areas of the City of Port Colborne. At present, there is no assessment of potential ecological risk in these urban areas.

#### 3.1 Identification of Study Area

57. Page 3-1 Section 3.1. The ERA does not provide any explanation for (inappropriately) combining the Primary (>500 ppm Ni in soil) and Secondary (>200 ppm Ni in soil) Study Areas into a single study area for subsequent data analysis. Combining the data from the two study areas into a single study area, and treating the two separate data sets as one data set, confounds the ability to determine if receptors in the "Primary Area" are at greater risk than those in the "Secondary Area". In fact, the report provides several reasons why these areas should be kept separate (e.g., page 3-1: elevated concentrations of COCs in primary area "is assumed to represent an area where ecological receptors would have a higher potential risk" and page 3-2: primary study area focus of field investigations since area has "been identified as significant natural areas by the Regional Municipality of Niagara").

#### 3.2 Assessment Methods for Site Characterization

- 58. Page 3-2. Several rare species and significant areas are identified here and a statement is made that field studies focused on natural habitats located in the Primary Study Area as they represent significant natural areas identified in the Regional Municipality of Niagara. The reader is referred to Section 3.4 for details but this Section deals with soil types; not significant areas. This discrepancy should be corrected.
- 59. Page 3-2. The winter surveys conducted between December 2001 and February 2002 provided an opportunity to document mammal tracks after snowfalls. We were unable to find any information in this report which summarizes the results of the winter surveys? Was this data collected?
- 60. Page 3-3. Four factors are provided for not including qualitative investigations into species richness of non-woody vascular plants in Study Area. It is very unfortunate that the opportunity was lost to investigate herbaceous species richness to determine if there was a change in species numbers, composition and absence/presence with increased distance from the refinery/COC levels in soil (e.g. species diversity could have been measured along several transect points). As no data is provided on the "inherent variability of plant species richness between sites", it is not possible to determine if this data would have been useful or not. Also, the argument of high variability in observations due to the presence of heavy clay soil, cattle grazing and micro-habitat conditions could also apply to the trees and shrubs which were surveyed (i.e. these factors would affect seedling establishment and growth). In fact, the study design could have been targeted to specifically address the importance of some of these potentially confounding factors. Finally, we note that some information is available in the Kitty 2002 report (Volume IV) on herbaceous species. This information should be evaluated and discussed in this RA.

61. Page 3-4. The authors state that most of the rare plants and animal species were recorded in the Wainfleet Bog wetlands, Mud Lake and The Clay Pits which are outside the Study Areas. Since these areas also have low concentrations of COCs, it is possible that rare plants and animals have not been recorded in similar habitats in the Study Area because of adverse effects resulting from the presence of elevated metal concentrations in the soil (or other factors may be involved). The ERA should address this issue. For example, is habitat present in the study area where these rare plants and animal species would be expected to occur? If so, what factors may be responsible for their absence?

### 3.4 Soil Types

62. Page 3-7. Five soil types are identified; heavy clay, shallow clay, clay loam, organic, and sandy. The organic soils (69-80% organic content) lay 40 to 160cm over silty to clayey mineral soil and have a soil pH 4.8 to 5.6. This soil is acidic compared to the clay soils, and is highly permeable with a high water holding capacity. Under these acidic conditions, it is possible that a relationship may exist between low pH in the organic soil and increased COC availability to plants and soil invertebrates. However, the elevated organic matter would act to reduce COC availability. The authors should discuss this relationship between soil pH, organic matter, and COC bioavailability in more detail in this report.

### 3.5 Known Significant Natural Features

- 63. Page 3-9. There are several significant natural areas located in the Primary and Secondary study area:
  - 1) Nickel Beach Wetland –PSW (Primary Area)
  - 2) Nickel Beach Woodlot ESA (Primary Area)
  - 3) Weaver Road Woodlot ESA (Secondary Area)
  - 4) Humberstone Swamp/Forest PSW, ESA, ANSI (Secondary Area)

However, the ERA does not provide any meaningful discussion on how COC may impact rare species or these specific areas of significance. The presence or absence of potential impacts to these four significant areas should be discussed in the ERA.

64. In addition, based on the soil sample locations described in the Figure in Tab 9 Volume III, no soil samples were collected from the Nickel Beach Wetland or Woodlot West of Reuters Road. This is surprising given that these are significant natural features. It appears that only the Weaver Road Woodlot has been comprehensively sampled (soil, surface water, leaf litter, maple leaf, woodland insect, earthworm, tadpole and frog survey). Based on the information provided in Map 1 and Map 2, it appears that only 1 surface water sample was collected from the Nickel Beach Wetland and that 2 surface water samples were collected from the Nickel beach woodlot. One sample was also collected from the Nickel beach woodlot for maple leaf and woodland insect analysis. Samples from the Humberstone Swamp/Forest are limited to maple leaf, woodlot insects, and frog survey and maybe one soil sample (see Tab 9 Volume III). Given that these are known significant areas and have elevated COC levels, the relevant chemical and biological data for all 4 of these significant natural areas should be discussed.

### 3.7 Significant Vegetation Communities

- 65. Page 3-12. The Nickel Beach Woodlot is an undisturbed Lake Erie shoreline dune complex supporting a number of rare Carolinian tree species. For this reason it is considered an environmentally sensitive area. In addition, the mature Red Maple swamp on the INCO site is part of a provincially significant area. Both features are located in the Study Area east of the refinery but potential impacts are not addressed in any detail in the ERA. Some discussion of potential impacts to these areas is warranted.
- 66. Page 3-13. How does the number of tree and shrub species identified in the primary study area compare to the numbers observed in the reference sites? These data indicate significant species richness for tree and shrub species but no data is provided to support the statements that over 90% of the tree species and 80% of the shrub species that should occur in the areas were recorded in the primary study area. In addition, please provide the data to evaluate the relationship between species richness and distance from the refinery within the primary study area to support the statement in the 3rd paragraph that "the vast majority of the tree and shrub species were found growing on the lands directly adjacent to the Inco refinery". While COC levels are highest here, the type of organic soil is also likely to dramatically reduce the bioavailability of these COCs. Hence, the reason for this enhanced species richness may be due to the lack of disturbance associated with agricultural practices. Also, please provide the data on relative abundance of these species by habitat type (we assume this information is available given the statement that "Most of the species occur in general abundance where suitable habitat is present").
- 67. Page 3-16. Several Carolinian zone tree and shrub species are present in the Study Area which lies at the extreme northern limit of the Carolinian vegetation zone. For this reason these species are provincially (and even nationally) rare. They are:
  - Pignut Hickory sand dune forest inland from Nickel Beach and dunes
  - Pin Oak wet forest around refinery
  - Swamp White Oak wet forest around refinery
  - Hop tree 5 individuals in SE corner of refinery site at sand dune forest interface.

There is no discussion to show whether any attempt was made to determine the status of populations of these rare trees/shrub species in the Study Area (e.g. tree health, recruitment measurements/seedling establishment). The ERA should

provide some information concerning the status of these five species in the Study Area. Is any information available in the Kelly 2002 report?

## 3.8.2 Birds

68. Page 3-16 to 3-23. Information on breeding birds was collected over two breeding seasons, 2000 and 2001. These data indicate significant species richness in the Study Area; however, for clarity, the section should indicate where the raw survey data is located in the ERA (e.g. provide details/data in an appendix or supporting document).

### 3.8.3 Mammals

- 69. Page 3-24 A total of 20 mammal species were recorded in Study Area (Table 3-8). As with the bird data, this section should indicate where the raw survey data is located.
- 70. Page 3-25. 2nd paragraph and Table 3-9. Where is the data and appropriate comparisons to control/reference sites to support statements that small mammals were "very abundant" and "in good numbers" in woodlots and field edges? Where exactly were the traps set and which traps were successful? Table 3-9 provides trapping results data from 2001; please add the trapping data from 2000.
- 71. Page 3-25, last paragraph. Please provide data to support and put into context the statements of "particularly high density" for the Eastern Cottontail and Gray Squirrel and "high densities" for deer.
- 72. Page 3-28, 3rd paragraph. Add information on where in this report the tadpole and frog tissue analysis is provided. For a large report of this nature, clear internal "signposts" are required to allow the reader to find relevant information quickly and easily within the report.

### 3.8.4 Reptiles and Amphibians

73. Table 3-10 indicates that 9 species of amphibian and 5 species of reptile were recorded in the study area. The eastern milk snake is considered provincially rare. The eastern red-back salamander was found in leaf litter and under logs in woodlots near the refinery. In addition, the snapping turtle has recently been listed as a special concern species in Ontario and nationally. The ERA does not provide any discussion of any potential impacts of Ni and the other contaminants of concern to these significant species. Some discussion should be provided. As before, data needs to be provided/summarized to support statements in this section. For example, the text on page 3-27, 1st paragraph should include information on the actual density of calling frogs estimated during this survey and the expected density based on observations in other areas of Southern Ontario.

74. In the census, spring peepers and chorus frog densities of calling adults were lower than expected compared to other areas in southern Ontario. American toad and wood frog were widely distributed but numbers were low in the study area. A rationale should be provided addressing why these numbers are low for the above species; i.e. is it related to COC concentrations in sediments and water or could other factors be important? Also, tadpoles and frogs were collected for tissue analysis, and to note deformities and abnormalities. This section should indicate where this tissue information is summarized in detail.

### 3.8.4.1Fowler Toad

75. The report states that specific lakeshore surveys were carried out with a number of calling sites; one primary breeding pond with 50 males was located near Lorraine Road. In the May to July 2001 survey, an estimate of 2000 to 3000 tadpoles were observed with full metamorphosis to young adults and complete emigration from the pond was completed in July 17th. Were any observations made of the frequency of deformities and abnormalities in the young?

### 3.10 Summary

76. The authors did not measure plant diversity quantitatively in the Study Area (e.g. utilizing randomly located quadrants in woodlots and field locations). Therefore, for non-woody plant species, the statement that diversity appears typical of the region is not based on quantitative measurements or observations. This should be clarified in the ERA and the lack of a quantitative assessment discussed in the uncertainty section.

### 4.0 RECEPTOR CHARACTERIZATION

#### 4.1 Criteria for VEC Selection

- 77. Detailed data collection of rare and significant species was not considered appropriate because of their low population density. On pg 4-4 the authors state that it is not known if the VECs selected for the Study are the "most sensitive". This suggests that the proposed soil standards may not provide adequate protection to the species declared rare or significant for the Niagara region or other species that the VECs are surrogates for. The issue of providing (or not) providing protection to sensitive species should be addressed in the ERA. This can be done by providing toxicity information on the relative sensitivity of the VEC species to the COCs for this site. That way, the results obtained for these VEC species can be evaluated with respect to the larger groups the VEC species represent.
- 78. Page 4-4 1st paragraph. 1st sentence. The "basic trophic levels found in the ... aquatic environment" are <u>not</u> well represented by the selected VECs. There is no

VEC species to represent phytoplankton, benthic invertebrates, aquatic plants, or fish.

- 79. Page 4-5, Table 4-2. Adult frogs would also be exposed to COCs from soil.
- 80. Page 4-6, last sentence is vague: "Some research has found measures of individual responses are not as sensitive as measures of population responses (CCME 1997)". Please add details on what was measured and if it is relevant to the COCs and VEC species evaluated in this risk assessment.
- 81. Page 4-7. 1st paragraph. A sustainable level of ecosystem functioning implies that some adverse effects/changes to ecosystem structure is considered acceptable as long as ecosystem function is not adversely altered (e.g., unacceptable toxicity to a species population may occur without altering ecosystem function). This possibility should be clearly stated in the report.
- 82. Page 4-7. 2nd paragraph. In general, we have no concerns with using the 20% effects level as a toxicity threshold to evaluate potential adverse effects to most VEC species. However, as noted previously, this level should not be referred to as a NOEC. In general, the use of a 20% effect limit is preferred (except for rare or significant species) since a NOAEL and LOAEL are based on the results of a statistical analysis and are highly dependent on the study design, doses selected, etc., of each individual study.
- 83. Page 4-7, 3rd paragraph. Please add a citation to support that tadpole survival is a particular sensitive lifestage for amphibians.

### 4.3 VEC Characteristics

84. One of the objectives of this ERA is to determine ecological risk at the population level. However, the ERA fails to provide any estimates of mortality rates, or emigration and immigration dynamics for any of the VEC animal populations within or outside of the Study Area. The ERA should clearly state what population measurements were made.

### **5.0 DATA COLLECTION METHODS**

- 85. Page 5-1, Table 5-1 indicates how many stations were sampled for each receptor; As noted previously, a Figure specific to each receptor is needed to show where these stations are located. Map 1 and 2 allows the reader to determine the overlap between the different receptors but is too confusing to be able to readily identify for each.
- 86. Page 5-2. It is troubling that "no rigorous selection criteria" was used to select sample sites. Overall, sampling needs to adequately characterize the spatial scale of the site and reflect potential confounding factors (clay vs. organic soil, woodlot

vs. open field, gradient of COCs based on distance to the refinery, etc.). It is not clear if these conditions were met.

### 5.2 Biological Field Data

- 87. Table 5-1 illustrates that at each station, a single composite sample was taken for tadpoles, arthropods, tent caterpillars, or wild grape; only two or three stations were sampled for tadpoles. Best practices usually dictate that one collects duplicate or triplicate samples from each given station to account for site/sample variability. A rationale should be provided for having only a single composite sample from each sampling site. The lack of an error estimate on these composite samples should also be discussed in the uncertainty section.
- 88. Table 5-1 Why are there limited number of stations for evaluating the meadow vole (n=1 to 3) and tent caterpillars (n=0 to 1)? This is inconsistent with the number of stations for frogs, earthworms, anthropods, maple leaves, and leaf litter where at least 5 stations were sampled from the reference, primary, and secondary areas. Why no bird survey from the reference areas?
- 89. Page 5-4. Please add a summary of the results of the Stantec oversight (e.g., data was collected as per protocols, duplicate samples collected by Stantec were typically within x%, etc). Since Jacques Whitford was purchased by Stantec, a footnote should be added here (or elsewhere) to indicate how the PLC consultant is not in a conflict of interest due to creation of WEG).
- 90. Table 5-5. It is our understanding that there is a lot of air monitoring data for this area. Why is air data limited to that collected between Aug and Sept (presumably in 2001)? How does this compare to the larger air dataset? Is it appropriate to use only this air data for this report?
- 91. Page 5-8. It is unclear why the composite samples for maple key soils, maple leaf soils, and vole soils are so small (n=1-2). Please provide supporting rationale.
- 92. Figure 5-1. Figure indicates that the analytical data was corrected for moisture content but is reported on a dry weight basis. Is this correct? Shouldn't the data be reported on a wet weight basis if corrected for moisture content? How was the data corrected for moisture content?
- 93. Page 5-10. Section 5.4.2. Add summary results of these SRM analysis (e.g., in general, SRM were within x% of nominal concentrations).
- 94. Page 5-11 Section 5.4.5. What type of plastic sample bottles was used (e.g., PE, PP, PET)? Where they cleaned and acid washed prior to water collection?
- 95. Page 5-12. Add a short summary of the results of the duplicate analysis.

### 6.0 EXPOSURE ASSESSMENT

- 96. Page 6-7, Section 6.3.1. Please add a brief summary of sources of contaminants. As currently written, the reader must consult other reports to find out even basic information on the source of COCs to the study area.
- 97. Page 6-7, Section 6.3.2. COCs from refinery emissions in receiving media should also include subsurface soils (via translocation from surface soils and new soil created after deposition occurred).
- 98. Page 6-7. Section 6.3.4. It may be appropriate to assume that exposure to COCs to a population of VEC species occurs through-out the entire Study Area for large home range species (e.g., deer). However, this assumption is not valid for small home range species or for ecosystem processes such as litter decomposition. For example, it is unreasonable to assume that the Meadow Vole (home range of between 300 and 900 m<sup>2</sup>) is exposed to average conditions across the entire Study area. In addition, given the significant relationship between COC levels in soil and distance from the refinery, assuming exposure to average COCs levels (i.e., exposure from the entire study area) inappropriately reduces the exposure and potential risk for species living in close proximity to the refinery. Additional discussion is warranted on what constitutes a population in the report. For example, we do not have a population of Woodlots. For small home range species and terrestrial plant species living within a woodlot, the "population" or "subpopulation" may be limited to each woodlot (depending on species-specific opportunities for interaction between woodlots).
- 99. Page 6-8. end of 2nd paragraph. Exposure from soil and water can also be evaluated.
- 100. Page 6-8, end of 3rd paragraph. Should indicate in the uncertainty section that it is recognized that additional exposure can occur (but was not assessed quantitatively) and that should be considered when discussing predicted risk results.
- 101. Page 6-9, 3rd paragraph, last sentence. Even though meadow voles prefer field habitat, they should be considered a VEC species for woodlots. Otherwise, there is no assessment of small mammals in woodlots. The meadow vole could be used as a surrogate species for small mammals that would be expected to reside in the woodlot (e.g., mice).

### 6.3.4 Whitetail deer

102. Page 6-8. Exposure of deer to Ni, Cu, Co and As was assessed in both field and forest habitats for the Study Area in general. It has been reported in the literature that moose livers in various parts of northern Ontario have been shown to bio-

accumulate elevated levels of cadmium. Were livers in whitetail deer analyzed from the Study Area for Ni, Cu, Co, and As to assess whether or not these metals were accumulating in that organ?

#### 6.3.5 Limitations of Predicted Exposure Routes

- 103. Page 6-9. Snakes were excluded from the Red-tail hawk diet. What percentage of their diet is made up of snakes? Overall, please provide details on what major components of the diet are missing and details on what food items were based on surrogate data.
- 104. Page 6-10. Red fox preys on rodents and birds. Bird COC tissue concentrations were not measured but were predicted using exposure and bioaccumulation factors from the literature. Without measured COC tissue values, the authors were unable to evaluate the accuracy of their predictions but expected that the actual COC concentrations in these birds would be lower than predicted using calculated exposure. No analytical evidence is provided to support this assumption. What if this is not the case? Some discussion should be provided on the uncertainty attached to this statement.

### 6.4 Assessment of Bioavailability

- 105. Page 6-10. Section 6.4.1 First paragraph. We agree that it is not necessary to provide illustrations of BAFs between different receptors for every location or study area. However, this information should be provided in a Table or in an Appendix. Specifically, information should be provided comparing BAF between primary, secondary, and control areas.
- 106. Page 6-10. Last paragraph. Information is presented to describe how the mean bioaccumulation factors (BAFs) were calculated as illustrated in Figure 6-6 and 6-7. No information is provided regarding the raw data used to calculate the mean concentration in surface water and sediments other that the sampling locations. This is insufficient, at a minimum; the relevant location in Volume V of the report should be identified so the actual data can be reviewed.
- 107. Page 6-16. Last paragraph. The fact that a BAF is low or not should not be used to conclude that "COCs are not accumulating to any appreciable degree in plant and animal tissues". The important factor is what is the concentration in these tissues and if levels are significantly elevated over control tissue concentrations. As shown in the frog tissue example (and for other tissue data see Figure 3 after comment 111), concentrations are elevated in tissue samples collected in the primary and secondary areas in relation to control areas. This information is important as it shows that COCs are bioavailable and elevated in tissues. The question of what is the significance of this exposure should be addressed in the risk characterization section. The BAFs values are useful for predicting tissue concentrations for those areas where only soil data is available. A spatial

assessment illustrating COC concentrations with distance to refinery is needed for all tissue samples (e.g., frogs, tadpoles, earthworms, voles, etc).

108. As currently presented, it is not clear how the BAF values were developed. For example, the text should indicate that the BAF is calculated from the weighted average concentration of COCs in whole frog tissue divided by the mean COC concentration in the sediment or the surface water. No information is provided to represent the uncertainty inherent in the BAF value. If we understand what was done correctly, the BAF was determined from collocated samples where data is available from the same sampling location for concentrations of COCs in the environmental media (i.e., water, soil, or sediment) and concentrations of COCs in the tissue levels in the selected VEC species. If that is the case, then BAF values can be determined for each collocated sample and the mean and standard deviation of BAF values can be provided (instead of just the mean). This information is important to evaluate the relative variability in the BAF values. We developed site-specific BAF values using all of the collocated sediment and frog tissue data to determine how variable the BAF values are using the raw data for sediment (Vol V, tab 27), and average frog total Ni concentration (Vol II, tab8) as an example (Table 1).

(Sediment data from Vol V, tab 27; Frog Tissue data from Vol II, tab 8)			
Area	[Ni] in Sediment (mean ± SD)	Total [Ni] in Frog Tissue (mean ± SD)	Mean BA (mean ± S
Primary Area (from Fig 6-6 in report)	$279 (n=4)^1$	4.56 (n=4)	0.02 (n=4
Primary	$432 \pm 354$ (n=5)	$4.04 \pm 2.97$ (n=5)	$0.015 \pm 0.0$ (n=5)
Secondary	76 ± 68 (n=5)	1.88 ± 1.43 (n=5)	$0.035 \pm 0.0$ (n=5)
Control	27 ± 8 (n=5)	$0.82 \pm 0.53$ (n=5)	$0.029 \pm 0.0$ (n=5)

This analysis presented in Table 1 is quite informative. For example:

- A clear relationship is observed in mean Ni concentrations in sediment and frog tissue based on proximity to the refinery (primary, secondary, or control areas); Ni concentrations are higher in sediment and frog tissue indicating elevated exposure in these areas over control areas.
- BAF values are variable within each category (likely due to the large variation in the frog tissue data because it is confounded with body weight).
- BAF values are lower in areas of higher Ni concentration than in areas of lower Ni concentration. Hence, area-specific BAF values should be used in subsequent analysis.

- 109. The text indicates that the COC concentrations in tadpoles and frog tissue represent weighted averages calculated from component tissues that were analyzed. The reader is directed to Volume III, tab 3 for more information. However, Volume III, tab 3 only provides the statistical results from a series of generalized linear models (glm); not information on the measured tissue concentration in frogs and tadpoles. After some searching, the reviewer found the tissue data in Volume II, tab 8. We note that not all the data was used to calculate the BAF for frogs. For some reason, the data from site FH3 was not used. Also tissue data was collected from frogs that varied considerable with respect to total body weight (suggesting large variation in age of individual frogs). It does not appear that any attempt was made to evaluate the potential relationship between body weight and COC accumulation in various tissues of these frogs and if the varying age/sizes of frogs is a source of uncertainty in the subsequent analysis.
- 110. Page 6-13. 1st paragraph. Please provide details on the qualitative or quantitative analysis of the amount of material in the GI tract of these collected frogs and tadpoles.
- 111. Page 6-13. Text states that: Goldenrod contains 0.3% of Ni concentration found in soil. Ni concentrations in field vole tissue were found to be higher than in goldenrod which suggests a degree of bio-accumulation is occurring in the vole. It is possible that the voles are getting the Ni from soil/dust ingestion as well as from ingestion of food and grooming their fur? Also, this section should indicate where the Bioaccumulation factor (BAF) calculations are located in the ERA. The reviewer could not find this information.
- 112. Page 6-16 2nd paragraph. Please provide BAF values from the literature from other metal contaminated soil sites to put these values reported here into context.

#### 6.4.2.1 Summary of Predictor Analysis

- 113. It is stated that soil type and habitat type are generally poor predictors. Did the authors look for correlations between soil pH to COC concentrations observed in biological receptors? Soil pH may be a significant predictor and should be considered in the statistical analysis.
- 114. Page 6-18, Section 6.4.2.1. Last sentence before Table. Volume III does not provide a discussion of the statistical analysis, just the output tables.
- 115. Page 6-18. Table 6-2. The fact that there are significant relationships between COCs in environmental media and biological tissue is very important since it demonstrates that COCs are bioavailable and exposure to VEC species is occurring in a dose-response fashion. In addition to soil type and habitat type, this analysis should also look at grouping the data by primary and secondary

study areas to determine if elevated COCs in biological tissues are related to distance from the refinery.

- 116. Page 6-19, 2nd paragraph. If soil type and habitat type are generally poor predictors, then that suggests that this data can be combined. Alternatively, these factors may be poor predictors because of high variability in the data because of merging the primary and secondary study areas. We don't agree that assessing bioavailability of COCs through a food chain is "well beyond the scope of this study".
- 117. Page 6-20. 1st paragraph. The high variability in the environment is also due to merging the data from the primary and secondary study areas and not controlling potential confounding factors (e.g., size/age of frogs).

#### 6.4.3 Key Receptor Data Used in glms

- 118. Page 6-21. Amphibian COC tissue results are presented in Tables 6-3 and 6-4 with data for the primary and secondary study area combined. In general, Ni, Cu, and Co concentrations are higher in tadpole and frog tissue from the Study Area than from reference area. In most cases, the highest concentrations were observed in the GI tracts of both tadpoles and adult frogs compared to whole body tissue; however, Cu in the frog liver was higher than other tissue sampled. However, there is no discussion of the potential impacts of elevated Cu in the livers of frogs in the ERA. In addition, this trend may not be restricted to frogs only; Cu may be bio-accumulating in livers of birds and mammals in the Study Area as well. Sampling and analysis of Ni, Cu and Co in bird and mammal livers should also have been conducted to determine if the liver results were restricted to frogs only (e.g. whitetail deer, voles, woodcock, etc.).
- 119. Page 6-21. Table 6-3 and similar tables. Data should be presented for COC levels in tissue based on primary and secondary study area and not the entire study area. Often significant accumulation of COCs is measured in tissue when comparing the overall study area to the reference areas. The magnitude of this increase would be expected to be much higher in the primary study area than the secondary study area since that is the area of significantly elevated COCs. However, this information is not provided in this report. As an example, the following figure (Figure 3) shows total Ni, whole body Ni (minus GI tract and liver) and Ni in liver (data from Vol II, tab 8). There is a clear relationship between elevated Ni in tissue and proximity to the refinery with the highest levels observed in the primary study area. This figure also provides a measure of how variable this data is (potentially a result of the large range of age/sizes of frogs collected from the site). Interesting, elevated Ni levels in the frog liver from the primary area is not elevated with respect to the secondary area. However, a clear pattern of increased exposure with distance from the refinery is apparent when examining total Ni or body Ni.

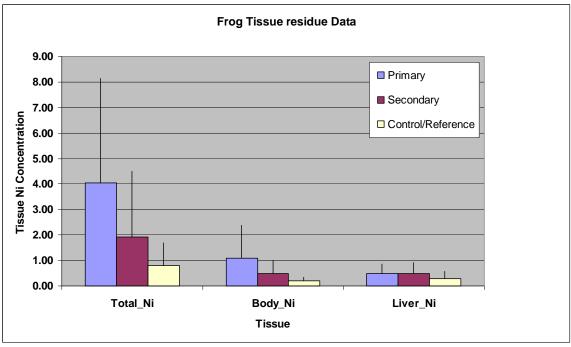


Figure 3

# 6.4.3.2 Maple Tissue

120. Table 6-5 shows that Ni and Cu concentrations were higher in leaves from the Study Area than the reference area although this was not the case for Co and As. Maple seeds were sampled from only 3 individual trees so the data set is very limited. Why was seed not collected and analyzed from as many woodlots as possible to build up a more robust data set. An opportunity was lost to determine possible trends in foliar concentration and distance for the refinery. How do these results compare to earlier MOE reports on Ni concentration in foliar tissue?

# 6.4.3.4 Earthworm Tissue

- 121. Page 6-27, Table 6-10 –The total COC concentrations of whole worm was considered bio-available to animals such as the robin. The authors state that this results in an over-estimation of the concentrations of COC actually available to the bird because the soil in the GI tract is expected to be less bioavailable than the tissue. A soil ingestion rate can be added to the exposure equation to account for the soil in the earthworm's GI tract.
- 122. Page 6-28, Table 6-10. Overall, these ratios have limited value given the low number of sample sites evaluated (between 1 to 4 depending on soil type), high variability in tissue concentrations for each COC for purged and non-purged earthworms, and the fact that the ratios reflect the overall study area and not the primary and secondary study areas separately. In addition, no information is provided on the total metal concentrations in the soils at these individual sites and

if there is a relationship between COC soil concentrations and the ratio observed at individual sites. This analysis should be provided as it is needed to support using this ratio for other earthworm data. Overall, there is considerable uncertainty in using these ratios as correction factors for estimating tissue concentration in earthworms (minus soil/metal in GI tract) that are consumed by VEC species. In addition, it is worth mentioning that the ratio observed from reference sites (about 1.0) is as expected since the soil is not contaminated and the vast majority of the COCs are incorporated in the tissues.

- 123. Page 6-28. Please provide the earthworm tissue data. We were unable to finds it in the material submitted for review. In addition, please clarify what information is presented for earthworms in Vol III, tab 1? The title does not provide enough information and there is no text describing this data (Note: this comment applies to several data tables provided in Vol III were data is provided with no or minimal context).
- 124. Page 6-29 last paragraph. Ni and Co did not "appear to be higher in anthropods", they were higher (by approximately 10-fold for Ni). The high variability may be due to inappropriately merging the data from the primary and the secondary study areas.

#### 6.4.3.6 Meadow Vole Tissue

125. Both Ni and Cu concentrations are much higher in carcass of voles from the Study Area compared to carcasses from the Reference Area; i.e. 14.8 ug/g Ni and 1.5 ug/g Ni, respectively. The ERA should state that based on these data, predators of these voles will be exposed to 10x more Ni than they would be exposed to preying on voles from outside the Study Area.

#### 6.4.4 Summary

- 126. One of the key findings in this ERA is that increases in soil and sediment values are reflected in the increases in tissue Ni concentrations in ecological receptors. The study results also show that Cu is also increasing in receptor tissue (e.g. frog livers). The accumulation of Cu in tissue should be included in the summary statement.
- 127. Page 6-32 1st bullet. What data/analysis is being used to support this statement that there is a soil-plant barrier that greatly reduces exposure to COCs? Is this the BAF data? If so, are the BAFs estimated for this site that much different than observed at other meal contaminated sites? Tissue data provided clearly show uptake is occurring as COC levels are elevated in plants and organisms from within the study area (hence COCs are bioavailable and exposure is occurring).
- 128. Page 6-32. 2nd bullet. The COCs at this site do not biomagnify. However, they do bioaccumulate.

- 129. Page 6-32. 5th bullet. The fact that soil type and habitat-type do not have a strong predictive relationship suggests they may not be important (and don't need to be treated as grouping variables in the statistical analysis). However, it also may be that the merging the data from the primary and secondary study sites is confounding these relationships. More robust statistical analysis is required to determine if these factors are important or not.
- 130. Page 6-33. 1st paragraph. We disagree that the magnitude of the difference (in tissue COC concentrations between the study area and the reference areas) are generally small. In addition, this summary should also identify that there are some limitations to the site-specific data collected for this site. For example, sample sizes are unequal between the primary and secondary study areas and are often low for specific receptors once separated out by soil type (clay/organic), habitat type (field/woodlot) and spatially (primary/secondary).
- 6.5 Exposure Magnitudes
- 131. Page 6-33. 2nd paragraph. The woodcock can also be exposed dermally via a "soil bath". This should be mentioned even thought it is not quantified in this RA.
- 132. Page 6-33. Last sentence. It is not usually done, but it is possible to assess potential risks associated with inhalation of COCs.
- 133. In Section 6.5.1, the authors indicate that air-to-flesh transfer factors were not available for inorganic chemicals. For that reason they used ingestion transfer factors as approximations (i.e. it is assumed that all COCs in air inhaled eventually enter the digestive tract and are absorbed as part of the whole body dose). Earlier in the report, it states that the inhalation pathway was not addressed in the ERA; hence the use of this factor in the hazard calculations is not clear and should be clarified.
- 134. Page 6-36. Please provide the basis for these uptake factors. Were the exposure parameters and the metal species tested from the Napier 1988 study appropriate for this site?

#### 6.5.3 Employed COC Concs.

135. The report states that data from sample sites within the Study Area, as well as sites within 2km to the east of the Study Area, were used to calculate the UCLM for each data set. The report states that this was done to capture areas with elevated soil COC concentrations noted by JWEL but which were not captured by MOE (2000a,b). This section should also include an assessment on the effect of including this additional data on the UCLM; i.e. did the value of the UCLM change as a result of this additional data? Given the unequal sample design where more sites are located in the secondary study area than the primary study area, it

seems likely that the mean, and the UCLM, is biased low and are not representative of conditions or potential environmental risks found in the areas of significant COC contamination (e.g., the primary study area).

#### **Bioavailability of Ni**

- 136. Page 6-31, Table 6-17. Please add UCLM or max values from the reference areas. Estimated exposure from reference areas should be calculated for all VECs as a measure of background exposure. In addition, the accompanying text should provide a brief summary of the data collected as part of the Crops Study. It is insufficient to simple cite the report.
- 137. Page 6-42. Table 6-18. It is surprising that COC concentrations in earthworms and anthropods are not influenced by soil type or by the very high COC concentrations from sites near the refinery. Please provide the earthworm tissue data and the UCLM analysis so we can examine this relationship further.
- 138. Page 6-42. Table 6-19. Please provide the raw bioaccessibility data (not just the mean) for each soil type and the results for with and without glycine added. The Table should also include the results for the experiments conducted with Ni.
- 139. Page 6-43. Bioavailability of Cu, Co: The report notes that other studies indicate similar results for birds (e.g. mallards) but because of uncertainty, the % Bioavailability for mammals was doubled (2X) for application to birds. A rationale should be provided to explain why a 2X factor was considered sufficient rather than a larger uncertainty factor of 5 or 10 which is usually used in interspecies extrapolation. The rationale should include a discussion on the digestion process in birds and how it is different from the digestive process in mammals. In addition, please provide the data from the Levengood and Skowron 2001 study to allow for a comparison with the data in Table 6-19.

#### 6.5.4 Calculated Receptor Exposure

- 140. A rationale is required to support the use of the UCLM based on data from all surface water samples taken within Study Area. The decision to combine all the surface water data from across the study area rather than assessing individual populations/water bodies within the Study Area is not appropriate since aquatic receptors are not exposed to the "average water quality" across the entire study area but the water quality at their particular location.
- 141. Page 6-44. Section 6.5.4.1. Please provide a rational supporting why the frog/tadpole was selected as the only aquatic VEC species given that the toxicity data in the literature is limited to surface water exposure only
- 142. Comment 114: Page 6-44, Table 6-20. Check units (should be mass per volume ug/L or mg/L).

#### 6.5.4.2-Fowlers Toad

143. Based on the information provided in the ERA, TRVs are only available for eggs/tadpoles in freshwater. Exposure calculations were based on exposure to COCs in breeding pond water (assuming 100% exposure). It is noted that Ni concentrations were highest in sediments and dune sand; however, these exposures were not assessed. In Section 8.3.1.1 the authors state that it is reasonable to conclude that the Ni concentrations in the sand do not pose significant risk to adult Fowler toads but there is no discussion of exposures to the juveniles. The ERA should examine whether or not Ni exposure of juvenile Fowler toads to the Ni in the sand could have a significant impact on their development and health (as they spend almost all time on the sand).

### 6.5.4.3 Earthworms

- 144. Exposure to earthworms is assumed to be through ingestion of surface soil (0-5cm) and it is also assumed that only soluble components are available for ingestion. There is no mention of the potential for Ni to be leached from soil particles by the strong acids in the digestive tract of the worm. For this reason, the acid ammonium oxalate extractions may likely a better representation of bioavailability than aqueous extractions (refer to table 6-23). This issue should be addressed in the ERA.
- 145. Table 6-22 (and similar Tables). Separate data for the primary and secondary study areas. Also, these tables should include data from the reference sites.
- 146. Page 6-49. Section 6.5.4.7. The Meadow Vole should be assessed for woodlots as well (see previous comment). This is similar to using the red-eyed verio to assess field habitat as was done in this report.

#### 6.5.4.8 Raccoon

147. Exposure for the raccoon was based on a diet of wild grape, corn, oats, earthworms, arthropods, voles and frogs. Incidental ingestion of soil and water was not included in the exposure assessment. A rationale should be provided as to why ingestion of soil and water is not included in the exposure calculations.

#### 6.5.4.9 (Red Fox) and 6.5.4.10 (Redtail hawk)

148. A rationale should be given as to why ingestion of soil and water is not included in the exposure assessments for red fox and red-tail hawk.

#### 6.5.4.11 Whitetail deer

149. The exposure assessment is based on maple leaves, goldenrod, oat seeds and corn seed. Deer love tree fruits and seeds (maple keys, acorns, etc.). It would have been more appropriate to include maple keys in the diet for calculating potential exposure. Again, a rationale should be provided for not including ingestion of soil and water in the exposure assessment.

## 7.0 HAZARD ASSESSMENT

150. Page 7-1. Risk is always present at some level – "safe" is a relative word and can be easily misinterpreted or misunderstood. It would be preferable to refer to "acceptable" levels instead of safe levels. Also, please update the references for the primary sources and verify the TRVs have not changed. Presumably, these documents are final now. Some of these reports are quite old (e.g., Toxicity summary for Arsenic (1993), Copper (1992) and Nickel (1995)). An examination of more recent toxicological information may be required to ensure that these TRVs are up to date and represent the most appropriate values to use in this risk assessment.

### 7.1.1 Arsenic to 7.1.4 Nickel

151. The references for all reported NOAELs, LOAELs, LC50s, LD50s and body burdens need to be provided in this report (currently, no citation information is available). These references should be included in sections 7.1.1 to 7.1.4.

### 7.1.3 Copper

152. In the published literature, it is shown that both eastern white pine and red maple are sensitive to Cu (i.e. injury can be observed when leaves contain more than 10 to 12 mg Cu/kg and extractable Cu in soil is greater than 60 mg/kg soil). The authors should compare maple leaf Cu concentrations and soil available Cu concentrations measured in the Study Area to these adverse effects limits from the literature.

### 7.1.4 Nickel

- 153. In this section it is stated that it has been shown in the literature that nickel can interact with other metals resulting in additive effects. As Ni is present with Co, Cu, and As in the soils within the Study Area, some discussion of the potential for additive effects is warranted.
- 154. Page 7-8 3rd paragraph. Please compare the plant tissue data collected at this site to this 50 mg/kg Ni level as an indication of potential toxicity.

- 155. Page 7-10. Please add the pH range measured in soil from this study. Is it similar to that found by OMAFRA in 1989?
- 156. Page 7-10, Table 7-1. Please provide a figure with measured soil Ni concentrations and measured CEC data to show this relationship. A Table of means by generic category of Ni concentrations (Reference, Very High) is not helpful.

## 7.2 Bioavailability of COCs

### 7.2.1 Arsenic

157. The authors state that the conditions in the Pt. Colborne area favour the oxidized state of arsenic (As+5) which is less available to plants and animals and conclude that based on the collection of plants (maple leaves, grapes and goldenrods) it would appear that only a small portion of soil arsenic is being translocated to above-ground biomass. This statement pertaining to the oxidation state of As should be substantiated with a summary table of the tissue concentrations and/or a reference to where this information is presented. In addition, a figure should be provided showing As uptake into plant tissues grouped by primary, secondary, and reference areas to clearly illustrate this relationship.

## 7.2.2 Cobalt

158. It is stated that organic chelates of Co are known to be easily mobilized and translocated in soils making them readily available. Clay soils have been cited in many studies as exhibiting a great sorption capacity, but can also readily release Co just as easily. Soil pH is also an important factor in Co availability. The organic soils in the Study Area are acidic (pH as low as 4.8); therefore based on pH levels, Co should be readily available in the Study Area. As Co availability could impact plants and soil organisms, additional discussion should be provided on the relative availability of Co in the organic soils in the Study area.

### 7.2.3 Copper

159. It has been demonstrated in the scientific literature that fish are more susceptible to soluble Cu cations in water than humans (e.g., Cu injury to gills). For this reason, the MOE ecological component value for Cu in the Brownfield Regulation is lower than the Ontario Drinking Water Objective value. ODWO values are not appropriate values to use when assessing potential risk to aquatic receptors. Environmental standards and/or toxicity values specific for aquatic receptors should be used instead. Additional discussion of the sensitivity of fish and other aquatic receptors to Cu in this section is needed.

### 7.2.4 Nickel

160. The MOE report (McLaughlin and Bisessar, 1994) indicated that chlorosis (yellowing of leaves) was observed in leaves of mature silver maples growing in the vicinity of the Pt. Colborne refinery. Therefore, the assertion that maple trees are not being exposed to quantities of Ni sufficient to cause phytotoxicity is incorrect. Unless evidence is available to suggest that this adverse effect is no longer occurring, then it is more appropriate to assume that trees in close proximity to the refinery have chlorotic leaves based on previous studies.

### 7.3 Toxicity Reference Values (TRVs)

- 161. Additional rational is required to support the Ni TRV for earthworms (3000 ppm).
  - a. More detailed information should be provided on the Nickel speciation soil study (e.g., what soil type was evaluated, how many samples, total Ni concentrations, etc.) and the actual report or Appendix cited.
  - b. Since earthworms burrow within the soil profile and not just in the top 5 cm, information on Ni speciation at depth is also needed to support exposure to only Ni oxide.
  - c. A discussion is required to reconcile the assumption of Ni oxide (and minimal Ni bioavailability) with measured Ni accumulation in earthworm tissues (indicating that Ni is in fact bioavailable) and toxicity tests that measured COC toxicity in organic soils and clay soils.
  - d. Additional information is required to summarize the critical studies used to develop this TRV (e.g., the Hartenstein paper and the two Malecki papers). For example, why was 12,000 ppm chosen from the Hartenstein et al. paper when it appears effects were also observed at lower concentrations?
- 162. The mammalian TRV for Copper needs to consider the study by Jenkins and Hidiroglou (1989). They fed calves milk replacer containing 10, 50, 200, 500 or 1000 ppm Cu from 3 to 45 days. Adverse effects were observed at 200 and 500 ppm Cu (reduced weight gain). Only 4 of 7 calves survived the 1000 ppm exposure. This experiment should be considered to ensure the selected Cu TRV is protective for cattle and other ruminants (deer) in the study area. Cite: Jenkin K.J. and M. Hidiroglou. Journal of Dairy Science. Vol. 72 Issue 1 pp 150-156. Tolerance of the Calf for excess copper in milk replacer.
- 163. Page 7-14, last paragraph. The EPA citation is readily available, so why cite it as "as cited in Suter and Tsao 1996"? In addition, the references to Cameco Corp 1994 and SENES 2001 are not appropriate since they are industry/consultant reports and not readily available, peer-reviewed, nor published in the primary literature.
- 164. Page 7-15. It is unclear whether references that observed adverse effects in frogs and/or tadpoles at concentrations less than background surface water levels are provided in this report? Please clarify.

## 7.3.1 Additive and Less than Additive Effects

165. This section indicates that few investigations have identified any additive or greater than additive effects between the four COCs. It is unclear from this statement if there were many investigations in the literature in which additive effects have been shown not to occur or that studies have shown an additive effect do occur but there have only been a few of these studies conducted. The intent of the statement should be made clear and supporting documentation cited.

### Table 7-2 TRVs and Test Endpoints

- 166. This section will need to be revised based on our comments provided on TRVS in VOLUME III: Supporting Data (TAB 4): Determination of Toxicity Reference Values (TRVs) for additional comments on TRVs.
- 167. Rationales for the selected TRVs are provided in Table 7-2; however, the TRV selection process was not transparent in all cases. The TRV selection process should be made clear to the reader..

## 8.0 RISK CHARACTERIZATION

### 8.2.3 Combined Effects of Chemical Mixtures

168. This section discusses the fact that for similar effects, the summation of doses is considered appropriate (U.S. EPA 2000). The authors identify that similar effects were observed for arsenic and cobalt. Therefore, there is some justification for a mixture risk assessment where HQs are added for the two COCs As and Co. This analysis should be done or a rationale provided stating why it was not.

### 8.2.4 Safe Levels

169. The calculations shown here are used for determining 'safe levels' for birds and mammals only, not soil organisms or vegetation. In addition, the statement that these calculations were used to estimate COC concentrations that provide 'a general level of safety to the natural populations or community' is unspecific as to the level of protection. The targeted level of protection and the VECs targeted for this protection should be clarified.

#### 8.3 Risk Characterization for Receptors

#### 8.3.1.1 Calculated Quotient for Tadpole/ 8.3.1.4 Summary of Effects of COCs on Frogs

170. The EC20 hazard quotient for Ni and Cu is 18 and 2, respectively. These ratios are significantly higher than 1, especially the ratio for Ni. Considering that the "safe" Ni level in surface water is 100 ug/L, these results suggest that 80% of the

ponds and ditches within the Study Area may put tadpoles at potential risk. The health of the local frog population was estimated by means of an adult frog breeding call survey. The data from the breeding call survey suggested that the distribution of calling males is not related to soil Ni concentrations and frog populations are typical of the region. What is unclear is how the survey results demonstrate that surface water Ni concentrations are not adversely impacting tadpole health and survival. Is it possible that Ni, as well as Cu concentrations in surface water and sediments in the Study Area are having a negative impact on frog survival at the tadpole stage of development? The ERA should clarify this issue.

171. Table 8-3. Please indicate the specific data that was used to determine the water exposure concentrations.

### 8.3.2 Maples

#### 8.3.2.1 Dose-Response Experiments with Maples

172. Table 8-4 shows that germination success, seedling height, and number of unhealthy leaves is significantly co-related with seed origin, soil Ni concentration and soil type (i.e. germination success of seeds from the reference area decreased with increased soil Ni concentration). These data also suggest that Maple seedlings, from seeds collected in the Study Area, may be more Ni tolerant than Maple seedlings from seeds collected in the reference area (since they grew better at higher Ni concentrations). These findings do not support the final statement (pg.8-12) "the Greenhouse study indicates that increased COC concentrations up to 3000 mg/kg Ni, do not negatively affect maple germination or growth". The growth of seedlings from the reference area was shown to be inhibited compared to growth of seedlings from the Study Area; therefore, the statement should be revised to more accurately reflect the results observed from these studies.

#### 8.3.2.2 Maples in the Natural Environment / 8.3.2.3 Woodlot Health Assessment

- 173. This section indicates that only 12 individual leaves were sampled and evaluated from various trees. There is no indication where the leaves were sampled from (i.e. new growth or old growth). Stand structure, basal area, etc. was investigated but condition of the leaf canopy was not assessed. The condition of leaves in the canopies would have also been a good screening approach of overall tree health prior to investigating individual leaves. It is unclear if overall canopy health (e.g. % of green vs. chlorotic leaves) was assessed. This is a significant uncertainty in the assessment of the health status of these trees.
- 174. Page 8-16, 2<sup>nd</sup> paragraph. Based on the results presented in this paragraph, only about 10% of the leaves were considered healthy (category #1); all others had some injury (category 2, 3, or 4).

175. Page 8-19. 2<sup>nd</sup> paragraph. Some woodlots in the study area had only 3 species of trees. This seems low. Which woodlots had this low species richness? What would the expected number of tree species be (i.e., how many are observed in the reference woodlots)?

### 8.3.3 Decomposers

#### 8.3.3.1 Earthworm Quotient Calculations

176. In Table 8-7 (exposure estimated using acid ammonium oxalate extraction), the hazard quotients for Cu and As were 30 and 4, respectively, in organic woodlot soil which contained 1,621ppm Cu and 83ppm As. The proposed 'safe levels' of 50 mg Cu/kg soil and 21 mg As/kg soil seem reasonable based on the observed results. However, a soil Ni concentration of 5,960 ppm in organic soil also produced a HQ of 2 in organic woodland soil yet the proposed 'safe level' (soil Ni value of 7,600 mg Ni/kg soil) is higher than the soil Ni concentration in the organic soil. There is no rationale provided for setting a 'safe level' for soil Ni that is higher than observed soil concentrations which gave a HQ >1. In contrast, the Cu and As 'safe levels' were set at much lower values relative to the corresponding woodlot organic soil Cu and As concentrations which gave a HQ>1.

### 8.3.3.2 Earthworm Dose-Response Experiment

- 177. The authors state that it is difficult to believe that COCs would be so much more bio-available in clay soils compared to organic soils considering the results of the chemical extractions (Section 6.5) and assessments of bioavailability (Section 6.4). There is no discussion provided to explain this phenomenon. It is possible that the digestive fluids of the worms are very efficient in removing metal cations from the clay particulates or that estimates of bioavailability are in error. Additional discussion of this issue is warranted including biogeochemical processes that may be influencing metal bioavailability in organic and clay soils (e.g., soil pH, metal binding to organic matter, cation exchange capacity, etc.) and/or a discussion of potential bias/confounding factors that may have occurred. Alternatively, this represents a data gap that needs to be addressed to resolve this apparent contradiction.
- 178. Table 8-8. It is unfortunate that the COC concentrations in the diluted test soils were not measured. Depending on the quality of the soil mixing, the actual COC concentrations may be different from the nominal values reported in this Table.
- 179. Page 8.26, Table 8-9. Please add statistics (e.g., from Dunnett's test) in order to determine which exposures were statistically significant different from controls.

### 8.3.3.3 Leaf Litter in the Natural Environment

- 180. This section will need to be revised based on our comments provided on the Leaf Litter Study in Vol. 4 Consultant Reports.
- 181. Page 8-33, 2<sup>nd</sup> paragraph. Why was the higher soil COC concentration considered an outlier and excluded from the statistical analysis?
- 182. Page 8-44. Table 8-19. Why no data from reference soils or soils from Secondary Study area? Biomass from Reuter Road woodlot appears to be quite low.

### 8.3.4 Birds

183. This section will need to be revised based on our comments provided on TRVS in Volume III: Supporting Data: TAB 4: Determination of Toxicity Reference Values (TRVs).

### 8.3.5 Mammals

184. This section will need to be revised based on our comments provided on TRVS in Volume III: Supporting Data: TAB 4: Determination of Toxicity Reference Values (TRVs).

### 9.0 INTEGRATION

#### 9.1 Approach

185. Three general lines of evidence were developed that were used for the interpretation of potential risk to the natural environment. It appears that the authors have put more emphasis on field observations over the results of controlled laboratory experiments and the Quotient Method in determining the ecological risk to VECs such as the earthworm. This approach is acceptable as long as sufficient field data has been collected from properly conducted field studies. However, the results from laboratory experiments should still be considered in the weight of evidence approach. This should be addressed in the report identifying the strengths and limitations of the laboratory data and the field data.

#### 9.2 Summary Discussion of Risk

#### Woodlots

186. It is stated in the report that the results of the greenhouse trials, which included seed germination success, sapling growth and assessment of leaf health, suggested that maple keys from the Study Area responded differently than maple keys taken from the Reference Area with the Study Area plants growing better in the more contaminated soil. The significance of this apparent metal tolerance could not be determined because of the extremely small size of the source population (i.e. seed

were collected from one reference tree and two adjacent trees in the study area). As the ability of plants to tolerate or adapt to high metal concentrations in the soil is important in ensuring long-term viability in the plant communities it is unclear why additional follow-up studies were not carried out to determine if there are significant differences in metal tolerance in the maple populations in the Pt Colborne area.

#### Inland Aquatic Environment

- 187. A number of concluding statements are made in the report indicating no adverse effect to aquatic receptors due to COC exposure. For example:
  - 'the potential risk (HQ) to tadpoles as a result of Ni and Cu concentrations in pond water does not appear to be supported by general field observations or analysis of field data'
  - 'may be adversely affecting local frog populations through small reduction in numbers of tadpoles surviving to adult stage'
  - 'field data identifying that long term (50+ yrs) exposure to Ni concentrations in surface water in ponds and swamps has not reduced the Study Areas high level of species diversity.

The wording of the above statements is not consistent with the study results; analyses of the COC concentration in sediment, water, and tissue, and exposure to Ni and Cu appears to present potential risk to frogs and tadpoles. Using available TRVs resulted in a hazard quotient of 18 and 2 for nickel and copper, respectively, indicating a potential risk to tadpoles. In fact, it was determined that Ni concentrations in surface water values for 80% of the ponds in the Study Area may pose a risk to tadpoles.

It is also stated in the report that based on the experience of the field biologist who conducted the frog calling survey, it was noted that although species were well represented throughout the Study Area, densities of calling adult frogs at quality breeding sites nearest the refinery were <u>not as high as expected</u> which suggests that there may be some suppression in population numbers due to reduced recruitment of tadpoles to adults in areas with very high soil Ni concentrations (>10,000 mg/g). The data suggests that within the Study Area there is a gradient of Ni/Cu impact to tadpoles/frogs vs. distance from the refinery but the authors have not emphasized this trend in their discussion. This analysis needs to be done.

# **10.0 UNCERTAINTY ANALYSIS**

#### 10.1 Uncertainties in the Problem Formulation

188. Table 10-1 indicates that there is no likely change to the risk conclusions by selecting a Primary Study Area (>500 mg/kg soil Ni) and a Secondary Study Area

(200 to 500 mg/kg soil Ni). This analysis needs to be conducted to demonstrate this fact. When warranted for large home range species, the primary and secondary study areas can be merged.

### 10.4 Uncertainties in Data Collection Methods

189. Table 10-4 indicates the author's belief that the constraint on sampling time likely did not cause any overestimation/underestimation of risk. However, the justification provided in the table suggests that data sampling was compromised (e.g. arthropods, earthworms, seasonal limitations affected the number of sampling sites for several VECs). In addition, no quantitative analysis of the vegetation community was conducted and the decomposition studies were modified as a result of time constraints. Additional rationale is required to justify that uncertainty due to the sampling constraints had no impact on the risk conclusions.

## 11.0 SUMMARY AND RECOMMENDATION

### 11.1 Summary

190. The Chapter will need to be revised to address the previous comments and more accurately reflect potential ecological risk to aquatic and terrestrial biota in the Primary and Secondary study area. For example, additional discussion is needed to support the statement that field surveys found that the Study Area supported high diversity and typical abundance of adult frogs for the species present. The HQ suggested impacts to the tadpole stage, the American Toad was found at all sites except two within the primary study area, and the breeding call count concluded that call frequency was rather lower than would be expected. The authors state that soil COC concentrations decrease with distance from the source in a north-easterly direction but fail to discuss what appears to be a relationship between likelihood of adverse effects vs. distance from the refinery (e.g. impacts were observed in maple foliage, earthworms and micro-organisms in woodlots that were closer to the refinery).

#### 11.2 Recommendations

191. A total of four rationales are provided for recommending that the safe soil COC values be based on the 'earthworm' for the purpose of assessing future management options. Some of the toxicity data and field data for other VECs (e.g. woodcock, tadpoles, decomposer) suggest that the fourth bullet may not apply in all parts of the Study Area; i.e. "a safe soil COC concentration for earthworms would be protective for other flora and fauna that inhabit these areas of high soil COCs". The authors should revise these recommendations to reflect this.

### 11.4 Conclusions

192. Table 11-5 lists the final 'safe' soil COC concentrations for earthworms. Rationales are given for the 'safe values' chosen for Ni, Co and As but no rationale is given for the Cu 'safe' value. This may be a simple error of omission which should be rectified.

### **12.0 CITED REFERENCES**

193. The reference list appears to be comprehensive but needs to be updated. Several JW references refer to draft reports that have been finalized and have a new date (e.g., COC selection reports).

## **VOLUME II: FIELD DATA COLLECTION and ANALYSIS PROTOCOLS**

### 9.0 Maple Seed Greenhouse Trials Protocols

194. Maple keys were collected from a single tree from one woodlot near the refinery and one residential tree in Welland (control). All greenhouse studies and analyses were carried out on seeds from only two trees. The study results suggest that these trees differ significantly in soil Ni tolerance. The objective of the ERA was to look at population effects; therefore, seeds should have been collected from several trees established in a number of woodlots across the Study Area. In this way the greenhouse trials may have been useful to demonstrate any given range of Ni tolerance in the tree populations across the Study area. An opportunity was lost here. A rationale should be provided to justify the seed collection procedure used.

#### 9.0 Earthworm Toxicity Tests and Field Sampling Protocol

195. In Table 1 (pg.4), the highest soil Ni concentration in organic soil is shown as 1490 ug/g. This value is likely in error as much higher Ni concentrations were measured in organic soils from this site.

# **VOLUME III: SUPPORTING DATA**

### TAB 4: DETERMINATION OF TOXICITY REFERENCE VALUES (TRVS)

### Allometric Dose Scaling

196. MOE no longer accepts the application of allometric scaling for estimating chronic effects data and recommends direct extrapolation of chronic TRVs from lab studies to wildlife species. All chronic exposure calculations should be recalculated without applying allometric dose scaling. Please refer to the 2009 MOE Technical Memo to QPRAs concerning the use of Allometric Dose Scaling.

### <u>Ni TRVs</u>

- 197. The TRV tables mix diet concentrations (mg/kg) and dose concentrations (mg/kg body wt/d). This is confusing to the reader and in many cases it is not possible to compare studies because of these inconsistencies. The TRV tables should be revised to provide both diet concentrations and dose concentrations for each contaminant of concern.
- 198. For the Fowler toad the selected TRV was based on LC10=0.4 mg/L from Birge et.al. 2000 which does not specify the chemical form of Ni, the stage of development of the toad, or the study duration (table 2). This information should be provided. The authors should also provide a rationale for not including other TRVs from other studies.
- 199. For frogs, the selected TRV is based on an embryo study of eastern narrow mouthed Toad even though a TRV (Birge et.al. 2000) was available for the leopard frog which resides in the Study Area. The authors should explain why preference was given to a TRV for a toad, rather than a TRV based on studies using leopard frogs.
- 200. Birds Table 4 and the paragraph below the table are confusing. The table should indicate that the mallard study by Cain and Pafford 1981 is the same study used in Sample 1996. Also, the TRV selection process should be more clearly presented as the same TRV is used for all of the avian receptors. Also, Table 4 should provide corresponding LOEL and NOEL values (mg/kg/d) from each study along with the LOECs and NOECs. For example, as it is presented, it is not possible to determine why the other listed mallard study (12.5 mg/kg Ni in diet) or the Plymouth Rock Chicken study (300 mg/kg Ni in the diet) were rejected. A lower avian TRV may have been derived using the results from one of these other two studies (i.e. toxicity causing reduced growth and elevated kidney levels of Ni). This should be addressed.
- 201. Mammals As in previous tables, Table 6 contains a mixture of LOECs (mg/kg in diet) and LOELs (mg/kg body wt/d) which is confusing to the reader. This should be rectified. The 30mg/kg/d LOEL for rat reproduction effects (Springborn 2000a) was selected as the TRV for all mammalian receptors but there is no rationale provided to support why this study was selected over the other studies. Also, why not use the LOEL for the 2 yr beagle study for red fox? The TRV selection process should be presented more clearly.

### <u>Cu TRVs</u>

202. Earthworms – the benchmark used for TRV appears valid but there are several other studies shown in Table 7 which are not discussed. The TRV selection process should be presented more clearly.

- 203. Fowler Toad determination of the TRV is based on a LC50 of 2.69 mg/L from Birge and Black 1979 (as shown in Table 8) but in the calculation of the EC20 of 5mg/L, the authors have used a value of 26.96 mg/L. Use of the reported LC50 value would result in EC20 of 0.5mg/L. This discrepancy should be clarified. Please check the units from this primary study carefully as these Cu concentrations are quite high and would be acutely lethal to most aquatic life.
- 204. Birds One TRV is used for all the avian VECs. It should be noted that studies with copper oxide or copper metal may represent the Pt. Colborne situation better than studies using either Cu chloride or Cu sulphate. There are several studies listed in Table 10, for which the chemical form of Cu is unspecified but which resulted in reduced growth in chickens and turkeys at lower concentrations than the study used to calculate a Cu NOEL of 47 mg/kg/d. The authors should provide arguments as to why these studies were not considered for this risk assessment. Also, NOAELs and LOAELs (mg/kg/d) have not been presented (or calculated) for several other studies listed in Table 10. Thus, one cannot compare potential TRVs resulting from these studies to the TRV which was selected. The authors should provide a rationale as to why these other toxicity data were not considered.
- 205. Mammals In Table 11, the TRV of 10 mg/kg/d, calculated from survival of mink kits (Aulerich et.al. 1982), appears to be an appropriately conservative value but may not be protective of sheep. In the literature it has been shown that sheep are very sensitive to Cu in diet (Adamson et al. 1969). Haemolytic crisis and jaundice was observed in lambs at a Cu dose of only 0.885 mg/kg/d Cu. Gopinath and Howell in Eisler 1998a demonstrated severe morphological changes at 7.5 mg/kg/d Cu sulphate in an 83 day study. The TRV selected for Cu (10 mg/kg/d) may not protect domestic sheep that graze in contaminated fields in the Study Area.
- 206. Lab rats and mice are more closely related to field voles and shrews than mink. The authors do not explain why the data from rat and mouse studies were not considered; no basis is provided for rejecting these studies. It is also unclear why a number of studies are included in Table 11 yet the results are not discussed or compared in any way to the chosen TRV. Justification for choosing the selected TRV should be provided.

#### Cobalt TRVs

207. Fowler toad – It is unclear why the LC10 of 0.2 mg/L (from Birge et.al. 2000) was selected as the TRV for the Fowler toad when the chemical form of Co and the duration of the test were not specified. Also, why was the EC20 not calculated as was done in the case of frog receptors? This should be discussed in the ERA.

- 208. Frogs Table 13 the selected TRV was based on a study for eastern narrow mouthed toad embryos (Birge et al. 1979) despite there being similar toxicity data available for the leopard frog (Birge et.al. 2000). The authors should provide a rationale for this decision.
- 209. Birds a conservative TRV has been used, based on a sub-chronic effects level (mortality to broiler chicks), as well as an uncertainty factor of 10 and 2 (because Co is in the form of a soluble chloride). Other chronic studies are listed which produced much higher TRVs (e.g. 7.8 to 17 mg/kg/d) apparently without applying an uncertainty factor. There should be some discussion as to why these chronic effects studies were rejected.
- 210. Mammals In Table 15, there are several other studies of similar duration as the study conducted with Norwegian rats (Mollenhauer et.al. 1985) which was selected for the TRV. Several other chronic effects studies, with lower LOAELs (4.2-5.7 mg/kg/d), are listed but have not been discussed. A rationale should be provided to justify the selected TRV (e.g. did the other studies utilize more soluble forms of cobalt which may not represent Co availability in Pt. Colborne soils?)

### Arsenic TRVs

- 211. Frogs Table 17 "pickerel frog" (R. palustris) is misnamed "leopard frog" (R. pipiens) in the Table.
- 212. Why was the Leopard frog LC10 of 0.01 mg/L (Birge et.al. 2000) not cited as the basis for the frog TRV instead of the narrow mouthed toad? Although it results in a similar value for calculating the EC20, the TRV would be based on data derived for the leopard frog.
- 213. Birds The selected TRV (5.14 mg/kg/d) was based on a NOEL value (100 mg/kg) for mallard duck (USWS 1964). A rationale should be provided to explain why the LOEL (7.38 mg/kg/d) from the copper acetoarsenate catbird study (Sample et al. 1996) was not suitable to be the basis for the selected TRV.

# TAB 5: EXPOSURE PARAMETERS for RISK CALCULATIONS:

Meadow Vole (Table pg. 2 of Section)

214. Soil – IR\*\* (food ingestion rate on dry wt. basis calculated to be 8.876 kg/day) – this value seems very large for this small VEC. It should be revisited and corrected if necessary.

### Red-tail Hawk (Table pg.16 of Section)

215. Diet – DFk is defined as 74% vole, 26% birds. It should be noted that 6 to 13% of the diet for red-tail hawks can be snakes which is not accounted for here. Also, the authors use the average COC concentration of the robin, vireo and woodcock in the calculations for red-tail hawk. A more conservative approach, would be to use the highest concentration of the three prey species rather than an average. This would have provided the maximum exposure risk to the red-tail hawk. The authors may wish to calculate both an average and a maximum exposure risk.

## TAB 6 EXAMPLE CALCULATIONS

216. The reviewer reviewed the American Robin example (woodlot – organic soil). For ADD soil \*, it is unclear how the bioavailability factor of 6.4% was determined. This factor has significant effect on the ADD total (it brings the total dose of 44.08 mg/kg/d down to 6.04 mg/kg/d. The reviewer was unable to find the calculations for this "bioavailability factor/bioaccessibility factor". As factor was applied in determining the exposure estimates for several of the VECs, how this factor was determined should be provided.

### TAB 8 CALCULATIONS of COC CONCENTRATIONS for COMPOSITE TISSUE SAMPLES

217. It is difficult to follow the COC concentration equations as they are currently presented. It would be easier to interpret if the equations were provided with symbols representing the variables (a legend could be added to explain the symbols).

### TAB 10 PREDICTORS FOR TISSUE COCS

#### 1.1 Amphibian tissue

218. The concentration of Ni in sediment is shown to be a significant predictor of tadpole GI tract Ni concentration but the authors state that sparseness of data and high variability restricted their ability to draw a conclusion. This should have been flagged as a deficiency in the ERA and attempts should have been made to collect enough samples to determine if the relationship is a strong one or not. Also, the sediment Ni concentration is a strong predictor of Ni concentrations in adult frogs. It is unclear if this relationship is reflected in the discussions and conclusions provided in the main ERA report.

### 1.2 Maple Tissue

219. The authors state that more sampling may be needed to clarify whether or not there is a significant relationship between soil Ni, Cu, Co, and As concentrations and metal concentrations in leaves. Does the main ERA report provides any additional information from the literature or additional sampling to determine if the soil metal levels are predictors of foliar metal concentrations?

### 1.3 Earthworm Tissue

220. Although the sample size was small, the analytical data indicates that worms in woodlots (organic soil) may have higher As concentrations than worms from clay soils in the Study Area. Does the ERA indicate whether feeding on worms from organic soil result in an adverse As effect on woodcock in the Study Area? Soil concentrations for all of the COCs were significant predictors of metals in earthworms (p<0.01) for both clay and organic soils. Why were only field habitats sampled for worms in 2002 and not woodlot soils as well? This was a missed opportunity to see if trends observed in organic vs. clay soils in fields also existed in the woodlots as well.

### 1.4 Arthropod Tissue

221. In Table 8m, soil Ni, Cu, and Co concentrations were all significant predictors of levels in arthropod tissue but not As. The authors do not explain the reason why As is acting differently from the other COCs. Some discussion should be provided in the ERA.

### 1.5 Meadow Vole Tissue

222. Only one vole specimen was caught in the secondary area of the Study Area. There is no explanation provide as to why As accumulation in vole tissue is acting differently from that of the other three COCs. Also, it is difficult to determine if this vole is representative of the meadow vole population without replicate samples. Voles are quite common in grassy fields across southern Ontario and it is unclear why more specimens were not obtained for analysis. Why was more effort not put into obtaining additional voles for analysis?

# **VOLUME IV: CONSULTANTS REPORT**

### **1. LEAF LITTER STUDY**

- 223. The authors assume that the total amount of decomposition that occurs in any single year at any one woodlot equals the amount of litter entering the system at that site. This leads to the conclusion (based on general observations) that no unusual litter accumulation was occurring; net decomposition is constant and there is no net litter accumulation occurring on the ground. However, contrary to this, the section also concludes that the decomposition process might be slowed in woodlots within the highest soil Ni and Cu concentrations because the amount of litter was much higher in high soil Ni woodlots. This discrepancy should be addressed in the main ERA report.
- 224. The proxy method used to measure decomposition rates is not a quantitative measure of rate of decomposition. There is no way to determine if a comparable

amount of litter has fallen in each of the selected woodlots. The author of this report states that he needed two years to do a litter bag study but was unable to do so because of time constraints. However, the ERA was not completed until 2004 (more than three years later). A proper leaf litter bag study could have been conducted. Therefore an opportunity was lost to provide quantitative, conclusive data to support the conclusions of the ERA. This limitation should be noted in the main ERA report.

- 225. For a current year litter study, one would normally choose to use standard litter traps and measure all the bits of litter caught over that given year. In this study, the authors collected leaves off the ground after the autumn leaf drop (on Nov. 2, 2001). This is a rather imprecise measure compared to the litter trap method. Also, only one sample site (consisting of five 1-m<sup>2</sup> sample grids) was established for each soil type and COC zone. A rationale should be provided for not establishing leaf litter sampling sites in more of the 21 selected woodlot sites with different soil types and soil metal concentrations.
- 226. Litter buildup can result in reduced nutrient availability to forest trees and shrubs. Did the author compare the health (e.g. vigor and size) of various trees at the litter study sites in the woodlots? Also, factors such as temperature, moisture, soil pH, soil structure, shade, etc. all influence litter decomposition. Were these factors measured at the various sample sites?
- 227. Figure 15 shows the number and composition of wood stems within the study plots is quite variable from site to site (e.g. Site #2 consisted of 5 trees, 55 shrubs whereas Site #3 consisted of 30 trees, 6 shrubs). The objective of the study was to select sites which were as similar as possible. This high plot-to-plot variability between trees and shrubs should be addressed in the report.
- 228. A very detailed discussion is provided on the composition of litter and of plant species, as well as bird species observed in woodlot sites; however, none of this discussion addresses the question of soil metal impacts on the 'rate' of decomposition.
- 229. It is stated that the results demonstrate that significantly higher amounts of standing litter were present in woodlots on organic soil with high metal concentrations  $(386 \text{ g/m}^2)$  compared to controls  $(138 \text{ g/m}^2)$ . After reading the previous statement, the following statements appear to be contradictory "Even though this decomposition pattern relationship with soil metals can be demonstrated, the total amount of decomposition that occurs in any single year at any one woodlot equals the amount of litter entering the system at that site. This conclusion is based on general observations that suggest no unusual accumulations of litter on the ground. The rate of average annual fresh litter input is essentially at equilibrium with amount decomposing each year". This discrepancy should be addressed in the report. Also, these conclusions are based

on very limited data (only five individual plots, one per zone). Statistically, the plots may not be representative of the entire Study Area.

- 230. The concept of Figures 21 and 22 (conceptual litter decomposition processes under two level of soil metal loading) is not clear nor is the process used to create them. This should be clarified.
- 231. The reviewer was unable to locate the calculations for expected decomposition rates using lignin content in foliage (Meetemeyer, ref 132) and potential evaporation using Thornthwaits [171]. This information should be provided with the report.
- 232. With the exception of the Reuter Rd. site, the average leaf weight loss was 43.3%, assuming weight of leaves in 2000 was the same as 2001, and no litter was older than one year. However, leaf litter weight losses vary considerably from site to site (3.2% to 81.5%). This should be discussed and a rationale provided to explain the large site to site variability.
- 233. It is stated in the report that slower decomposition rates were observed at the Reuter Rd woodlot but these slower rates were not due to metal concentrations in the fresh foliage; it was some other agent. No discussion is provided to address what that agent might be or the agent's relationship to high metal concentrations in litter or soil, or both. It is possible that soil metal concentrations have reduced soil invertebrates, nematodes and fungi numbers which could result in slower decomposition rates. Additional rational is required to explain possible reasons for the observed slower decomposition rates.
- 234. The author of this consultants report states that the study is not 'best science' and that the study should have included the following:
  - collection of fresh litter fall over at least one full year using formal litter collection devices
  - exposure of leaf litter in mesh bags at selected study sites over a 2 yr+ period
  - exposure of leaf litter to known metal concentrations under controlled but realistic conditions
  - conducting bioassays (e.g. removal of large soil cores from different woodlot locations and relocating them together in other woodlots topped with fresh litter).

The reviewer concurs that the above mentioned procedures would have taken two to three years to complete but it would have likely provided a more complete picture of the impacts of historical emissions. It is unfortunate that this work was not carried out because of perceived time constraints. These limitations should be included in the main ERA report.

## 2. EARTHWORM TOXICITY STUDY (E. Andrei)

235. Phase 1 consisted of four undiluted site soils and a control. Tables are provided in the Appendices which show physiochemical data on the four soils; however, COC concentrations (Ni, Cu, Co, and As) are not shown. The COC concentrations should be provided in these tables for comparative purposes. Phase 2 involved dilution tests to derive effects concentrations. Again COC concentrations of the eight soil treatments (0-100% mixtures) are not provided. This information should be provided. Data for Phase 2 results (% soil mixtures) are shown but no discussion of results or statistics is provided.

## 3. WOODLOT HEALTH ASSESSMENT STUDY

## SITE PRODUCTIVITY

236. There were no significant differences between mean maximum height for the PSAC and CTLC but on average the PSAC was 16 yrs younger than CTLC. The authors claim this is a reflection of the site selection process rather than a growth or age inhibitor. This is a limitation of this study. Why did the authors not attempt to select sites of similar age?

## WILDLIFE HABITAT

237. The author's state that the COCs may have a role in the increased amount of wildlife habitat trees in SWD3-4 sites especially Ni, which has greater effect on sites with lower soil pH. More discussion should be provided here concerning changes to the forest as a result of the soil COCs, especially in acidic soils.

## **III. MOE Comments of Vale CBRA HHRA**

The following comments pertain to the December 2007 Port Colborne Community Based Risk Assessment (Volumes *I* to *VI*). The review focussed on identifying if the risk for potential adverse effect to human health has been characterized appropriately in a scientific and defensible manner and that the conclusions of the human health risk assessment (HHRA) are supported by the data, information and interpretations included in the HHRA.

It was stated in the HHRA that the primary objective was to determine whether the soil concentrations of Chemicals of Concern (CoCs) in the Port Colborne area present an unacceptable risk to human health in the Port Colborne community. In addition to this, the HHRA has the second objective of estimating the environmental concentrations of CoCs in soil at which no adverse effects on human health are expected to occur. According to the HHRA these have been termed Risk Based Soil Concentrations (RBSCs) and are defined as "*an estimate of the concentration of that CoC in soil that is expected to be protective of human health for a worst case exposure of sensitive receptors*". The calculations of the RBSCs are dependent on the assumptions of the HHRA.

The proponent concluded in the report that "The results of the assessment of conservative exposure scenarios indicate that the concentrations of nickel, copper, cobalt and arsenic in the Port Colborne environment do not pose an unacceptable risk to residents as defined by the MOE target risk levels".

Furthermore, the proponent derives a site-specific RBSC for nickel of 20,000 mg/kg that it indicates would serve as a human health based soil remediation guideline. The proponent also indicated that RBSCs would not be required for copper or cobalt because *"the computed values were less than the maximum measured"* whereas, in the *"quantitative evaluation of uncertainties, arsenic oral/dermal exposures were found to have uncertainties too large to make the evaluation reliable"*.

As a consequence of this review, MOE has identified concerns in this memo that must be satisfactorily resolved and are likely to influence the recommended RBSC's for the CoC's including nickel. As a result, MOE will not provide final comments on the derivation of the RBSC until the concerns identified have been resolved.

A key determinate of the proponent recommended RBSC of 20,000 mg/kg for nickel is based on the site-specific relative oral bioavailability (ROB) factor of 4%. While MOE believes that there is sufficient site-specific bioavailability information to deviate from the default 100% used for the Ontario generic based soil criteria<sup>1</sup>, MOE does not share the proponent's confidence in the 4% ROB as determined by their weight of evidence analysis. Instead MOE recommends that an ROB of 19% as was previously relied upon

<sup>&</sup>lt;sup>1</sup> The generic soil standards for Ontario use a 100% ROB (or relative bioavailability factor of 1 as in MOE 2009) in the absence of site-specific information.

by the Ministry for the Rodney Street risk assessment (MOE 2002) be used for the purpose of determination of a RBSC for nickel and in risk characterization for Port Colborne. The consequence is that the RBSC of nickel would result in a lower more stringent RBSC.

The following are MOE findings as they relate to the HHRA conclusions. Comments are provided as Part A specific comments, and Part B responses to previous comments made by MOE.

## Part A: Specific Comments

#### Site Characterization

1) Screening Process for Selection of CoCs: According to Section 2.3 CBRA Chemicals of Concern of the HHRA: "For the CBRA, the definition of a CoC is a chemical found in Port Colborne soils originating from the Inco Refinery where all of the following conditions are met:

Condition 1) Chemicals that were historically used or generated by the Inco Refinery or its processes, and Condition 2) Chemicals that are present at a community level at concentrations greater than MOE generic effects-based guidelines (MOE, 1997), and Condition 3) Chemicals whose presence in soil shows a scientific linkage to the historical operations of the Inco Refinery.

The CoCs considered in the HHRA are nickel, copper, cobalt and arsenic. The identification and selection of CoCs for the CBRA is reported elsewhere (Jacques Whitford, 2001a; 2001b; 2001d). This documentation was used by Jacques Whitford in the CoC selection process and although standard practice is to review CoC selection at the time of submission of the HHRA, the CoC selection was preformed in 2001. In order to facilitate the review of the current HHRA, CoC selection was not considered as apart of this review. Therefore, MOE's comments are limited to the identified CoC's - nickel, copper, cobalt and arsenic.

MOE notes that in December 2009 Brownfields soil criteria (component values and revised soil standards) "Rationale for the development of soil and ground water standards for use at contaminated sites in Ontario" were updated. As such the proponent is encouraged to ensure that the submission would satisfy these criteria, first to help place the current assessment in the context of the current Ontario regulatory environment with best science practice, and second to increase the openness and transparency of the document such that it could be read as the contemporary accepted practice of risk assessment.

It is important that appropriate relevant criteria be used to determine the study area (Section 2.2), and in CoC selection (Section 2.3). As indicated by the proponent in Section 1.2 CBRA process *"the components of the CBRA process include: An* 

*evaluation to confirm that all relevant CoCs have been considered;* ", the proponent should ensure that the submitted risk assessment satisfies these criteria.

- 2) Section 2.7 Soil Parameters. The reviewer was not able to fully evaluate the site soil characterisation information provided. The proponent has provided contour maps for CoC's (Figures 2-6 to 2-8) which present a good visual aid. However, the combined soil data used in the assessment as provided in Appendix 20, and soil sampling locations provided in map Figure 2-3, Soil Sampling Locations Port Colborne, are not clearly presented. Specific details are required to aid in the understanding of the rationale behind the soil EPCs selection process used by the proponent in the HHRA model, including a detailed spatial presentation of the information. It would be more appropriate if the following information is provided for each of the zones:
  - A map showing sampling locations of all the data used in the HHRA.
  - For each sample location, the soil land use (category) as a recreational (woodlot), commercial, residential, school yard or garden type etc. should be indicated.
  - For each sample location CoC concentrations including the max with an indication of the soil depth.

This will enable the reviewer and future readers to gain a better understanding of the selected data and support the statistical representation of the data used in the HHRA. MOE also has concern due to insufficient data for the following zones:

		0
Zone	Soil by Land Use	Sample Locations
A	Recreational	4
A	Commercial	2
A	Schools	2
С	Schools	7
D	Commercial	3

Without sufficient sampling data the reviewer is not in a position to determine the adequacy of the exposure assessment. While there is some general guidance on sampling requirements for conducting a site-specific risk assessment, specifics for a CBRA are lacking. MOE recommends that a data gap analysis be conducted when less than 10 distinct sample locations are used and for residential properties especially when the sampling represents less than 10 % properties within each zone.

3) Section 2.7 Air Quality. The proponent indicated that the results of the ambient air monitoring program for Port Colborne were evaluated using the MOE 2001 Ambient Air Quality Criteria (AAQC) and that all the ambient air CoC concentrations obtained from Port Colborne were below the associated AAQC guidelines (Section 2.7.1 Ambient Air Monitoring). However, AAQCs are used in compliance assessment of a facility and are not necessarily TRVs, may not be human health risk-based, or may not reflect current knowledge. Therefore, the appropriateness of the AAQC in context of health protection within a HHRA as "*safe*" (e.g. Page 2-37) should be readdressed by the proponent. It is noted that the MOE is currently reviewing and updating the respective AAQC's for Nickel (Ni), Arsenic (As) and Copper (Cu).

4) Section 2.7.1.1 Nickel Speciation Scan of Ambient Air Samples. The proponent indicates that according to ambient air filter samples, oxidic forms of nickel (about 80% of total) were found in particulate. This information is inconsistent with the MOE data (2001-2002) for Port Colborne, which indicated that up to 85% of the  $PM_{10}$  sample is nickel sulphate (MOE 2009, EBR posting # 010-7188). The proponent should review the evaluation to resolve the inconsistency and incorporate appropriate changes into the report. All information necessary to demonstrate that the assessment undertaken is appropriate for the HHRA should be included.

#### **Problem Formulation**

5) Section 3.2.4.1 Concentrations in Drinking Water: The proponent has used the MOE's Drinking Water Surveillance Program (DWSP) data (Appendix 15, Table 18) to estimate the drinking water exposure for HHRA Zones A, B, C, and E (Sections 2.6.3 and 3.2.4.1). According to the report the data set is based on water samples obtained from the distribution system and not the tap. Drinking water exposure from a community-based perspective is most applicable from the tap where water is obtained. This introduces a limitation to the HHRA, as relying on the distribution system water samples may not account for the exposure at the tap. This is potentially significant for the CoC Cu, where due to water-based corrosive activity Cu can be leach from copper piping. As such, the use of the distribution system versus tap water data is likely to underestimate Cu exposure from drinking water. The lack of this information should be discussed in the uncertainty section.

In the determination of the drinking water exposure from the drilled well supply the proponent has combined the non-tap (Table 7) and tap (Table 8) collected data as they assert that the data sets are "*similar*". The combined data set (Table 9) was used as the EPC for Zone D and E. It is not apparent if a statistical analysis was performed to support this statement. Furthermore, specifically, Cu tap water samples are preferred (mean Cu concentration: non-tap = 0.0040 mg/L verses tap = 0.059 mg/L) for use in the HHRA. Data sets for dug wells were also combined, but due to low sample numbers combining of data might be required. A statistical analysis of these data should be provided.

It is stated in this section that the MOE DWSP data from Dunnville, Fort Erie (Rosehill), Haldimand-Norfolk, Port Dover and Port Rowan water distribution systems were used for Zone F background EPC drinking water. However, according to Appendix 15, Section 5.6 data were taken from taps serviced by water treatment plants throughout the Niagara region, including treatment plants at Dunnville, Fort Erie, Grimsby, Hamilton, Nanticoke, Niagara Falls, Ohsweken, Port Colborne, Port Dover, Port Rowan, St. Catharines (De Cew), Simcoe, Waterford, and Welland. This inconsistency should be resolved and appropriate changes made to the report. Furthermore, the proponent should confirm that the water samples were obtained from the tap (preferred) as opposed to the distribution system as indicated elsewhere in the HHRA.

6) Section 3.2.5.3 Concentrations in Indoor Air: The proponent has selected 0.6 as the ratio of indoor air to outdoor (ambient) air (Appendix 13, Indoor Air and Dust Study). The selection of a 0.6 ratio was based on an analysis of 24 hour indoor air samples collected at 10 residences in each of the 3 air zones, totalling 30 residences as identified in Figure 2 (Samples Zones Used in the Indoor Air Sampling Study Port Colborne). The data was pooled from the 3 air zones (Table 3 Definition of the Three Sampling Zones used in the Indoor Air and Dust Study) to provide a comparison to monitoring data collected at the baseball diamond (Rodney and Davis Street). The monitoring data at the baseball diamond was the site used as the source for Zone B EPC for air and used to limit the maximum modelled air concentrations for other Zones.

The reviewer is not confident that this ratio represents the Port Colborne area-wide and between-Zone ratios, as the sampling of indoor air is highly variable, and was not preformed with co-localized outdoor air sampling. Therefore, while the HHRA relies on the ratio of 0.6, MOE recommends that a ratio of 1.0 also be tested in the sensitivity analysis and in the assessment of the maximum exposed individual. (See also related Comment 29).

- 7) Section 3.2.5.4 Concentrations in Indoor Settled Dust: The indoor dust pathway can be a significant exposure pathway particularly for the toddler, which is likely to have greater time spent indoors and greater hand to mouth activity than adults. The proponent has adopted the US EPA equation (1997) for estimating dust ingestion for the toddler (Appendix 2, Section 2.2, Ingestion of General Household Dust). The reviewer has concerns about the assessment of the dust route of exposure in the HHRA because:
  - the data is based on a limited number of pooled residential homes (30 locations),
  - the data is highly variable, no background exposures for Zone F were determined (thus direct comparisons can not be made),
  - the soil relative bioavailability adjustment was used to approximate the dust specific relative bioavailability, and
  - there is a lack of assessment of the dust maxima found.

Therefore, MOE recommends that the maximum dust concentration be used in the Risk Characterization for Maximally Exposed Individuals (Chapter 7) and that in the absence of a verified measurement, the relative oral bioavailability (ROB) of 1.0 be tested for dust as part of a sensitivity analysis (Chapter 8) to help improve the transparency of the report, and to provide a more complete risk characterization.

#### 8) Section 3.2.8 Table 3-8: Selected Exposure Point Concentration (EPC) for Zone

**B:** The proponent indicates in the report that an objective of the HHRA is to evaluate current risks to human health in Port Colborne. For the determination of the soil EPC for the residential Zone B receptor the proponent has relied on soil sampling data prior to 2002 (Appendix 20, Section 3.2.1 Zone B Residential Soils). Since Zone B includes the Rodney Street community and remediation has occurred it is not apparent how the soil-clean up has been incorporated into the HHRA. As the

proponent has indicated throughout the HHRA that the assessment is of "*current*" risks, the proponent should clarify how this objective is being met.

- 9) Section 3.2.8 Tables 3-8 to 3-11: Selected Exposure Point Concentration (EPC) for Zone A, B, C and D: As indicated by the proponent seven school soil samples were analyzed for Ni, Co, Cu, and four samples for As. Since the number of samples collected for Zone C schools was less than 10 the proponent used the maximum concentration measured for the RME EPC scenario for soil (Appendix 20, Section 3.3.3, Zone C School Soils). Given that zone delineation for HHRA is somewhat arbitrary, the school soil sampling is limited, and the close proximity of schools in zone D (across the street), the near schools within zone D should be incorporated with Zone C schools. Additionally, for the Zone D receptor it is not apparent why Zone C versus Zone D school soil was used in the assessment.
- 10) Section 3.2.8 Table 3-13: Selected RME Exposure Point Concentration (EPC) for Zone F: Ontario typical range (OTR98 from MOE, 1997), EPC for Zone F was used as the Niagara region background (e.g. Table 3-1: HHRA Zones and Rationale, Section 3.2.3, Appendix 20, Section 5.0, Derivation of Background Soil Concentrations) in order to compare receptors in Port Colborne zones. The use of the 98<sup>th</sup> percentile of the Ontario data set is not the same as the RME (i.e. UCLM) EPC used for the Port Colborne selected soil EPC. Since the OTR98 is used throughout the HHRA (e.g. Section 5.3.1 Background Exposures, Tables 5-6 Zone F Background Doses of CoCs), comments and results pertaining to Zone F should be reviewed and revised where appropriate, to take into consideration a more appropriate soil concentration.

## TRV Selection

Comments (11 through 16) refer to the Toxicity Assessment Appendix 7 and Tables 4-2 and 4-3 of the main report. In many cases, insufficient information is provided on the critical study or how the TRVs were selected.

- 11) **Arsenic Inhalation non-cancer TRV:** The proponent has not evaluated the inhalation non-cancer risks for arsenic (As) as it was reported that no TRV was found. MOE recommends that the proponent use the MOE (2009) chronic inhalation non-cancer Arsenic TRV of  $0.03 \ \mu g/m^3$  based on Cal EPA (2000). If the proponent elects to use a different value from another authoritative body, a scientific rationale should be provided.
- 12) **Cobalt Oral non-cancer TRV:** The proponent has relied on U.S. EPA's Region III (2001) oral Reference Dose (RfD) of 0.02 mg/kg-day for cobalt (Co) as it was considered the most appropriate by the proponent for use in the HHRA. MOE notes that U.S. EPA Region III no longer supports this value and has adopted a more conservative value of  $0.3 \mu g/kg$ -day although a rationale is not apparent. MOE recommends that the proponent use the MOE (2009) oral TRV of  $1.0 \mu g/kg$  bw day based on the intermediate MRL of ATSDR (2004), with the application of an additional uncertainty factor of 10 times for subchronic to chronic extrapolation. The

TRV should be replaced and any estimations or calculations relying on this value reviewed and appropriate revisions incorporated into the report.

- 13) **Copper Oral non-cancer TRV:** The proponent has used the Institute of Medicine (IOM, 2001) oral copper (Cu) non-cancer TRV of 130  $\mu$ g/kg bw –day. This TRV is less appropriate than the TRV value of 30  $\mu$ g/kg bw –day derived by Health Canada (HC DWQ, 2004) and preferred by the MOE (2009). MOE recommends that the proponent consider the use of the MOE (2009) chronic oral non-cancer Copper TRV of 30  $\mu$ g/kg bw –day based on Health Canada (HC DWQ 2004). If the proponent elects to use the IOM (2001) TRV a more fulsome scientific rationale to justify selecting this TRV values should be provided.
- 14) **Nickel Oral TRV:** The selection of the nickel (Ni) Oral TRV has been considerably debated as part of this risk assessment. Whereas, the Ministry has maintained a preference for using the US EPA RfD (1998) based on the analysis of Ambrose (1976) at 20  $\mu$ g/kg bw –day to assess potential non-cancer effects from estimated intakes from all exposure routes, the proponent has maintained its preference of 20  $\mu$ g/kg bw –day based on its analysis of the Springborn (2001) study.

In MOE's view, the limitations of the Springborn study (2001), particularly the lack of a dose response or identifiable LOAEL, renders it less reliable than the Ambrose (1976) study used by the US EPA. It should be noted that two credible agencies have considered the Springborn 2001 study as a supporting study for a lower RfD (11  $\mu$ g/kg bw/ day (California OEHHA, 2005, 2010; WHO 2007)).

Furthermore, use of the US EPA RfD would be consistent with:

- Brownfield (2004) program and recently re-endorsed (2009).
- Rodney Street RA (2002) HHRA as recommended by an international expert panel for the Port Colborne RA
- Sudbury Soil Study as conducted by SARA 2008 and independently endorsed by its International Expert Review Panel.

In the context of the use of this value, as indicated by US EPA, the RfD is believed not to cause an individual to become sensitive to Ni but, those who already are hypersensitive to Ni "may not be fully protected". A similar statement (is not intended to protect hypersensitive individuals) was also made by the Working Group who supported a 20  $\mu$ g/kg bw - day TRV based on the Springborn study (2001). As such, it is the expectation that the qualitative statement be brought forth in all communications on the findings of the report as a limitation in the quantitative assessment and in reference to the proponent's Ni RBSC. Note: oral elicitation of dermatitis in individuals who are already sensitized to nickel has been observed following oral Ni dosing which has resulted in lower, more stringent oral TRV's for Ni (WHO, 2007).

15) **Nickel Inhalation cancer TRV:** The proponent's assessment of the inhalation carcinogenic potential of Ni was performed by reviewing several (I to IV) approaches

(Appendix 7, Section 2.4.2.2.). The various approaches combined a cancer threshold and non-threshold (unit risk) analysis for comparative evaluation. According to the HHRA, "the threshold approach was concluded to be more appropriate and the unit risks and resulting cancer risk estimates were concluded to over state actual risks". The cancer threshold approach (proponent Approach III) employed a point of departure analysis of the Copper Cliff refinery worker cohort with the application of uncertainty factors to derive the  $0.6 \,\mu g/m^3$  value based on the analysis of the European Commission (EC, 2001) and Lewis and Caldwell (1999). However it is noted that, while the EC did develop a cancer threshold estimate for Ni, they also developed a threshold non-cancer and a non-threshold cancer estimate. Ultimately the EC developed an air limit of  $0.02 \,\mu g/m^3$ , which was intended to be protective of both cancer and non-cancer effects. The Copper Cliff refinery worker cohort is also used by the US EPA IRIS to develop its unit risk estimate and the EC in its cancer non-threshold approach I (unit risk) (this report ( $0.24 \,mg/m^3$ )<sup>-1</sup>). It was also endorsed by the Ministry in its update to the Brownfield Program (2009).

MOE has proposed an annual limit of  $0.02 \ \mu g \ \text{Ni/m}^3$  as part of consultation for the development of air standards for nickel and nickel compounds for Ontario (O. Reg. 419/05) consultation (EBR posting # 010-7188). The air standard review and rationale indicates that no regulatory agency reviewed has adopted the cancer threshold approach for establishment of a limit for nickel mixtures. Thus MOE recommends that for the quantitative risk assessment of inhalation in Port Colborne, Approach I (refinery dust) and II (oxidic nickel) should be used to bracket the potential range of risks in the quantitative assessment. Reference to approach III (cancer threshold approach) is not supported and should not be part of the assessment.

Note also: Appendix 7, page 108. Approach III. The  $1.1 \,\mu g/m^3 EC$  (2001) value based on a cancer threshold approach represents the upper estimate of a range of values; a low end, middle and upper end of a range have also been developed (0.06, 0.6 and  $1.1 \,\mu g/m^3$ ). The text should clearly indicate and discuss the range of values, derived by the EC (2001).

16) **Nickel Inhalation non-cancer TRV:** The proponent has used the ATSDR (2005) chronic inhalation MRL for nickel sulphate TRV of 0.09  $\mu$ g/m<sup>3</sup>. MOE recommends that the proponent consider the MOE preferred (2009) TRV of 0.06  $\mu$ g/m<sup>3</sup> TERA (1999) with the application of an additional uncertainty factor of 3 times for animal to human extrapolation, and the EU (2004) limit of 0.02  $\mu$ g/m<sup>3</sup>. If the proponent elects to use the ATSDR (2005) TRV a more fulsome scientific rationale to justify selecting this TRV values should be provided.

**Relative Bioavailability Adjustments** 

The following comments (17, 18 and 19) refer to the proponent's selection of relative oral bioavailability (ROB) used in the HHRA, Appendix 8 and Tables 4-4 in the report:

#### 17) Weight of Evidence Criteria Evaluation Criteria Summary:

For the purpose of determining a ROB adjustment factor, the proponent has outlined the evaluation criteria (Appendix 8, Table 13) used in its weight of evidence. Attributes were selected in order to evaluate the weighting that they believed should be placed on each measure of bioavailability or bioaccessibility. In general, the proponent ranked the attribute (importance – low, moderate or high), as well as the criteria in which to evaluate whether the attribute was satisfied or not (ranking – low, medium, or high). While this has aided MOE's review there are specific concerns with the evaluation criteria used by the proponent:

a) "Site-specificity and spatial representation" attribute was ranked to be of "Moderate" importance in the assessment of ROB; however, MOE recommends that this attribute be ranked as "High", as the confidence in the ROB estimate is intended to be site-specific. Furthermore, within the evaluation criteria of this attribute, the proponent has indicated the following ranking criteria, "Low" confidence be assigned to "Artificial substances not site-specific", "Medium" confidence assigned to "Few samples or soils not including all of clay, organic and fill" while assigning the "High" to "10 or more soil samples including clay, organic and fill". MOE recommends that since this is a community-based risk assessment, and that heterogeneity and distinct soil types are found throughout the subject community that a greater weighting should have been allotted to the use of statistically robust sitespecific information. For example, the assignment of "Low" may be reserved for "Few samples or soils not including all of clay, organic and fill", "Moderate" for "10 or more soil samples including clay, organic and fill" and "High" for "10 or more soil samples including clay, organic and fill" and "High" for "10 or more soil samples for each of the soil type including clay, organic and fill".

b) "*Test Vehicle*" and "*Strength of Method*" attributes are both ranked "*High*" importance by the proponent, it is not apparent if some overlap exists in these attributes. In the absence of a more fulsome explanation, MOE recommends that they should not both be ranked as "*high*". Alternatively, the two attributes could be combined to form a single attribute for evaluation purposes and/or there should be a thorough explanation and selection rational provided.

c) Furthermore, it is noteworthy that while the importance of the "*Strength of Method*" is ranked "*High*" by the proponent, there is a difference between method validation, which means the method is only acceptable if it has adequately been evaluated, documented and undergone independent peer review, and regulatory acceptance.

As was previously noted by MOE (referred to in Part B), authoritative bodes have only accepted two methodologies for Arsenic (As) (State of Hawaii) and lead (Pb) (US EPA, 2007), both of which are highly dependant on the consideration of in vivo validation. As such, a high overall ranking does not necessarily dictate that the analysis as performed by the proponent be relied upon for the HHRA. Overall confidence in the proponent's weight of evidence criteria is limited as it is not apparent how the ROB evaluation criteria have taken into account absorption of CoC's for the toddler. As a consequence of this limitation, as well as the lack of assessment ROB for these CoC's in the primary literature, MOE feels that the certainty associated with the use in vivo and in vitro data to make a ROB adjustment dictates cautious interpretation and use in the HHRA.

## 18) Summary: Ni TRV and ROB

The ROB of Ni is a risk driver for both the estimated risks, as well as for the development of the risk based soil level (RBSL). There are no known validated procedures for the evaluation of Ni bioavailability in soil, although general guidance is available for the evaluation of methods to assess bioavailability of metals from soil.

In consideration of the available TRV's for Ni, and with the available information to make a ROB adjustment, MOE recommends that the US EPA (1996) RfD of 20  $\mu$ g/kg bw /day be used (See Comment 14).

Two paths forward were considered by MOE regarding the ROB:

- in vitro bioaccessibility data underlying the 19% ROB used for the Rodney Street (2002) risk assessment, and
- the in vivo bioavailability data underlying the 4% used in the proponents weight of evidence analysis,

MOE continues to recommend a ROB of 19 %, as previously supported by the Ministry be used for the reasons discussed within, which includes accounting for exposure to toddlers and in consideration of the criteria for weight of evidence evaluation (Comment 17).

#### Previous MOE analysis: The Rodney Street (2002)

In the Rodney Street (2002) risk assessment the MOE used the ROB of 19 % (mean within range from 11.8 to 23.3 %) based on the in vitro determination of bioaccessibility data of fill soil samples (n = 10). In general, bioaccessibility data as determined by the in vitro analysis of the fill soil likely represents an upper estimate of bioavailability and was previously relied upon in the development of the soil remediation level. While the ROB of 19% was developed to represent the Rodney Street area, the applicability of this parameter for the different soil types found in the greater community wide Port Colborne (e.g., Welland Clay or Organic) was outside the scope of the 2002 assessment. Based on the additional data provided by the proponent, it is reasonable to interpret that of the soils tested, the fill soil may contain the least bioavailable Ni, as determined in both the in vivo (Fill = 2.5%, Welland Clay 4.5%, and Organic 4.1%) and in vitro (Fill = 6.9%, Welland Clay 14%, and Organic 26%) analyses. However, given the lack of descriptive nature of the fill soil it is more appropriate to conclude that the estimate of 19% bioaccessible as used by the MOE (2002) is within the range of the bioaccessible Ni as determined by the proponent.

MOE appreciates that there are constraints associated with the 19% estimate gleaned from in vitro data but notes that it is based on an established procedure, and is more statistically robust. Based on the information outlined above MOE does not share the proponent's interpretation that bioaccessibility determination of a ROB via in vitro data be ranked "*low*". Furthermore, the intent of a bioaccessibility data is only directed at providing an estimate of the available Ni from the soil under stomach physiological conditions. The use of a ROB based on bioaccessibility information enables the direct relative comparison to the TRV as an intake dose (an in vitro measurement), thus it does not require assumptions to be made on the absorption of Ni into blood (an in vivo measurement).

Additionally, in the absence of toddler specific absorption information, a sufficiently conservative estimate of bioaccessibility is deemed by MOE to be warranted from a regulatory perspective. Bioaccessibility data has previously been used by the MOE (2002) and was relied upon in the Sudbury Soils Study (SARA, 2008).

#### Proponents Weight of Evidence Approach:

In the current HHRA, the proponent has supported the use of a ROB factor of 4 % based on a weight of evidence approach. The approach considers site-specific in vivo and in vitro determination of bioavailability and bioaccessibility respectively, and includes an indirect analysis using soil Ni speciation information. The proponent considers the in vivo data as a "*high*" overall attribute in its weight of evidence evaluation to support the recommended 4 % ROB. However, in review of this material MOE does not share the proponent's confidence in reliance on the very limited in vivo data and, in turn, MOE lacks confidence in the derived ROB of 4% (Appendix 8, Table 14).

The following concerns are raised in regard to the in vivo bioavailability determination of a ROB of 4%, ranked "*high*" by the proponent:

#### 1) Limited sampling

Only 3 soil samples representing Fill, Welland Clay and Organic soils were tested (i.e., n=1 for each soil type). The variability of the bioavailability of the Port Colborne soils introduced by this limited number of soil samples is a concern and may not truly represent area soil variability. A larger sample size is needed to ensure that the bioavailability assessment yields a more reliable estimate.

#### 2) Single oral dose

The in vivo determination of bioavailability was based on rats administered a single oral gavage dose of test vehicle, Ni-sulphate, or test soil. This was undertaken in order to make a comparison of the bioavailability of the Ni from Port Colborne soils to the oral Ni TRV. A key assumption inherent to this approach is that the relative absorption comparison between the Ni-sulphate in water and Ni in soil by a single administered dose is representative of the long-term absorption of Ni in the development of the oral Ni TRV. While this would

not preclude the use of the in vivo information submitted by the proponent, the dosage regimen of the in vivo study is considered to be a significant limitation to the reliance on this data for the determination of the ROB.

In the context of this HHRA, the intent of the ROB adjustment is to determine a relative factor that is site-specific and takes into consideration the Ni speciation and protocol utilized in the TRV. In this case, the preferred US EPA (1996) RfD of 20  $\mu$ g/kg bw /day was based on Ni-sulphate fed (spiked rat chow) to rats for 2 years. In this report the proponent has used a single administered dose of Ni-sulphate in water by gavage to relate the Ni absorption into blood of Ni-sulphate to the test soil. This has introduced some uncertainties to the applicability of this surrogate approach.

It is important to note that ROB adjustment is not intended to directly account for the absorption of Ni, as the adjustment applied to the oral TRV as an intake dose not an uptake dose. In fact, the determination of absorption of Ni from soil requires the added considerations of an understanding of the fed versus fasted state, use of the rat model to mimic human absorption, and whether the absorption rate is sufficiently conservative to account for a toddler.

#### 3) Overall data quality

MOE is concerned that the proponent has assigned greater quality to the in vivo data than may be warranted. For example, the proponent has developed a ROB by comparing the absolute bioavailability determined by blood Ni levels absorbed over a 72 hour period to the area under the curve (AUC) of Ni-sulphate for each of the three soil types. The blood Ni concentration - time curves based on mean data are presented (Appendix 8, Figures 7 and 8). MOE notes the following: (Appendix 8, Attachment A), the blood Ni levels are highly variable, with the Ni blood levels from the soil dosed animals within the variation of the vehicle treated group, thus making differences between the vehicle and soil treated group hard to differentiate.

Together, the proponent's overall ranking of this line of evidence as "*high*" is not shared by MOE, because of the use of a single oral gavage dosing regime to make a relative prediction to the long-term bioavailability of Ni in rats, a lack of soil samples tested, and data quality limitations.

MOE is further concerned that the proponent has considered the in vitro bioaccessibility data ranked "*low*" by the proponent, to support a ROB of 17-21 %.

Previously MOE has commented on the proponent's derived in vitro data as presented in earlier drafts. Those comments stated that the information provided was insufficient and unacceptable to support the interpretations and conclusion of the report because: 1) an insufficient number of samples, 2) ROB values did not meet standards for statistical acceptance, and 3) the lack of validation of the bioaccessiblity data. The proponent responded by combining its bioaccessibility data with the data obtained as part of the Rodney Street Risk Assessment (MOE, 2002) in this version of the report. This was done to account for the broad range of characteristics and indicated that it is suitable for analysis as a statistical pooled data set to cover the range of soil characteristics found in the area (Appendix 8, Section 5.3 Bioaccessibility – In vitro Study). It is not apparent if an analysis was undertaken to determine if data from two different labs could be pooled to generate the 21 % ROB estimate.

In the absence of an appropriate methodology to pool the data sets, the in vitro bioaccessibility data as used by the MOE (2002) is more robust (n = 10) and hence warrants further consideration. Given the more site-specific nature of the data, MOE does not share the proponent's assessment of a "*low*" overall ranking.

Data pertaining to the in vitro stage 2, as conducted by ESG, is not a generally accepted method for assessment of bioaccessibility and therefore, is not considered in MOE's analysis.

Lastly, the proponent has used soil Ni speciation information in an indirect assessment of a ROB of <5%, ranked from "*low*" to "*high*" by the proponent. MOE's concerns with this approach are:

The proponent indicates that, based on Ni speciation work of soil samples of the exchangeable Nickel (soluble), the bioavailability of Ni in soil "would be less than 5 %" (Appendix 8, Section 2.7 Expected Bioavailability Based on Soil Nickel Speciation Data). While the exchangeable Ni fraction provides (Table 5) an indication of the potential or readily available Ni in soil, reliance on this fraction only has not taken into consideration biologically relevant processes that contribute to the leaching of Ni from the soil matrix. The Ni bound to carbonates or subsequent to degradation /dissolution of carbonate, will also be a contributor of Ni bioavailability (Table 5 reported soil samples 4.0 and 5.3%). In addition, the Ni bound to organic matter may be leachable at lower pH conditions and thus, may also be a contributing source (Table 5 reported soil samples 41.3 and 12.6 %). As such, the proponent has not fully accounted for all the Ni that could leach from soil. The result of this omission is that the bioaccessibility fraction is likely higher than the estimated < 5%. Furthermore, due to the limited number of soil samples analyzed, it is not apparent that there is adequate information to support the proponent's assertion.

In predicting the bioavailability of the Ni from soils based on Ni speciation information, combined with human literature reports, the proponent considered the human absolute bioavailability of 7.1% by Nielsen et al., 1999 as being the *"most applicable to a long term average exposure"*. Using this human absolute bioavailability factor resulted in a calculated ROB of approximately 2.8% (Table 7). The use of 7.1% was based on the judgement of the proponent that the absorption rate, as determined in the pre-feed participants (eggs given 1.5 hours prior to dosing), as being the most appropriate of the scenario's preformed by Nielson et al., (1999) in reflecting the typical behaviour of a child (expected to eat prior to playing outside). Nielson et al., (1999) determined the human bioavailability ranged from 3.4 to 25.8 % depending on the fed or fasted conditions. While a rationale to support the selection of 7.1% is provided, it is not apparent how the absorption of the adults in the Nielson et al., (1999) paper can be used to represent a toddler's absorption rate. In lieu of specific child data, MOE recommends that the maximum human adult absorption rate of Nielsen et al., (1999) of 25.8% be used in this line of evidence.

The use of Ni speciation information combined with human and rat absorption rates from the literature are not a generally accepted methodology for making site-specific ROB adjustment. This indirect method in not preferred over the direct determination of in vivo bioavailability, nor the in vitro determination of bioaccessibility. As direct methods are preferred, MOE does not share in the proponent's confidence in assessing an overall ranking of "*high*".

MOE acknowledges the potential contribution of the in vivo data to refine the approach used by the MOE (i.e., 19% ROB based on in vitro data). However, the concerns detailed above lead to an overall lower confidence in the data and resulting 4% ROB, than attributed by the proponent. See additional Comment 17 on weight of evidence evaluation criteria.

#### Added Consideration – the exposure of toddlers

In deliberation of the proponent's weight of evidence assessed in this version of the report and in context of the Ni TRV, it is noted that OEHHA (2005) has developed a child specific Ni TRV (chRD) for non-cancer effects of 11  $\mu$ g/kg bw /day based on Smith (1993) and Springborn (2000) studies. As part of the analysis, a deliberation of matrix effect and child specific differential absorption rates was considered. Using the assumption that the absorption of Ni from water is about 10 times greater than that from food, and that the matrix effect of soil and food are equivalent in retarding absorption, the water based TRV could have a 10 times greater absorption than that of soil. In consideration of an adult versus child's absorption rate of Ni. Thus, in consideration of the retardation of absorption by the soil matrix and the higher GI absorption in children in totality, OEHHA determined that a child specific absorption factor is not required. In addition, OEHHA has noted that since they had considered bioavailability of Ni in developing the chRD, that a further correction for oral bioavailability would not be required in conducting an exposure assessment.

While OEHHA uses a more conservative ROB of 100% than previously used to assess the risks of Port Colborne soils from Ni by either the Ministry (2002) or the proponent, the importance of a children perspective in consideration of absorption rates is noted and warrants a prudent health practice.

#### Conclusion

In evaluation of the bioavailability of the Port Colborne soils for the purpose of conducting a human health risk assessment, MOE believes that there is sufficient site-specific bioavailability information to deviate from the default 100% used for the Ontario generic based soil criteria<sup>2</sup>.

Historically, by considering the data underlying the Ministry's (2002) previous use of 19% along with new data and the weight of evidence provided by the proponent, it is reasonable to suggest that the value of 19% is likely conservative and thus the predicted bioavailability of Ni from Port Colborne soils is likely less than 19%.

Nonetheless, while the provision of much needed in vivo data adds considerably to the site-specific information, MOE does not share the proponent's confidence in the 4% ROB, for key reasons discussed above, notably the single-dose regimen of the in vivo experiment, the minimal number of soil samples, and the ability to the rat model to account for child's absorption. Even so, the new analysis adds weight to the suggestion that the historical approach of the MOE (i.e., 19%) tends to be conservative, yet the information provided does not provide MOE with sufficient confidence to rely on the proponent's weight of evidence for the characterization of risk for Port Colborne or in the determination of the RBSL.

Finally, as the site-specific ROB is a risk driver for Ni, and that there exists uncertainty in the estimation of potential risk characterization of Ni in the Port Colborne soils, it is suggested that this uncertainty be reflected as part of the risk communication.

Final ROB recommendation: 19%

#### 19) Weight of Evidence evaluation for As, Cu and Co ROB's

In the assessment the ROB for the CoC's, As, Cu and Co, the proponent has relied on the in vitro bioaccessibility data determined by the Exponent Environmental Group as used by the MOE for the Rodney Street HHRA (2002). In the weight of evidence evaluation, the proponent (Appendix 8, Section 6.0 Weight of Evidence Criteria Evaluation Criteria) has assigned a "*Low*" confidence to Cu and Co and "*Medium*" confidence to As, thus the rationale for selecting the 95<sup>th</sup> UCLM versus the maxima has not been sufficiently substantiated. MOE recommends that given the limited number of soil samples tested and the proponents weighting that the soil maximum ROB be considered and factored into the sensitivity analysis.

Clarification of Appendix 8, Table 19 Summary of Selected ROB values. According to Table 18 the UCLM (bolded) was used in the HHRA, yet summary Table 19 indicates that the mean ROBs were used. Spread sheets provided to the MOE (July, 24, 2010), indicate that the UCLM data was used. The proponent should ensure that

 $<sup>^{2}</sup>$  The generic soil standards for Ontario use a 100% ROB (or relative bioavailability factor of 1 as in MOE 2009) in the absence of site-specific information.

the UCLM data was used in the HHRA as indicated and resulting appropriate changes to the table(s) be incorporated.

### Exposure Assessment

- 20) 5.1.3 Literature Review: The proponent has omitted the MOE's December 2009 updated Brownfields soil criteria (component values and revised soil standards) "Rationale for the development of soil and ground water standards for use at contaminated sites in Ontario" from its literature review. This document contains the MOE preferred receptor characteristics recommended to be used in HHRA's and in the development of site specific soil standards. The proponent should ensure that the current submission would satisfy/fulfill these criteria, especially when the proponent has used less conservative receptor characteristics. However, it is also noted that sitespecific receptor characteristics have been incorporated into this HHRA and if sufficiently supported, may be acceptable. A comparison of receptor characteristic from the MOE preferred criteria (2009) to the characteristic used is the submitted HHRA should be incorporated into Appendix 3, Receptor Characterisation; this would increase the transparency of the report. Additionally, other citations should be updated, such as the US EPA Child-Specific Exposure Factors Handbook (2008, 2009). Where appropriate updated or MOE (2009) preferred receptor characteristics should be integrated into the exposure assessment of the HHRA.
- 21) 5.3.5.1 Uncertainty in Arsenic Exposures: The proponent indicates that "the arsenic oral and dermal exposures were concluded to have too great uncertainties associated with them for the valuation of exposure to be reliable" (Page 5-32). Based on this assessment, risk estimates were not generated in the report, despite As being a CoC and TRVs being selected. The uncertainty in estimation of the exposure to As due to undetectable levels in samples of well water, municipal water, supermarket foods and garden produce is discussed in Section 5.3.5.1, Uncertainty in Arsenic Exposures of the HHRA. In Table 5-13, when the Estimated Quantification Limit (EQL), Method of Detection Limit (MDL), ½ MDL or zero for As was used in the exposure assessment, the reported variation between these default assumptions in exposure in comparison to the variation among zones was deemed by the proponent insignificant.

An uncertainty in the arsenic exposure estimate, due to samples being below the detection limit, is an insufficient reason to not complete the quantitative arsenic risk characterization (Section 6.2.4.2). It is important to note that only 1 of the soil samples (Appendix 20 Statistical Analysis of the Soils Database) was considered non-detect (ND). Thus, as the focus of this HHRA is a soil study, while the risk estimates for other media may introduce uncertainty in the overall risk estimate, the uncertainty of the soil exposure is reliable to make a risk prediction. Thus, a comparison of the arsenic exposure estimates to the arsenic TRVs is required.

#### **Risk Characterization**

As many of the MOE comments (including Part B) would influence the risk characterization, various statements made by the proponent in this section would require additional justification, and may also change once MOE comments are addressed or incorporated by the proponent. Comments are limited to concerns not identified by earlier comments.

- 22) Section 6.1 Risk Estimation Equations (Page 6-3): The proponent includes the following statement "Where background doses are used, these are used for comparative purposes only; effects smaller than 10 to 20% above natural background cannot be reliably distinguished or quantified". The statement is not supported. If the proponent elects to retain this statement in the document a rationale supporting it should be provided.
- 23) Section 6.1 Risk Estimation Equations (Page 6-3): The proponent includes the following statement "For each non-threshold acting chemical, the incremental lifetime cancer risk (ILCR) was estimated for the incremental dose discernible from background (see Equation 6-3) or the incremental concentration in the case of inhalation risks (see Equation 6-4)". The statement is not supported. The proponent has confused a compliance assessment wherein a facility's incremental contribution is assessed and a community based risk assessment for which background (total) exposures are to be taken into consideration. See also Part B Comment 34 where this has been previously commented on by MOE. The original comment remains valid, and the response by the proponent is not accepted.

For the purpose of evaluating the inhalation cancer risk in the CBRA, MOE considers the Total Lifetime Cancer Risk (TLCR) data as being relevant only to the characterization of inhalation risk for the community, provided that the background air concentrations are confirmed to be included in the risk estimation.

24) Section 6.1 Risk Estimation Equations (Page 6-4): The proponent has indicated that "All estimated ILCRs and HQs in the following sections have been rounded to the number of significant digits in the selected TRVs". The use of significant digits of a converted number in relationship to the selected TRV has resulted in a tendency to reduce the accuracy of the estimated reported data i.e. the measures or modelled exposure data used in the report. For example, as indicated in Table 7-22, for the zone B resident, the Max value HQ for the infant is reported as "1" (1 significant digit); however, due to rounding this could represent an HQ from 0.7 to 1.4. The result is that the rounding methodology used by the proponent has tended to loose information. Consequently the risk manager is not in a position to assess whether an HQ of 1.0 has been exceeded.

It should be noted that the HQ and ILCR designation are converted ratios, in that the analysis culminates in the expression of the report data as a ratio to the TRV. The precision of the report data should be retained such that the accuracy is neither

sacrificed nor exaggerated. As a consequence of excess rounding based on the TRV, forming a converted number has resulted in the loss of useful information. Given that the HHRA consists of mixed data based on varying degrees of precision and accuracy, and with the intended use of this information, it is recommended that both hazard quotients and cancer risks be reported to 2 significant figures.

For the purpose of risk management, the significance of exceedance of an HQ of 1 or ILCR of 1 in a million, especially when small differences are identified, should also be taken into consideration in the overall error/uncertainty of the risk estimation. The risk assessment report should provide sufficient information to inform risk management decisions.

- 25) Section 6.2.4.1: In Section 6.2.4.1, Inhalation, the proponent concludes that "All of the maximum measured air concentrations fall within the range of typical Ontario ambient air concentrations of arsenic and no incremental (i.e., above background) health risk is indicated". This statement is not supported. In context to the HHRA, as mentioned in comment 3, this should be re-addressed by the proponent as health based statements should only be made in reference to a TRV and not an AAQC. Furthermore, it is noted that As compounds have been targeted for review by the Ministry as recent studies have identified new toxicological information since the previous guideline was set in 1981.
- 26) **Section 6.2.4.3:** The Section 6.2.4.3, Historical Use of Arsenic Trioxide, is more appropriately considered as part of a discussion of results versus within risk characterization, as it was not specifically investigated as part of this HHRA.
- 27) Section 6.2.4.4 Findings from Studies Involving Bioassays: The proponent has by "extension" and for comparative purposes suggested that residents of Port Colborne would not be expected to have adverse health effects from As exposure, by comparing three urinary health studies conducted in Ontario (Volume III, Appendix 7, Attachment B). These previous Ontario studies, while providing context to the Port Colborne scenario, should not be used to make declarations that there are "no health effects from arsenic exposure are expected to residents of Port Colborne", because the previous studies were not based on an urinary As exposure limit associated with a clinical effect, but were used to make comparisons to other As exposure sites. Furthermore, no urinary health-based study has been conducted in Port Colborne. Comments on As exposures should be limited to comparisons to other communities, and health claims should be removed.
- 28) Section 7.2 Maximum Concentration in Soil at All Sample Depths. In order to assess potential maximally exposed individuals, the maximum concentration in soil scenario was used. However, the proponent states "the maximum concentrations in soil scenario is likely unrealistically conservative but provides an upper estimate of potential for exposures to soil". This statement is not supported. While on a community-based level the use of the maxima would not be representative of the typical or average exposure for most human receptors, a given toddler's exposure

may be limited too a residential property, thus the maximum soil concentration should be considered. Furthermore, limitations in the site characterization may also indicate that the use of the maxima is warranted, including depths below the 0-5 cm range, due to insufficient information (see Comment 2).

29) Section 7.5 Maximum Ambient Air Concentrations: As part of the risk characterization for the RME scenario and the maximally exposed individual, the ambient air exposure point concentrations for various Zones were assessed. The assessment relies on a combination of both measured and modelled air data. In general, it is difficult to readily understand how the air concentrations were derived for use in the exposure assessment and if they are reflective of the ambient air. For example, for Zone B, the maximum ambient air concentration, as measured at receptor location 25 referred to as the baseball diamond, was considered in the RME scenario. For Zones B, C, and D, the Zone B maximum ambient air concentration was used to assess the maxima at these Zones. However, it is noted that the estimated ambient air data was modelled for Zones A, C, and D, yet these predicted air concentrations were used as long as they were not higher than the Zone B highest year averages (Section 3.2.5.3 Concentrations in Indoor Air). The rationale for excluding the modelled predicted air concentrations for Zones A, C, and D requires additional justification in the assessment of maxima. Additional clarity in presentation of material is required.

Furthermore, since indoor air concentrations were evaluated as being proportional to ambient air at a ratio of 0.6 and, given MOE's hesitation for reliance on this estimate, it is recommended that the outdoor air concentration be compared directly too the TRV or a ratio of 1.0 be assessed. In accordance with comment 15, Table 7-17 using Ni approach III should also be omitted.

Overall, as a consequence of the above concerns, this report does not provide enough information to support the proponent's claim that "the results of the assessment of maximum ambient air concentrations indicates that inhalation health risks associated with the highest evaluated maximum ambient air concentrations (i.e. highest location) are not expected" (page 7-16). Additional rationale and justification is required to support this concluding statement.

30) Section 7.6 Maximum Indoor Air Concentrations: As part of the risk characterization for maximally exposed individuals, the indoor air exposure point concentrations for Zone B were assessed. Despite the reservations of the proponent to include home IAS 102 because it may be being a statistical outlier, the observed air concentration should be assessed as a maximum indoor air concentration (Appendix 13, Section 3.0 Sample Outliers). The inclusion of this observation is supported, given that the indoor air data was based on a limited number of residential homes tested in the most impacted air zone (n = 10), and that the data is highly variable. However, MOE acknowledges that the sample IAS 102 does not represent the community exposure.

In characterizing the Ni inhalation risks associated with the maximum;

- the proponent's cancer Ni approach I and II are noted to predict cancer risks above a one in a million benchmark,
- reference to the proponent's approach III (cancer threshold approach), is not supported (See Comment 15), and
- confidence in the risk characterization of inhalation non-cancer is hampered by rounding (See Comment 24).

The proponent's conclusion "*There is unlikely to be an elevated risk from nickel inhalation, even for residents of the home with the maximum measured indoor air nickel concentration*" (Page 7-19), is not supported because of the potential exceedances of cancer and non-cancer endpoints and, the insufficient site characterization information available. Additional rationale and indoor air sampling would be required to substantiate the supposition.

#### Sensitivity Analysis

It is anticipated that once MOE comments are addressed, this section would be expanded. Thus the following comments are reserved for information presented that has not been addressed through other comments.

#### 31) Table 8-1 Sensitivity Analysis for Site Characterization and Problem

**Formulation** For the risk analysis study factor "*Changes in future land use – agricultural*" the proponent indicates that a "*change of agricultural areas to other land uses would not be expected to increase potential exposures*". It is not apparent, how the proponent has arrived at this conclusion. A rationale to support the statement should be provided. It is noted that the agricultural land is located in the predominate down wind footprint from the facility. Thus the potential for increased exposure to CoC's is likely.

- 32) Table 8-1 (continued) The risk analysis study factor "Changes in future land use-recreational" the proponent has indicated that for the Reuter Road woodlot residential development would "increase exposures and may lead to higher risks". This statement is supported. However, the proponent also indicates that concentrations in other woodlots are less than those found in the current residential location, thus the statement is limited to the Reuter Road woodlot. Given that higher CoC levels are detected in woodlots (Figure 2-4, CoC Concentrations in Selected Woodlot Soils (0-5 cm Deep) Port Colborne, ON) than the surrounding residential area, this too would be expected to increased exposures for the residential receptor. Consequently, the limiting of the comment to the Reuter road woodlot warrants additional elaboration and or justification. Due to some woodlots being characterized by a single soil sample, this limitation should also be discussed as part of the confidence in the proponent's response.
- 33) Table 8-3 Sensitivity Analysis for Toxicity Assessment: In this Table the proponent has indicated that through the incorporation of uncertainty factors (UF) the oral TRVs for Ni and Cu, and the inhalation TRVs for Ni and Co, inherently "overestimate" risk. MOE does not share the proponent's interpretation. UFs are intended to account for

deficiencies or gaps in the original study that they are derived from, therefore can not contribute to the risk overestimation. UF are not equivalent to "safety factors" although historically were referred to as such. In general, as the body of scientific information increases TRVs are more likely to become more stringent with time, not less. Thus the application of UF is deemed to be appropriate, when applied at the time of establishment of the TRV. Including the discussion on the uncertainties associated with the TRV in the sensitivity analysis is unconventional and is more appropriately included in the toxicological (hazard) assessment.

34) Section 8.5.5 Nickel Contact Dermatitis. The proponent has indicated, based on a "extreme maximum estimate of potential soluble nickel loading to skin from soil exposure at the maximum concentration" would yield an estimated 0.7  $\mu$ g Ni/cm<sup>2</sup> dermal exposure. The HHRA compares this estimate to <0.1 to1  $\mu$ g/cm<sup>2</sup> concentration range, a range identified by Menne (1994) as being unlikely for the elicitation of nickel dermatitis assumed for sensitized individuals, but not hypersensitized individuals (as low as 0.0075  $\mu$ g/cm<sup>2</sup> estimate of Menne (1994) when exposed on inflamed skin under occlusion). From this, the proponent asserts that "a dermatological response to nickel in Port Colborne soils was concluded to be highly improbable for nickel-sensitized individuals". It is not apparent from the information provided how the proponent has calculated this estimate. Therefore, MOE can not substantiate the proponent's conclusion. A detailed calculation of the estimate, including a rationale supporting key assumptions used by the proponent is required. It is noted that MOE recommends the use of 0.2 mg soil/cm<sup>2</sup> skin soil adherence factor (MOE, 2009) versus 0.1 mg soil/cm<sup>2</sup> as was indicated (page 8-45).

Confidence in the proponent's conclusion is also limited as the toxicological assessment of Ni dermatitis is abbreviated (Sections 4.4.1 Nickel Contact Dermatitis and Appendix 7 Section 2.4.3 Dermal Toxicity). A more fulsome hazard assessment of Ni dermatitis is required. Furthermore, MOE notes that the most recent scientific paper cited was in 1994, an updated review of the science literature of Ni dermatitis is warranted.

35) Section 8.5.7 Soil Pica Behaviour in Children: As part of the sensitivity analysis, the proponent has attempted to account for pica behaviour of children (deliberate ingestion of soil) Section 8.5.7, Soil Pica Behaviour in Children. The proponent indicates that "For the purpose of the Port Colborne HHRA, the US EPA (1997) upper percentile estimate of 400 mg/day was chosen as the representative soil ingestion rate relevant to soil pica behaviour." The toddler for Zone B is used to demonstrate the influence of a more conservative SIR of 400 mg/day versus 100 mg/day on the calculated ingestion dose and hazard quotient (HQ). This is intended to account for the soil pica versus RME scenario (Table 8-11, Sensitivity of Inhalation Hazard Quotients to a Pica Toddler Scenario). MOE notes that the SIR of 400 mg/day is an upper percentile (95<sup>th</sup>) whereas, 100 mg/day SIR is considered by the US EPA (2007) to be the best estimate of the mean for children under 7 years of age. Thus the use of 400 mg/day is inappropriate to account for soil pica and instead would be appropriately used in a RME scenario. It is noted that MOE (2009) SIR of

200 mg/day is preferred as a conservative estimate of the average SIR (95 UCLM) for the toddler for use in HHRA's in Ontario and in the development of soil standards.

36) Section 8.5.10 Assessment Verification. The proponent has adopted some of the key assumptions of the MOE Rodney Street assessment (MOE, 2002) into its model as outlined in this section. The corresponding changes are reported in Table 8-14 Ingestion/Dermal Hazard Quotients for Nickel. Details of the changes adopted for use and additional model assumptions are required to indicate how each of the parameters was modified by the proponent. The analysis was not reproducible given the supplied information. Detailed model inputs and or modifications may also be required. Furthermore, confidence in the proponent's assessment is limited as multiple variables (12) were simultaneously modified. Preferably a percentage change in HQ should be indicated, first for each modified variable before combining of variables. Additionally, site-specific variables from the MOE 2002 report should be incorporated, whereas, the receptor characteristics should be obtained from the MOE 2009 Brownfields rationale document where available.

## Risk-Based Soil Concentrations (RBSC)

- 37) 9.1 Derivation of RBSCs. Many of the concerns outlined in this memo have not been satisfactorily resolved and are likely to influence the recommended RBSC's for the CoC's. As a result, MOE will not provide final comments on the derivation of the RBSC until the concerns appropriate to this issue have been resolved. The proponent requests a RBSC of 20,000 mg/kg for Ni; however, MOE is not confident that the proposed level will be protective of human health for the citizens of Port Colborne. Furthermore, many of the considerations of the RBSC rely upon risk management, thus a broader/general Ministry approach is warranted. MOE offers the following comments in the interim to facilitate this review:
  - The proponent has not provided the Hazard Quotient or Cancer Risk associated with the determined RBSCs. This key information should be incorporated into the report and communicated in the executive summary.
  - The proponent should indicate that not all exposures have been qualitatively accounted for in the HHRA; specifically, the omission of consumer products should be mentioned.
  - The decision to not derive a RBSC for Co, Cu, and As has resulted in the stated objective of the report not being satisfied.

Additional discussion with the Ministry is anticipated.

# <u>Part B:</u> Proponent's Responses to Previous Comments Made by MOE (September 26, 2007)

**Part Two: Responses to Ontario Ministry of the Environment's Comments** - for tracking of responses, blocks within tables have been sequentially numbered. Responses and clarifications are provided as groupings with additional sub- related comments made. Where appropriate, emphasis on the Part A new MOE comments are highlighted. For the most part, Part A of this review, above, addresses ongoing MOE concerns.

#### Comments 1 and 2 (Preamble)

Responses are acknowledged. While the application of O.Reg 153/04 as mentioned, to the Port Colborne community-based risk assessment process, is more of a legal issue and outside the context of this review, from a Human Health perspective the regulation, as mended (2009), provide the proponent with MOE's expectation of scientifically acceptable methodology and criteria (e.g. TRV's and receptor characteristics) that the Ministry prefers to be used in an HHRA or in the development of soil criteria. These criteria have been used in the assessment of the submitted HHRA.

Comments 3, through 12 (Soil and dust in vitro extraction issues)

The proponent has addressed the concerns by providing a weight of evidence evaluation for the determination of the oral bioavailability adjustment (ROB) factor, Part A Comment 17, 18 and 19 apply.

#### Additionally

#### Comment 7

Response is partially supported. There are many factors that may contribute to differences in oral bioavailability between soil and house hold dust that can be attributed to facility emission. Forefront in this consideration is the influence of particle size on bioavailability, that is the fraction which is likely to enter through aerial deposition in the house from outdoors and is likely a smaller size fraction then that which deposits outdoors. It is not uncommon to observe higher bioavailability adjustments for co-localized dust than soil, likely attributable to particle size differences. The lack of dust sampling remains an outstanding limitation of the HHRA, Part A Comment 7 applies.

#### Comments 9 and 10

The response does not address the statistical limitations or methodology used to assess the data.

#### Comments 11

Response is acknowledged. MOE's comment should have clarified that it is only when the in vitro data had been well supported by in vivo data it is considered a generally accepted and validated method. This would not preclude in vitro data in of its self invalid, but does highlight a significant limitation of the information provided.

Comments 13, 14, and 15 (Inhalation cancer risk factor for Nickel) The proponent has made modifications to the inhalation cancer hazard assessment for Ni. Part A Comment 15 applies.

Comments 16, through 22 (Assessment of Soil and other media exposure point concentrations in the context of CBRA)

The proponent has addressed the concerns by providing an assessment of the maximally exposed individuals, however, MOE has identified concerns with the proponent's

analysis, and has recommended additional criteria to be assessed. Part A Comments 5, 6, 28, 29 and 30 apply.

Additionally,

Comment18

The response by the proponent is not supported. While extensive soil sampling has occurred in the highest impacted area, the uncertainties in other zones or in other media have introduced limitations and uncertainties in the assessment. Part A Comments 2, 5, 6, 7, 9, and 28 apply.

Comment 23 (Proposed SSTL exceed soil maximum for each zone) The proponent has provided a risk based soil concentration for Nickel of 20,000 mg/kg. see Comment 37.

Comments 24 through 28 (Soil Dermal Absorption Adjustment) The response is acknowledged, additional clarification is required see Part A Comment 34.

Comments 29 and 30 (Intake of nickel form supermarket food issues) The proponent has provided additional rationale to support the use of daily dietary intake method 2 for use in the estimation of doses and risks for the HHRA. The use of method 2, by larger food category is assumed to be dependent on the combination of mean data for each food item. Given the lack of food items sampled by the proponent, the justification of using mean data is not warranted; the statistical procedure as outlined in Appendix 4, should be used for each food item. Additional clarity and justification is required.

Comment 31 (Oral Nickel RfD Issue) See Part A Comment 14.

Comment 32 (Requirements for both CTE and RMA assessments) The response is reasonable and no further response is required.

Comment 33 (Arsenic assessment issues) The response is not supported, a quantitative assessment is requested see Part A Comment 21 and 25.

Comments 34 to 39 (Subtraction of background from lifetime risk calculation). The response is not acceptable. Part A Comment 23 apply. Additionally

Comments 35 and 37 The response is provisionally acceptable, contingent on the proponent clearly indicating the HQ or ILCR that the determined RBSC represents. Part A Comment 37 applies. Comment 39 The response is not accepted. Comment 40 (Surface soil depth issue) The response is reasonable and no further response is required.

Comment 41 (Exclusion of woodlot soil data) The response is accepted, clarification should be gained by addressing site characterization concerns Part A Comment 2.

Comment 42 (Soil ingestion rate)

The response is acknowledged, the soil ingestion rates of 100 mg/day and 400 mg/day published by the US EPA have been used in the final report. Part A Comment 20 and 37 apply.

Comment 43 (Soil and dust in vivo bioavailability issue) The response is not acceptable. Part A Comment 17, 18 and 19 on the weight of evidence to support the ROB apply.

Comment 44 (Soil CoC speciation issues) The response is acknowledged.

Comment 45

The response is accepted; however, the proponent should organize the material such that it can be readily located. The reviewer was forced to search all disks to find the attachment as referenced "*Attachment C Electronic copy of referenced reports*" does not indicate the location of the material.

#### Comment 46 (Model sensitivity)

The response is not acceptable. The proponent has been requested to conduct additional sensitivity and/or uncertainty analysis to address the MOE concerns; Part A Comments 5, 6, 7, 18 and 37 apply.

Comment 47 (Use of chronic TRV to calculate SSTL) The response is reasonable and no further response is required.

Comment 48 (Adjustment of cancer risks in early life stages) The response is reasonable and no further response is required.

#### Comment 49 (SSTL Calculation)

The response is provisionally acceptable contingent on the proponent including the "*Hand Calculation of RBSC for Nickel*" as an appendix of the main report versus an appendix of the Stantec Consulting Ltd. draft report "*Responses to PLC consultants* report Human Health Risk Assessment Port Colborne, Ontario" dated February 23, 2010.

Comment 50 (Clarity and errors/discrepancies) The response is reasonable and no further response is required. Comment 51 (Air data) The response is acknowledged, additional clarification is requested (Part A Comment 29).

Comment 52 (use of adjusted air concentrations to assess inhalation risks) The response is reasonable and no further response is required.

Comment 53 The response is reasonable and no further response is required.

Comment 54 The response is reasonable and no further response is required.

Comment 55 (Infant diet exposures) The response is reasonable and no further response is required.

Comment 56 (Potential effects of mixtures and cumulative effects) The response is reasonable and no further response is required.

Comment 57 (Attachment 1) The comment and responses have been addressed above, and no further response is required. Appendix 5B

Literature review and EC25 meta-analyses of crop studies from the Port Colborne area



Appendix 5B: Literature Review and EC25 Meta-Analysis on Studies of Crops grown in Organic muck soils of the Port Colborne Area



Prepared for:

Vale Canada Limited

Prepared by:

## Stantec Consulting Ltd.

70 Southgate Drive, Suite 1 Guelph, ON N1G 4P5

File No. 122210662 September 12, 2014

# Sign-off Sheet

This document entitled Appendix 5B: Literature Review and EC25 Meta-Analysis on Studies of Crops grown in Organic muck soils of the Port Colborne Area was prepared by Stantec Consulting Ltd. for Vale Canada Limited. The material in it reflects Stantec's best judgment in light of the information available to it at the time of preparation. Any use which a third party makes of this report, or any reliance on or decisions made based on it, are the responsibilities of such third parties. Stantec Consulting Ltd. accepts no responsibility for damages, if any, suffered by any third party as a result of decisions made or actions based on this report.

Prepared by (signature) Wai Ma lengo Reviewed by (signature)

Tereza Dan



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## APPENDIX 5B: LITERATURE REVIEW AND EC25 META-ANALYSIS ON STUDIES OF CROPS GROWN IN ORGANIC MUCK SOILS OF THE PORT COLBORNE AREA

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#### 1.0 Introduction

As part of Vale Canada's community-based risk assessment (CBRA) process, field and greenhouse crop studies were designed and conducted in 2000 and 2001 (Jacques Whitford, 2004) to:

- 1. determine how chemicals of concern (CoC) at varying low to high concentrations would affect crop growth in metal-impacted soils in the Port Colborne area;
- 2. establish acceptable soil and plant tissue concentrations for CoC that would not cause significant phytotoxic effects; and,
- 3. evaluate the effectiveness of select remediation treatments. A biomonitoring field study was also conducted in 2001 to provide a suitable comparison for results generated from the greenhouse study.

The Effective Concentrations causing a 25% reduction in yield (EC25) calculated from the yield (biomass) of oats grown in four types of blended soils found in the Port Colborne area (sand, organic, Welland clay, and till clay) in the 2001 greenhouse study were determined to be 1350, >2400, 1880, and 1950 mg/kg of nickel (Ni) in soil, respectively.

In the case of organic soils, the site-specific objective of >2400 mg Ni/kg soil was derived because a 25% reduction in oat relative yield (i.e. relative to plants grown on "control" soil with low Ni) (expressed as plant biomass rather than grain yield) was not observed, even in organic soils with the highest Ni concentration (2400 mg/kg) used in the study. The calculated EC25 values were proposed as site-specific (toxicological) threshold level (SSTL) values for the protection of crops in the affected area.

The purpose of this appendix is to re-evaluate the pertinent literature from 1981 to 2001 (including Ontario Ministry of the Environment (MOE) reports) regarding the phytotoxicity of Ni to a variety of field crops grown in the Port Colborne area. It happens that this literature related exclusively to organic muck soils, as it was these soils that were present on the farms that were most severely impacted by the refinery's emissions until the refinery ceased Ni production in 1984. It is the crop damage from the emissions on these farms on organic soils that were studied by the MOE and its predecessor, the Air Pollution Control Branch, which resulted in several study reports and publications. These earlier reports had been excluded from consideration in the Crops Risk Assessment Report (Jacques Whitford, 2004) because (a) the studies were typically not designed in such a way that EC25 values could be readily calculated and (b) they were conducted when the refinery was still actively releasing Ni. This is an important point, since the emissions included soluble Ni and Cu in considerable proportions in the high production years in the 1950's and 1960's (Air Pollution Control Branch, 1959). In 1979 and 1980, it was determined that 70% of the Ni associated with silver maple leaves within 2 km downwind of the refinery was due to active emissions (MOE, 1981).



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The exposure of plants to elevated airborne Ni doesn't occur today, so the role of foliar metal exposure to phytotoxicity has to be carefully considered. Nevertheless, fruitful discussion with the MOE during the review process resulted in this appendix, which has brought this earlier literature into the discussion surrounding agricultural crop risk assessment at Port Colborne. Emphasis is placed on how the site-specific studies relate to soil Ni concentrations where significant phytotoxicity (represented by yield loss) was observed on crops grown in organic muck soil.

No similar re-evaluation was completed on EC25 values generated for clay or sand soils from the 2001 greenhouse study as the MOE was satisfied that the EC25 values for clay and sand soils were reflective of the actual phytotoxicity conditions independently observed by the MOE in the field.

There are two aspects related to the incorporation of these older data into the Crops risk assessment. First, the relative value of the papers under review had to be determined. A process was developed for ranking the papers (presented in section 1.1). Second, it had to be determined whether EC25s could be estimated from the data. In some cases, "control" data was not included in the original study. In such cases, the potential use of surrogate values from other sources as control data was evaluated so that EC25s could be estimated in a common sense way.

#### 1.1 SCORING AND RANKING OF RE-EVALUATED LITERATURE

In the time since the original Crops Risk Assessment was completed in 2004, the field of evaluating published data has advanced considerably, as a result of the REACH (Registration, Evaluation, and Authorisation of Chemicals) Regulation in the European Union (EU)<sup>1</sup>. More than 12,000 unique chemical substances have been registered for use in Europe, and one goal of the REACH Regulation is to use existent data as much as possible to minimize testing. The approach of Klimisch et al. (1997) has been broadly utilized under REACH to assign reliability estimates to existing scientific articles to determine whether the information in the articles is reliable. The "Klimisch Criteria" provide a means of assessing the value of information from the scientific literature for use in risk assessment. The Klimisch approach identifies 4 categories of reliability: Klimisch 1 - "reliable without restriction"; Klimisch 2 - "reliable with restrictions"; Klimisch 3 - "not reliable"; and Klimisch 4 – "not assignable". These categories span a wide range of quality of scientific papers which reflect the varying standards associated with scientific journals (which themselves have a wide range of quality, with the highest tier journals having stringent standards of acceptance and lower tier journals having lower standards for acceptance). Included in the assessment was the so-called "grey literature" (non-independently-peer-reviewed) comprising reports from a wide range of sources, including both industry and government. The general approach of Klimisch is that the best-designed and most transparent (i.e. best documented)

<sup>&</sup>lt;sup>1</sup> <u>http://ec.europa.eu/enterprise/sectors/chemicals/reach/index\_en.htm</u>



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work conducted according to standard scientific approaches and principles should have higher acceptance for risk assessment than poorly documented studies<sup>2</sup>.

As will be seen below, an approach was developed (based on a preliminary plan provided by the MOE) to rate the agricultural studies conducted as early as 1980. The methodology was developed independently from the Klimisch approach, and has some robust aspects to it, although, in the final analysis, professional scientific judgment is an important part of the approach and the resulting numerical scoring. This is also true of the Klimisch approach.

The main objective of the literature re-evaluation was to derive and recommend an EC25 value for soil Ni (as a SSTL) that includes all studies of merit conducted on organic soils in Port Colborne from 1981 to 2001. Because of the varying study objectives, experimental designs, and confounding factors noted in the re-evaluated papers, a standardized and objective process was needed to evaluate the quality of the reported or calculated EC25 values from these various reports for inclusion in the dataset from which the SSTL would be derived. A process similar to the US EPA's *Guidance for Developing Ecological Soil Screening Levels* (Eco-SSLs) was followed (US EPA, 2003). This process included:

- a) Formulating a key comprising the scoring criteria to objectively assign a numerical value (score) to each endpoint based on the scientific quality of its source study;
- b) Endpoints above a certain score (e.g., greater than 55%) were included for calculation of an overall EC25 for organic soil;
- c) The scores were used as "weights" to weight the value of each EC25; and,
- d) Calculate the SSTL as the weighted average of the individual EC25s from all studies.

In consultations that occurred throughout 2012 between representatives of the MOE, Vale, and Stantec, a scoring key was developed. Every effort was made to produce a scoring key that was objective and impartial. However, by the nature of the process, the scoring key development may have included elements of subjectivity as the scoring categories and their assigned scores were chosen pragmatically. The finalized key included 12 scoring categories based on various relevant scientific, economic, and practical considerations. Only those endpoints from references that scored 55% or higher were considered to be of sufficient quality to be included for further consideration.

A consensus was reached on the scoring categories comprising the scoring key; however, consensus was not reached for the scoring criteria in three of the scoring categories (e.g.,

<sup>&</sup>lt;sup>2</sup> A major aspect of the scientific approach is that the science should be sufficiently rigorous and documented such that it can be reproduced by others and therefore, a published study, to be credible, has to provide enough information that it could be reproduced by others in order to verify the results. Poor documentation and poor experimental design are obstacles that make verification challenging or less likely. Klimisch 3 and 4 reliability categories are intended to classify such studies and caution us to be wary of using these types of scientifically unsound and poorly documented studies.



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scientific, economic, and /or practical merits). In the interest of advancing the process, the scoring key presented by the MOE was adopted (summarized in **Table 5B-1**).

It should be noted that professional judgment could have resulted in a different scoring approach, as some of the scoring categories and criteria include assumptions that are clearly precautionary and conservative. For example, the "Study Type" scoring category assumes that field studies are "better" (i.e., a field study receives a score of 3) than greenhouse studies (which would receive a score of 1). This is a simplistic view. Greenhouse studies allow confounding influences to be removed from consideration and allow considerable experimental control, whereas field studies have considerably more inherent variability and there is little control over the influence of confounding factors. What is relevant about field studies is that they relate directly to field-grown crops. Similar biases are present in several of the other scoring categories and in the final determination of "study confidence". The scoring approach is limited by these considerations, but it is more quantitative than the Klimisch approach and is still a worthwhile exercise in that it allowed more data to be used for the Crops Risk Assessment in this 2014 Update Report.

Scoring Categories (Range of Scores)	Scoring Criteria
Study Type (1 to 3)	1=pot in greenhouse or growth chamber 2=pot in field 3=field
Soil Type (1 to 3)	1=other 2=agricultural and other (woodlot, vacant field, beach etc.) 3=agricultural soils
Test Species (0 to 2)	0=non-crop species 1=crop of minor economic importance 2=crop of major economic importance
Agricultural Practices (1 to 3)	<ul> <li>1=non-standard (no statement regarding agricultural practices</li> <li>2=more or less standard (statement of using standard practices but no detail)</li> <li>3=Standard Practice (OMAFRA (Ontario Ministry of Agriculture, Food and Rural Affairs) best practice or detailed description of best practice)</li> </ul>
Number of Replicates (0 to 2)	0=only one pot or field plot with single plants 1=multiple plants in one pot or field plot

## Table 5B-1Scoring categories and criteria used to evaluate the quality of the effects-based<br/>data and studies from which they were derived.



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Scoring Categories (Range of Scores)	Scoring Criteria
	3=three or more pots or field plots
Number of Treatments (1 to 3)	1=one or two 2=three 3=four or more
Dose-Response Relationship (0 to 5)	One point for each one of the following five lines of evidence: 1=increasing Ni concentrations correlated with increasing biological response; 2=treatment captures the full range of effects from no effect to severe
	effects; 3=at least two treatments have intermediate biological response (i.e., not 0 or 100%); 4=ECx can be calculated; 5=NOAEL and LOAEL can be determined
Presence of Control Study (0 to 2)	<ul> <li>0 =no control; no appropriate soil treatment or other standard of comparison</li> <li>1=surrogate control; yield or other suitable measure of productivity for the same crop grown under comparable conditions (e.g., regional soybean yield data for that year)</li> <li>2= acceptable control; appropriate soil treatment that shows no nickel effect at the lowest concentrations (i.e., the soil must be well matched with treatment soils but have background concentrations of CoC)</li> </ul>
Endpoint Relevance (1 to 3)	1=other (e.g., predicted or theoretical yield) 2=measured emergence/growth/biomass 3=measured crop yield
Evidence of Effect (0 to 2)	0=low; no evidence given of an effect 1=moderate; one of the above lines of evidence of an effect 2=strong; plant tissue Ni concentrations exceed the threshold for phytotoxicity (26 µg/g Ni) and classical Ni phytotoxicity symptoms (e.g., longitudinal chlorosis and necrosis of the leaves, stunting of roots) are reported
Confounding Factors/Limitations (0 to -3))	0=unlikely; treatment soils are well matched and nutrient deficiencies unlikely -1=may impact the study; confounding factors observed by readers/reported by authors that may have a reasonable effect on results



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Scoring Categories (Range of Scores)	Scoring Criteria
	-3=factors that seriously impact the study; presence of confounding factors / limitations that could seriously affect the interpretation of the results; confounding factors observed by readers or reported by authors that affect results
Study Date: adequacy and relevance of the data to the current site conditions (operating times of the refinery (0-1)	0=study was conducted outdoors in Port Colborne in or prior to 1984 2=study was conducted after 1984
Total Score (Highest score possible = 29)	Sum of above scores
Score (%)	(Sum of Score per Endpoint/Highest score possible)*100
Study Confidence	High Confidence - score from 22-29 (>76%) Medium Confidence - score from 16-21 (55 to 72%) Low Confidence - score from ≤15 (≤ 52%)

#### 1.2 ESTIMATION OF EC25 VALUES FROM THE PUBLISHED SCIENTIFIC LITERATURE FROM PORT COLBORNE

Several of the studies on soil Ni phytotoxicity in this review were not designed as dose-response experiments for the purpose of determining "effect-levels", and so contained only two data points (yield/growth in control and contaminated soil). The MOE studies were in response to complaints from local farmers, and the studies evaluated impaired crop growth or yield at the sites. Only three of the reviewed studies (Bisessar and Palmer; Frank *et al.*, 1982; and Rinne, 1984) had three or more data points for calculating an EC25 estimate (though such calculations were not made by the authors).

EC25 values were estimated from the summary data (e.g. treatment means) provided in the papers. The approach was guided by Environment Canada test methods for deriving EC25 values from ecotoxicity testing using earthworms (e.g., *Eisenia andrei*) and terrestrial plants (EC, 2004 and 2005) with some required adjustment to account for the types of data available. Briefly, the procedure was as follows:



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- a) In studies where there was no Control treatment (i.e., production of crop in an organic muck soil with elevated soil Ni concentration in the Port Colborne area; e.g., Frank et al., 1982), 100% production was assumed at a soil nickel concentration of 37 mg/kg. This value was chosen because it is the Ontario Regulation (O.Reg.) 153/04 Table 1, generic site condition standard of full depth background soil for agricultural property use that are not contaminated by point sources (MOE, 2011) and is believed to be associated with no Ni toxicity. The production levels that would be associated with this control Ni concentration were taken from other literature sources, as appropriate. In cases where a surrogate control response value could not be identified, an EC25 was not calculated.
- c) The soil Ni concentration and plant response data were tabulated and the concentration-response curves were evaluated to determine the best-fit relationship within the constraints of physical reality. This included fitting straight lines for studies that had only control and one treatment level.
- d) EC25 values were then calculated based on the 25% reduction of the best-fit estimation of yield, growth, or biomass.

The EC25 values for the various crop endpoints are presented in the following sections.

#### 1.3 REVIEW OF THE LITERATURE ON PORT COLBORNE AGRICULTURAL TOXICITY

#### 1.3.1 Temple and Bisessar, 1981

**Summary:** A greenhouse study where lettuce (n = 7), celery (n = 6), and onion (n = 6) grown in organic soil collected from muck farms within 1-3 km of the refinery were compared to those grown in organic soil from an unaffected research farm. The confounding effect of root-knot nematode on crop growth was also evaluated by using both sterilized (autoclaved) and non-sterilized soil in a greenhouse study. This review only considers the sterilized soil, as the growth impairment seen in the non-sterilized soil was confounded by the root-knot nematode (which impaired the growth of plants in the control soils as well as in the Ni-impacted soils.

The organic soil from the Site used in the greenhouse study averaged 7300 mg Ni/kg soil. Growth of all three crops was reduced when grown in the contaminated Site organic soil when compared to the Control organic soil.

Dry mass of lettuce leaf grown in sterilized Site soil was reduced by 36% when compared to the lettuce grown in the sterilized Control soil. Celery stalk dry weight was reduced by approximately 40% (39 in sterilized and 46% in non-sterilized) when grown in the Site soils in comparison to control soils. Celery leaf dry weights were also reduced by an average of 40% when grown in the Site soil; however, this reduction was not found in celery roots.

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Growth of onions (expressed as dry weight of onion bulbs) did not appear to be impacted in Site soil (there was arguably a positive effect). Onion leaves were found to be impacted when grown in the Site soil, with a reduction of 72% (in sterilized Site soil). Onion roots (excluding the bulb) were similarly impacted.

This experiment provided only two exposure concentrations (7,300 ppm Ni and 25 ppm Ni) from which growth and metal accumulation data could be derived (

**Figure** 5B-1). A straight line could be drawn between the response values and an EC25 could be calculated. Such data could be misleading, as the true shape of the dose-response curve is not known. Nevertheless, the EC25's are as follows (**Table 5B-2**):

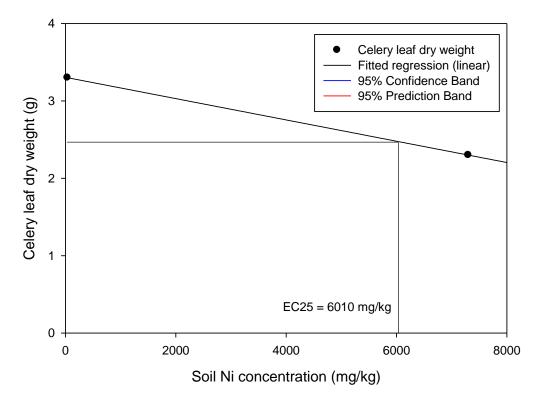


Figure 5B-1 Derivation of the EC25 for celery leaf dry weight from Temple and Bisessar, 1981.



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## Table 5B-2Score assigned (based on MOE criteria), EC25 (model-derived), and WeightedEC25 (Score x EC25) for crop endpoints from Temple and Bisessar, 1981.

Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Celery	Leaf Weight	69	6010	414690
Celery	Root Weight	69	NA*	NA*
Celery	Stalk Weight	72	4630	333360
Lettuce	Leaf Weight	72	5090	366480
Lettuce	Root Weight	69	3780	260820
Onion	Bulb Weight	59	NA*	NA*
Onion	Leaf Weight	69	2530	174570
Onion	Root Weight	69	2960	204240

**NA\*** The authors noted that either there was no significant difference between control/background soil or the value in the contaminated soil was greater than that of the control/background soil. Therefore, an EC25 value was not calculated.

#### 1.3.2 Bisessar and Palmer (Date Unknown – possibly 1983)

**Summary:** The most recent paper cited in this report was published in 1983, so this paper is circa 1983. Amongst the literature reviewed for the growth response of crop plants grown in Ni impacted Site soil, this is the only study where the objective was to determine the concentration of Ni in soil required to produce phytotoxic symptoms in plants. In this case, the plants used for testing were celery and lettuce. Five soil Ni concentrations (35 (Control soil), 920, 3,000, 3,800, and 5,000 mg Ni/kg soil) were created by mixing varying proportions of a highly impacted organic soil from the Site with a similar organic soil from a non-impacted location (Control). This soil blending approach was also used by Jacques Whitford in the 2001 Greenhouse experiments (Jacques Whitford, 2004).

Seedlings of both crops were transplanted singly into pots containing soil with one of the five different Ni concentrations. Each plant/Ni treatment combination was replicated nine times (n = 9). Celery was grown under greenhouse conditions, while lettuce was grown in pots in a field plot adjacent to the greenhouse.

Foliar toxicity symptoms were only observed at the highest tested soil Ni concentration (5,000 mg Ni/kg soil) for both celery and lettuce, where tissue Ni concentrations were 75 and 41 mg Ni/kg tissue, respectively.



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However, there was a significant negative correlation between tissue dry mass of both species and soil Ni concentration. Celery growth reduction of greater than 10% in stalk and foliage compared to the yield of celery in the Control soil (35 mg Ni/kg soil) was observed even at 920 mg Ni/kg soil. Lettuce was less sensitive than celery as only a 3% reduction in root growth was observed at 920 mg Ni/kg soil. Celery accumulated approximately 2 to 3 times more Ni in the corresponding tissue than lettuce.

The EC25's derived from this study from the metal-contaminated soil treatments are presented in **Table 5B-3** based on interpolation of best-fitting linear and non-linear regression model to the control and contaminated soil plant responses (using the treatment mean values) (e.g., **Figure 5B-2**).

## Table 5B-3Score assigned (based on MOE criteria), EC25 (model-derived), and WeightedEC25 (Score x EC25) for celery and lettuce growth endpoints from Bisessar andPalmer (date unknown).

Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Celery	Leaf Weight	86	3580	307880
Celery	Root Weight	86	1960	168560
Celery	Stalk Weight	86	3230	277780
Lettuce	Leaf Weight	86	3080	264880
Lettuce	Root Weight	83	4320	358560

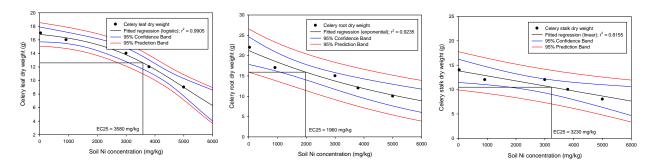


Figure 5B-2 Figures depicting various best-fitting regression models used to derive EC25 for the celery leaf (logistic), root (exponential), and stalk (linear) growth endpoints from Bisessar and Palmer (date unknown).



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#### 1.3.3 Frank et al., 1982

**Summary:** The impact of soil Ni concentrations on crop health and crop yields were investigated for beetroot, cabbage, celery, lettuce, and radish in a field study. Crops were grown in a study area 1 km east of Port Colborne in organic soil that had 70% organic matter. Soil Ni concentrations in the study area ranged from 600 to 6455 mg Ni/kg soil. Crop yields in 1980 were determined for beetroot, cabbage, celery, lettuce and radish on the basis of the number of marketable roots, stalks or heads. Crop yields were determined for celery and lettuce only for 1981. Note that crop yield loss was calculated relative to theoretical and practical expected yield because a comparison to yield from a Control site was not conducted.

Beetroot yield (defined as roots of marketable size) was reduced 100% (the entire crop was not marketable) in soils at two planted plots with a mean concentration of 2,075 and 4,470 mg Ni/kg soil. The fresh weight of roots and tops were reduced at all concentrations, and ranged from a high of 10.0 and 41.0 g, respectively, when grown in soil with 1,570 mg Ni/kg soil, to 1.8 and 6.3 g (82 to 85% reduction) when grown in soil with 4,675 mg Ni/kg soil. The corresponding nickel tissue concentrations in roots and tops (dry weight) were found to be 95 and 94 mg Ni/kg tissue, respectively, for beets grown in lower nickel concentrations and 280 and 201 mg Ni/kg tissue for beets grown in higher nickel concentrations.

Like beetroot, cabbage yield was considered to be a total loss (not marketable) at all Ni concentrations, with fresh weight of roots and tops declining from a high of 27 and 547 g respectively, when grown in soil with 2,400 mg Ni/kg soil, down to 4 and 20 g (85 to 96% reduction), respectively, when grown in soil with 6,400 mg Ni/kg soil. Nickel concentrations in root and top tissues increased from 150 and 76 mg Ni/kg tissue to 730 and 400 mg Ni/kg tissue in those same soils.

In 1980, the celery crop yield was reduced by 59% (as compared to the expected yield) when plants were grown in soil with a low Ni concentration of 1,180 mg Ni/kg soil. Nickel concentrations in root and stalk tissues were 340 and 78 mg Ni/kg tissue when grown in soil with 1,820 mg Ni/kg soil. In 1981, crop yield was reduced by 66% in soils with a low Ni concentration of 1,200 mg Ni/kg soil. Plants grown in soil with 1,330 mg Ni/kg soil had tissue concentrations of 98 and 15 mg Ni/kg tissue in roots and tops, respectively.

Head lettuce yield in soil with Ni concentration of 1,300 mg Ni/kg soil was 8% higher than the expected yield during the 1980 growing season. However, in 1981, head lettuce yield was reduced by 36% (relative to the expected yield) in soil with the same soil Ni concentration.

The mixed lettuce crop consisted of Boston, endive, escarole, leaf and romaine lettuce. For 1980, overall yields were reduced by 26% in soils with 1,180 mg Ni/kg soil and reduced by 82% in 1981 for plants grown in 3,605 mg Ni/kg soil. Tissue concentrations were only reported for Escarole lettuce in 1981, with root and top tissues having 210 and 35 mg Ni/kg tissue, respectively, when grown in soils with 3,625 mg Ni/kg soil.

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Radish yield was reduced by 93% when grown in soil with 4,800 and 5,070 mg Ni/kg soil. Tissue concentrations of Ni at the lowest soil concentration (2,570 mg Ni/kg soil) were found to be 24 and 56 mg Ni/kg tissue for roots and tops, respectively, and up to 140 and 135 mg/kg, respectively, when grown in in soil with Ni concentration of 6,550 mg/kg. A decrease of 90 and 59% in root and top biomass was reported for growth at 2,570 versus 6,550 mg Ni/kg soil.

EC25 values were not calculated for marketable yield. There are two reasons for this. First, this is a chemical risk assessment, not a socioeconomic risk assessment. Second, the concept of marketable yield essentially loosely contains the information present in the growth endpoints, but with a commercial overlay. It was decided to only consider biological responses from the Frank study.

EC25 values were estimated for the endpoints of root weight, and top weight, in Table 5B-4.

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Beet (1980)	Top & Root Weight	72	410	29520
Cabbage (1980)	Top Weight	76	4040	307040
Celery (1980)	Top Weight	76	260	19760
Celery (1981)	Top Weight	76	380	28880
Escarole (1981)	Top Weight	76	450	34200
Head Lettuce (1980)	Top Weight	76	3410	259160
Head Lettuce (1981)	Top Weight	76	370	28120
Radish (1980)	Root Weight	72	1960	141120

## Table 5B-4Score assigned (based on MOE criteria), EC25 (model-derived), and WeightedEC25 (Score x EC25) for various crop growth endpoints from Frank et al., 1982

## 1.3.3.1 The use of Surrogate Values to constrain Datasets without a "Control": Frank et al. (1982) as an Example

A central requirement for the derivation of EC<sub>x</sub> values (and in scientific experimentation) is the need for controls. In particular, a negative control is required in order to determine the expected measurement of the toxicological endpoint (e.g., fresh weight of beet root and top) if the stressor of interest (soil Ni concentration) is present at a concentration that has no detectable effect on the endpoint. Negative controls were not reported for any endpoint reported by Frank *et al.*, 1982.

In the absence of negative controls in the field experiments, it was necessary to find other data sources for the relevant crops for the years that the studies took place (1980 and 1981) that were geographically relevant. These other data sources for biomass of unexposed plants were



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assumed to occur at an assumed background soil Ni concentration of 37 mg/kg (from MOE O.Reg. 153/04, Table 1 generic site condition standard)

For head lettuce from Frank et al. (1982), a surrogate for negative control biomass was obtained from OMAFRA (1981), which studied lettuce grown on the Overholt farm in Port Colborne during the same period. In the OMAFRA (1981) study, the average weight of head lettuce in control soils in 1980 was 744 g. This value was used for developing an EC25 for lettuce for both 1980 and 1981 (**Figure 5B-3**).

For beetroot, cabbage, celery, and radish, OMAFRA statistics were obtained for the OMAFRA (2014) internet site (www.omafra.gov.on.ca/english/stats/hort). The statistics are provided as average yields (tonnes/ha). Frank *et al.* (1982) did provide values (plants/ha) for "theoretical" and "practical" expected yields. The expected weights of individual plants of the various crop species could be derived from these two values. For example, the average Ontario yield of cabbage in 1980 was 38.4 t/ha and Frank reported (Table 2 of Frank *et al.*, 1982) that 70,200 plants were expected per hectare. The field planted with cabbage was 0.12 ha in area, so 20,348 cabbage plants were expected on the field. The estimated weight per cabbage when Ni toxicity is not expected (i.e. with 50 mg/kg in the soil) would have been 547 g, inserting these values in the equation below.

Weight per Plant =  $\left( Yield\left(\frac{tonnes}{ha}\right) \times Area\left(ha\right) \right) \div \left( Yield\left(\frac{Plants}{ha}\right) \times Area\left(ha\right) \right) \times 1,000\left(\frac{kg}{tonne}\right)$ 

Using this approach, it was possible to obtain estimates of weight that could be used for control plants in the Frank et al. study. These were: beets (166 g), cabbage (547 g), celery (886 g in 1980 and 956 g in 1981), and radish (22 g).

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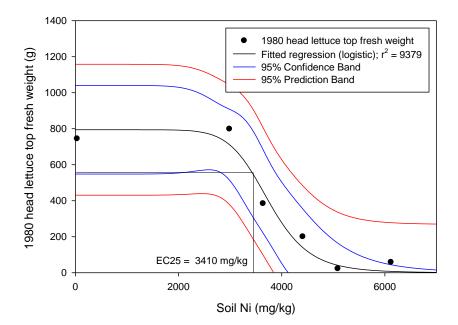


Figure 5B-3 Logistic model fitted to the 1980 head lettuce top fresh weight data from Frank et al., 1982, augmented with estimated "Control" data of 744 g lettuce top fresh weight (OMAFRA, 1981) at a soil Ni concentration of 37 mg/kg (O.Reg. 153/04, Table 1 generic site condition standard). The estimated EC25 in this scenario is 3,410 mg/kg.

#### 1.3.4 Bisessar et al., 1983

**Summary:** This is the companion paper to Temple and Bisessar (1981). Where the previous paper was a greenhouse experiment, this article reports on the results from a field plot experiment where effects of Ni toxicity and root-knot nematode infection on the growth of celery were further explored. Nematodes are a common pathogen for agricultural crops in Ontario, and the authors were exploring potential interactions between soil metal contamination and nematode infestations on phytotoxicity.

The experiment was conducted using Ni impacted organic soil (Site soil) at a farm located 1 km east/northeast of the refinery. Half of a 3.6 m x 3.6 m plot was excavated and filled with an organic soil low in metals (Control soil). Nematode population, metal concentration and pH of both soils were characterized prior to the start of the experiment using the methods outlined in Temple and Bisessar (1981). Individual celery seedlings were grown in pots from seeds for 8-week duration. Initially, some of the seedlings were inoculated by injection into the potting soil with approximately 1000 second-stage root-knot nematode larvae suspended in 7.5 ml of water. Control seedlings were similarly injected with water. Eighteen (18 of each nematode treatment) celery seedlings were planted into each subplot. This produced four treatments: 1) Control soil; 2) Control soil with nematode; 3) Site soil; and 4) Site soil with nematode.



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Nickel concentrations in the Control and Site soils (regardless of nematode treatment) were approximately 60 and 7,360 mg Ni/kg soil, respectively. Injury symptoms were obvious for celery in both treatments grown in Site soil. Above-ground celery biomass (fresh weight of stalk and leaf) accumulated more Ni in the Site soil (24.5 to 94.8 mg Ni/kg tissue) in comparison to celery grown in the Control soil (4.3 to 12.7 mg Ni/kg tissue). The authors stated that the presence of nematode infestation in the roots of celery inhibited Ni translocation to above ground biomass (which was observed in Temple and Bisessar, 1981). However, the presented data (Table 2) shows the opposite. It is uncertain whether the authors' statement or results presented in Table 2 were in error. The latter is likely because root-knot nematode infestation should decrease the function of the root system, based on previous studies such as Temple and Bisessar, 1981.

Unlike the 1981 study, where above ground celery biomass in sterilized soil did not differ from the non-sterilized soil (regardless of Site or Control), additive effects between Ni toxicity and nematode infestation were observed. The pattern of decline in shoot weight and height amongst the treatments relative to celery grown in the Control soil were as follows: Site and nematode (86 and 47% reduction in shoot weight and height, respectively) > Site (79 and 35% reduction in shoot weight and height, respectively) > Control and nematode (12% reduction in shoot weight). Root fresh weight was unaffected by treatments.

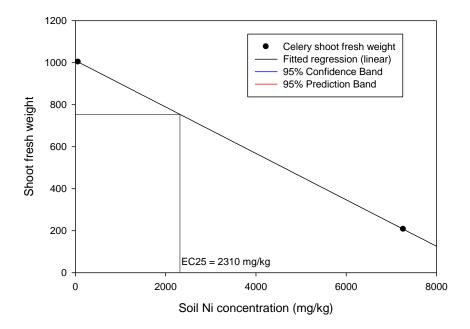
The EC25's derived from this study from the metal-contaminated soil treatments were 2,310 mg/kg (shoot fresh weight) and 5,120 mg/kg (shoot height) (**Table 5B-5**) based on a linear interpolation between the control and contaminated soil plant responses (using the treatment mean values) (e.g., **Figure 5B-4**).

Table 5B-5	Score assigned (based on MOE criteria), EC25 (model-derived), and Weighted
	EC25 (Score x EC25) for celery growth endpoints from Bisessar et al., 1983.

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Celery	Root Weight	69	NA*	NA*
Celery	Shoot Height	66	5120	337920
Celery	Shoot Weight	69	2310	159390

**NA\*** The authors noted that either there was no significant difference between control/background soil or the value in the contaminated soil was greater than that of the control/background soil. Therefore, an EC25 value was not calculated.

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### Figure 5B-4 Derivation of the EC25 for celery leaf dry weight from Bisessar *et al.*, 1983, using linear model (only model possible).

#### 1.3.5 Bisessar, 1989

**Summary:** This study was conducted to evaluate the effectiveness of liming to improve the tolerance of celery to Ni toxicity in impacted organic soil from a muck farm located adjacent to the Inco refinery (Site soil). Lime (CaCO<sub>3</sub>) increases the sorption of metals to soil (by increasing pH), thereby decreasing metal bioavailability (and therefore resulting in a decrease in toxicity). The average Ni concentration in the soil used in this study was 5,700 mg Ni/kg soil, while average copper and cobalt (Co) concentrations were found to be 650 mg Cu/kg soil and 90 mg Co/kg soil. This study was conducted by trucking Site organic soil (containing 37% organic carbon) and Control organic soil (containing 18% organic carbon) to a study area in Brampton where field plots (4.5 m x 1.0 m in size) were prepared. The Site soil had a pH of 5.7 which increased to 6.9 following liming (similar to the Control Soil). The celery crops were fertilized three times and soils were maintained at field capacity until harvest. Total Ni concentration in the limed and un-limed Site soil was 5,550 and 6,000 mg Ni/kg soil, respectively.

Liming decreased the ammonium acetate-extractable (bioavailable) Ni in the Site soil from 52 to 33 mg Ni/kg soil (in comparison, extractable Ni in the Control soil was 1 mg/kg). A statistically significant negative correlation existed between the increase of pH as a result of liming and the decrease in Ni bioavailability.



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Although there was no difference in the height of celery grown in the limed Site and Control soils (celery height was decreased by 29% when grown in the Site soil with 5,550 mg/kg Ni), yield (dry weight) of celery stalk and root growth in the limed Site soil declined by 19 and 15%, respectively, when compared to those grown in the Control soil. Shoot and root weight declined by 28 and 22%, respectively, for the celery grown in the un-limed Site soil. This might be attributable to the observation that although root, stalk, and leaf Ni (at concentrations of 332, 21, and 66 mg Ni/kg tissue, respectively) declined in celery grown in limed Site soil when compared to un-limed Site soil (concentrations of 475, 28, and 78 mg/kg, respectively), the ratio of Ni in root to either stalk or leaf remained the same. This indicated that the rate of Ni translocation remained the same even though the bioavailability of Ni in the site soil is assumed to have decreased with liming.

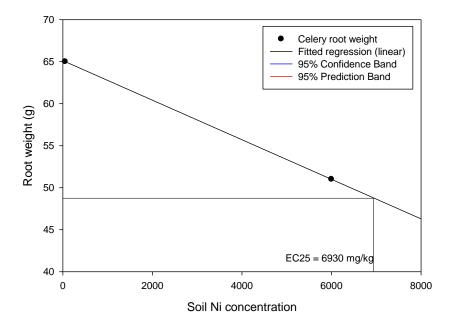
Therefore, although Ni bioavailability was decreased by 36% (total Ni declined by 7.5%) with liming, it remained at a bioavailable concentration that was sufficient to result in phytotoxicity in celery when translocated from root to shoot and leaf.

The EC25's derived from this study from the metal-contaminated soil treatments were 6,930 mg/kg (root weight), 5,200 mg/kg (shoot height), and 5,250 mg/kg (shoot weight) (**Table 5B-6**) based on a linear interpolation between the control and contaminated soil plant responses (using the treatment mean values) (e.g., **Figure 5B-5**).

Table 5B-6	Score assigned (based on MOE criteria), EC25 (model-derived), and Weighted
	EC25 (Score x EC25) for celery growth endpoints from Bisessar, 1989.

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Celery	Root Weight	79	6930	547470
Celery	Shoot Height	79	5200	410800
Celery	Shoot Weight	83	5250	435750

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### Figure 5B-5 Derivation of the EC25 for celery root weight from Bisessar, 1989, using linear model (only model possible).

#### 1.3.6 McIlveen and Negusanti, 1994

**Summary:** The article by McIlveen and Negusanti is a review of current information (at the time) on Ni behavior in terrestrial environments and how it relates to exposure of humans and animals through food consumption. This study also incorporated data from Sudbury and Port Colborne.

Studies reporting the Ni concentrations in plant tissues associated with phytotoxicity, physiological effects of Ni on plants (and a variety of organisms), and the Ni toxicity thresholds to a variety of plants grown in solution culture was provided in this review.

Ni concentrations in the tissues of 15 crop, forage, and tree species where phytotoxicity was reported ranged between 11 (barley) and 332 (celery) mg Ni/kg tissue. In general, the reported values where phytotoxicity occurred were below 80 mg Ni/kg tissue. Phytotoxicity to oat was observed at 17 to 135 mg/kg tissue.

From a review of studies on phytotoxic thresholds of Ni in culture solution, the majority of the critical concentrations ranged between 2 to 15 mg Ni/L solution. In flax, Ni at a concentration of 0.5 mg/L was reported to have toxic effects.

No numeric values for EC25s were derived from McIlveen and Negusanti (1994) because it is a literature review that could not be scored according to the MOE scoring criteria.



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#### 1.3.7 Kukier and Chaney, 2000

**Summary:** A pot experiment was conducted with two Ni-contaminated organic soils collected from Port Colborne to determine the influence of two soil amendments on the amelioration of Ni toxicity to three species of plants with different nickel sensitivities: wheat, oat, and red beet.

The two field-collected nickel-contaminated soils were amended with either a limestone mixture of calcium and magnesium carbonates and/or hydrous ferric oxide (HFO). The two unamended control soils were considered to have high (3,090 mg Ni/kg soil) and low (1,360 mg Ni/kg soil) nickel concentrations, respectively. Seeds (20, 30 and 10 seeds for wheat, oat, and red beet respectively) were sown in each of the three replicate pots for each (low and high) control soil. The pH of the control soils (*i.e.*, un-amended) was 5.7.

Ni uptake was species-specific (20% greater uptake in red beet than wheat), and reflected species sensitivity (i.e., red beet was more sensitive than wheat). Uptake was greater for plants grown in soil with the high Ni concentration in comparison to those grown in soil with the low Ni concentration, based on both total soil and extractable Ni measurements.

Wheat grown in both high and low Ni soils were suspected to be Manganese (Mn) deficient as Ni levels in wheat shoots were not sufficiently high to cause Ni toxicity or adversely affect growth. Oat grown in high-Ni soils was deficient in Mn and exhibited Ni toxicity (not quantified). Red beet grown in high-Ni soil suffered Ni toxicity (not quantified; qualitative – marbling and spots) while red beet grown in low-Ni soil were stunted but not chlorotic. Therefore, adverse impacts to growth were attributed to Mn deficiency.

In the un-amended soils, yields of wheat, oat, and red beet were reduced by 30, 56, and 22%, respectively, when crop yield in the high Ni soil is compared to that for the low Ni soil.

Crop yield for all species exposed to low-Ni soils exhibited adverse growth effects attributable to Mn and phosphorous (P) deficiencies as it was determined that tissue Ni levels were not sufficiently high to result in toxicity.

Numeric values for EC25s were not derived from Kukier and Chaney (2000) because: 1) the endpoints for beet and wheat scored below 55% according to the MOE scoring criteria; and 2) a control value could not be derived for oat shoots – OMAFRA does not have records of oat shoot production even though this endpoint did score 55%.

#### 1.3.8 Kukier and Chaney, 2001

**Summary:** A pot experiment was conducted with two Ni-contaminated soils; 1) an organic (72% organic matter content) soil, Orthic Humic Gleysol; and 2) a mineral soil, Terric Mesisol, collected from Port Colborne to determine the influence of two soil amendments on the amelioration of Ni toxicity to three species of plants with different nickel sensitivities: wheat, oat, and red beet.

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The two soils were amended with a limestone mixture of calcium and magnesium carbonates and/or hydrous ferric oxide (HFO). The un-amended control organic soil had a concentration of nickel of 2,210 mg Ni/kg soil (358 mg Ni/kg soil DTPA-extractable; 2.48 mg Ni/kg soil SrNO<sub>3</sub>-extractable) and a soil pH of 5.66. The mineral soil, which was a Welland silt loam soil, had a concentration of 2,930 mg Ni/kg soil (634 mg Ni/kg soil DTPA-extractable; 54.2 mg Ni/kg soil Sr(NO<sub>3</sub>)<sub>2</sub>-extractable) and a soil pH of 5.24. The number of pots per treatment was not specified. All pots were fertilized with a standard formulated mixture which was further supplemented to compensate for Mn and P deficiency.

The yields (biomass reduction) of the three crop species grown in un-amended organic and mineral soils were: 1) wheat – 3.56 g and 0.98 g, respectively; 2) oat – 4.98 g and 0.20 g, respectively; and 3) red beet – 6.58 g and 0.0 g, respectively. The tissue Ni concentrations of the three crop species grown in un-amended organic and mineral soils were: 1) wheat – 7.98 and 271 mg Ni/kg tissue, respectively; 2) oat – 62.9 and 692 mg Ni/kg tissue, respectively; and 3) red beet – 32.6 mg Ni/kg tissue for organic soils only (no growth was observed in mineral soils).

Numeric values for EC25s were not derived from Kukier and Chaney (2001) because all endpoints from this reference scored below 55% according to the MOE scoring criteria;

#### 1.3.9 Rinne, 1984

**Summary:** In response to a complaint by the Overholt Farm, the MOE conducted an investigation of alleged sulfur dioxide (SO<sub>2</sub>) injury to celery grown at the muck farm after a temporary breakdown of the SO<sub>2</sub> scrubber occurred at the Inco No. 2 Research Station in 1983. Signs of Ni-related stunting, necrosis, chlorosis, and cupping of celery leaves were observed in plants grown in the allegedly impacted field. Samples of normal (~60 cm tall celery grown in the field opposite to the affected area with soil Ni concentration of 1,310 mg Ni/kg soil), moderately stunted (celery ~ 25 cm tall; *i.e.*, 58% reduction in stalk height at 4,900 mg/kg), and severely stunted plants (celery ~ 15 cm tall; *i.e.*, 75% reduction in stalk height at 5960 mg/kg) along with the soil from the base of these plants were collected for chemical analysis.

All nutrient and trace elements in soil and tissue were similar except for levels of Ni and phosphorus. The acidic soil might have exacerbated Ni toxicity because of an increase of nickel bioavailability resulting from the acidic pH. Unlike previous complaints filed by the complainant, there were no significant confounding issues such as root-knot nematode infestation or fungal disease. As there were no signs of SO<sub>2</sub>-related plant injuries, it was concluded that celery stunting was caused by high Ni concentration in the soil.

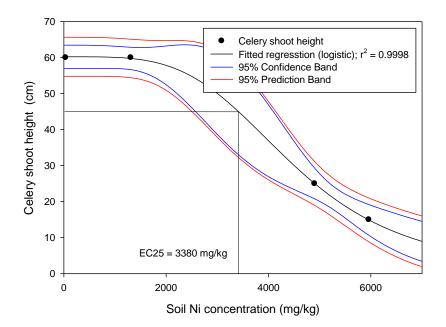
The EC25 derived from this study is 3,380 mg/kg (celery shoot height) (**Table 5B-7**) based on interpolation of the logistic model fitted to the data which required the addition of the control point of 37 mg Ni/kg soil where the normal celery height of 60 cm (according to Rinne, 1984) may be produced (e.g., **Figure 5B-6**).



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### Table 5B-7Score assigned (based on MOE criteria), EC25 (model-derived), and WeightedEC25 (Score x EC25) for celery shoot height from Rinne, 1984.

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Celery	Shoot height	76	3380	256880



#### Figure 5B-6 Logistic model fitted to the celery shoot height (cm) data from Rinne, 1984, augmented with estimated "Control" data of 60 cm normal celery height (Rinne, 1984) at a soil Ni concentration of 37 mg/kg (O.Reg. 153/04, Table 1 generic site condition standard).

#### 1.3.10 Bisessar, 1991

**Summary**: A complaint by the Davison Farm concerning the poor performance of crops was investigated by the MOE through a pot experiment where wheat was used as the test species. Organic (1,300 mg Ni/kg soil) and mineral (1,000 mg Ni/kg soil) soils were collected from the allegedly impacted farm and mixed with respective control soils to create four organic soil treatments with approximately 15 (control), 535, 955 and 1,200 mg Ni/kg soil and four mineral soil treatments with approximately 11 (control), 330, 600, and 975 mg Ni/kg soil. Three (n = 3) replicate pots of each soil treatment were seeded with wheat and fertilized at recommended

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agronomic rates. Pots were placed in trenches in a field plot and watered by rainfall and supplemented with irrigation.

Observable Ni-related injuries in wheat were detected at a soil Ni concentration of 955 and 975 mg/kg for organic and mineral soils, respectively. Growth of wheat relative to the control soil was decreased by up to 38%, 46%, 36%, 44% and 36% in the shoot height and respective grain, leaf, stem, and root dry weights depending on whether the soil was organic or mineral. The report concluded that soil Ni concentration above 600 and 955 mg Ni/kg soil in the respective mineral and organic soils decreased the growth and yield of wheat and restricted farming options.

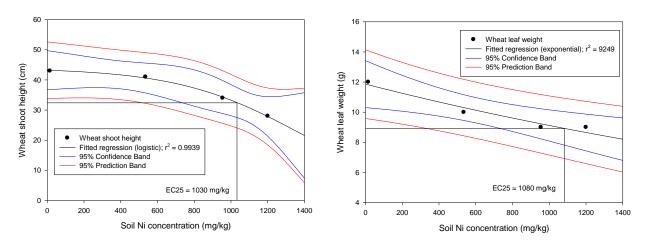
The EC25 values derived from this study (**Table 5B-8**) are based on interpolation of the logistic (shoot height, grain weight, and root weight) or exponential model (leaf weight and stem weight) fitted to the data (**Figure 5B-7**).

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Wheat	Grain Weight	93	970	90210
Wheat	Leaf Weight	90	1080	97200
Wheat	Root Weight	93	1320	122760
Wheat	Shoot Height	90	1030	92700
Wheat	Stem Weight	90	1050	94500

### Table 5B-8Score assigned (based on MOE criteria), EC25 (model-derived), and WeightedEC25 (Score x EC25) for wheat growth endpoints from Bisessar, 1991.



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### Figure 5B-7 Examples of the logistic and exponential models fitted to the wheat shoot height (left) and leaf weight (right) growth endpoints, respectively.

#### 1.3.11 Jacques Whitford, 2004 (Biomonitoring)

**Summary:** The biomonitoring study was conducted concurrently with the Greenhouse and Field Trials during 2001. The goal of the biomonitoring study was to characterize the extent of the contamination of CoC (e.g., Ni) in the natural vegetation and in the soils of the Port Colborne area, and to characterize the relationship between CoC concentrations in soils and accompanying natural vegetation in the area. Golden rod (representing soft tissue vascular plants) was collected from sites (n = 3 or 4 depending on soil type and Ni concentration) with clay, sand, and organic soil types within a range of Ni concentration representative of Reference (background), Medium (500 to 4,000 mg/kg; except for organic), and High (>4,000 mg/kg; except for sand) concentrations.

The highest concentration of nickel was found in organic soil at the High site, both for soil concentrations and tissue concentrations. This site also had the lowest pH and the highest CEC recorded for this study. Overall, tissue nickel concentrations increased as soil nickel concentrations increased. No tissue nickel concentration exceeded 67.3 mg Ni/kg.

Correlation between soil pH, CEC, and soil concentrations of iron and manganese showed that CEC was positively correlated with iron and manganese overall, and negatively correlated with pH overall. Iron and manganese were correlated across soil types. Organic soils had the highest CEC, followed by clay soils and sandy soils. Lower pH was observed in the organic soils when compared to the clay and sand sites. Any differences in CoC uptake by plants likely reflected this variation in soil chemistry.

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#### 1.3.12 Jacques Whitford, 2004 (Field Trials)

**Summary:** Several experiments/trials with different but integrated objectives were conducted for the Port Colborne CBRA Crops report (Jacques Whitford, 2004). Whereas the Greenhouse Trials of 2000 and 2001 were designed as dose-response experiments used to derive the recommended site-specific toxicological threshold values for CoC (e.g., Ni) in the various soil types found in the Port Colborne area, the objective of the Field Trials was to examine the effects of dolomitic limestone amendments on mitigating Ni-related phytotoxicity (measured as decreases in plant yield) through its influence on bioavailability of soil Ni as a function of soil pH and plant CoC uptake as represented by plant tissue Ni concentration. Furthermore, the field trials were to provide context for interpreting the results from the Greenhouse Trials.

In the Year 2000 Preliminary Field Trial, oat, soybean, corn and radish were grown in plots at sites Clay 1 (Till Clay; 600 mg Ni/kg soil), Clay 2 (Welland Clay; 5,000 mg Ni/kg soil) and Organic (1,500 to 9,000 mg Ni/kg soil). Replicate plots were prepared with one of three levels of limestone amendment at each site: 1) no limestone (unamended); 2) 1X (7.5 t/ha) OMAFRArecommended rate of limestone application; and 3) 2X (15 t/ha) OMAFRA-recommended rate. Only sites Clay 2 and Clay 3 (Welland Clay; 3,000 mg Ni/kg soil; similarly prepared with limestone amendments as other sites in 2000) were planted in the Year 2001 Structured Field Trial. An additional Calcareous treatment (limestone added in 1999 at a rate of about 100 t/ha) was included in 2001. Late planting (end of July) and excessive moisture caused by inclement weather conditions limited results obtained for the Year 2000 Preliminary Field Trial. The general observations from this field trial were that liming decreased plant tissue Ni concentration in agronomic, toxicological, and crop yield samples while concurrently increasing plant biomass production. Variation in the soil types in this trial precluded the interpretation of phytotoxic effects on plant yield as a result of soil Ni concentration. For example, plant biomass for oat and radish (above and below ground) were greater at Clay 2 than Clay 1, where the soil Ni concentrations were approximately 5,000 and 600 mg Ni/kg, respectively, indicating that factors other than soil Ni were adversely affecting growth of the crops grown at Clay 1.

For the Year 2001 Field Trial, two Welland Clay sites (Clay 2 and Clay 3) were used in order to remove the confounding factors relating to soil type. Plant tissue Ni concentration decreased with an increase in limestone amendment. Soil pH in limestone amended soils was significantly higher than unamended soils, but it was not significantly different between liming rates.

However, the level of tissue Ni concentration varied greatly between plants grown in unamended Clay 2 and Clay 3. For example, Ni concentrations in agronomic tissues were 2.6, 21.8 and 52.2 mg/kg for corn, oat and soybean when grown at Clay 2. Tissue Ni concentrations were 19.6, 135, and 158, respectively, when the same plants were grown in Clay 3. These tissue concentrations reflect a 3- to 6-times increase in tissue Ni concentration even though soil Ni concentration was lower in Clay 3 than Clay 2. It may be possible that these findings are related to an increase soil Ni bioavailability in Clay 3, as reflected in the soil pH and cation exchange capacity being lower in Clay 3 soil than Clay 2 soil.



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Oat and soybean were the highest Ni accumulators in Clay 3 (both accumulated in excess of 100 mg Ni/kg in agronomic tissues in Year 2001). However, radish is likely the highest Ni accumulator given it had the highest tissue Ni concentration (71.1 mg/kg) amongst all plant species grown at Clay 2.

The tissue concentrations for corn, oat, and soybean grown in unamended Clay 2 soil in Year 2001 were within the lower end of the range of concentrations for the respective species where phytotoxicity was reported (McIlveen and Negusanti, 1994). Tissue Ni concentration for radish grown in Clay 2 and for corn, oat and soybean grown in Clay 3 were high relative to the range of tissue Ni concentration reported in studies where phytotoxicity was observed in McIlveen and Negusanti (1994).

The limestone amendments did demonstrate that: 1) limestone amendment can increase the soil pH thereby decreasing Ni (and other CoC) bioavailability; 2) Ni uptake in all tested plant species decreased with an increase in rate of limestone amendment; and 3) soil Ni concentration cannot directly predict tissue Ni concentration as metal bioavailability in soil is influence by factors such as pH and CEC. However, it was speculated that excessive liming induced pH-dependent nutrient deficiencies (e.g., symptoms of Fe and Mn-related deficiencies were observed) in corn, radish and soybean which led to decreases in crop yield. This is similar to observations by Kukier and Chaney (2000 and 2001).

The results from the field trials are not included in the meta-analysis of this Appendix because of the noted confounding factors.

#### 1.3.13 Jacques Whitford, 2004 (Greenhouse Trials and Engineered Field Plot)

**Summary:** The Greenhouse Trials in 2000 and 2001 formed the basis for the derivation of the recommended SSTL values for soil Ni concentration. The objective of the Greenhouse Trials was to determine the CoC (e.g., Ni) concentrations in various Port Colborne area soils that induce CoC-related toxicity (phytotoxicity) in select agricultural species. The CoC in soil were measured as both total and bioavailable concentrations, and plant response was related to soil metal concentration by a dose-response relationship for each soil type (organic, clay (further divided into Welland clay and Till clay for 2001), and sand).

The Year 2000 Greenhouse Study involved growing corn, oat, and soybean in soils collected from various locations representing a range of soil Ni exposure concentrations (Control = <100; Low = 200 - 500; Medium = 500 - 1,250; High = 1,250 - 3,500; Very High = >3,500 mg Ni/kg soil) for any given soil type. Soils were amended with one of three types of limestone amendments: 1) unamended; 2) 1X OMAFRA recommended rate; and 3) 2X OMAFRA recommended rate.

For the Year 2001, instead of collecting soils that represented the range of soil Ni exposure concentrations, a given type of soil with background level of CoC was blended with the same type of soil with very high CoC concentration in various proportions to achieve a range of Ni exposure concentrations (background (Control), 250, 500, 750, 1,000, 1,500 (except sand), 2,000,



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and 3,000 mg Ni/kg soil). Oat (on all soil types) and radish (Welland clay) were grown in 2001. Carbonate (e.g., CaCO<sub>3</sub> and MgCO<sub>3</sub>) was added to the potting soil at OMAFRA recommended rates to achieve a pH of approximately 7 in the amended soils.

An Engineered Field Plot (EFP) Trial was also conducted at Clay 3 (Field Trial) in 2001. Oats were partially grown on Welland Clay in the greenhouse and then were transferred to a field plot. The bottoms of the pots were removed to allow the roots to access the underlying soil, and the plants placed in a trench in the plot and exposed to ambient conditions for the remainder of the growing season. The potting soil was prepared by the mixing of Ni-contaminated Port Colborne Site soil and uncontaminated Control Site soil to achieve nominal target Ni concentrations as described for the 2001 Greenhouse Trial. CaCO<sub>3</sub> and MgCO<sub>3</sub> were added to the potting soil for the amended treatment as described for the 2001 Greenhouse Trial.

Confounding variables associated with the use of soils collected from various locations representing a range of soil Ni exposure concentrations for the Year 2000 Greenhouse trial produced highly variable yield results. Consequently, the derivation of a threshold toxicological value for soil Ni was highly problematic. For example, the Weibull model fitted as the dose-response curve to the data for oat and soybean grown in organic soil (and soybean in sand) had a curve critical value approaching zero (a horizontal line) resulting in a soil Ni EC25 > 5,000 mg/kg (>1,400 mg/kg for soybean in sand) (*i.e.*, greater than the highest tested soil Ni concentration). Similar problems for oat and corn grown in sand and clay produced undefined results because the fitted models were horizontal lines.

Alternatively, EC25 derived for corn grown in organic soil was approximately 800 mg/kg (2,000 mg/kg for soybean in clay); however, the variability in the data produce 95% prediction limits that ranged between 0 and 150% relative yield.

To improve on previous results, the Year 2001 Greenhouse Trial used potting soil prepared by the mixing of Ni-contaminated Port Colborne Site soil and uncontaminated Control Site soil to achieve nominal Ni exposure concentrations. The current recommended site-specific toxicological threshold values (EC25) of 1,350, 1,880, 1,950, and >2,400 mg/kg for sand, Welland clay, Till clay, and organic soils were derived from the dose-response results for cultivated oat.

The toxicological threshold for soil Ni from the EFP for oat grown in Welland clay was 1,425 mg/kg. The EC25 for tissue Ni was 42 mg/kg.

For both Greenhouse Trials and the EFP, tissue Ni concentrations were found to decrease as a result of limestone or carbonate amendment. Crop yield in the clay soils improved with amendment; however, crop yield had mixed results in crops grown in organic and sandy soil during the Greenhouse Trials. It is possible that this discrepancy is related to pH-dependent Mn deficiency caused by limestone or carbonate amendment.

Direct comparison of the Greenhouse/EFP Trials to the Field Trials is not possible as the two components were designed to meet separate objectives. However, the results from both



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components were not that disparate. For example, soil factors (pH and CEC) affected Ni bioavailability which in turn affected the level of uptake and corresponding phytotoxicity.

The results of the re-evalution of the 2000 greenhouse trial are presented in Section 1.3.14.

The 2001 oat greenhouse trial formed the basis for the recommended SSTL (Table 5B-9).

## Table 5B-9Score assigned (based on MOE criteria), EC25 (reported in Jacques Whitford,<br/>2004), and Weighted EC25 (Score x EC25) for oat shoot biomass from Jacques<br/>Whitford, 2004.

Сгор	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Oat	Shoot Biomass	86	2400	206400

## 1.3.14 Reanalysis of crop data for organic and clay soils from the year 2000 greenhouse studies

The MOE and the independent reviewer of the Crops Risk Assessment consistently pressured to include the Crops data for the year 2000 studies. Stantec and the proponent (Vale) have resisted the inclusion of the year 2000 data for the purposes of calculating toxicity thresholds (EC25s or equivalent) because the year 2000 studies were preliminary.

The study approach and design were modified in the following year (2001) in which much better data was generated and more reliable results were obtained. In scientific activities, this is a common sequence, with preliminary or range-finding studies being used initially, followed by more definitive studies that provide better and more reliable results. The reluctance to use the year 2000 data is for these very reasons. Nevertheless, the MOE has persistently requested that these earlier preliminary data be used to derive toxicity thresholds, and failure to do so would not meet MOE's regulatory request. This section is intended to meet this regulatory request, even though it counters the essential sequential nature of the scientific approach.

In the year 2000 preliminary Greenhouse Trials, soils were collected from selected field locations and were used "as-is" (i.e., without any soil blending) for experimentation. This was referred-to as option 1 in the Crops Risk Assessment (Jacques Whitford 2004 – volume I, part 2 (see Appendices 1J-1L). Option 2 (blending soils) was used in 2001 due to the inadequacies of option 1 in year 2000. Corn, oat and soybean were grown in these preliminary Greenhouse Trials, and plant biomass was used as the measure of response in the plants. The wide variation in composition of soils collected in this manner led to complications in the analysis and interpretation of results due to the heterogeneity in soil properties.

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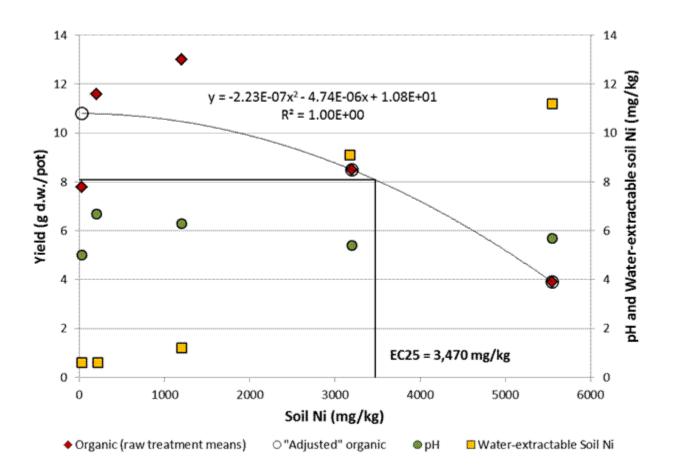
Five classes of Ni soil contamination were targeted: Control (~43 mg Ni/kg), "Low" (200 - 500 mg Ni/kg), "Medium" (500 – 1,250 mg Ni/kg), "High" (1,250 – 3,500 mg Ni/kg), and "Very High" (>3,500 mg Ni/kg). Ten 200L drums of each soil type were collected for use in the year 2000 greenhouse trials.

#### 1.3.14.1 Soybean

For soybeans grown in organic soil, the dose-response between yield and soil Ni concentration was not straightforward (**Figure 5B-8**). The raw yield data are plotted as red diamonds in the figure and show that the yield for the controls was low and similar to that seen for soybeans in the High treatment. An EC25 could not be calculated from the raw data, but an examination of the water-extractable soil Ni and tissue Ni indicated that the bioavailable soil Ni for the three lowest Ni concentrations were similar. Therefore, to facilitate analysis, the yield data were pooled for the three lowest treatments and the average was used to represent the control yield (necessary to calculate an EC25). A polynomial fit of the adjusted data was used to derive an EC25 for soybeans. Seventy-five per cent of the control yield of 10.8 g/pot was calculated to be 8.1 g/pot. The polynomial equation in **Figure 5B-8** was solved iteratively to give y=8.1. The corresponding x value was 3,470 mg Ni/kg soil. This was the estimated EC25 using the adjusted (censored) data. It would also have been possible to omit the control data entirely and consider that the yields from the Low and Medium treatments were surrogates for control yield. This would also have been possible, based on water-extractable soil Ni and tissue Ni (**Figure 5B-8**). In that case, the EC25 would be 2,645 ppm.



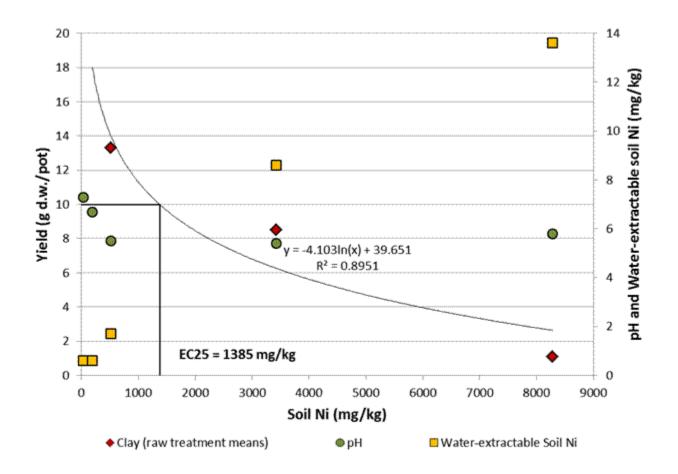
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## Figure 5B-8 Derivation of an EC25 for soybean plants grown in organic soil in the Year 2000 greenhouse studies (Jacques Whitford, 2004). The EC25 interpolated from the fitted polynomial model is 3470 mg Ni/kg soil.

The yield of soybean (soybean plant biomass, not bean biomass) in clay soil from the Year 2000 Greenhouse Studies is provided in **Figure 5B-9**. There was no germination of the control seeds, so no control growth data are available. The EC25 was estimated using the dose-response from the Low Ni treatment to the Very High Ni treatment. The EC25 generated in that way was 1,385 mg Ni/kg soil. The lack of true control data make the reliability of this value somewhat questionable, but the attempt to derive an EC25 was made to satisfy the MOE's ongoing demand to assess the Year 2000 experiments.

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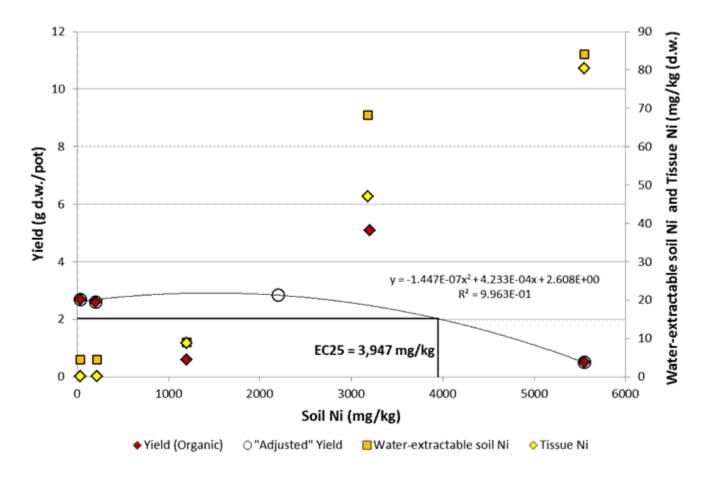
## Figure 5B-9 Derivation of an EC25 for soybean grown on clay soil in the Year 2000 greenhouse studies (Jacques Whitford, 2004). The EC25 interpolated from the fitted polynomial model is 1385 mg Ni/kg soil.

#### 1.3.14.2 Oat

For oats grown on organic soil in Year 2000 Greenhouse experiments, the yield was low in the Medium treatment (and similar to the reduced yield seen in the Very High treatment). In comparison, the High treatment had very good yield. These data were not suitable for deriving an EC25. If the yield data from the Medium and High treatments are pooled and if it is assumed that the soil Ni concentration is the average of the Medium and High concentrations, a dose-response curve can be generated (**Figure 5B-10**). A dose-response curve could be derived from the adjusted data. The EC25 calculated in this way was 3,947 mg Ni/kg soil.



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## Figure 5B-10 Derivation of EC25 for Oats in organic soil. In the "Adjusted" yield curve (open circles), the medium and high yield and soil concentrations were "averaged" in order to obtain a calculable EC25.

#### 1.3.14.3 Corn

In the year 2000 Greenhouse Studies, corn germination in organic soil was poor (control germination failed entirely) and a second experiment (Organic II) was undertaken. The treatment averages for these two experiments are plotted in **Figure 5B-11**. The raw data were not amenable to calculating an EC25. There was no control yield data for one experiment and a lack of monotonically decrease in yield against soil Ni. There was fairly good reproducibility for yield between the Organic and Organic II experiments, although the yield in the High Ni treatment in the Organic experiment was higher than that in the Low Ni treatments from both experiments. Due to the lack of fit, data were pooled to facilitate analysis:

• The average yield from the Control treatment in Organic II was pooled with the average yield from both Low Ni treatments. The water-extractable soil Ni was very similar between

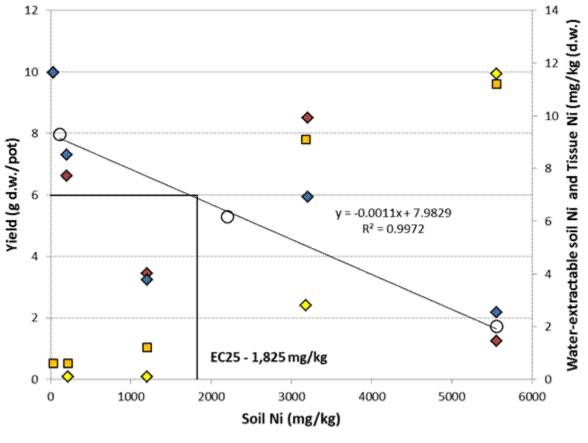
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these treatments, which provide some justification for such grouping. The resulting yield was 7.97 g/pot (**Figure 5B-11**)

• Due to the lack of a monotonic decreasing dose-response, the Medium and High yield data from both Organic and Organic II treatments were pooled and averaged. The soil concentration values for these two treatments were also averaged, and the "Pooled and adjusted" yield (open circle in **Figure 5B-11**) was used in the three-point regression line for the resulting dose-response curve.

The resulting EC25 from this exercise was 1825 mg Ni/kg in soil.



## Figure 5B-11 Derivation of an EC25 for corn yield in organic soil in the year 2000 greenhouse studies.

For corn grown in clay in the Year 2000 Greenhouse Studies, large reductions in yield in the High Ni and Very High Ni treatments correspond to high tissue Ni concentrations (Fig. E), and represent real phytotoxic responses. No yield data were available for the Control treatment, so



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a dose-response relationship was fit using a power function (**Figure 5B-12**) for the soil Ni versus yield dose-response pairs. This was solved iteratively for the point at which the response (yield) was 75% of the control yield. In this case, the Low Ni treatment was considered to provide the "control" response, and the water-extractable soil Ni for the Control and Low Ni soils were very similar, so this decision appears to be supportable. The EC25 estimated by this method is 315 mg Ni/kg soil.

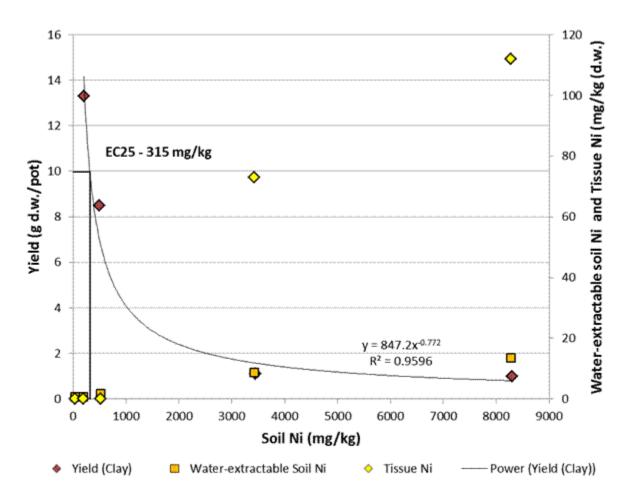


Figure 5B-12 Derivation of an EC25 for corn in clay soil in the year 2000 greenhouse studies.

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#### 1.3.14.5 Summary of the reassessment of the year 2000 greenhouse data

Greenhouse<sup>3</sup> (2000 and 2001) and field studies<sup>4</sup> (2001) were conducted by Jacques Whitford as dose-response experiments designed to generate data from which to derive suitable SSTLs. The Greenhouse Trial in 2001 formed the basis for the derivation of the recommended SSTLs for Ni in soil for the Port Colborne CBRA (Jacques Whitford, 2004) because the data from the 2000 Greenhouse Trial were unreliable as discussed in the Addendum Report<sup>5</sup> and summarized below. The objective of the Greenhouse Trials was to determine the CoC (e.g., Ni) concentrations in various Port Colborne area soils that induced CoC-related toxicity (phytotoxicity) in select agricultural species. The CoC in soil were measured as both total and bioavailable concentrations, and plant response was related to soil metal concentration by a dose-response relationship for each soil type (organic, clay (further divided into Welland clay and Till clay for 2001), and sand).

In 2000, corn, oat, and soybean plants were grown in soils collected from various locations representing a range of soil Ni exposure concentrations (Control = <100; Low = 200 – 500; Medium = 500 - 1,250; High = 1,250 - 3,500; Very High = >3,500 mg Ni/kg soil) for any given soil type<sup>6</sup>. Soils were amended with limestone at one of three rates: 1) un-amended (0 T/ha); 2) 1X OMAFRA recommended rate (7.5 T/ha); and 3) 2X OMAFRA recommended rate (15 T/ha). For the Year 2001, un-contaminated and contaminated sandy, organic muck, heavy clay, shallow (Till) clay soils were blended in various proportions to achieve a range of Ni exposure concentrations. The range of CoC concentrations (expressed in terms of Ni, the major CoC) were: background (Control), 250, 500, 750, 1,000, 1,500 (except sand), 2,000, and 3,000 mg Ni/kg soil. Oat (on all soil types) and radish (Welland clay) were grown in 2001. Carbonates (CaCO<sub>3</sub> and MgCO<sub>3</sub>) were added to the blended soils at OMAFRA-recommended rates to achieve a pH of approximately 7 in the limestone-amended soils<sup>7</sup>.

In the original Crops risk assessment, the results of the Greenhouse Trial in 2000 were not used to derive the SSTLs for the site because a number of confounding factors unrelated to the concentration of nickel in soil affected the outcome of the trial.

In response to the MOE's concerns that exclusion of some of these data relating to soil factors from the SSTL derivation process was somehow limiting, the data were re-examined to determine if any of the data could be included in the revised dataset.

<sup>&</sup>lt;sup>7</sup> Jacques Whitford Ltd. 2004. Port Colborne Community Based Risk Assessment: Ecological Risk Assessment: Crop Studies. Greenhouse Trials 2000 and 2001. Volume 1 – Part 3, pp. 3-14. A report prepared on behalf of Inco, Dec. 2004.



<sup>&</sup>lt;sup>3</sup> Jacques Whitford Limited (Jacques Whitford), prepared on behalf of Inco Limited. 2004. Port Colborne CBRA – Ecological Risk Assessment: Crop Studies. Greenhouse Trials 2000 & 2001. Volume 1 – Part 3. December, 2004.

<sup>&</sup>lt;sup>4</sup> Jacques Whitford Limited (Jacques Whitford), prepared on behalf of Inco Limited. 2004. Port Colborne CBRA – Ecological Risk Assessment: Crop Studies. Field Trials 2000 & 2001. Volume 1 – Part 4. December, 2004.

<sup>&</sup>lt;sup>5</sup> Jacques Whitford Ltd. 2006. Port Colborne Community Based Risk Assessment: Ecological risk assessment – Crops. Addendum report prepared on behalf of Inco Ltd. September, 2006 for Inco Ltd.

<sup>&</sup>lt;sup>6</sup> Jacques Whitford Ltd. 2004. Port Colborne Community Based Risk Assessment: Ecological Risk Assessment: Crop Studies. Greenhouse Trials 2000 & 2001. Volume 1 – Part 3, pp. 3-15. December, 2004.

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These data were included in the re-evaluation and scored and weighted accordingly. The field trials designed and implemented in 2000 and 2001 to corroborate or verify the findings of the Greenhouse Trials failed to produce reliable or definitive data for various reasons (Jacques Whitford Ltd., 2004)<sup>8</sup>. Nevertheless, the data were re-evaluated (Sections **1.3.14.1** to **1.3.14.3**).

Amongst the corn, oat, and soybean shoot biomass endpoints from the Year 2000 greenhouse trial, only soybean scored greater than 55% based on the scoring criteria from the MOE (**Table 5B-10**). Corn and oat are excluded from further consideration. The method for deriving the EC25 for soybean shoot biomass production in response to soil Ni concentration is illustrated by **Figure 5B-8**.

# Table 5B-10Score assigned (based on MOE criteria), EC25 (calculated as described in<br/>Section 1.3.14.1 to 1.3.14.3), and Weighted EC25 (Score x EC25) for corn, oat, and<br/>soybean shoot biomass from the Year 2000 greenhouse trials reported in Jacques<br/>Whitford (2004) and reanalyzed in this section.

Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 (Score x EC25)
Corn	Shoot biomass	52	NA*	NA*
Oat	Shoot biomass	52	NA*	NA*
Soybean	Shoot biomass	76	3470	263720

**NA\*** Endpoints for these crops scored below 55% based on the MOE scoring criteria. Therefore, the endpoints were excluded from further evaluation.

<sup>&</sup>lt;sup>8</sup> Jacques Whitford Limited (Jacques Whitford), 2004. Port Colborne CBRA – Ecological Risk Assessment: Crop Studies. Greenhouse Trials 2000 and 2001. Volume 1 – Part 3, A report prepared on behalf of Inco, December, 2004.



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#### 1.4 SAMPLE CALCULATION OF EC25

**Section 1.2** provided the rationale and described the process of calculating EC25 values from the available literature for crops grown in Ni-impacted muck soil of Port Colborne. In this section, the method of calculating the EC25 value from the 1980 head lettuce top fresh weight data from Frank *et al.* (1982; Table 10) is used as an example to illustrate the process.

# Table 5B-11Soil Ni concentration (mg/kg) and corresponding 1980 head lettuce top fresh<br/>weight (g) from Frank et al., 1982.

Soil Ni Concentration (mg/kg)	Lettuce Top Fresh Weight (g)
37°	744 <sup>b</sup>
2990	798
3640	384
4410	200
5090	22
6120	58

a "Control" soil Ni concentration based on MOE O.Reg. 153/04, Table 1 site condition standard (MOE, 2011).

<sup>b</sup> Control data from OMAFRA (1981)

The reported data from Frank *et al.* (1982) for 1980 head lettuce top fresh weight is augmented with the "Control" value from the Overholt study (OMAFRA, 1981) presented in **Table 5B-11**. The values were imported into SigmaPlot, and linear and non-linear (exponential, logarithmic, and logistic) regression models were fitted to the data.

The best-fitting regression model is accepted as the one with the highest adjusted r<sup>2</sup> value as calculated by SigmaPlot. The adjusted R<sup>2</sup> value was the criterion used for determining the best-fitting regression model because the data presented in Frank *et al.* (1982) comprised the mean of the dataset rather than the actual data used to calculate the means. In such a situation, where a sample of the dataset (e.g., the mean values) rather than the empirical data is used in the regression analyses, the adjusted r<sup>2</sup> is a better measure of the goodness of fit.

Based on the adjusted  $R^2$  value, the logistic model (adjusted  $r^2 = 0.9379$ ) was the best regression to model the 1980 head lettuce top fresh weight data (**Figure 5B-3**).

An EC25 can be calculated from the equation of the logistic model. The logistic model fitted to the data is,



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$$y = 794 / (1 + (x / 3,750)^{9.50})$$
 Eq. 1

where, x = soil Ni concentration (mg/kg), and y = head lettuce fresh weight (g).

Given that at a soil concentration of 37 mg/kg (MOE, 2011) and the expected head lettuce top fresh weight is 744 g (OMAFRA, 1981), the 1980 head lettuce fresh weight at EC25 is calculated to be,

$$y_{EC25} = 744 \text{ g} * 0.75 = 558 \text{ g}$$
 Eq. 2

The EC25 based on 1980 lettuce fresh weight is then calculated to be **3,410 mg/kg** by solving for "x" in **Eq. 1** and substituting  $y_{EC25}$  (**Eq. 2**) for y. Alternatively, it can be interpolated from the logistic model fitted to the data as illustrated in **Figure 5B-3**.

#### 1.5 SAMPLE CALCULATION OF WEIGHTED EC25 FOR A CROP SPECIES

Here is an example using lettuce is provided to further elaborate on the process to calculate a weighted EC25 value for an individual crop species.

Source	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 by Score
Temple & Bisessar 1981	Root Weight	69	3780	2608
Temple & Bisessar 1981	Leaf Weight	72	5090	3665
Frank et al. 1982 (1980 head)	Top Weight	76	3410	2592
Frank et al. 1982 (1981 head)	Top Weight	76	370	281
Frank et al. 1982 (1981 escarole)	Top Weight	76	450	342
Bisessar & Palmer	Root Weight	83	4320	3586
Bisessar & Palmer	Leaf Weight	86	3080	2649
Sum	15722			
Weighted EC25 for lettuce	2920			

# Table 5B-12:The calculation of weighted EC25 values for individual lettuce endpoints including<br/>how they were used to calculate a weighted EC25 for lettuce

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Table 5B-12 lists EC25 values calculated (as described in Sections 1.2 and 1.4; best-fit regressionmodels presented in Section 1.3) for all lettuce endpoints with their corresponding literaturesource and score assigned to that endpoint based on the MOE scoring key. The weighted EC25for any given endpoint is calculated by multiplying its calculated EC25 value by its score.

Using the lettuce root weight from Temple and Bisessar, 1981, as an example,

Weighted EC25 = EC25 \* (Score / 100) Eq. 3 Weighted EC25 = 3,780 mg/kg \* (69% / 100) Weighted EC25 = 2,600 mg/kg Eq. 4

The weight given to an endpoint is to normalize the calculated EC25 based on the scientific, economic, and practical merits/qualities of the source article as described by the MOE scoring key. The weighted EC25 value for an endpoint (e.g., **Eq. 4**) is not a theoretical "safe" concentration for a particular endpoint. Rather, it is an attempt to relate the confidence in an EC25 value as a result of the score assigned to the endpoint.

The weighted EC25 for a particular crop is the sum of the weighted EC25 values of all endpoints for a crop divided by the sum of all the scores.

Weighted EC25 for lettuce =  $\sum$  Weighted EC25 / ( $\sum$  Score / 100) Eq. 5

Weighted EC25 for lettuce = 15,700 mg/kg / (538%/100) = 2,920 mg/kg Eq. 6

To be conservative, the weighted EC25 for lettuce (and all crops included in the meta-analysis) is rounded down to the nearest 10 mg/kg regardless of the value of the last digit.

#### 1.6 META-ANALYSIS OF EC25 VALUES

A total of 56 crop endpoints were evaluated. Eighteen (18) endpoints were eliminated from further consideration because: 1) seven (7) endpoints did not have a "Control" datum because no OMAFRA value was found (e.g., lettuce root); 2) one (1) endpoint was eliminated when two (2) endpoints from Frank *et al.*, 1982 (beet root and top), were amalgamated into a single endpoint because the value from OMAFRA was a combination of the two endpoints (i.e., whole plant); 3) three (3) were noted by the authors to be not significantly different than control; and, 4) seven (7) endpoints scored less than 55%. Furthermore, as the CBRA is a chemical-based risk assessment, six (6) socio-economic based endpoints of marketable yield from Frank *et al.* (1982) were excluded from further consideration.

The resulting meta-analysis was conducted on the remaining 32 endpoints that scored at or greater than 55% (at least 16 out of 29 points). The highest score reported was 93% (27 of 29 points) for two endpoints calculated from Bisessar, 1991. The lowest scoring endpoint (66%) that



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was included in this evaluation came from an endpoint derived from Bisessar et al. (1983) for celery shoot height.

The calculated EC25 values derived from the procedures described in **Section 1.4** for each endpoint were multiplied by its score to produce a weighted EC25 value for that particular endpoint (as described in **Section 1.5**). The weighted EC25 value of a crop species was calculated by dividing the sum of the scores of the crop's endpoints (e.g., root weight, % yield) by the sum of the crop's weighted EC25 values. The weighted EC25 value for nine (9) crop species in this meta-analysis derived by this manner are presented in **Table 5B-13**. A weighted EC25 values by the geometric mean of the score.

Species	Weighted EC25 Values (mg/kg) Based on MOE Scoring Key	Weighted Geometric Mean EC25 (mg/kg)
Beet	410	NA
Wheat	1090	1080
Radish	1960	NA
Oat ª	2400	2400
Onion	2740	2730
Lettuce	2920	2030
Soybean	3470	NA
Celery	3680	2730
Cabbage	4040	NA

# Table 5B-13:Weighted and Geometric Mean EC25 values for individual crop species for<br/>organic muck soil

<sup>a</sup> Recommended SSTL from Jacques Whitford, 2004.

NA - Not applicable because there was only one included endpoint.

The weighted EC25 values for three (3) of nine crop species, specifically beet (410 mg/kg), wheat (1090 mg/kg), and radish (1960 mg/kg) are less than the recommended SSTL value of 2400 mg/kg for organic soils (Jacques Whitford, 2004). If the weighted geometric mean is considered as the standard for comparison, further risk evaluation is needed for an additional species (lettuce; 2030 mg/kg).

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The results of this meta-analysis may indicate a potential for yield loss for beet, wheat, radish, and lettuce in the event that they are cultivated in Port Colborne organic soil with Ni concentration at the recommended SSTL of 2400 mg/kg.

Instead of comparing the weighted EC25 value for each crop to the recommended SSTL from Jacques Whitford (2004), one could use the weighted EC25 from all the endpoints included in the meta-analysis to derive a new SSTL. One approach may be to divide the sum of all weighted EC25 values by the sum of all scores – similar to the approach used for the individual crop species. This resulted in a combined weighted EC25 value and a weighted geometric mean EC25 value of **2810** and **2100 mg Ni/kg soil**, respectively (**Table 5B-14**).

# Table 5B-14Summary of all endpoints used to derive a weighted EC25 and weightedgeometric mean EC25 that could be used as a Site-Specific Threshold Level.

Source	Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 by Score
Bisessar & Palmer	Celery	Leaf Weight	86	3580	3079
Bisessar & Palmer	Celery	Root Weight	86	1960	1686
Bisessar & Palmer	Celery	Stalk Weight	86	3230	2778
Bisessar & Palmer	Lettuce	Leaf Weight	86	3080	2649
Bisessar & Palmer	Lettuce	Root Weight	83	4320	3586
Bisessar 1989	Celery	Root Weight	79	6930	5475
Bisessar 1989	Celery	Shoot Height	79	5200	4108
Bisessar 1989	Celery	Shoot Weight	83	5250	4358
Bisessar 1991	Wheat	Grain Weight	93	970	902
Bisessar 1991	Wheat	Leaf Weight	90	1080	972
Bisessar 1991	Wheat	Root Weight	93	1320	1228
Bisessar 1991	Wheat	Shoot Height	90	1030	927
Bisessar 1991	Wheat	Stem Weight	90	1050	945
Bisessar et al. 1983	Celery	Shoot Height	66	5120	3379



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Source	Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 by Score
Bisessar et al. 1983	Celery	Shoot Weight	69	2310	1594
Frank et al. 1982	Beet	Top and Root combined	72	410	295
Frank et al. 1982	Cabbage	Top Weight	76	4040	3070
Frank et al. 1982	Radish	Root Weight	72	1960	1411
Frank et al. 1982 (1980 head)	Lettuce	Top Weight	76	3410	2592
Frank et al. 1982 (1980)	Celery	Top Weight	76	260	198
Frank et al. 1982 (1981 escarole)	Lettuce	Top Weight	76	450	342
Frank et al. 1982 (1981 head)	Lettuce	Top Weight	76	370	281
Frank et al. 1982 (1981)	Celery	Top Weight	76	380	289
JW 2000 (GH)	Soybean	Shoot biomass	76	3470	2637
JW 2001 (GH)	oat	Shoot biomass	86	2400	2064
Rinne 1984	Celery	Shoot height	76	3380	2569
Temple & Bisessar 1981	Celery	Leaf Weight	69	6010	4147
Temple & Bisessar 1981	Celery	Stalk Weight	72	4630	3334
Temple & Bisessar 1981	Lettuce	Leaf Weight	72	5090	3665
Temple & Bisessar 1981	Lettuce	Root Weight	69	3780	2608



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Source	Crop	Endpoint	Score (%)	EC25 (mg Ni/kg soil)	Weighted EC25 by Score
Temple & Bisessar 1981	Onion	Leaf Weight	69	2530	1746
Temple & Bisessar 1981	Onion	Root Weight	69	2960	2042
		Sum	2517		70953
			Weighted EC25		2810
			Weighted Geometric Mean EC25		2100

#### 1.7 UNCERTAINTY ANALYSIS

The process developed between the proponent (Vale), its consultant (Stantec) and the MOE for conducting this meta-analysis presented in this Appendix resulted in potential SSTL values for Ni in Port Colborne muck soils of **2,100** (weighted geometric mean EC25) or **2,810 mg Ni/kg soil** (weighted EC25). Both of these values generally agree with the original CBRA recommendation (Jacques Whitford Ltd., 2004) that soil Ni concentrations greater than 2400 mg/kg in muck soil would be required to impair production of most crop species that are reportedly grown in organic soils of the region. Impaired production (up to 25% reduction) of most crop species is not expected until soil Ni concentration is above 2000 mg/kg even if the weighted geometric mean EC25 (**2100 mg/kg**) from the meta-analysis is considered a possible SSTL.

This meta-analysis also indicated that there is potential for significant yield decrease (up to 25%) if a producer chooses to cultivate beet, wheat, radish, and lettuce (depending on which value is adopted as the SSTL) in organic soil of Port Colborne with Ni concentrations of 410, 1090, 1960, and 2030 mg/kg, or higher, respectively. There is, however, uncertainty for this contention and the assumptions associated with the derivation of these values, including a lack of concomitant control data and the presence of active Refinery emissions during some of these studies. The endpoints used to derive the calculated EC25 values for beet, cabbage, and radish came from the reference Frank *et al.*, 1982. Data for the derivation of the EC25 for wheat came from the reference Bisessar (1991). The value for lettuce is skewed by two endpoints (370 and 450 mg Ni/kg soil when four other endpoints from two other sources had EC25 values above 3000 mg/kg) with low EC25 values for Frank *et al.*, 1982.



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Although many factors were considered in the meta-analysis, a number of key assumptions were made to facilitate the calculation of weighted EC25 values for each crop species. These assumptions were convenient for the purposes of the meta-analysis, but they bear limited semblance for the original reality, circumstances, and purposes of the collected data intended by the authors. The following uncertainty analysis examines these key assumptions to determine whether the calculated EC25 values for beet, wheat, radish, and lettuce are applicable.

#### 1.7.1 Assumption of Dose-Response from Field Data

An important assumption of a dose-response experiment (an experimental design that can be used to derive ECx values) is that the measured effect on an endpoint (e.g., decrease in beet root fresh weight) is caused by the increasing concentration of the stressor of interest alone (soil Ni concentration). Although tissue fresh weight data were collected for beet, cabbage, and radish grown in the field over a range of soil Ni concentrations, other field factors inevitably impacted on the results. These confounding factors may include the following:

- Phytotoxicity caused by aerial deposition these studies were conducted on organic muck soil at a farm within 1-km of Port Colborne that has produced vegetables commercially for 20 to 40 years. It can't be ruled-out that the effects observed by the MOE authors in 1980 and 1981 might be event-driven, e.g., aerial deposition of Ni (and other particulates) and sulfur dioxide emissions, rather than a chronic issue such as soil Ni concentration.
- Insufficient water the authors recognized irrigation was needed during the 1980 growing season (the year when data for the included endpoints were collected). This implies there was insufficient rainfall. Insufficient information is provided by the authors to determine whether the planted crops were irrigated to levels that would have supported unhindered growth.
- 3. Potential of root rot nematodes and other pests although the authors indicated standard OMAFRA-recommended agronomic practices were followed, it is uncertain why nematocides were used for most crops reported in Frank et al. (1982) except for beet and radish. These two crops were noted in Table 5B-13 as having lower weighted EC25 values compared to that of oat which was the crop used in the Jacques Whitford (2004) report to establish a common EC25 for all crops grown in organic muck soils. The picture of cabbage in Frank et al. (1982) also showed signs of insect predation.

Based on these three confounding factors alone, the likelihood of measuring a dose-response relationship between the reported endpoints for beet, radish, and lettuce and soil Ni concentration in a field trial as described in Frank *et al.* (1982) is highly suspect. The calculated EC25 values from these results likely represent an overestimation of risk due to soil Ni phytotoxicity for beet, radish, and lettuce.

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#### 1.7.2 Likelihood of Crop Species to be cultivated in the Port Colborne Area

Information regarding the likelihood/probability of the crop species of beet, lettuce, radish, and wheat was collected to assess the potential economic impact on producers in the Port Colborne area if these crops were cultivated in organic soils with soil Ni concentrations at the respective EC25 values or the SSTL. The following information (**Table 5B-15**) was reported in the 2006 Statistic Canada Census of Agriculture (Statistics Canada, 2014; <u>http://www.statcan.gc.ca/pub/95-629-x/2007000/4123849-eng.htm</u>).

Table 5B-15	Estimate of acres of beet, cabbage, radish and wheat crops grown in Port
	Colborne based on 2006 Statistics Canada Census of Agriculture

Species	# of Farms	Acres
Beet	2	8a
Lettuce	2	x
Radish	0	0
Wheat	12	2,067

<sup>a</sup> Estimated based on 27 farms in the Niagara region reporting the cultivation of 70 acres of beet in 2006 with 11 farms not in Port Colborne accounting for 5 acres; therefore, the estimate = 65 acres/16 farms = 4.1 acres/farm.
 <sup>b</sup> Estimated based on 18 farms in the Niagara region reporting the cultivation of 75 acres of beet in 2006 with seven (7) farms not in Port Colborne accounting for 50 acres; therefore, the estimate = 25 acres/11 farms = 2.2 acres/farm.
 x – Suppressed to meet confidentiality requirements of the Statistics Act.

At the recommended SSTL of 2,400 mg/kg, wheat is likely the crop of greatest economic importance. Radish is realistically of no consequence because no producer reported its production during the 2006 Census. Beet only accounted for an estimated 0.4% of the cropped acres relative to the acres cultivated to wheat in Port Colborne. Information for lettuce was redacted because of confidentiality. These findings suggest the apparent EC25 values for beet and radish likely overestimates the potential economic impact to producers given the limited to no acreage cultivated to these crops in Port Colborne.

#### 1.7.3 Effect of Aerial Deposition from past Refinery Activity

As discussed in **Section 1.7.1**, aerial deposition of phytotoxic particulates and sulfur dioxide emissions might have contributed to crop injuries reported for beet, radish, and lettuce in Frank *et al.* (1982). It is well documented that aerial deposition of particulates from Ni refineries has often caused injuries to nearby agricultural crops. In fact, crop producers in parts of Ontario in similar situations have complained to the MOE about damages to their crops related to aerial depositions. This in turn triggered the many phytotoxicity studies that were carried out by the MOE in the 1980s that generated the reports which were published and used in the current meta-analysis.



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The Port Colborne refinery has not processed Ni since 1984. Therefore, the phytotoxicity plant studies that were conducted in the Port Colborne area in 2001 (Jacques Whitford, 2004) provide site-specific information to derive recommended SSTL values during a period of time when there was no atmospheric deposition of nickel-laden particulates from the local refinery emissions. In comparison, the work by Frank *et al.* (1982) was completed at a time when there were ongoing atmospheric deposition of nickel-laden particulates and sulphur dioxide from the local refinery emissions. Therefore, the plants grown by Frank *et al.* (1982) were likely exposed to soil Ni by uptake through the roots as well as to through exposure to Ni (and other emission products) deposited on the surface of the plants.

Results of the field trial with radish reported by Jacques Whitford, 2004 (Appendix F-2, p. 2), further illustrates the difference in field conditions between the 1980s and 2000s. The reported dry weight of radish grown in four field plots of organic soils with a mean Ni concentration of 3,590 mg/kg ranged between 4.6 and 6.9 g per plant (dry weight). The reported radish has a wet weight of 22 g per plant (as calculated based on OMAFRA data in **Section 1.3.3.1**) or 2.2 g per plant dry weight (based on 90% water content; University of Kentucky, 1997). This indicates organic soils of Port Colborne with elevated Ni concentration can produce crops such as radish that meets or exceeds what is expected for Ontario. This contrasts with the results from Frank *et al.* (1982) where radish of approximately 12.9 g wet weight (1.3 g dry weight) was produced in muck soil with 2,570 g Ni/kg soil. Clearly, soil Ni concentration alone cannot account for the difference in the size of the radishes produced in between the two studies.

The historic data used to derive EC25 is only of consequence if the circumstances under which the data were collected are applicable and reproducible today. The calculated EC25 values for beet, lettuce, and radish likely overestimated the current-risk from soil Ni concentration to these species because it is not possible to distinguish the phytotoxic effects of Ni from aerial deposition versus effects attributable to soil Ni concentration in the historic data.

#### 1.7.4 Model Selection used to calculate EC25 Values

The calculation of EC25 values conducted in this meta-analysis relied on the selection of the best-fit model to the available data in the reported literature. The model used to describe the dose-response relationship has obvious impacts on the resultant EC25 value. It is possible to fit any model to a dataset in order to generate a desired estimation of risk. From **Table 5B-16**, the estimated EC25 value based on the data from Frank *et al.* (1982) fitted to logistic, linear, exponential, and logarithmic models are 3410, 2300, 1660, and 340 mg/kg, respectively.

It is arguable that the most conservative model should be chosen to estimate the EC25 in order to offer the highest risk protection possible. However, model selection was based on its ability to account for the natural variability in the available dataset and on its biological plausibility.

As described in **Section 1.4**, the model chosen to describe the dataset was based on the model's adjusted R<sup>2</sup> value. To further elaborate, the best-fit model also has the lowest standard error of the estimate (SE) and the lowest residual mean square (MS). These two parameters are



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direct measurements of how much the dataset itself deviates from the fitted predictive models. To simplify, the data that are being model are situated closer to the modeled regression line of the best fit model. The adjusted r<sup>2</sup>, SE, and MS values for the 1980 head lettuce example are presented in **Table 5B-16**.

Model	Estimated EC25 (mg Ni/kg soil)	SE	MS	Adjusted r2
Logistic (best fit model)	3410	84	7084	0.9379
Linear	2300	198	39062	0.6577
Exponential	1660	243	59239	0.4809
Logarithmic	340	290	84047	0.2635

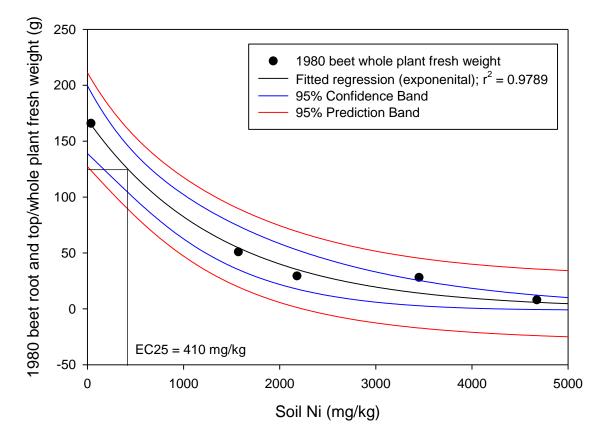
Table 5B-16	Standard error of the mean (SE) and the residual mean square (MS) for the models
	fitted to the 1980 head lettuce data from Frank et al., 1982.

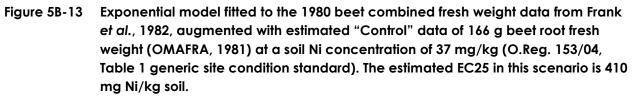
For 1980 head lettuce, the logistic model (**Figure 5B-3**) also conformed to the known biological response of plants and animals to metal toxicity. That is to say, a threshold soil Ni concentration is reached prior to its toxic effects to lettuce are observed.

For beet (Figure 5B-13) and lettuce (1981 head lettuce and escarole), the best fit model was the exponential model. An exponential model indicates there was no threshold response to soil Ni toxicity for beet and lettuce, i.e., soil Ni-related toxicity occurs at relatively low concentrations. Although possible, this is counter to what is commonly known in regards to soil Ni toxicity to plants because Ni is a required micronutrient (*i.e.*, required at trace amounts). It is likely that the OMAFRA and MOE values used to constrain the beet and lettuce datasets (as discussed in Sections 1.2 and 1.3.3.1) artificially created a non-threshold response. Therefore, the exponential model used to estimate the EC25 values for beet and lettuce (1981 head lettuce and escarole) likely overestimated the potential risk to these two crop species.



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#### 1.7.5 Exclusion of Year 2000 Corn and Oat Data

The MOE requested in 2012 the re-evaluation and potential inclusion of the experimental data for soil Ni phytotoxicity to corn and oat that were generated in the Jacques Whitford greenhouse trials in 2000. The re-evaluation was completed (**Section 1.3.14**), and it was found that soil nutrient deficiencies (manganese and iron) and organic matter content were the primary determinants of crop yield rather than soil Ni concentration. When soil Ni was forcibly included as a predictor of yield in the statistical model, EC25 values for soil Ni toxicity in organic soil to corn and oat based on the Year 2000 trials were calculated at 1825 and 3947 mg Ni/kg soil, respectively. These two endpoints were excluded from the meta-analysis because the respective studies scored less than 55%.

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However, if they were included, they would represent an overestimation of the risk to corn and oat because soil Ni concentration was not a true predictor of phytotoxicity in the respective studies.

#### 1.7.6 The Effect of Recommended Agronomic Practice on Nickel Phytotoxicity

The addition of lime to agricultural fields is an OMAFRA recommended practice to control soil pH. This practice was demonstrated in experiments on contaminated organic muck soils in Port Colborne to reduce soil Ni phytotoxicity as well (Kukier and Chaney, 2000, 2001).

For example, wheat biomass was increased by 50% when grown in limestone-amended muck soil with soil Ni concentration of 2210 mg/kg (Kukier and Chaney, 2001). In the same experiments, beet was cultivated with relative success even though pH-related manganese deficiencies precluded conclusions on the effectiveness of liming for beet cultivation in the tested organic soil. In another experiment with beets, there was a 92% increase in plant biomass when a muck soil with 3,090 mg Ni/kg soil was amended with limestone (Kukier and Chaney, 2000).

Liming was a risk management recommendation made by Jacques Whitford (2004) for soils in the Port Colborne area with soil Ni concentrations exceeding the EC25-derived soil Ni SSTL values to mitigate soil Ni phytotoxicity. It can significantly decrease the severity of Ni-related phytotoxicity to crops such when applied as recommended.

#### 1.8 SUMMARY AND CONCLUSIONS

The proposed SSTL for organic soil Ni concentration for the protection of crops in the Port Colborne area from the Crops Risk Assessment (Jacques Whitford, 2004) was 2400 mg/kg (EC25). This value was derived from experimental data collected from dose-response greenhouse trials in 2001. This was completed using oat grown in a representative sample of Port Colborne organic muck soil of elevated Ni concentration collected from an area within a zone of high Ni particulate deposition and blended with a sample of negative control organic muck soil from a background area of Port Colborne unaffected by historic Ni particulate depositions to produce a range of organic muck soil samples with varying soil Ni concentrations. The suitability of this 2001-derived EC25 value as an SSTL for organic muck soils in Port Colborne was re-evaluated within the context of the body of published previously-completed field crop phytotoxicity studies in the 1980s conducted on organic muck soils in the Port Colborne area.

The majority of the previously-conducted studies on Ni crop phytotoxicity in organic muck soils of the Port Colborne area in this review were found not to have been designed as dose-response experiments for the determination of effect concentrations of soil Ni that could impact crop growth or yield in the Port Colborne area. To overcome this limitation in the reviewed literature, values of EC25 were calculated and documented in this report using what data was available in the reviewed literature and applying the Environment Canada test methods (2004 and 2005).



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Applying these test methods, it was found that there was limited statistical power in calculating EC25 values from the literature data because each literature data point was reported as the mean value of the whole dataset rather than an individual entry in the dataset itself. Therefore, the variability of the datasets was unknown.

Best-fit linear or non-linear regression models were ascribed to the available data to determine EC25 values for each crop endpoint for Port Colborne organic muck soils found in the literature. In a number of cases, assumptions regarding production, yield, or growth parameter at "Control" soil Ni concentrations were necessary because controls were not included in the respective studies. The main assumption was that maximum production, yield, or growth of any crop, based on values from OMAFRA (1981 and <u>www.omafra.gov.on.ca/english/stats/hort</u>) can occur at a soil Ni benchmark control value of 37 mg/kg (MOE, 2011).

A standardized and objective process was needed to evaluate and integrate the quality of the reported or calculated EC25 values from the various studies in the literature review. In consultations between representatives of the MOE, Vale and Stantec in 2012, a scoring key was developed. A consensus was reached on the scoring categories comprising the scoring key; however, consensus was not reached for the scoring criteria in three of the scoring categories (*i.e.*, scientific, economic, and/or practical merits). In the interest of moving the process forward, the scoring key as presented by the MOE was adopted.

Thirty-two (32) biological response endpoints for nine (9) crops species scored at or above (ranged between 55 and 93%) the minimum inclusion score (55%) for this literature review. The calculated EC25 values for these endpoints were multiplied by their respective scores to produce a weighted EC25 value for each endpoint. All weighted EC25 values were summed and then divided by the sum of all scores. This resulted in a combined weighted EC25 value of 2,810 mg Ni/kg soil and a weighted geometric mean EC25 value of 2,100 mg Ni/kg soil.

The weighted EC25 value (**2810 mg/kg**) generally agrees with the original CBRA recommendation (Jacques Whitford Ltd., 2004) that soil Ni concentrations greater than 2400 mg/kg in muck soil is required to impair production of most crop species that are reportedly grown in organic soils of the region. Impaired production (up to 25% reduction) of most crop species is not expected until soil Ni concentration is above 2000 mg/kg even if the weighted geometric mean EC25 (**2100 mg/kg**) from this meta-analysis is adopted as the SSTL. Therefore, the proposed SSTL of 2400 mg/kg derived for oat (a species that was recognized as the most Nisensitive crop at the time of the Crops Risk Assessment completion in 2004 (Jacques Whitford, 2004)) is protective of the majority of crop species that might be grown in the Port Colborne area.

However, based on the results of this literature review, there is potential for decreased yield of beet, lettuce, radish and wheat if a producer chooses to cultivate these crops in Port Colborne organic soils with Ni concentrations exceeding their respected weighted EC25 values. Those crop species that were not considered in this meta-analysis must also be considered.

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Stantec recommends the development of a risk management plan that includes the addition of limestone to soil in order to mitigate the potential loss in yield that might occur if an agricultural producer chooses to cultivate crops where site-specific soil Ni concentration exceeds the weighted EC25 values or data is not available to make conclusions related to soil Ni-related toxicity for the Port Colborne area. This is an adoption of an OMAFRA-recommended agronomic practice for soils where pH is known to affect metal bioavailability and toxicity.

Alternatively, given the limited quantity and quality of data used for deriving the weighted EC25 values for crop species such as beet, lettuce, and radish grown in organic soils with elevated Ni concentrations, incentivizing (e.g., compensation for liming) the cultivation of these crops (or other crops of interest) by cooperative producers in affected areas could aid in generating a more robust dataset to make policy decisions.

It is important to note that agricultural producers are unlikely to use muck soil to cultivate beet, lettuce, and radish in the Port Colborne area as the total acreage (regardless of soil type) that cultivated the three species were reported to be 8, unknown, and 0 for the three respective crops according to the 2006 Statistic Canada Census of Agriculture. Furthermore, the EC25 values estimated for beet, lettuce, and radish are highly conservative because of the inordinate number of conservative assumptions that were made in order to include their respective endpoints (where the data came from a single reference (Frank *et al.*, 1982) in this meta-analysis).

Wheat is likely the only crop species that might be of economic concern if cultivated in organic soil at the recommended SSTL of 2400 mg/kg. However, most of the available plots of organic soils in the affected area where soil Ni concentrations would exceed 2400 mg/kg are found in woodlot areas and very little open space is available for crop production.

It should be reiterated that historical data (prior to 1984) used to derive the weighted EC25 values for phytotoxicity related to soil Ni concentration reported within this document for the Port Colborne area likely does not reflect current environmental exposure conditions. This is because Ni-related phytotoxicity prior to 1984 was commonly attributed to event-driven, emissions related aerial deposition from refinery activities rather than chronic, soil-bound Ni exposure.

It is recognized that agricultural producers in the area have the right to cultivate any crop of their choosing. However, producers must acknowledge there might be inherent limitations if their site-specific organic soil Ni concentration exceeds the weighted EC25 values of the respective crop or the SSTL of 2400 mg/kg. Vale is committed to working in goodwill with those producers that might be affected by assisting in the implementation of the recommended risk management measures.



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# Appendix 5B-1

# Derivation of EC25 values for crop species endpoints from the available literature for Port Colborne

(refer to enclosed electronic media)



# Appendix 5B-2

# Scoring and weighting of calculated EC25 values based on the MOE-approved scoring key

(refer to enclosed electronic media)



CHAPTER SIX SUMMARY OF CONCLUSIONS IN CBRA UPDATE



Prepared for: Vale Canada Limited

Prepared by: Stantec Consulting Ltd. 1-70 Southgate Drive Guelph ON N1G 4P5

122210662 September 12, 2014

#### CHAPTER SIX SUMMARY OF CONCLUSIONS IN CBRA UPDATE

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#### CHAPTER SIX SUMMARY OF CONCLUSIONS IN CBRA UPDATE

## 1.0 INTRODUCTION

The Port Colborne Community-Based Risk Assessment (CBRA) is the first of its kind in Ontario – a "wide area" risk assessment – which began in the year 2000, after the proponent, Inco Limited (now Vale Canada Limited), accepted accountability for the contamination of soils with nickel, copper, cobalt, and arsenic in the vicinity of Inco's Port Colborne Refinery. Inco acknowledged in 2000 that historical Refinery particulate emissions in Port Colborne was the cause of the southwest-to-northeast depositional plume of soil metal concentrations observed in the MOE phytotoxicity soil investigations. To address any human or environmental health concerns that may have resulted from the historical deposition of the identified CoCs in soil, Inco made a commitment to the community of Port Colborne, the City of Port Colborne, and the MOE, to conduct a CBRA. The management of the risks identified in the CBRA would be addressed in a separate "Integration Report".

Work on the CBRA data gathering activities, data interpretation and reporting were well underway before the MOE issued, in October 2004, the Province of Ontario's Regulation 153/04 (O.Reg.153/04) made under Part XV.1 of the *Environmental Protection Act* and then later on December 29, 2009, with amendments to O.Reg.153/04 through O.Reg.511/09. The regulatory requirements of O.Reg.153/04 or O.Reg.511/09 are not applicable to the CBRA.

The design and purpose of the CBRA was never to follow the path of a regular O.Reg.153/04 process, though there are elements of the CBRA that do mirror the requirements under O.Reg.511/09. Instead, the CBRA had been designed in the year 2000 to follow a new community-specific risk assessment process with collaborative input by all members of the Port Colborne community and the various government agencies, including the MOE, Regional Niagara Public Health, and the City of Port Colborne. The CBRA process had more continuous and extensive communication with the Port Colborne public throughout the 2000 to 2007 CBRA duration than would have otherwise occurred if the CBRA had followed the minimal requirements for public input under O.Reg.511/09. The CBRA process was and still is to this date voluntary for Inco/Vale.

Work on the CBRA between 2000 and 2007 was designed and implemented to complete three different types of risk assessments for each type of potential receptor, including a Human Health Risk Assessment for the human receptors, an Ecological Risk Assessment on receptors of the Natural Environment and a "Crops" Risk Assessment on agricultural crop receptors. Between 2000 and 2007, the CBRA was conducted by Jacques Whitford Limited (and by Stantec after 2011) on behalf of Inco/Vale, with results and findings documented in various Jacques Whitford-produced reports in 2004 and then in 2007.

The MOE review process of the 2004- and 2007-produced CBRA reports was such that the MOE committed that it would begin its official review only after the date that it had received all of the final CBRA reports and only after receipt of additional public review comments that materialized



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well after the deadlines that had been originally set for the public. The official review process by the MOE began in August, 2010 and MOE comments were finally prepared on May 11, 2011 and submitted to Vale.

Responses by Stantec and Vale to the MOE 2011 comments were presented to the MOE at a meeting held on August 25, 2012. Remaining outstanding issues that could not be resolved by consensus with the MOE required additional analyses of the existing data by Stantec and Vale in an effort to address unresolved/outstanding issues and to provide an opinion and discussion on how 'new science' since 2007 up to 2014 may lead to different conclusions from those presented in the 2004- and 2007-produced CBRA reports. Some limited follow-up research was conducted for Vale beginning in 2012 to address new issues identified in the MOE review that was presented to Vale eleven years after the CBRA had been initiated. Conclusions from the additional analyses and updated interpretation of the existing 2000 to 2007 accumulated data set are presented in individual chapters of this CBRA 2014 Update Report, i.e. **Chapter 3** for HHRA, **Chapter 4** for the ERA Natural Environment and **Chapter 5** for the ERA Crops Studies, as well as summarized in the following sections.

### 2.0 UPDATE TO HUMAN HEALTH RISK ASSESSEMENT

A number of modifications were made to the HHRA approach based on the May 2011 comments by the MOE and through consideration of new science since 2007. As documented in **Chapter 3**, these included the following:

- Changes to the approach to dust ingestion;
- Re-evaluation of dietary intakes from supermarket foods and backyard produce;
- Changes to the approach of interpreting predicted ambient air modeling data to measured air concentration data;
- Changes to the toxic reference value (TRV) selection for the cobalt and nickel oral RfDs and the nickel inhalation cancer TRV;
- Expansion of, and revision to the evaluation of dermal exposure to nickel including nickel contact dermatitis and absorption both into the bloodstream and into the skin;
- Inclusion of a more robust nickel bioavailability data set and CoC bioaccessibility data set from 2013-completed laboratory studies; and,
- Conduct of additional sensitivity analyses.

Revised risk estimates were completed for the RME and Maximum Scenarios:

- All hazard quotients were less than or equal to the MOE benchmark of 1.0 applicable to a multimedia pathway assessment; and
- Estimated cancer risks for arsenic inhalation were below the MOE benchmark of one in one million.



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RBSCs were developed for cobalt, copper and nickel in various soil types within (i) the residential community immediately next to the refinery as defined by HHRA Zone B and (ii) the agricultural farms and dwellings downwind of the refinery as defined by HHRA Zone D. Specific RBSC values are summarized in **Table 2.1** below:

HHRA Zone	Nickel (mg/kg)	Copper (mg/kg)	Cobalt (mg/kg)
Zone B (fill soil)	48,000	21,000	18500
Zone D (farm, clay soil)	20,500	20,500	22000
Zone D (farm, organic soil)	11,900	22,500	13400
Zone D non-farm (not organic soil)	24,000	17,800	17800

#### Table 2.1 RBSCs for Specific HHRA Zones and Soil Types

Specific RBSCs for nickel, copper and cobalt as shown in the above table will be used in all future risk management activities, addressing contamination by HHRA zone area and by soil type.

#### 3.0 UPDATE TO ERA NATURAL ENVIRONMENT

**Chapter 4** contains a completely-revised risk assessment of the natural environment of the Port Colborne area based on consideration of the May 2011 comments by the MOE and an updated and revised evaluation of the historical emissions from the refinery regarding whether they present an unacceptable risk to the natural environment. This revised risk assessment still relies on earlier information presented in the 2004 risk assessment report but has incorporated additional data, analyses and risk calculations. Every effort was made to incorporate technical advances in the area of risk assessment as well as any new science that may have evolved since 2004.

The revised risk assessment re-evaluated whether particulate soil deposition from historical emissions of nickel, copper, cobalt and arsenic from the Inco Port Colborne presents an unacceptable risk to the natural environment. This re-evaluation considered two worse-case study areas (woodlot and adjacent field) based on their proximity to the refinery, and where previously-collected data showed soil nickel concentrations of 200 mg/kg or greater (i.e., exceeding the MOE generic guideline at the time prior to 2004 for soil nickel). Data used to represent the soil quality within these areas were taken from the earlier 2004 CBRA sampling and inventory program on the natural environment.



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The "safe" soil CoC concentrations (the concentrations at which adverse health effects to ecological receptors are not expected) generated from this re-evaluation in 2014 are summarized below in **Table 3.1**:

Soil Type	Nickel (mg/kg)	Copper (mg/kg)	Cobalt (mg/kg)	Arsenic (mg/kg)
Organic	3500	550	3000	40
Clay	3000	350	3000	25

Table 3.1	"Safe" Soil COC Concentrations for the Natural Environment by Soil Type	e
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These 2014-re-evaluated "safe" soil CoC concentrations are exactly the same as those determined and documented in the earlier 2004 ERA on the natural environment.

## 4.0 UPDATE TO ERA CROPS STUDIES

The MOE May 2011 review comments acknowledged some of the challenges that the Crops Risk Assessment faced between 2000 and 2004. Some of these challenges included studying the effects of historical particulate deposition on four different soil types within the agricultural area downwind of the refinery and determining present day risk to agricultural crops forty years after emissions ceased. Preliminary year 2000 crop studies were not adequately designed to address and control confounders in variance of soil texture, soil chemistry, soil pH and soil COC concentrations. After lessons learned, the design of the year 2001 studies adequately addressed many of these confounders using an approach involving the blending of contaminated and uncontaminated soils to obtain common contaminated soils for each of the four soil types.

At a meeting with the MOE on August 25, 2012 and subsequent meetings thereafter, consensus was reached that the information and data for the mineral soils were sufficient to support the derived site-specific target levels (SSTLs) for Ni, but not however with the Ni SSTL for the organic muck (highly organic) soil. Following recommendations made by the MOE, Stantec re-evaluated all of the past studies that had been conducted on soils from Port Colborne, including published scientific literature and unpublished reports provided by the MOE, as well as the prior data from the crop studies of 2000 and 2001, with the purpose of extracting data (e.g., EC25) that could contribute, in a scientifically reasonable way, to the derivation of SSTLs.

This re-evaluation as presented in **Chapter 5** of this report resulted in derivation of new SSTLs for organic muck soils through the inclusion of additional information – earlier data from Port Colborne that had not been used in the earlier CBRA, as well as more recent research findings. It was found that the earlier literature data generally supports the 2004-determination of SSTL for organic muck soils. **Table 4.1** below presents the new SSTLs for organic muck soils as well as the earlier 2004 SSTL values.



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#### Table 4.1 Site-Specific Threshold Levels (SSTLs) for Four Soil Types in Port Colborne

Soil Type	2004-SSTL for Ni (mg/kg)	2014-SSTL for Ni (mg/kg)			
Sandy Soil	750 <sup>1</sup>	750 <sup>1</sup>			
Organic Muck Soil	2,350 <sup>1</sup>	2,350 <sup>1</sup> (>2,400) <sup>2</sup>			
Welland (Heavy) Clay	1,650 <sup>1</sup>	1,650 <sup>1</sup>			
Till (Shallow) Clay	1,400 <sup>1</sup>	1,400 <sup>1</sup>			
<sup>1</sup> Determined using the PNEC approach (EU, 1996) <sup>2</sup> Determined using regression analyses of the Greenhouse Trial site-specific data (Jacques Whitford Ltd., 2004)					

