

HEAVY METAL TESTING AROUND THE HURON QUARRY MONOFILL

I. **PURPOSE:** To test for the presence of heavy metals--iron (Fe), zinc (Zn), Nickel (Ni), and cobalt (Co)--in the highland "wetlands" (adjacent to the Huron Quarry Monofill) and in the sediment of the stream flowing past/ out of the Huron Quarry Monofill. In addition to the above metals, sediment from Outfall 001 (into Huron River from the Huron Quarry Monofill) will also be tested for the presence of lead (Pb) and Cadmium (Cd).

These test results may help to determine whether or not the Huron Quarry Monofill is compromising Great Lakes' watershed quality and biota through the leaching of potentially toxic metals into the Great Lakes' basin. It may better be stated that these results may help to determine to what extent the Huron River watershed in the area of the Huron Quarry Monofill is being degraded.

It is hoped that future studies of aquatic biota--both macro- and micro-invertebrates--in the Spring/Summer of 1994 will shed more light on the health or "ill-health" of this particular area of the Huron River watershed.

II. **MATERIALS:**

EQUIPMENT/ APPARATUS:

-Ponar Grab Sampler	-Graduated Cylinders
-Hach One pH Meter w/ temp. probe	-Graduated Mixing Cylinders
-Hach DR/2000 Spectrophotometer	-Beakers
-Hot Plate	-Glass Pipets
-Mechanical Vacuum Pump	-TenSette Pipet w/ plastic pipet tips
-Clippers	-500-ml Separatory Funnel
-Neoprene/ Rubber Gloves	-Filtering Flask w/ filter holder & filter paper
-Latex Gloves	-25-ml Matched Sample Cells
-Rubber Safety Aprons	-Glass Membrane Filter (for Pb and Cd samples)
-Safety Goggles	-500-ml Plastic Sampling Bottles
-Fume Hood	
-5-Gal. Sampling Buckets	
-Plastic/Rubber Tubing for vacuum pump	
-10-Gal. Containment Vessel for Waste Storage	
-Marking Pencils	
-Cotton Balls	
-Scupula	
-Balance	
-Wire Brushes/ Cleaning Brushes (and Dial Anti-bacterial Gel Soap)	
-Sediment-Water Samples around Huron Quarry Monofill (as delineated below)	
-Hach DR/2000 Spectrophotometer Procedures Manual	
-Filtering Pans	

REAGENTS/ CHEMICALS:

*Ni/ Co Tests (PAN Method)--	-Nitric Acid (1:1)
-Phthalate-Phosphate Powder Pillows	-Hydrochloric Acid (1:1)
-EDTA Powder Pillows	-AbsoPure Distilled Water
-0.3% P.A.N.(1-[2-Pyridylazo]-2-Naphthol) Indicator Solution	-NaOH (5N)
	-NaOH (1.00N) and Household Bleach (for Cyanide Waste Disposal)
*Fe Test (FerroVer Method)--	
-FerroVer Iron Reagent Powder Pillows	

*Zn Test (Zincon Method)--
-ZincoVer 5 Reagent Powder Pillows
-Cyclohexanone

*Pb/Cd Tests (Dithizone Method)--
-Buffer Powder Pillows (Citrate Type for Heavy Metals)
-DithiVer Metals Reagent Powder Pillows
-Chloroform
-Potassium Cyanide
-50% w/w NaOH Solution (for Cd Test only)
-5N NaOH (for Pb Test only)

III. PROCEDURE:

1. All glassware and sampling buckets/bottles acid-washed with nitric acid and then rinsed with distilled water prior to sample collection and analysis.
2. Samples of water/sediment layer from three sites around the Huron Quarry Monofill were taken with the Ponar grab sampler and deposited in collecting buckets as follows:
 - a. Ponar grab sampler (PGS) and collecting buckets were immersed in water to be sampled prior to collection of sediment samples.
 - b. PGS then slowly lowered into water until sediment layer encountered.
 - c. One or two tugs on the lowering rope triggered the spring-pin on the PGS to be released with the subsequent trapping of sediment materials.
 - d. Contents of PGS then transferred to sampling bucket.
 - e. Before each sampling at the three different sites, the PGS was thoroughly scrubbed with Dial Gel soap and brush, and then rinsed with tap water.
 - f. The three sites sampled are described (and designated) as follow:
 - 1.) "Headwaters" or "wetlands" adjacent to the Huron Quarry Monofill approximately 100 yards from the Monofill's westernmost fenceline, which will be referred to as the **Highland "Wetlands"**.
 - 2.) Dredged portion of the Wagner and Pink "Drain" approximately 60 yards from its Monofill exiting, which will be referred to as the **Dredged Monofill Stream**.
 - 3.) Huron Quarry discharge pipe into the Huron River along its southern shoreline, which will be referred to as **Monofill Outfall 001 (to Huron River)**.
3. The samples were then taken back to the Mount Carmel High School lab in Wyandotte, MI. where they were transferred to 500-ml plastic sampling bottles, and then acidified to a pH<2 with nitric acid for storage purposes.
4. Prior to analysis, all samples digested (with the exception of the Ni/Co samples analyzed with the PAN Method) in accordance with the "E.P.A. Mild Digestion" procedure as delineated in the "Hach DR/2000 Spectrophotometer Procedures Manual" (HDR2-SPM); however, instead of using deionized water to bring the digested samples to volume, distilled water was substituted.
5. All samples filtered prior to analysis (after digestion where required) as follows:
 - a. Samples to be analyzed for lead and cadmium were filtered with a glass membrane filter.
 - b. Samples to be analyzed for iron, zinc, nickel, and cobalt were filtered with filtering apparatus and filter paper.
6. Before testing, the pH of samples were adjusted with 5N NaOH as follows:
 - a. pH of samples to be tested for Ni/Co was adjusted to between 3 and 8.
 - b. pH of samples to be tested for Fe was adjusted to between 3 and 5.
 - c. pH of samples to be tested for Zn was adjusted to between 4 and 5.
 - d. pH of samples to be tested for Cd was adjusted to 2.5.

- e. pH of samples to tested for Pb was adjusted to between 2.5 and 4.5.
- 7. The samples were tested with the DR/2000 Spectrophotometer in accordance with the procedures detailed in the HDR2-SPM (see data table titled "Flat Rock Quarry Monofill" for results and manual page numbers for individual tests).

IV. DATA: (Refer to Data Spreadsheet entitled "Flat Rock Quarry Monofill")

V. Discussion:

Since numerous studies have revealed the toxicity of incinerator ash resulting from the concentration of heavy metals therein, it has been hypothesized in this study that leachate contaminated with potentially toxic, bioaccumulative heavy metals may be entering the Huron River watershed/ecosystem via run-off and ground water seepage from/through the Huron Quarry Monofill. It is also well documented that several of the heavy metals analyzed in this study--notably nickel, lead, cadmium and cobalt--can cause/contribute to the development of cancers, lung disease, respiratory ailments, reproductive damage, neurological impairment, and a host of more common maladies. Of very real concern is the health hazard which improperly transported and covered incinerator ash (as documented by local residents) poses to the inhabitants living in close proximity to the Huron Quarry Monofill.

Needless-to-say, it is beyond the scope of this study to postulate exposure levels of residents to airborne heavy metal-laddened ash particles. Rather, it is within the realm of this study to provide evidence for a more insidious, though far-reaching, health hazard that may impact the well-being of future generations (and which may already be impacting the present generation). The dispersion of heavy metals in the Great Lakes' Basin results in the bioaccumulation of these metals in the flesh of aquatic organisms, which subsequently are consumed by unsuspecting fishermen and diners (as well as other wildlife). It is rather ironic that this study has been undertaken at a time when Friday fish consumption is at its yearly high during the Easter Season.

From the data, there appears to be a clear trend pointing toward heavy metal contamination of the Huron River aquatic ecosystem stemming from the Huron Quarry Monofill. All of the metals analyzed at the three sites--Ni, Co, and Zn--show a significant increase in concentrations from the Highland "Wetlands" to the Dredged Monofill Stream to the Monofill Outfall 001, with the exception of iron. The latter finding is not surprising as iron is ubiquitous to the Great Lakes' Ecosystem and is comparatively non-toxic, even in high concentrations. Also, the dredging of the Wagner and Pink Drain adjacent to, and flowing from, the Huron Quarry Monofill may possibly explain the finding of a lower total iron concentration in the Dredged Monofill Stream as compared to the Highland "Wetlands" area. It is postulated here that the other metals show no such trend because they are not as ubiquitous to the area, and they are/have been leaching into the Wagner and Pink Drain from the Huron Quarry Monofill, such that not even dredging could possibly eliminate the insidious leaching of such metals into the stream.

However, with regard to the other metals, the test concentrations reveal the following:

	<u>Highland "Wetlands" Dredged Monofill Stream</u>		<u>Monofill Outfall 001</u>	
Zinc	0.07 mg/L		0.11 mg/L	0.55 mg/L
Nickel	0.002 mg/L	0.029 mg/L	0.029 mg/L	0.243 mg/L 0.316 mg/L
Cobalt	0.00 mg/L	0.10 mg/L	0.10 mg/L	1.89 mg/L 0.66 mg/L

As can be noted above, when comparing Monofill Outfall 001 with the Dredged Monofill Stream, the Zinc concentration increases 5x, the Nickel concentration approximately 8-11x, and the Cobalt concentration approximately 7-18x. When the Monofill Outfall 001 is compared with the "pristine" Highland "Wetlands", the increase in concentration is much more marked and dramatic.

The presence of Cadmium and Lead, albeit in very low concentrations, should not be dismissed without further studies. It will be the scope of a subsequent study to test the Outfall 001 wastewater directly, rather than sediment, as well as portions of the Dredged Monofill Stream and the Highland

"Wetlands" (for comparison purposes) in order to more accurately assess the extent of possible Lead and Cadmium contamination into the Huron River Ecosystem.

However, it is of interest to note that the test results reveal concentrations of Lead (18-51 ug/L) and Cadmium (16 ug/L) which exceed their monthly average discharge limits of 14 ug/L and 1.5 ug/L, respectively (according to Permit NO. MI0045110). Of course, the aforementioned limits are for final effluent discharges; but, nevertheless, the test results imply that more testing needs to be performed before final conclusions can be proffered with regard to discharge violations.

It must be mentioned here that this study in no way attempts to provide absolute proof of the Huron Quarry Monofill's role in contaminating the Huron River watershed with heavy metal pollution. However, the results reported herein should be regarded as conservative estimates of heavy metal contamination into the Huron River Basin for the following reasons:

- 1.) Vigorous digestion was not utilized to digest the samples; but, rather, mild digestion procedures were followed.
- 2.) Volume additions were NOT corrected for; therefore, results obtained may be less than the actual concentrations present.
- 3.) Due to the inexperience of the testing group, some portions of testing may have not been as expertly performed as they may have been by someone with more expertise. For instance, during digestion procedures, some sample may have been lost due to unwanted boiling of samples for brief moments.
- 4.) Snow melt and rain during late winter and early spring may have caused a dilution of metal concentrations in the areas tested.

One area of concern which may have resulted in overly high concentrations for the metals noted is the fact that "Accuracy Checks", as outlined in the HDR2-SPM, were not undertaken. This is a concern which will be ameliorated in future studies.

In conclusion, it is obvious that more testing needs to be done. Though financial restraints may restrict the depth of future studies surrounding the Huron Quarry Monofill, the DCSE-OLMC Stream Team will continue to monitor the Huron River Watershed throughout the year. The Stream Team will do so because it seems rather hypocritical to incinerate waste and supposedly safely dispose of the ash by-product in a "self-contained" Monofill, only to find inordinate amounts of potentially toxic heavy metals possibly seeping from it into the surrounding environment. It is not morally responsible to knowingly allow citizens to be exposed to a toxic hazard that is in their own "backyard". It is questionable why such a quarry situated so close to a waterway that is utilized yearly by thousands of citizens for such recreational purposes as fishing and swimming--a waterway that is currently having a fish-ladder put into place to help restore gamefish populations in the area--has been allowed to operate a facility which cannot totally prevent toxic metals in the ash it stores from leaching into the waterways (and which may, in fact, be directly pumping them into the Huron River via Outfall 001). It is the authors' hopes that the above information will be of assistance in assessing the course of future operations at the Huron Quarry Monofill, and that prudent measures will be taken to insure the safety and welfare of the people living in the Huron River Basin area, as well as the health of the voiceless creatures who unfortunately now depend on responsible human stewardship of their ecosystems.

Lastly, the authors would like to add the following to clarify future environmental heavy metal water quality studies:

- 1.) The "Heptoxime Method" for Nickel analysis (after digestion) will be utilized in order to more rigorously meet USEPA standards for reporting.
- 2.) Copper, Silver, and Manganese concentrations will also be evaluated in future studies (where funding is available) in order to more thoroughly evaluate heavy metal contamination in Michigan waterways.
- 3.) Accuracy Checks, as noted previously, will be conducted in future studies.
- 4.) A northern Lower Peninsula study near Grand Lake in Presque Isle, MI. will be undertaken in the summer of 1994 in order to better provide "background" data on water quality for comparison purposes.
- 5.) Any information, advice, or guidance which USEPA personnel can provide for our benefit relating to future water quality analysis and reporting will be greatly appreciated.

Date: March 30, 1994

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