Work Plan for Sediment Pore Water Sample Collection in Secondary Pond

RACER Nodular Industrial Land

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List of Acronyms

DI	Deionized
DODI	Deoxygenated Deionized
HDPE	High Density Polyethylene
QAPP	Quality Assurance Project Plan
USEPA	United States Environmental Protection Agency
WQC	Water Quality Criteria
Work Plan	Work Plan for Sample Collection

1. Introduction

GHD Inc. has prepared this Work Plan for Sample Collection of sediment pore water for the Secondary Pond at the RACER Saginaw Site. Previous sampling of the sediments have shown very elevated concentrations of several metals, notably manganese and zinc (GHD 2017). These and other metals were well above screening benchmarks for bulk sediment chemistry in almost all sediment samples, potentially suggesting widespread toxicity to benthic invertebrates. However, there are concerns about the scientific validity of the benchmarks (e.g., see National Academy of Science 2001, Smith and Jones 2006, 2012) and also the ability of bulk sediment chemistry to assess bioavailability. Therefore, a limited number of AVS/SEM (Acid Volatile Sulfide/Simultaneously Extractable Metals) analyses were also conducted in the pond's sediments. AVS/SEM analyses are superior to bulk sediment chemistry because these analyses consider bioavailability of metals in sediments (USEPA 1995). These more refined AVS/SEM analyses suggested considerably less toxicity than the initial screening of bulk sediment chemistry. According to AVS/SEM, the potential for toxicity in about half of the sediments could be dismissed as unlikely.

However, AVS/SEM analyses are limited in two ways. First, the AVS/SEM analyses pertain to bioavailability/toxicity of about five divalent metals (cadmium, copper, lead, nickel, silver, and zinc) and chromium, but not the potential toxicity of manganese. As there are no reliable sediment benchmarks for manganese, this problem cannot be resolved with further sampling of bulk sediments. In addition, most of the AVS/SEM sample had results that were intermediate between likely to be non-toxic and likely to be toxic. A last source of uncertainty is that there are also very high concentrations of black carbon in the Secondary Pond sediments. Black carbon is known to be much more sorptive, than typical organic carbon, to hydrophobic substances; however, it is unknown whether black carbon also greatly reduces metals' bioavailability as well.

Given these sources of uncertainty, it was agreed that further sampling of sediment pore water would be the most effective method to assess the potential for settlement toxicity from metals in Secondary Pond sentiments. Thus, the intent of this sampling program is to collect sediment pore water for metals and hardness in a preliminary analysis. In turn, that information will be used to refine the assessment of risks of metals to benthic invertebrates, and, if necessary, used to develop site-specific clean up levels and the areas requiring remediation.

The samples will be packaged and shipped in accordance with GHD standard procedures. Samples will be submitted to the laboratory on a standard 2-week turn. A summary of the proposed testing is presented in the following sections.

2. Sediment Pore Water Sampling

Sediment pore water will be collected at 10 nearshore sample locations using peepers (small passive sampling devices (see photos provided in Appendix A). Because there are no currently well-developed methods to install peepers in deep water without scuba divers, these peepers will be placed by hand in shallow water from either a small boat or through the ice. Appendix A presents a photo of how the samples were placed in shallow water at another location. Since the peepers will be emplaced by hand, the pore water samples will be limited to shallow water that is about an arm-length deep. The Secondary Pond has been drained about 8 feet since the summer of 2016. The current shoreline represents about the 8 ft depth contour of the totally-filled pond. Perusal of results of sampling of bulk sediment shows that sediment samples near this depth contour were as contaminated with metals, notably zinc, lead, and manganese, as the rest of the main portion of the Secondary Pond (Figure 3). Thus, these now nearshore samples should provide results that are representative of the Pond's sediments. Note that the J-shaped section of the Secondary Pond is now mostly drained and will not be sampled for pore water. However, this section tends to have lower concentrations than the main body of the Pond, making this sampling somewhat conservative for the Pond as a whole.

The peepers have membrane windows that are permeable to dissolved metals. The peepers will be buried in sediment and left in place for approximately two weeks to allow equilibration between the concentrations of metals in the sediment pore water and the peepers. The peepers will be constructed as described below, using approved methods acceptable to USEPA.[1] Peepers will be placed at the appropriate depth by pushing them into the sediments by hand. To the extent practical, the peepers will be pushed into place with the least possible disturbance of the surrounding material. The sediments in the pond are very loose, and our experience with peeper placement in loose sediments shows that the sediments just close overtop the peepers after they are pushed into the desired depth. The semipermeable window of the peeper will be located at the desired depth of sampling into the sediments.

After equilibration, peepers will be retrieved and pore water will be analyzed for relevant metals and hardness. These pore water results will then be used to assess risk by comparison to water quality criteria and other relevant toxicological data based on water exposures.

The sediments in the bottom of the pond are very soft mucks, which are likely to be anoxic just below the sediment-water interface. Consequently, the biologically active zone (BAZ), or zone where benthic macrobenthos occur, is likely limited to the top two or three inches or less. To measure pore water in this BAZ, the peeper window will be placed 1.5 inches below the sediment-water interface. At each sediment locations, a pair of peepers will be placed since the water volume of one peeper does not provide sufficient volume for metals analyses and hardness.

3. Construction, Deployment, Retrieval, and Analyses of Peepers

Pore water samples will be collected using field peepers (small passive sampling devices) that will be buried in the sediment. Pore water will be sampled at 10 locations in the nearshore area of the pond, equally distributed around the two lobes of the pond (see Figure 3). Each field peeper will be

[1] See "*Standard Operating Procedure AQ-3 – Peeper Method for In-Situ Sampling of Pore Water*", http://newtowncreek.info/docs2/2%20Remedial%20Investigation/Phase%202%20Remedial%20Investigation%20Work%20Plan%20-%20Volume%202/01%20Appendix%20A%20-%20Quality%20Assurance%20Project%20Plan%20Version%203/QAPP%20Attachment%20A/Anchor%20QEA/QAPP%20SOP_AQ-3_PeepersforMetals.pdf. In addition, GHD just used these peepers, successfully, in a study of small stream in New York, with sediments having very high concentrations of nickel and chromium.

constructed using a low-density polyethylene snap-cap vial (50-ml) and a PES filter membrane (0.45-µm pore size, 47-mm diameter). Several holes will be punched into the vial cap, and caps and vials will be cleaned and soaked in deionized (DI) water overnight. The field peeper will be prepared by submerging the vial in deoxygenated deionized (DODI) water. While holding the vial at the water surface, a PES filter membrane will be placed over the top, and the punched cap will be closed to seal the membrane. Once the membrane is seated, it will be inspected for rupture or bubbles by inverting it above the water momentarily to check for leaks. The finished peepers will be transferred to a wide-mouth, 1-liter (L) or 2-L high-density polyethylene (HDPE) or polypropylene bottle containing DODI water. Once the storage bottle is full, the remaining head space will be replaced with DODI water, and the storage bottle will be tightly capped and stored in a refrigerator.

The peepers will then be transported to the Site in the storage bottles in a cooler on wet ice. A length of wetland flagging tape will be tied to the peeper and left above the sediment surface to allow locating and retrieving the peeper. At each sample location, the peepers will be inserted into the sediment to the pre-determined depth. The porous semi-permeable membrane will be set at the applicable depth interval so that the peepers sample the pore water in the identified surficial sediment horizon. A stake will be driven into the sediments near the peeper location to mark the location and, with the flagging tape, allow retrieval. Once deployed, the peepers will be left in place for approximately two weeks. After this period of equilibration, the peepers will be removed from the sediment by pulling on wetland flagging tape or carefully digging the peeper out. The peeper will be rinsed thoroughly in DI water until all visible sediment particles are displaced from the peeper.

Once the peeper is removed and cleared of particulates, the membrane and cap assembly will be carefully opened to prevent the membrane from falling into the liquid inside the vial. Liquid will be transferred directly to a pre-preserved sample bottle supplied by the laboratory. Sample bottles will be stored in a cooler on wet ice, and the peeper vial and membrane discarded. The pore water samples from the peepers will be analyzed for hardness, select dissolved metals, and the results compared to chronic Water Quality Criteria (WQC) for the dissolved metals and to other appropriate toxicological benchmarks. According to the screening of bulk sediment chemistry, zinc, manganese, lead, and copper are most problematic in terms of potential risks to benthic invertebrates (see Table 1, which is excerpted from Table 4 of Draft "Ecological Screening Assessment for Secondary Pond under Future Use Scenarios").

Barium and beryllium also had high frequencies of exceedance of sediment screening benchmarks, but these exceedances were due largely to overly conservative screening values. Neither barium nor beryllium are significantly elevated above background concentrations. See the background concentrations in the EcoSSL documents for both metals). Thus, neither barium nor beryllium will be assayed in sediment pore water.

4. Schedule

The planned schedule for implementing this Work Plan is within 2 to 4-weeks of U.S. EPA approval, assuming conditions are safe to do so (ie. ice is thick enough).

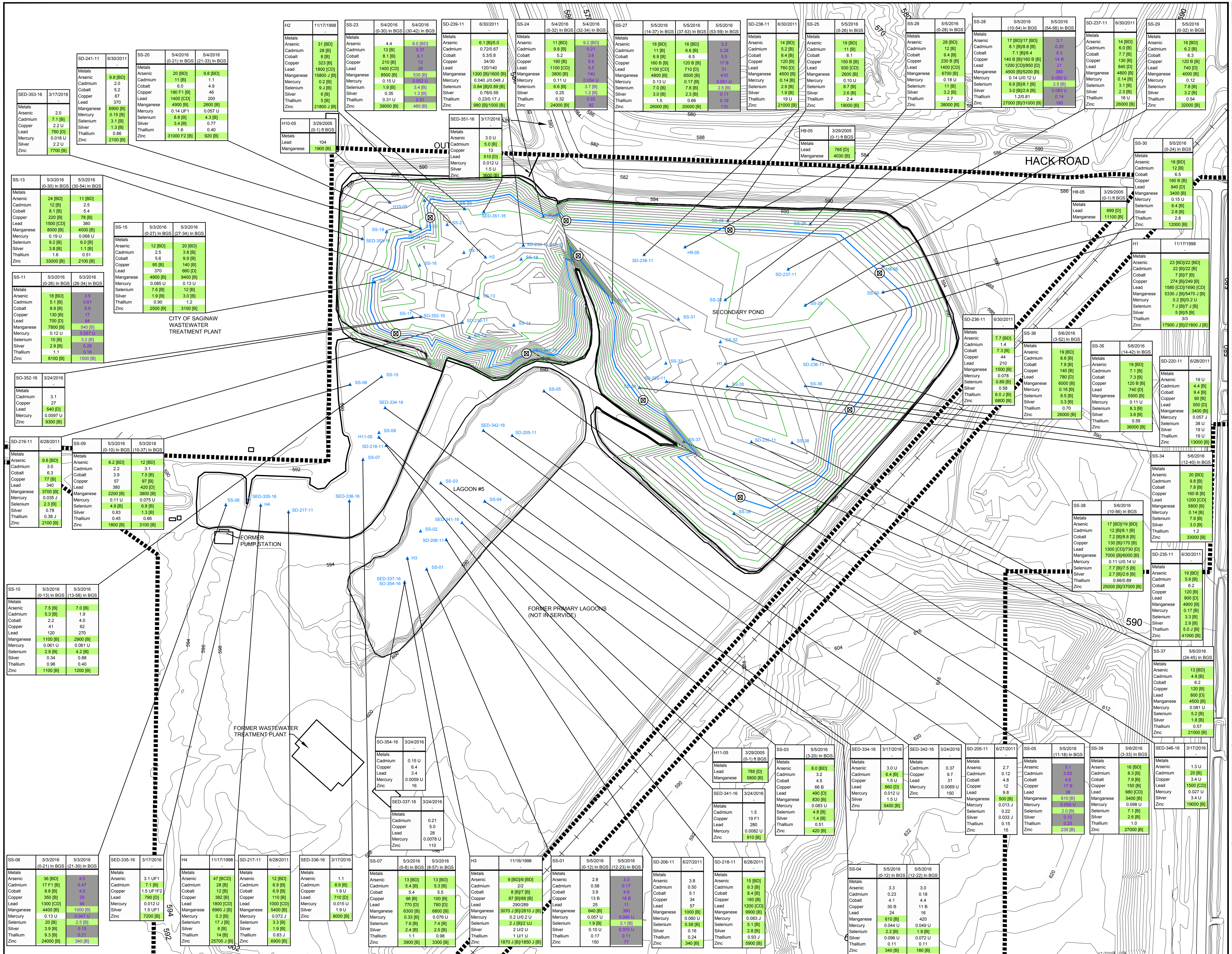
5. References

National Academy of Sciences Board. 2001. A Risk-Management Strategy for PCB-Contaminated Sediments. Committee on Remediation of PCB-Contaminated Sediments. National Academy of Sciences Board on Environmental Studies and Toxicology. National Research Council. National Academy Press, Washington, D.C. 432 pp.

Smith, D.W., and Jones, S.M. 2006. It's time to abandon co-occurrence sediment quality benchmarks (SQBs). Learned Discourse, Society of Environmental Toxicology and Chemistry. March 2006.

Smith, D.W. and S.M. Jones. 2012. Ecological risk assessment and natural resource injury assessment: when policy masquerades as science. Environmental Litigation, Winter 2012.

USEPA. 2005a. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metal Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc). EPA/600/R-02/011.



0 60 120 ft

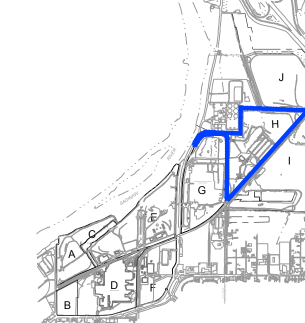
LEGEND

A — INVESTIGATIVE UNIT BOUNDARY AND IDENTIFIER
APPROXIMATE LIMITS OF RACER PROPERTY
590 EXISTING GROUND CONTOUR (NGVD)
CURRENT SHORELINE (APPROXIMATE)
SEDIMENT SAMPLE LOCATION
PROPOSED PORE WATER SAMPLE LOCATION
SAMPLE LOCATION
SAMPLE DATE
SAMPLE DEPTH
RESULT (mg/kg)
PARAMETER
EXCEEDANCE OF CRITERIA
0.050 CLAY SAMPLE

Parameter	A	B	C	D	Unit
Arsenic	5.8	4.6	37	7.6	mg/kg
Cadmium	1.2	3.7	2100	550	mg/kg
Cobalt	6.8	2	9000	2600	mg/kg
Copper	32	74.73	73000	20000	mg/kg
Lead	21	5170	900	400	mg/kg
Manganese	440	57.5	90000	25000	mg/kg
Mercury	0.13	0.1	580	160	mg/kg
Selenium	0.41	0.4	9600	2600	mg/kg
Silver	1	0.1	9000	2500	mg/kg
Thallium	-	4.2	130	35	mg/kg
Zinc	47	169.2	630000	170000	mg/kg

Notes:
A: Res/Non_Res/Statewide Default Bkgd Levels
B: Res/Non_Res/GW Prot_GW SW Interface Prot
C: Non_RES/Direct Contact
D: Res/Direct Contact_Direct Contact

SOURCES:
EXISTING GROUND CONTOURS ARE DERIVED FROM:
TOPOGRAPHY DRAWING RECEIVED FROM SANBORN (AN AERIAL PHOTOGRAPHY COMPANY)
JANUARY 3, 1996 - STATE PLANE;
2009 SURVEY OF CLAY PILE BY SPICER;
2013 SURVEY OF SAND/CLAY PILES BY WILCOX.
2016 SURVEY OF SEDIMENT SAMPLES BY NORMANDEAU ASSOCIATES, INC.



KEY MAP

SCALE VERIFICATION

THIS BAR MEASURES 1" ON ORIGINAL. ADJUST SCALE ACCORDINGLY.

REVITALIZING AUTOMOTIVE COMMUNITY ENVIRONMENTAL RESPONSE

SAGINAW, MICHIGAN

SECONDARY POND AND LAGOON CHARACTERIZATION SUMMARY OF EXCEEDANCES METALS, CURRENT SHORELINE AND PROPOSED PORE WATER SAMPLE LOCATIONS

Source Reference:
MICHIGAN STATE PLANE SOUTH, NAD 83 USING INTERNATIONAL FEET, NGVD 88
TOPO - SANBORN, 1996

Project Manager:	Reviewed By:	Date:	
I.R.	M.T.	JANUARY 2018	
Scale: 1" = 120'	Project №: 58502-T02	Report №: 017	Drawing №: figure 1

58502-T02(017)GN-WA001 JAN 29, 2018

Table 1

Screening of Sediment in Main Body of Secondary Pond
Sediment Pore Water Work Plan
Nodular Industrial Land
Saginaw, Michigan

Parameters	Units	ESV	ESV Source	# Samples	Freq. of Detection	Max Detection	Mean Detection (ND = 1/2 DL)	Mean Detection (ND = 0)	Max SQ	Mean SQ (ND=1/2 DL)	Mean SQ (ND = 0)	Freq. of Exceedance ND = 0
Metals												
Aluminum	mg/kg	Not Toxic	-	49	100%	32000.00	14695.92	14695.92	**-**	**-**	-	-
Antimony	mg/kg	25.00	Region 4	60	88%	43.00	4.89	4.31	**1.72**	0.20	0.17	2%
Arsenic	mg/kg	33.00	PEC	67	94%	47.00	12.39	12.19	**1.42**	0.38	0.37	3%
Barium	mg/kg	60.00	Region 4	62	100%	280.00	116.31	116.31	**4.67**	**1.94**	**1.94**	**79%**
Beryllium	mg/kg	1.20	Dutch	62	92%	2.70	1.21	1.20	**2.25**	1.01	1.00	**48%**
Cadmium	mg/kg	4.98	PEC	72	99%	28.00	6.05	6.05	**5.62**	**1.22**	**1.21**	**51%**
Chromium	mg/kg	Not Toxic	AVS Present	67	100%	190.00	94.94	94.94	**-**	**-**	-	**-**
Cobalt	mg/kg	50.00	Region 4	62	100%	12.00	6.47	6.47	0.24	0.13	0.13	0%
Copper	mg/kg	149.00	PEC	70	94%	382.00	98.19	98.13	**2.56**	0.66	0.66	**24%**
Iron	mg/kg	Not Toxic	-	49	100%	90000.00	46297.96	46297.96	**-**	**-**	-	**-**
Lead	mg/kg	128.00	PEC	77	100%	1800.00	639.09	639.09	**14.06**	**4.99**	**4.99**	**75%**
Manganese	mg/kg	1100.00	Region 4	66	100%	15800.00	4203.64	4203.64	**14.36**	**3.82**	**3.82**	**77%**
Mercury	mg/kg	1.10	PEC	72	28%	0.33	0.07	0.04	0.30	0.06	0.03	0%
Nickel	mg/kg	48.30	PEC	73	99%	60.00	31.50	31.46	**1.24**	0.65	0.65	14%
Selenium	mg/kg	20.00	Region 4	62	97%	20.00	5.79	5.47	1.00	0.29	0.27	0%
Silver	mg/kg	Not Toxic	AVS Present	67	81%	6.00	1.96	1.71	**-**	**-**	-	**-**
Thallium	mg/kg	2.60	Dutch	62	90%	14.00	1.81	1.34	**5.38**	0.70	0.51	15%
Tin	mg/kg	22000.00	Dutch	6	100%	170.00	110.17	110.17	0.01	0.01	0.01	0%
Vanadium	mg/kg	56.00	Dutch	62	100%	94.00	22.90	22.90	**1.68**	0.41	0.41	2%
Zinc	mg/kg	459.00	PEC	72	100%	41000.00	11737.78	11737.78	**89.32**	**25.57**	**25.57**	**79%**
Metals (AVS/SEM)												
CNE-SEM (more conservativ	umol/g OC	130.00	EPA 2005	16	100%	7570.93	1878.59	1878.59	**58.24**	**14.45**	**14.45**	**81%**
CNE-SEM (less conservative	umol/g OC	3000.00	EPA 2005	16	100%	7570.93	1878.59	1878.59	**2.52**	0.63	**14.45**	**25%**

Notes:

ESV = Ecological Screening Value
CNE-SEM = Carbon normalized excess SEM. See text.
BOLD = SQ > 1.0 or Freq. of Exceedance > 20%

Appendices

Appendix A
Photographs

Photo 1 Image of peepers

Photo 2 Placement of peepers in sediments in small stream in New York

Photographs

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