

Port Colborne Community-Based Action Plan (PCCAP)

Preliminary Draft Aquatic Survey Report (surface water and sediment)

June 25, 2021



Concise Summary

This report documents preliminary findings of the Aquatic Survey being conducted as part of the Port Colborne Community-Based Action Plan (PCCAP). The Aquatic Survey is intended to address perceived shortcomings of the Port Colborne Community-Based Risk Assessment (CBRA) with respect to the aquatic environment.

No systematic concentration-dependent toxicity was observed in toxicity tests conducted on water and sediment from the Wignell Drain watershed in fall 2020 and spring 2021. Nickel concentrations in test water was as high as 140 μ g/L and sediment Ni concentrations ranged between 377 and 2,167 mg/kg. For comparison, the Provincial Water Quality Objective (PWQO) for Ni is 25 μ g/L and the 'severe effect level' (SEL) for Ni in sediment is 75 mg/kg.

Biotic ligand models (BLMs) for Ni and Cu were used as a supplementary method for assessing aquatic risk. An Excel-based BLM tool (Bio-met) was used for that purpose. The aquatic toxicity test samples and 10 additional water samples collected along a Ni and Cu concentration gradient were assessed using the bio-met BLM tool. The BLMs calculated Risk Characterization Ratios (RCRs) below 1 (well below 1 for Cu), predicting an absence of risk to the aquatic systems receiving these metal inputs. The BLM findings corroborate the aquatic toxicity testing findings.

Water samples exhibited similar CoC concentrations whether measured as dissolved (0.45 μ m filtered) or 'total' (unfiltered), indicating that the CoCs present in the water represent metals that have been leached from poorly soluble CoC-containing particles in the soil and sediment rather than being CoC-containing particulates transported from soil and sediment. It is possible that particulate deposition could occur around major precipitation events, however.

The historical emissions from the Port Colborne Nickel Refinery from the period between 1918 and 1984 are very unfortunate. The aerially deposited metals now represent a soil source of Ni, Cu, Co, and As that will contribute loadings to the Wignell agricultural drainage basin that can be expected to continue long into the future. The loadings do, however, appear to be below a threshold level that would lead to increased risk to these aquatic environments.

The PCCAP Aquatic Survey is not complete as of June 15, 2021. One additional sampling event has been planned to occur around a major precipitation event. In addition, survey work specifically examining amphibian risk in the affected aquatic environments is underway, and will be reported separately.



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Introduction

The Natural Environment Risk Assessment completed under the Port Colborne Community-Based Risk Assessment (CBRA) was initially conceived as a soil study, and included a scopelimited aquatic risk assessment (JWEL, 2004; JWEL, 2005). In the 2014 CBRA Update Report (Stantec, 2014), water samples collected in the Wignell and Beaverdam Drains were riskassessed using biotic ligand model<u>s</u> (BLM<u>s</u>), but the sample size was too small and the metal concentrations too low to meaningfully assess aquatic risk. The aquatic risks of the CBRA chemicals of concern (CoC) (i.e., Ni, Cu, Co, and As) still remain to be assessed conclusively.

Vale Canada Limited (Vale) proposed the Port Colborne Community-Based Action Plan (PCCAP) as a means to address the limitations of the previous aquatic risk assessment efforts (Vale, 2017; Vale, 2020). The PCCAP documented the findings of the Niagara Peninsula Conservation Authority's (NPCA) watershed report card, which identified Ni concentrations in the agricultural drainage basin occupied by the Wignell Drain as being elevated (as high as 100 μ g/L). The Wignell Drain is located east of the Vale-owned lands adjacent to Reuter Road. The drain runs in a north-to-south direction, draining into Lake Erie via a defunct weir structure. The most heavily contaminated land from the historical refinery emissions are found in the woodlots immediately east of Reuter Road, with a gradient of decreasing soil metal concentrations being present eastward towards the drain.

The PCCAP aquatic survey was intended to:

- 1. Evaluate the nature of the Ni, Cu, Co, and As in the agricultural drains nearest the contaminated soils (establishing whether the waterborne concentrations reflect shedding of particulate metals from soil to water, or whether the metals reflect leaching of metals from the metal-containing particles into soil porewater with subsequent transport to the drains via surface runoff and shallow groundwater).
- 2. Evaluate the toxicity (risk) of CoCs in surface waters east of Reuter Road. Toxicity would be assessed using chronic and (or) sub-chronic toxicity tests (*Ceriodaphnia dubia* survival and reproduction and fathead minnow larval growth and survival tests). Risk would be assessed using the 'bio-met' bioavailability tool (version 5.0). The site-specific toxicity testing would be used as a check on the BLM findings, the intention being to rely on the BLM going forward.
- 3. Evaluate the toxicity of the CoCs in sediments using chronic and sub-chronic toxicity tests (survival and growth using *Chironomus dilutus* and survival, growth, and reproduction using *Hyallela azteca*)
- 4. Evaluate risk to amphibia, particularly frogs and toads, including the endangered Fowler's Toad (to be addressed in a separate report).

The covid-19 pandemic delayed the start of the aquatic survey due to lack of availability of toxicity testing slots for non-essential (i.e., non-regulatory) tests early in the pandemic. The PCCAP aquatic survey was intended to collect data over an approximately one year period, capturing seasonal differences in risk that might occur, the intention being to not underestimate risk. The aquatic survey field work began in November, 2020, the November sampling event collected data under relatively low-flow conditions, when transport of CoCs by water from the



surrounding lands would be expected to be lower than under conditions of higher flow. The 2021 spring sampling event occurred in late March, when flow in the system was greater, supplemented by flow from adjacent lands via open ditches.

Materials and Methods

Water

Two 10 L grab samples were collected on Nov. 9, 2020 from each of two locations in the agricultural drainage basin east of Port Colborne (Fig. 1). One sample was collected from the Port Colborne Drain¹ on the south side of Highway 3. The second sample was collected at the western bank of the Wignell Drain from Vale-owned property at the concrete foundation of the former bridge that crossed the drain near the northern property line of the former Grotelaars property (Wignell Drain South). For the spring 2021 testing, two 10 L grab samples were collected at each of two locations on March 30, 2021. The first sample was collected at Grotelaars Bridge again (Wignell Drain South), while the second sample was collected from a drain that flows west-to-east on the south side of Grotelaars Bridge from the eastern edge of the Reuter Road woodlot, emptying into the Wignell Drain ('Grotelaars' Drain).

Water samples were delivered to AquaTox Testing and Consulting Inc.in Puslinch, Ontario for testing. Environment Canada's 7-day static renewal toxicity tests (reproduction and survival using the cladoceran *Ceriodaphnia dubia* (EC, 2007), and larval growth and survival with fathead minnows (EC, 2011)) were used to characterize aquatic toxicity. Associated with each test, analytical chemistry data were collected from subsamples of the undiluted field-collected water at test initiation and again on day 5 of the test (before renewing the test solutions)².

A set of 10 water samples were collected from the Grotelaars Drain and Wignell Drain on March 31, 2021. The sample locations were the same as for 10 sediments samples (SED11-20) that had been collected the previous day (see below). These water samples were labelled 'SED11 water' to 'SED20 water' and were analyzed for dissolved metals and DOC by Bureau Veritas, Mississauga, Ontario.

¹ This sample was mistakenly labelled as "Wignell Drain North" on the laboratory submission form, but the western branch of the Wignell Drain is now known as the Port Colborne Drain.

² Analytical chemistry of the Port Colborne Drain water sample was not collected on day 5 of testing.





Figure 1. Surface water sample collection locations used for PCCAP aquatic toxicity tests. Figure elements from Niagara Navigator (https://maps.niagararegion.ca)

Sediment

Ten sediment samples were collected in November, 2020 (samples SED1-10) and again in March, 2021 (samples SED11-20) (Fig. 2). Aliquants of sediment were dried at 70°C for 24 hours, then gently disaggregated by hand using a mortar and pestle. The powdered sediment was loaded into sample cups (Chemplex 1330 SE, Chemplex Industries, Palm City, Florida) sealed with mylar film (Chemplex No. 257) and analyzed by handheld XRF (Olympus Delta).

Sediment toxicity tests were conducted using two organisms (*Chironomus dilutus* and *Hyallela azteca*) using Environment Canada methods (EC, 1997; EC, 2017). The general approach was to collect sediments on a concentration gradient with the intention to develop a concentration-response relationship including all data from both sampling events. Samples collected in Nov. 2020 (SED1-SED10) were tested without methodological deviations, but the testing on the Mar. 2021 samples (SED11-SED20) had the following deviations: (1) In the *Chironomus dilutus* assay, no organisms were found in the SED14 exposure vessel, so the individual sample was retested with five replicate controls. As a result, there were 15 control data points available for the *Chironomus dilutus* data analysis, including the Nov. 2020 testing. (2) In the *Hyallela azteca* test, no control organisms were found at the end of the test, so the entire test was repeated. As



a result, there were duplicate test results for survivorship and biomass data available for the 10 metal-exposed organisms from the Mar. 2021 sediment data set.



Figure 2. Sediment sample collection locations used for PCCAP sediment toxicity tests. Figure elements from Niagara Navigator (https://maps.niagararegion.ca)

Biotic ligand model (BLM)

BLM analyses used the bio-met bioavailability tool (available at <u>https://bio-met.net</u>). The biomet tool is an Excel spreadsheet-based tool based on biotic ligand models for Cu, Ni, Zn, and Pb. As mentioned previously, for both the Nov. 2020 samples and the Mar. 2021 samples, analytical chemistry data suitable for BLM analysis were collected at the toxicity testing lab (Aquatox) from subsamples of the undiluted field-collected water both at test initiation and again on day 5 of the test (before renewing the test solutions)³.

In addition, a set of 10 water samples was collected from the Grotelaars Drain and Wignell Drain on March 31, 2021 and analyzed for BLM-relevant parameters. The sample locations were the same as for 10 sediments samples (SED11-20) that had been collected the previous day (Fig. 2). These water samples were labelled 'SED11 water' to 'SED20 water' and were

³ Analytical chemistry of the Port Colborne Drain water sample was not collected on day 5 of testing.



analyzed for relevant BLM parameters, including dissolved metals and DOC, by Bureau Veritas, Mississauga, Ontario.

Findings

Under the low flow conditions in autumn of 2020, no CoCs exceeded their respective Provincial Water Quality Objectives (PWQOs) (Table 1). The dissolved Ni concentrations in Port Colborne and Wignell Drains at that sampling event were the lowest observed (12 and 13 μ g/L) (Table 1). Under the spring runoff conditions present when the March, 2021 samples were collected, the Ni concentrations were much higher, up to 190 μ g/L in sample 'SED11 water', well in excess of the Ni PWQO (Table 1). Cu and Co PWQOs were also exceeded in most samples. The interim As PWQO (5 μ g/L) was not exceeded in any sample (Table 1).

Table 1. Relevant water chemistry in surface water from the drainage of the agricultural lands east of Port Colborne. This agricultural drainage basin includes the most metal-contaminated land adjacent to the west bank of the Wignell Drain. Values exceeding the PWQOs are bolded.

| | | - | | | | | | |
|------------------------------------|-----------|--------|------|----------|----------|----------|----------|----------|
| | | DOC | | Diss. Ca | Diss. Cu | Diss. Co | Diss. Ni | Diss. As |
| Sample Name | Date | (mg/L) | рН | (mg/L) | (µg/L) | (µg/L) | (µg/L) | (µg/L) |
| Port Colborne Drain at Hwy 3 | 09-Nov-20 | 5.6 | 7.9 | 400 | <0.9 | <0.5 | 12 | <1 |
| Wignell Drain at Grotelaars Bridge | 09-Nov-20 | 6.9 | 7.5 | 260 | <0.9 | <0.5 | 13 | 1.1 |
| Wignell Drain at Grotelaars Bridge | 30-Mar-21 | 19 | 7.4 | 57 | 9.7 | 0.78 | 57 | <1 |
| Grotelaars Drain | 30-Mar-21 | 39 | 6.9 | 84 | 7.2 | 4.4 | 140 | 2.3 |
| SED 11 water | 31-Mar-21 | 42 | 7.36 | 99 | 6.9 | 4 | 150 | 4.2 |
| SED 12 water | 31-Mar-21 | 42 | 7.42 | 100 | 9 | 8.8 | 190 | 1.7 |
| SED 13 water | 31-Mar-21 | 44 | 7.48 | 92 | 7.4 | 5.2 | 170 | 2.2 |
| SED 14 water | 31-Mar-21 | 45 | 7.38 | 93 | 5.7 | 5.2 | 150 | 3.5 |
| SED 15 water | 31-Mar-21 | 44 | 7.48 | 99 | 6.1 | 5.7 | 160 | 3 |
| SED 16 water | 31-Mar-21 | 43 | 7.42 | 110 | 6.8 | 6.5 | 150 | 3.7 |
| SED 17 water | 31-Mar-21 | 29 | 7.71 | 95 | 6.4 | 5 | 110 | ND |
| SED 18 water | 31-Mar-21 | 40 | 7.68 | 84 | 5 | 1.8 | 71 | 1.4 |
| SED 19 water | 31-Mar-21 | 24 | 7.58 | 46 | 3.4 | 0.59 | 40 | 1.2 |
| SED 20 water | 31-Mar-21 | 20 | 7.83 | 120 | 5 | 1.7 | 57 | 1.2 |
| Ontario PWQO (µg/L) | | | | | 5 | 0.5 | 25 | 5* |
| | | | | | | | | |

^{*}interim

The CoC concentrations in the dissolved (0.45 μ m filtered) and particulate phases were quite similar (Table 2), indicating that the majority of the CoCs were present due to leaching from CoC-containing particles present in the soils into soil porewater and then into the agricultural drains. It is possible that particulates containing the CoCs could be present in surface water after heavy rainfall events, due to erosion, but it is reasonable to believe that leaching of metals from the contaminated soils present in the drainage basin of the Wignell Drain is the primary source of the Ni, Cu, Co, and As in the surface water there.



| subsampled from the | | • | Wignell Drain | Wignell Drain | Wignell Drain | | Grotelaars | Grotelaars | Ontario |
|-----------------------------------|-------|-----------------|-----------------|---------------|-----------------|---------------|-----------------|---------------|-------------|
| | | Drain (initial) | South (initial) | South (day 5) | South (initial) | South (day 5) | Drain (initial) | Drain (day 5) | PWQO |
| Analyte | Units | Nov. 2020 | Nov. 2020 | Nov. 2020 | Mar. 2021 | Mar. 2021 | Mar. 2021 | Mar. 2021 | (µg/L) |
| Dissolved organic carbon (DOC) | mg/L | 5.6 | 6.9 | 6.4 | 19 | 21 | 39 | 39 | |
| рН | | 7.9 | 7.5 | 7.6 | 7.4 | 7.7 | 6.9 | 7.3 | 6.5-8.5 |
| Dissolved Nickel (Ni) | μg/L | 7.6 | 13 | 12 | 57 | 62 | 140 | 140 | |
| Total Nickel (Ni) | μg/L | 7.6 | 13 | 14 | 86 | 70 | 140 | 150 | 25 |
| Dissolved Copper (Cu) | μg/L | <0.9 | <0.9 | 0.99 | 9.7 | 8.9 | 7.2 | 7 | |
| Total Copper (Cu) | μg/L | <0.9 | 1.3 | 1.4 | 17 | 13 | 8.1 | 8.5 | 5 |
| Dissolved Cobalt (Co) | μg/L | <0.5 | <0.5 | <0.5 | 0.78 | 0.58 | 4.4 | 3.9 | |
| Total Cobalt (Co) | μg/L | <0.5 | <0.5 | <0.5 | 2.1 | 1.2 | 4.5 | 4.3 | 0.9 |
| Dissolved Arsenic (As) | μg/L | 1.0 | 1.1 | <1.0 | <1 | <1 | 2.3 | 2.1 | |
| Total Arsenic (As) | μg/L | 1.0 | 1.1 | 1.2 | 1.7 | <1 | 2.6 | 2.9 | 5 (interim) |
| Dissolved Calcium (Ca) | mg/L | 400 | 260 | 250 | 57 | 60 | 84 | 86 | |
| Total Calcium (Ca) | mg/L | 410 | 260 | 270 | 60 | 60 | 88 | 93 | |

Table 2. Relevant chemistry in water samples from *Ceriodaphnia* toxicity tests in Nov. 2020 and Mar. 2021. 'Initial' samples were subsampled from the first sample container at test initiation.' Day 5' data were from the sample container at renewal on day 5 of the test.

The first level of analysis of aquatic risk involves comparing measured values with relevant environmental guidelines or standards, exceedances of which provide a screening level assessment of risk. In Ontario, the PWQOs for the CoCs from the CBRA are 25 μ g/L (Ni), 5 μ g/L (Cu), 0.5 μ g/L (Co), and 5 μ g/L (As). The worst-case risk characterization ratio (RCR) using the PWQO for Ni and the data from Table 1 would be 7.6 (i.e., 190 μ g Ni/L÷25 μ g/L).

Aquatic Toxicity Tests

Toxicity testing provides site-specific information to enhance risk assessments. Here, any observed toxicity could be related to a range of potential toxicants, such as agricultural chemicals, road runoff, and quarry dewatering effluent from the limestone aggregate pit at the source of the Port Colborne Drain. The degree to which the CoC-contaminated soils in the agricultural drainage contribute to aquatic risk was not resolved conclusively in the CBRA, so this testing was initiated to address those outstanding issues. The toxicity test using *Ceriodaphnia dubia* is a chronic, 3-brood static-renewal toxicity test that determines both mortality and reproductive output (EC, 2007).

No concentration-dependent mortality was observed in Ceriodaphnia in the four tests conducted (Fig. 3).



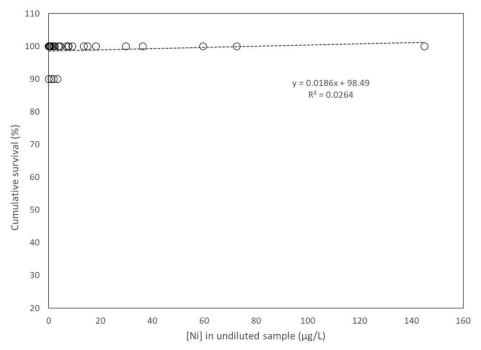
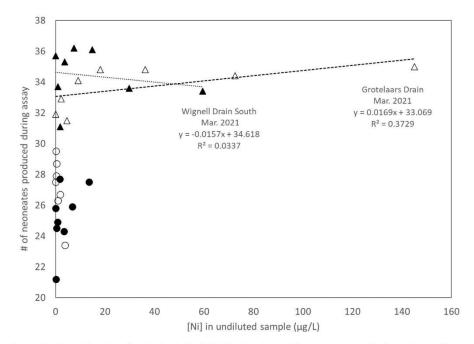
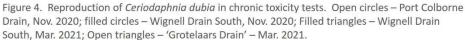


Figure 3. Survival of *Ceriodaphnia dubia* in chronic toxicity tests. All tests combined.

In the absence of systematic chronic mortality in these samples, the reproductive endpoint provides valuable additional information for assessing aquatic risk (reproduction being a more sensitive indicator of toxicity than mortality – reproductive toxicity occurring at lower exposure concentrations over longer time frames). No concentration-dependent impairment of reproductive output was seen in these tests, however (Fig. 4). Because the laboratory brood stock of *Ceriodaphnia* were different between the November and March tests, the reproductive output of the two sets of tests can only be compared with each other in absolute terms.







However, when these data are expressed as a percentage of reproductive output in control (unexposed) animals, it can be seen that the reproduction endpoint showed no concentration-dependent impairment in *Ceriodaphnia* reproduction despite Ni concentrations almost 6 times higher than the PWQO ($25 \mu g/L$) (Fig. 5).

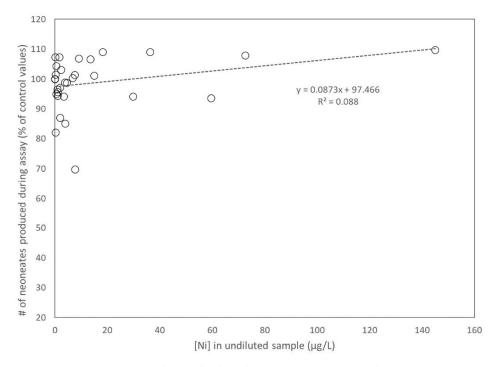


Figure 5. Reproductive output of *Ceriodaphnia dubia* in all four tests combined, expressed as a percentage of the control values for each test.



The 7-day fathead minnow (*Pimephales promelas*) toxicity test is a sub-chronic test, too short to be considered chronic (less than a tenth of the lifespan of the test organism), but longer in duration than acute aquatic toxicity testing using fish (typically 96-hours for fish species). The test uses larval (less than 24 hours old) fish, the most sensitive life stage, and provides a reasonable estimate of the likely chronic toxicity.

As was the case for the *Ceriodaphnia* tests, there was no systematic concentration-dependent mortality observed in these larval minnows (Fig. 6).

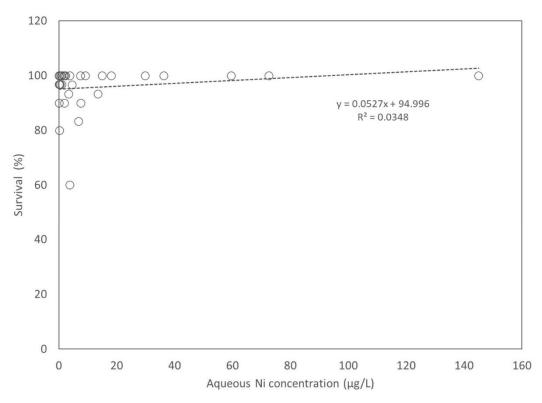


Figure 6. Survival of fathead minnow in 7-day toxicity tests. All tests combined.

For the growth endpoint, which is a more sensitive indicator of toxicity than the mortality endpoint, there was also no systematic concentration-dependent response observed at the concentrations range tested when considered on a test-wise basis (Fig. 7) or as pooled data from all four tests (Fig. 8).



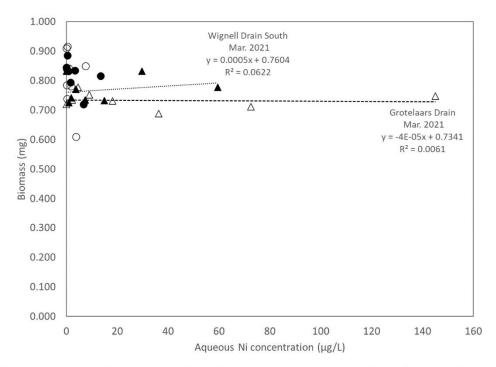


Figure 7. Fathead minnow biomass after 7-days exposure. Open circles – Port Colborne Drain, Nov. 2020; filled circles – Wignell Drain South, Nov. 2020; Filled triangles – Wignell Drain South, Mar. 2021; Open triangles – 'Grotelaars Drain' – Mar. 2021.

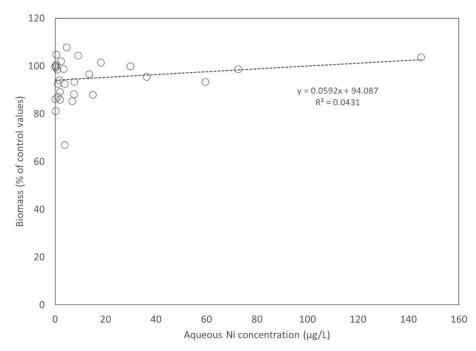


Figure 8. Fathead minnow biomass in all four tests combined, expressed as a percentage of the control values for each test.



Biotic Ligand Model

Biotic ligand models have been developed to extend our ability to express metal toxicity in freshwater organisms as a function of key variables responsible for the toxicity. The key variables for Ni, Cu, and Co are (in addition to the metal concentrations themselves): hardness (Ca concentrations), dissolved organic carbon (DOC), and pH. This aquatic survey used the freely available 'bio-met' excel-based BLM to estimate the local (i.e., site-specific) HC₅ values for Cu and Ni (Table 3).

| abricate and a damb initial initian initial in | | DOC | | | Diss. Cu | Local Cu | Bioavail. | RCR | Diss. Ni | Local Ni | Bioavail. | RCR |
|--|-----------|--------|------|--------|----------|---------------|-----------|--------|----------|-----------------|-----------|------|
| Sample Name | Date | (mg/L) | рН | (mg/L) | (µg/L) | HC_5 (µg/L) | Cu (µg/L) | (Cu) | (µg/L) | HC ₅ | Ni (µg/L) | (Ni) |
| Port Colborne Drain | 09-Nov-20 | 5.6 | 7.9 | 400 | <0.9 | 25 | 0.04 | 0.002 | 7.6 | 11.3 | 2.7 | 0.2 |
| Wignell Drain S | 09-Nov-20 | 6.9 | 7.5 | 260 | <0.9 | 34 | 0.03 | 0.0008 | 13 | 16.3 | 3.2 | 0.2 |
| Wignell Drain S | 30-Mar-21 | 19 | 7.6 | 57 | 9.7 | 76 | 0.13 | 0.0017 | 57 | 34.4 | 7.1 | 0.2 |
| Grotelaar Drain | 30-Mar-21 | 39 | 7.1 | 84 | 7.2 | 115 | 0.06 | 0.0005 | 140 | 46.7 | 12.9 | 0.3 |
| SED 11 water | 31-Mar-21 | 42 | 7.36 | 99 | 6.9 | 167 | 0.04 | 0.0002 | 150 | 47.9 | 15.9 | 0.3 |
| SED 12 water | 31-Mar-21 | 42 | 7.42 | 100 | 9.0 | 121 | 0.07 | 0.0006 | 190 | 47.9 | 15.9 | 0.3 |
| SED 13 water | 31-Mar-21 | 44 | 7.48 | 92 | 7.4 | 121 | 0.06 | 0.0005 | 170 | 46.7 | 14.6 | 0.3 |
| SED 14 water | 31-Mar-21 | 45 | 7.38 | 93 | 5.7 | 120 | 0.05 | 0.0004 | 150 | 46.7 | 12.9 | 0.3 |
| SED 15 water | 31-Mar-21 | 44 | 7.48 | 99 | 6.1 | 121 | 0.04 | 0.0003 | 160 | 46.7 | 13.7 | 0.3 |
| SED 16 water | 31-Mar-21 | 43 | 7.42 | 110 | 6.8 | 167 | 0.04 | 0.0002 | 150 | 46.7 | 12.9 | 0.3 |
| SED 17 water | 31-Mar-21 | 29 | 7.71 | 95 | 6.4 | 107 | 0.06 | 0.0006 | 110 | 43.4 | 10.2 | 0.2 |
| SED 18 water | 31-Mar-21 | 40 | 7.68 | 84 | 5.0 | 107 | 0.05 | 0.0005 | 71 | 43.4 | 6.6 | 0.2 |
| SED 19 water | 31-Mar-21 | 24 | 7.58 | 46 | 3.4 | 124 | 0.03 | 0.0002 | 40 | 37.6 | 4.3 | 0.1 |
| SED 20 water | 31-Mar-21 | 20 | 7.83 | 120 | 5.0 | 93 | 0.05 | 0.0005 | 57 | 28.9 | 7.9 | 0.3 |
| Ontario PWQO (µg/L) | | | | | 5 | | | | 25 | | | |

Table 3. Relevant water chemistry and associated BLM estimates of local HC_{5} , bioavailable Cu and Ni, and associated Hazad Quotients (HQ) in agricultural drains influenced by runoff from metal-contaminated lands adjacent to the drains.

The dissolved Cu concentrations among these samples were as high as 9.7 μ g/L, but under the water chemistry conditions associated with these samples, the predicted bioavailable Cu concentrations were all below 1 μ g/L, and the predicted site-specific (local) HC₅ values ranged from 25 to 167 μ g/L (Table 3). The RCRs calculated as the ratio of bioavailable Cu to local HC₅ were 0.002 or lower, indicating no unacceptable risk for that metal.

Ni concentrations were much higher than Cu (7.6-190 μ g/L). However, under the relevant local conditions of dissolved Ca, DOC, and pH, the predicted bioavailable Ni concentrations were 2.7-15.9 μ g/L, local HC₅ were 11.3-47.9 μ g/L, and RCRs ranged between 0.1 and 0.3, again indicating no unacceptable risk for the agricultural drainage basin east of the Port Colborne Refinery site.

Although a BLM exists for Co, Co is not incorporated into the bio-met BLM software. Bioavailable Co concentrations, local HC_5 values and RCRs have not been reported at this time. They are, however, expected to demonstrate a lack of risk, as per Ni and Cu. Given the lack of toxicity observed in these surface water samples, the absence of cobalt data from this report is not a critical deficiency. The Co BLM results will be included in final PCCAP Aquatic Survey reporting.



Sediment Toxicity Testing

The sediments were collected on a concentration gradient, ranging from 377-2,167 mg Ni/kg (Table 4). Samples SED1-SED10 were tested separately from SED11-SED20, but the results have been analyzed jointly here. Co was below the XRF detection limit in all 20 sediment samples, the average detection limit (D.L.) being 76 ppm, 95% CI [70,82].

Table 4. Ni, Cu, and As concentrations in

| sediment from the Wignell Drain agricultural | | | | | | | | | |
|--|---------|---------|---------|--|--|--|--|--|--|
| drainage basin. Co concentrations were | | | | | | | | | |
| below the detection limit of the XRF | | | | | | | | | |
| instrument. | | | | | | | | | |
| | Ni | Cu | As | | | | | | |
| | (mg/kg) | (mg/kg) | (mg/kg) | | | | | | |
| Sample ID | (d.w.) | (d.w.) | (d.w.) | | | | | | |
| | | | | | | | | | |
| SED9 | 377 | 80 | 8.1 | | | | | | |
| SED15 | 388 | 73 | 8.4 | | | | | | |
| SED8 | 450 | 150 | 23.9 | | | | | | |
| SED16 | 470 | 83 | 12 | | | | | | |
| SED18 | 565 | 80 | 15.2 | | | | | | |
| SED17 | 593 | 102 | 14.6 | | | | | | |
| SED10 | 645 | 100 | 8.3 | | | | | | |
| SED20 | 733 | 92 | 13 | | | | | | |
| SED14 | 752 | 172 | 23.9 | | | | | | |
| SED19 | 778 | 129 | 10.2 | | | | | | |
| SED7 | 939 | 177 | 10.7 | | | | | | |
| SED6 | 972 | 177 | 18.1 | | | | | | |
| SED2 | 1053 | 194 | 13.4 | | | | | | |
| SED11 | 1267 | 221 | 23.3 | | | | | | |
| SED4 | 1530 | 206 | 18.7 | | | | | | |
| SED1 | 1727 | 289 | 43.4 | | | | | | |
| SED3 | 2009 | 277 | 18.5 | | | | | | |
| SED13 | 2035 | 356 | 25.6 | | | | | | |
| SED5 | 2053 | 249 | 20.2 | | | | | | |
| SED12 | 2167 | 304 | 33.3 | | | | | | |

Despite the elevated sediment Ni, Cu, and As concentrations, the sediments were not lethal to either *Chironomus dilutus* or *Hyallela azteca* (Fig. 9), and showed no obvious meaningful trend in growth impairment in either *Chironomus dilutus* (Fig. 10) or *Hyallela azteca* (Fig. 11).



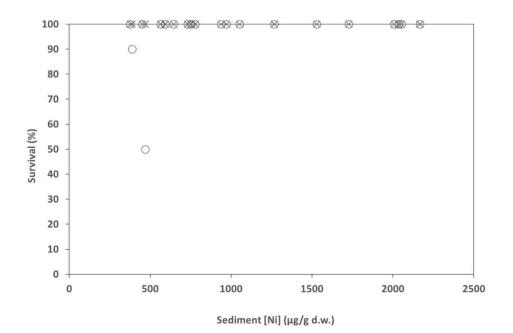


Figure 9. Survival of *Chironomus dilutus* (circles) and *Hyallela* azteca (x) in relation to sediment Ni concentration.

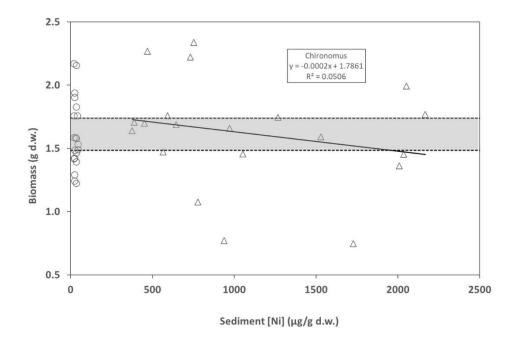


Figure 10. Biomass of *Chironomus dilutus* in relation to sediment Ni concentration. Symbols: open circles – controls; Open triangles – Ni-exposed. Shaded band represents the 95% confidence limits for controls.



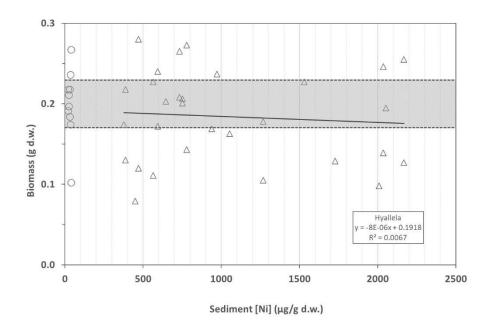


Figure 11. Biomass of *Hyallela azteca* in relation to sediment Ni concentration. Symbols: open circles – controls; Open triangles – Ni-exposed. Shaded band represents the 95% confidence limits for controls.

Synthesis

The PCCAP aquatic survey is intended to address gaps in the aquatic risk assessment component of the CBRA. The PCCAP (Vale, 2020) provided a general outline of the expected approach to be used, including pesticide analyses of water and sediment. This was under the assumption that toxicity would be observed in the water and sediment samples, and the toxicity would need to be apportioned to different sources. The absence of toxicity in the aquatic and sediment toxicity tests obviates the need for such testing. The aquatic sampling approach selected for the March, 2021 sampling event was changed to a gradient approach from an "upstream-downstream" sampling approach, which had been outlined in the PCCAP (Vale, 2020). This change was made upon the realization that spring runoff from the 'Grotelaars Drain' and other inflows to the Wignell Drain from the contaminated lands on the west bank of the Wignell Drain contained elevated DOC, and important moderator of metal toxicity in freshwater. The DOC plume from the Grotelaars Drain is visible at the inflow from Grotelaars Drain to the bottom right of Fig. 1. The change to a gradient sampling approach was an improvement to the sampling design. Small changes to sampling and analytical chemistry approaches were necessary to adapt the aquatic survey to field conditions that were unanticipated during the desktop planning for the PCCAP.

The chronic (*Ceriodaphnia*) and sub-chronic (fathead minnow) aquatic toxicity tests conducted in the autumn (low flow conditions) and spring (high flow conditions) demonstrated a lack of toxicity, in spite of elevated concentrations of the CBRA CoCs (Ni, Cu, Co, and As) in the spring samples (Ni as high as 150 μ g/L in the Grotelaars Drain test sample, six times higher than the



PWQO for Ni). The Biotic Ligand models for Cu and Ni predicted no unacceptable risk to aquatic organisms from these metals, based on the water chemistry in the Wignell Drain and its inflows during the period of elevated spring runoff. The transport of CoCs from the Grotelaars Drain likely represents the largest such source of metals to the Wignell Drain because it originates very close to the most contaminated lands supplying the agricultural drainage system. The high DOC in the 'Grotelaars Drain' likely reflects the transport of soluble degradation products of leaf litter and organic material (as well as Ni, Cu, Co, and As) from the organic muck soils present in the woodlots along Reuter Road. Taken together, the findings of no unacceptable risk by the BLM corroborated the toxicity test findings, which showed a lack of toxicity. Any further sampling of surface water for the purposes of assessing risk, should use the BLM as the basis for such assessment.

Although it was expected that there would be a number of confounding variables affecting sediment toxicity in the aquatic environment east of the refinery, including agricultural chemicals, there was no observed toxicity in the sediments using chronic (*Chironomus*) and sub-chronic (*Hyallela*) toxicity tests. This absence of toxicity obviates the need for pesticide and other analyses of these sediments. The lack of toxicity was seen for a range of sediment samples containing 377-2,167 mg Ni/kg, all well above the provincial 'severe effect level' of 75 mg Ni/kg. The lack of sediment toxicity in these sediments is most likely related to the chemical form (chemical species) of the CoCs in these contaminated sediments, which are expected to be the same as in the soils in the surrounding lands, dominated by poorly soluble species (Dutton et al., 2019).

The findings reported here support the perception that, in spite of the extremely unfortunate nature of the historical contamination of the terrestrial and aquatic environments east of the Port Colborne Refinery, the risk associated with the contamination is low. The CoCs will continue to slowly be transported from the soils and sediments in the low-lying lands adjacent to the Wignell Drain 'watershed' into the drains and some portion of that will ultimately be transported into Lake Erie.



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Supporting Documentation