CORRESPONDENCE/MEMORANDUM — **State of Wisconsin**

DATE: January 11, 2001 FILE REF: 3200

TO: Jim Hosch - NOR/Superior

FROM: Tom Janisch - WT/2 Tom Janisch

SUBJECT: Preliminary Evaluation of the Sediment Sampling Results From Cores Taken From the Superior Harbor Inlet Potentially Impacted by the Former Operations of the Superior Manufactured Gas Plant.

Summary

Sediment samples were collected on September 19, 2000 from an inlet of the Superior Harbor navigational channel next to the City of Superior's wastewater bermed lagoon. The inlet potentially received historical discharges of wastes associated with a manufactured gas plant that was a few hundred feet to the west of the inlet. A 4 ft. diameter storm sewer outfall pipe exists at the head end of the inlet that may have served as a transport route for MGP wastes from the plant site to the inlet.

Core samples from two depths were taken at 6 locations along the longitudinal length of the inlet and analyzed for 8 metals and 19 unsubstituted PAH compounds.

Based on comparisons with consensus-based sediment guidelines derived to protect benthic organisms, the general conclusions based on the sediment concentrations of individual and combined metals and total PAHs are summarized as follows in terms of prediction of risks to benthic organisms:

<u>On an individual metal basis</u>

- No to minimal exposure risks - arsenic, cadmium, chromium, copper, lead, nickel, zinc,
- Moderate to high exposure risks - mercury (also considers risks due to methyl mercury production and uptake in fish)

<u>On a combined metal basis</u>

- Low to moderate exposure risk assuming an additive or synergistic effect of the combined metals (note on a combined basis mercury does not stand out other than how it might increase the overall averaging associated with the calculations and assigning the level of risks)

<u>On a TPAH Basis</u>

- Moderate to high exposure risks

Summary of Additional Assessmen. .eeds

Given the findings in this preliminary assessment, the following is recommended:

- Additional assessment work is needed, preferably in a phased fashion
- The parties currently responsible for the former coal gas manufacturing site need to be identified.
- In association with additional sediment assessment work in the inlet, assessments should be conducted on the groundwater and soils at the former plant site which includes identifying the location of all former building and structures.
- Coring at more locations and deeper into the sediments is needed focusing on the head end of the inlet to determine the degree and extent of contamination..
- Provisions should be made in any study to try to distinguish between coal tar contributed PAHs and those that may originate from the coal piles along the northwest shore of the inlet.
- Any decisions on future remediation of the inlet will depend on the results of further assessments including a laboratory toxicity component and field studies of such components as the benthic community in the inlet.
- A number of factors may need to be considered in any remediation decisions for the inlet including the setting and the feasibilty of source controls (if the coal piles are identified as a source of mercury and/or TPAHs to the inlet).

Background

The focus of the sediment sampling was an inlet adjacent to the Superior navigational channel and which is between a filled pier and a bermed area for Superior's wastewater treatment lagoons. On September 19, 2000, we collected a series of 6 cores beginning at the head end of the inlet near the storm sewer outfall pipe and proceeded in a northeasterly direction toward the mouth of the inlet with the Superior Harbor. The sampling locations are shown on the attached map of the inlet which you had previously provided. The purpose of the sediment sampling was to do an initial screening of the sediments both visually and analytically to determine if there might have been any waste discharges from the former operations of the manufactured coal gas that was located a few hundred feet to the southwest of the head end of the inlet. The city of Superior's wastewater holding lagoon berm forms the southeast side of the inlet . Coal storage piles on a filled pier are along the northwest side of the inlet. An observation made at the site was the presence of a 4 foot diameter storm sewer pipe at the head end of the inlet that may have may have served as a transport route for wastes, either inadvertently or purposely, generated from the coal gas manufacturing operations to Superior Bay.

The core samples were taken with our 3 in. diameter piston core sampler. Depth of sediments obtained at each coring site are shown on the following tables. The cores obtained at each site were divided into two sections for analysis. The surface segments were approximately 4 to 6 inches in length which approximates with the bioactive zone or the zone inhabited by benthic infaunal organisms. Analyses of contaminant concentrations in the surface segments allows realistic comparisons with various sets of sediment quality guidelines that are based on predicted effects to benthic organisms in the bioactive zone.

I developed the following tables of chemical results based on the tables you had e-mailed to me. Some of the values in the tables, especially the metals, had a number of notes indicating some of the results were qualified. I have repeated the qualifying notes in the following tables but didn't have the qualifier explanations. I did not access the SLOH data base to get this information. In the evaluation below, I assumed the data was generally useable for the purposes.

Results of Metal Analyses

Two points of comparison for the metal results are: 1) representative background concentrations in sediments for the region and harbor area, and 2) effect-based guideline concentrations developed to be protective of benthic macroinvertebrate organisms.

Comparison of Metal Concentrations in Sediment Samples With Representative Background Concentrations.

Table 1 presents a summary of background or reference site concentrations for the metals from six different published sources. The data represents both nearshore littoral area and offshore depositional basin sampling data and surface and deeper strata representative of pre-development conditions in Lake Superior. A general conclusion based on these studies is that the fine-grained silts, clays and organic matter which predominate in the offshore depositional basins of the lake would contain higher concentrations of metals while concentrations in coarse-grained nearshore sediments would be lower. Concentrations of metals in lower pre-development sediment strata would be lower than surface sediments.

Table 2 shows the analytical results from both the surface and deeper cored sediments from the study inlet. Note that the sample sites in the table are in the order from the head end of the inlet (SPG-3) out to the mouth. The question is what is the most appropriate set of reference site concentrations to use for comparison purposes with the Table 2 results. Given that the sediment load of the St. Louis and the Nemadji rivers carry a heavy clay component and clay parent materials were encountered during the inlet sediment sampling, comparing metals concentrations to sand-dominated reference substrates may not be totally appropriate. The nature of the study inlet sediments may put the metal concentrations somewhere between sand-dominated and fine-dominated reference site levels assuming no source inputs other than ubiquitous sources..

In doing a comparison of site metals concentrations with the Table 1 reference site concentrations, the following are results that look to be potentially elevated from various anthropogenic sources around the inlet.

Metal	Site	mg/kg	Metal	Site	mg/kg
Arsenic	SPG-3S	32	Zinc	SPG-3D	159
Copper	SPG-3D	104	Zinc	SPG-1D	100
Lead	SPG-3D	78.4	Zinc	SPG-6D	110
Lead	SPG-4D	110	Mercury	SPG-2D	0.56
Lead	SPD-6D	100	Mercury	SPG-6S	0.64
			Mercury	SPG-6D	0.98

Depending on what set of reference site values are used, the above metals may be somewhat elevated above what might be expected at an unimpacted site. With the exception of mercury, the levels of the other metals would represent only a low level of elevation. Mercury concentrations are greatly elevated over what may be expected compared to reference site concentrations. If a concentration range of 0.020 to 0.100 mg/kg can be used as the range of expected natural variability, the concentrations in the cores in the inlet are 20 to 50 times greater than this at the upper end of the concentrations found.

Some general observations of the distribution of the metals in the core samples are:

- Metals concentrations were generally greater in the deeper strata of the cores compared to the surface strata for 60% of the results (8 metals analyzed for at 6 sites gives 48 paired results for comparison), versus 19% of the results where the surface concentrations where greater than lower strata. There were essentially no differences in concentrations at the remaining 21% of results.
- Zinc, lead, and mercury concentrations were consistently greater in the lower strata at all the sample sites compared to the surface strata.
- The highest concentrations of arsenic, chromium, and copper were found in the two sample sites (SPG-3 and SPG-1) which are nearest to the head end of the inlet.
- The highest concentrations of mercury were at sample sites toward the mouth of the inlet (SPG-4 and SPG-6).
- For the other metals, there generally was not a lateral distribution pattern along the sampling transect based on a concentration gradient.

<u>Comparison of Metal Concentrations In Sediment Samples With Effect-Based Sediment Quality Guidelines</u>

Within the last couple of years a number of sources have published sediment quality guidelines based on effects to benthic macroinvertebrate species. Currently, some authors have combined and integrated the low and high effect concentrations for each metal from several guidelines to yield single low and high effect values that are based either on the arithmetical or geometric mean of the values from all the guidelines. The mean effect values from the combined guidelines are called consensus-based guidelines. Appendix A shows how low and high effect consensus-based concentrations were derived from several sets of guidelines. The derived values summarized in the table on the first page of Appendix A are comparable to the referenced literature source given (MacDonald *et al.* 2000).

The next step in the evaluation process is to calculate a hazardous quotient (HQ) for each metal for both the low and high effect concentrations. Derivation of the HQ involves dividing the sediment concentration by the effect-based concentration as follows:

HQ LEL (Hazardous quotient based on the low effect concentration)

$$\text{HQ LEL} = \frac{\text{Sed. Concen. for metal mg/kg}}{\text{LEL Concen. For metal mg/kg}}$$

HQ PEL (Hazardous quotient based on probable effect concentration)

$$\text{HQ PEL} = \frac{\text{Sed. Concen. for metal mg/kg}}{\text{PEL Concen. For metal mg/kg}}$$

A calculated HQ value of less than 1 predicts no impacts or exposures. An HQ greater than 1 predicts impacts and effects with the degree and severity determined generally by the amount greater than 1. Calculated HQ LEL and HQ PEL values for each metal at each sample site are shown in Table 2.

Metals Exceeding HQ LEL and HQ PEL Values of 1

Metals that exceed the HQ LEL values in order of degree and frequency are in the following table. All the HQ LEL values for all the other metals are less than 1.

Metal	No. of Samples	No. of Sample Sites that Exceed HQ LEL of 1 (No. of sites where lower strata involved)	Range of HQ LEL Values Greater than 1	Ave. of HQ LEL Values Greater than 1
Mercury	12	9 (5)	1.3 - 5.0	2.68
Arsenic	12	8 (5)	1.1 - 2.7	1.41
Lead	12	4 (3)	1.3 - 2.3	1.7
Copper	12	1 (0)	2.1	2.1
Chromium	12	1 (0)	1.3	1.3

The potential degree of risks to benthic organisms from arsenic, lead, copper, and chromium concentrations at the sites involved above would generally be considered low. While the LELs are exceeded, the PEL concentrations are generally not approached or exceeded as indicated by HQ PEL values of less than 1 for any of the metals with the exception of mercury which is discussed below. Based on the fact that some of the HQ LEL exceeding 1 are found in the lower strata which are presumed to be below the bioactive zone, there would be no exposure risks at these depths unless the lower strata with their associated metals become exposed by removal of overling sediments.

Mercury concentrations exceed the HQ LEL values by much greater than 1 at some sites which is also associated with the HQ PELs being approached at these same sites. The strata where the HQ LELs are exceeded the greatest and the HQ PEL values of 1 are equaled are in the lower strata which is assumed to be below the bioactive zone. An additional consideration for mercury in sediments is that the mercury can be methylated to form organic forms of mercury that can be readily bioaccumulated in fish tissue. There is a fish consumption advisory in Lake Superior based on mercury levels in walleye. The St. Louis River and associated harbors are a likely contributing source of mercury. Given the levels of mercury found in the sediments of the inlet under study, and considerations of potential impacts to both the benthic community and human health based on the bioconversion ability and uptake in fish, mercury concentrations in sediments at the site would be rated at moderate to high risks. One source of mercury found in the inlet sediments may be the runoff and particulate wind transport from the coal piles on the pier along the northwest shore.

Alternate Evaluation Tool For Metals

Another way to predict potential toxicty based on the results at a site is to total all the HQ PEL values for the individual metals and divide by the number of metals to derive a mean PEL quotient for the metals. Based on correlating ranges of these mean PEL quotients with incidences of toxicity at a number of sample sites, Ingersoll et al. (2000) have predicted the level of toxicity that may be found associated with these mean PEL values. Based on results from the *Hyalella azteca* 28 to 42 day tests and metal concentrations in the sediments at the sites tested, Ingersoll et al. (2000) predicted the following incidences of toxicity associated with the mean PEL value ranges.

Incidence of Toxicity (%) Based On Mean PEL Quotients (number of samples in parentheses) based on metals							
Mean PEL Quotients	< 0.1	0.1 to < 0.5	0.5 to < 1.0	1.0 to < 5.0	> 1.0	> 5.0	Total Number of samples
% of Samples Toxic	8 (50)	20 (51)	62 (37)	NC	86 (22)	NC	160

The bottom of Table 2 shows the calculated mean HQ-PEL or PEL quotients for comparison with the above values. The Table 2 PEL quotients and the percentage of sites that had associated toxicity at them based on the above table is shown below. Based on the PEL quotient values it would appear that there is a 20% chance that sediment samples taken from the study inlet would have some degree of toxicity associated with them which somewhat confirms the above assessment of low to moderate risks to the benthic organisms present. If mercury is looked at alone, I would estimate that there is a moderate to high overall risk when both benthic organism and human health risks are of concern.

Prediction of Toxicity in the Inlet Samples Based on Combined Metal Concentrations												
	SPG-3S	**SPG-3D**	**SPG-1S**	**SPG-1D**	**SPG-2S**	**SPG-2D**	**SPG-4S**	**SPG-4D**	**SPG-5S**	**SPG-5D**	**SPG-6S**	**SPG-6D**
PEL Quotient	0.3	0.29	0.23	0.29	0.24	0.29	0.13	0.43	0.16	0.20	0.26	0.13
Esimated % Sites where toxicity found at the PEL Quotient	20	20	20	20	20	20	20	20	20	20	20	20

Ingersoll et al. 2000. Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines. EPA 905/R-00/007. June 2000.

Results of PAH Analyses

Table 3 shows the results of the PAH analyses. The individual PAHs are grouped into low (LMW) and high (HMW) weight PAHs with both groups totaled to yield a total PAH (TPAH) concentration.
Some things to note about the lateral and vertical distibution of the PAHs includes:

- Generally in the sediment strata with the high PAH concentrations, it was noted in the field that the strata had a black color and odors typically associated with coal tars were present.
- At the two sample sites (SPG-3 and SPG-1) at the head end of the inlet nearest the storm sewer outfall, TPAH concentrations are greatest in the surface strata compared to the deep strata. At the remainder of the sample sites out toward the mouth of the inlet from these sites, TPAH concentrations are greater in the lower strata compared to the surface. The transition from the TPAH greatest in the surface to greatest in the lower strata appears to take place between SPG-1 and SPG-2. The two sites are located relatively close together so just by random sampling we apparently selected sites just on either side of the transition line where the concentrations become reversed.
- There is a concentration gradient associated with TPAH concentrations with the highest concentrations found at the head end of the slough near the stormwater outfall and decreasing at the sample sites out toward the mouth. This is different from the metal concentrations that generally did not show any lateral concentration gradients .
- Generally the LMW PAHs were greater (SPG-3S) or equal (SPG-3D) to the HMW PAH concentrations in the surface sediments at the sample site nearest the storm sewer outfall. At all the remaining sample sites out from this site, HMW PAHs were greater than LMW PAHs in both the surface and deeper strata.
- Based on the above observations, it appears high concentrations of relatively unweathered coal tars may still reside in surface sediments near the storm sewer outfall based on the presence of greater amounts of LMW PAHs. At samples sites out from this point, the coal tars have been buried under deposited sediment and based on the greater concentrations of HMW PAHs, have under went a greater degree of weathering which may account for the loss of the LMW PAHs through volatilization, solubilization, and biodegradation.
- An additional source of PAHs to the study inlet besides the coal tars may be from runoff and wind blown particulates from the coal piles along the northwest shore of the inlet.

Background Concentrations of TPAHs

Depending on the sources and sample locations, TPAH concentrations can vary in waterways associated with urban areas. In sampling related to dredging projects in the navigational channel of the Superior Harbor and the St. Louis River, the U.S.ACOE typically found 1,000 to 3,000 ug/kg TPAHs (Janisch, 1992). The lowest TPAH concentration in the inlet sediments was found at SPG-6S at 6,055 ug/kg.

Janisch, T. 1992. Appendix D. Sediment quality assessment for the St. Louis River Area of Concern. The St Louis River System Remedial Action Plan. Stage 1. April 1992. WDNR.

Comparison of TPAH Concentrations In Sediment Samples With Effect-Based Sediment Quality Guidelines.

Sediment quality guidelines exist for individual PAHs, LMW PAHs, HMW PAHs, and total PAHs. To evaluate the potential effects of the PAHs in the study sediments, LEL and PEL consensus sediment quality guidelines from MacDonald et al. (2000) were used to compare with the Table 3 results. The consensus-based LEL and PEL concentrations from MacDonald et al. are 1,600 ug/kg and 23,000 ug/kg, respectively. Following the procedure above, these values were used to calculate HQ - LEL and HQ - PEL values for TPAHs in the surface and deeper strata at each of the sampling sites. The results of the calculations are shown at the bottom of Table 3.

The HQ - LEL values are greatly exceeded at all of the sites to the degree that the HQ - PEL values at 5 of the strata sampled are also greatly exceeded. Three of the 5 strata involved are the lower strata at three sample locations. There is a high potential for effects to benthic organisms associated with the surface sediments at the two sample locations nearest the storm sewer outfall. To get an idea of the overall toxicity that may be found at the site, the system of Ingersoll et al. as was used above for metals where ranges of PEL quotients are used to predict the incidence of toxicity in the *Hyalella azteca* 28 to 42 day toxicity tests was used based on the concentrations of TPAHs. The toxicity in the inlet sediments is predicted in the table below.

Incidence of Toxicity (%) Based On Mean PEL Quotients (number of samples in parenthese) for TPAHs							
Mean PEL Quotients	< 0.1	0.1 to < 0.5	0.5 to < 1.0	1.0 to < 5.0	> 1.0	> 5.0	Total Number of samples
% of Samples Toxic	17 (98)	61 (46)	56 (9)	NC	86 (7)	NC	160

Prediction of Toxicity in the Inlet Samples Based on TPAH Concentrations												
	SPG-3S	**SPG-3D**	**SPG-1S**	**SPG-1D**	**SPG-2S**	**SPG-2D**	**SPG-4S**	**SPG-4D**	**SPG-5S**	**SPG-5D**	**SPG-6S**	**SPG-6D**
PEL Quotient	15.8	8.6	11.8	0.98	0.77	11	0.53	3.9	0.37	0.44	0.32	0.70
Esimated %Toxicity	86	86	86	56	56	86	56	86	61	61	61	56

Given the high incidence of toxicity that is predicted at the sample sites, especially in the surface strata containing the bioactive zone the risk level predicted to benthic organisms is moderate to high.

Cc: Bob Masnado - WT/2
Lee Liebenstein - WT/2
Ted Smith - NOR/Superior
Jim Killian - WT/2

Table 1. Concentrations of Metals in Near Shore and Off Shore Depositional Areas and in Surface and Pre-development Substrata.

Metal	Undeveloped Tributary Mouths OF Lake Superior [1.]		L. Superior Pre-cultural Substrata Duluth Sub-basin [2.]	Mean Concentrations (SD) of Metals in Lake Superior Sediments [3.]		
	Average	Range		Total Lake	Non-depositional Zone	Duluth Sub-basin
Arsenic	NA	NA	5	1.7 (2.5)	1.3 (2.2)	2.6 (3.4)
Cadmium	0.48	0.1 - 1.3	0.9	1.2 (0.8)	0.8 (0.6)	1.7 (0.5)
Chromium	6.4	0.9 - 11.4	50.7	163 (104)	124 (95)	195 (66)
Copper	10.6	0.6 - 19.6	69	82 (67)	49 (40)	90 (26)
Lead	7.0	2 - 12.3	18	44 (27)	26 (18)	62 (20)
Mercury	0.028	< 0.010 - 0.060	0.080	0.083 (0.056)	0.053 (0.030)	0.136 (0.046)
Nickel	10.7	1.1 - 22.5	63.5	95 (46)	72 (47)	123 (40)
Zinc	24.5	3.0 - 55.5	117	97 (48)	63 (41)	127 (35)

Table 1. (Continued).

Metal	Wisconsin Point Sand-Average [4.]	Lake Superior Near Shore - Duluth Superior [5.]		Lake Superior Depositional Basins [6.]	
		Average	Range	Range - Surface	Range - Subsurface
Arsenic	6.9	NA	NA	NA	NA
Cadmium	1.0	0.97	0.83 - 1.3	1.4 - 2.4	0.4 - 0.7
Chromium	64	9.0	4.3 - 18.5	29.5 - 60.2	26.1 - 73.1
Copper	41.5	4.5	1.8 - 9.9	113 - 173	30 - 84
Lead	5	6.4	3.6 - 12	74.9 - 138.2	20.5 - 68.01
Mercury	< 0.020	NA	NA	0.094 - 0.160	0.044 - 0.68
Nickel	33.5	8.2	4.8 - 15	28.9 - 66.4	24.4 - 69.8
Zinc	59	15.1	7.6 - 30	143 - 195.2	53 - 137.1

Table 1 Notes. Sources of background concentration data:

1. Fitchko, J. and T.C. Hutchinson. 1975. A comparative study of heavy metal concentrations in river mouth sediments around the Great Lakes. J. Great Lakes Res. 1(1):46-78.

2. IJC. 1988. Procedures for the assessment of contaminated problems in the Great Lakes. Report to the Great Lakes Water Quality Board by the Sediment Subcommittee and its Assessment Work Group. International Joint Commission Great Lakes Regional Office. Windsor, Ontario. December 1988.

3. IJC. 1977. The waters of Lake Huron and Lake Superior. Volume III (Part B). Lake Superior. Report to the International Joint Commission by the Upper Lakes Reference Group.

4. Mason, J.W., M.H. Albers, and E.M. Brick. 1985. An evaluation of beach nourishment on Lake Superior Shore. Technical Bulletin No. 157. Wis. Dept. of Natural Resources.

5. 5. IJC. 1977. The waters of Lake Huron and Lake Superior. Volume III (Part B). Lake Superior. Report to the International Joint Commission by the Upper Lakes Reference Group.

6. Mudroch, A., L. Sarazin, and T. Lomas. 1988. Report. Summary of surface and background concentrations of selected elements in the Great Lakes Sediments. J. Great Lakes Res. 14(2):241-251.

Table 2 . Analytical Results (mg/kg) and Calculation and Summing of Hazardous Quotients (HQs) For Metals In Sediments in the Bay Associated With Potential Discharges from the Superior MGP Site.

Metal	SPG-3S	SPG-3D	SPG-1S	SPG-1D	SPG-2S	SPG-2D	SPG-4S	SPG-4D	SPG-5S	SPG-5D	SPG-6S	SPG-6D	Units	LOD	LOQ
Arsenic	**32**	**14**	**9**	**15**	**19**	**13**	**7**	**14**	**13**	**8**	**9**	**13**	**mg/kg**	**3**	**9**
HQ - LEL	2.7	1.2	0.8	1.3	1.6	1.1	0.6	1.2	1.1	0.7	0.8	1.1	—		
HQ - PEL	0.8	0.3	0.2	0.4	0.5	0.3	0.2	0.3	0.3	0.2	0.2	0.3	—		
Cadmium	ND	ND	ND	ND	ND	ND	ND	**0.6**	ND	ND	ND	**0.7**	**mg/kg**	**0.4**	**1.2**
HQ - LEL	—	—	—	—	—	—	—	0.4	—	—	—	0.5	—		
HQ - PEL	—	—	—	—	—	—	—	0.1	—	—	—	0.1	—		
Chromium	**67**	**27**	**20**	**23**	**27**	**18**	**8**	**36**	**13**	**13**	**16**	**15**	**mg/kg**	**0.4**	**1.2**
HQ - LEL	1.3	0.5	0.4	0.4	0.5	0.4	0.2	0.7	0.3	0.3	0.3	0.3	—		
HQ - PEL	0.4	0.2	0.1	0.1	0.2	0.1	0.1	0.2	0.1	0.1	0.1	0.1	—		
Copper	***26.1**	***40.8**	***104 a**	***38.9 e**	***43.6**	***31**	**9.4**	**58**	**13**	**21**	**28**	**35**	**mg/kg**	**0.7**	**2.4**
HQ - LEL	0.5	0.8	2.1	0.8	0.9	0.6	0.2	1.2	0.3	0.4	0.6	0.7	—		
HQ - PEL	0.1	0.2	0.5	0.20	0.2	0.2	0.1	0.3	0.1	0.1	0.1	0.2	—		
Lead	***33**	***78.4**	***28.5 b**	***65.4**	***29.3**	***57.2**	**8**	**110**	**17**	**37**	**61**	**100**	**mg/kg**	**2**	**8**
HQ - LEL	0.8	1.8	0.7	1.5	0.7	1.3	0.2	2.5	0.4	0.8	1.4	2.3	—		
HQ - PEL	0.2	0.5	0.2	0.4	0.2	0.4	0.1	0.8	0.1	0.3	0.4	0.7	—		
Nickel	**20**	**9**	**10**	**12**	**17**	**11**	**6**	**15**	**7**	**9**	**11**	**11**	**mg/kg**	**1**	**4**
HQ - LEL	0.8	0.4	0.4	0.5	0.7	0.5	0.3	0.6	0.3	0.4	0.5	0.5	—		
HQ - PEL	0.4	0.2	0.2	0.2	0.3	0.2	0.1	0.3	0.1	0.2	0.2	0.2	—		
Zinc	***49.2**	***159**	***62 c**	***100 g**	***53.2**	***82.3**	**26**	**180**	**43**	**67**	**88**	**110**	**mg/kg**	**2**	**6**
HQ - LEL	0.4	1.2	0.5	0.7	0.4	0.6	0.2	1.3	0.3	0.5	0.6	0.8	—		
HQ - PEL	0.1	0.4	0.1	0.2	0.1	0.2	0.04	0.4	0.1	0.2	0.2	0.3	—		
Mercury	***0.051**	***0.20**	***0.26 d**	***0.45 h**	***0.18**	***0.56**	***0.31**	***1.0**	***0.26**	***0.34**	***0.64**	***0.98**	**mg/kg**	**0.007**	**0.021**
HQ -LEL	0.3	1.0	1.3	2.3	0.9	2.8	1.6	5	1.3	1.7	3.2	4.9	—		
HQ - PEL	0.05	0.2	0.3	0.5	0.2	0.6	0.3	1.0	0.3	0.3	0.6	1.0	—		
Ave. HQ-LEL	0.97	0.81	0.89	1.07	0.81	1.04	0.47	1.74	0.57	0.69	1.06	1.53			
Ave.HQ-PEL	0.3	0.29	0.23	0.29	0.24	0.29	0.13	0.43	0.16	0.20	0.26	0.13			
Depth of Sample inches	0 - 8.7	8.7 - 23.4	0 - 6.9	6.9 - 13.8	0 - 8.9	8.9 - 17.4	0 - 4.2	4.2 - 16.2	0 - 4.8	4.8 - 10	0 - 6.6	6.6 - 13.3	inches	—	—

Table 3. PAH Concentrations (ug/kg) in the Bay Potentially Impacted by Discharges from the Superior MGP.

LMW PAHs	SPG-3S	SPG-3D	SPG-1S	SPG-1D	SPG-2S	SPG-2D	SPG-4S	SPG-4D	SPG-5S	SPG-5D	SPG-6S	SPG-6D
Acenapthene	12000	6000	3600	880	740	4200	590	1300	92	170	68	150
Acenaphthylene	16000	7700	4700	1200	930	5700	770	2000	130	240	93	230
Anthracene	15000	6800	7100	1000	900	5300	610	1900	180	230	150	390
Fluorene	13000	6200	5100	670	600	8900	380	2400	130	280	120	370
Phenanthrene	54000	31000	50000	3900	3300	57000	2100	17000	680	1000	640	2300
Naphthalene	76000	26000	2700	430	410	3800	370	760	130	210	76	220
1-methlynapthalene	25000	8800	1300	670	450	1700	370	820	66	140	63	170
2-methylnapthalene	31000	5900	650	210	180	1200	200	450	100	200	90	190
Σ LMW PAHs	242000	98400	75150	8960	7510	87800	5390	26630	1508	2470	1300	4020
HMW PAHs												
Fluoranthene	23000	21000	52000	3200	2300	45000	1400	17000	1500	1700	1400	2800
Pyrene	35000	23000	43000	3400	2600	37000	2000	14000	1500	1600	1200	2200
Chrysene	12000	9500	17000	E	990	15000	760	6600	700	810	650	1400
Benz(a)anthracene	12000	8700	15000	1400	1000	14000	790	5800	660	680	520	1100
Benzo(a)pyrene	12000	8700	14000	1400	960	13000	760	5300	700	730	560	1100
Benzo(e)pyrene	E	4900	8200	750	E	6200	410	2800	380	400	310	E
Benzo(b)fluoranthene	7400	7200	15000	1100	730	12000	E	3900	610	700	630	1200
Benzo(k)fluoranthene	5000	4100	7400	640	430	6900	300	2900	330	370	320	660
Dibenz(a,h)anthracene	600	450	750	65	55	750	35	275	35	35	35	55
Indeno(1,2,3-cd)pyrene	6500	5400	11000	800	540	8100	E	E	E	E	E	790
Benzo(g,h,I)perylene	7400	5800	12000	870	620	8300	450	3700	480	510	430	760
Σ HMW PAHs	120900	98750	195350	13625	10225	166250	6905	62275	6895	7535	6055	12065
Total PAHs	362900	197150	270500	22585	17735	254050	12295	88905	8403	10005	7355	16085
TPAH HQ - LEL [1]	227	123	169	8.5	11	159	7.7	55.6	5.3	6.3	4.6	10.1
TPAH HQ - PEL [1]	15.8	8.6	11.8	0.98	0.77	11	0.53	3.9	0.37	0.44	0.32	0.70
Depth of Sample (inches)	0 - 8.7	8.7 - 23.4	0 - 6.9	6.9 - 13.8	0 - 8.9	8.9 - 17.4	0 - 4.2	4.2 - 16.2	0 - 4.8	4.8 - 10	0 - 6.6	6.6 - 13.[illegible]

Notes:

1. The Hazardous Quotients for the Lowest Effect Concentration and Probable Effect Concentrations were calculated based on an LEL and PEL values of 1,600 ug/kg and 23,000 ug/kg TPAH. These are consensus based effect concentrations derived from MacDonald et al. 2000a and 2000b.

Appendix A

Consensus Sediment Quality Guidelines For Metals For the Protection of Benthic Macroinvertebrates

"Consensus" Sediment Quality Guidelines are derived from the integration of the low and high effect concentration values from seven different sets of sediment quality guidelines from different sources. Each of the sources has used different data bases and approaches to derive the effect-based concentrations for each metal. The lower effect concentrations (e.g. Lowest Effect Level, Effect Range-Low, Threshold Effect Level) are associated with no or minimal impacts to benthic invertebrates (growth, reproduction, survival). The high effect concentrations (e.g. Severe Effect Level, Effect Range-Median, Probable Effect Level) are associated with probable effects and toxicity. It is assumed that as the concentrations of metals increase between the low effect levels and the upper effect levels, the frequency and severity of effects will also increase. Metal concentrations that exceed the LEL value but are less than the PEL value would be considered to have low to moderate risks to benthic organisms associated with them. The effect levels from each set of guidelines are summed and an arithmetical mean of the summed values is derived. The effect level concentration for each metal from each guideline is shown on the following pages along with statistical calculations. The effect level concentrations for each metal are summarized in the table below.

Metal	Low or Minimal Effect Concentration mg/kg	High or Probable Effect Concentration mg/kg
Arsenic	**12**	**41**
Cadmium	**1.5**	**6.0**
Chromium	**52**	**166**
Copper	**50**	**222**
Lead	**43**	**136**
Mercury	**0.2**	**0.91**
Nickel	**24**	**51**
Zinc	**138**	**428**

The low and effect concentrations derived through the methodology on the following pages and summarized in the above table compare favorably with the consensus-based levels for metals derived by MacDonald *et al.* 2000.

MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Archives of Environmental Contamination and Toxicology. 39:20-31.

Arsenic

(mg/kg)

Summary of Sediment Effect Concentration Levels for Arsenic for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines	
Lowest Effect Level	Severe Effect Level
6	**33**

NOAA Biological Effects of Sediment Sorbed Contaminants	
Effect Range - Low	Effect Range - Median
33	**85**

ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)	
Effect Range - Low	Effect Range - Median
13	**50**

Freshwater Sediment Quality Assessment Values (Smith et al. 1996)	
Threshold Effect Level	Probable Effect Level
5.9	**17**

Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (Unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (Likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
11	5	**17**	10

Canadian Sediment Quality Guidelines (1999)	
Interim Sediment Quality Guidelines (TEL)	Probable Effect Level
5.9	**17**

Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)	
Effect Range - Low	Effect Range - Median
8.2	**70**

Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**11.9**	Average	**41.3**
Minimum	**5.9**	Minimum	**17**
Maximum	**33**	Maximum	**85**
LOWEST EFFECT LEVEL 12 mg/kg		**Highest Effect Level 41 mg/kg**	

Cadmium
(mg/kg)

Summary of Sediment Effect Concentration Levels for Cadmium for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
0.6		**10**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
5		**9**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
0.7		**3.9**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
0.6		**3.5**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (Unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (Likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
2	0.2	**3.5**	0.4
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		Probable Effect Level	
0.6		**3.5**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
1.2		**9.6**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**1.53**	Average	**6.14**
Minimum	**0.6**	Minimum	**3.5**
Maximum	**5**	Maximum	**10**
LOWEST EFFECT LEVEL 1.5		**HIGHEST EFFECT LEVEL 6.0**	

Chromium
(mg/kg)

Summary of Sediment Effect Concentration Levels for Chromium for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
26		**110**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
80		**145**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
39		**270**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
37.3		**90**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
64	1.0	**90**	2.0
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		Probable Effect Level	
37.3		**90**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
81		**370**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**52**	1666.4Average	**166.4**
Minimum	26	Minimum	90
Maximum	80	Maximum	370
LOWEST EFFECT LEVEL 52 mg/kg		**HIGHEST EFFECT LEVEL 166 mg/kg**	

Copper

(mg / kg)

Summary of Sediment Effect Concentration Levels for Mercury for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
16		**110**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
70		**390**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
41		**190**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
35.7		**197**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
120	2.0 – 9.0	**200**	4.0 - 18
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		Probable Effect Level	
35.7		**197**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
34		**270**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**50.3**	Average	**222**
Minimum	28	Minimum	110
Maximum	120	Maximum	390
Lowest Effect Level 50 mg / kg		**Highest Effect Level 222 mg / kg**	

Lead

(mg / kg)

Summary of Sediment Effect Concentration Levels for Lead for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
31		**250**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
35		**110**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
55		**99**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
35		**91.3**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
63	4.0 –16 ug/L	**91**	8.0 - 32
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		**Probable Effect Level**	
35		**91.3**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
46.7		**218**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**43**	Average	**135.8**
Minimum	31	Minimum	91
Maximum	63	Maximum	250
LOWEST EFFECT LEVEL 43 mg/kg		**HIGHEST EFFECT LEVEL 136 mg/kg**	

Mercury (total)

(mg / kg)

Summary of Sediment Effect Concentration Levels for Mercury For Protecting Benthic Invertebrate

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
0.2		**2.0**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
0.15		**1.3**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
No Value		No Value	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
0.174		**0.486**	
Draft Criteria for Managing Contaminated Sediment In British Columbia			
Level I Criteria (Unlikely to cause unacceptable impacts to benthic organisms)		Level II (Likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug /L)	Sediment	Pore Water
0.33	0.02	**0.49**	0.04
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		**Probable Effect Level**	
0.17		**0.49**	
Sediment Guidelines for Marine and Estuarine Sediments ((Long et al. 1995)			
Effects Range - Low		Effects Range - Median	
0.15		**0.71**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic / Probable / Severe Effect Level	
Average	**0.20**	Average	**0.91**
Minimum	0.15	Minimum	0.486
Maximum	0.33	Maximum	2.0
LOWEST EFFECT LEVEL 0.2 mg/kg		**HIGHEST EFFECT LEVEL 0.91 mg/kg**	

Nickel
(mg/kg)

Summary of Sediment Effect Concentration Levels for Nickel for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
16		**75**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
30		**50**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
24		**45**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
18		**36**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
36	25	**49**	50
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		Probable Effect Level	
No Value		**No Value**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
20.9		**51.6**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**24.2**	Average	**51.1**
Minimum	**16**	Minimum	**36**
Maximum	**36**	Maximum	**75**
LOWEST EFFECT LEVEL 24		**HIGHEST EFFECT LEVEL 51**	

Zinc

(mg/kg)

Summary of Sediment Effect Concentration Levels for Zinc for Protecting Benthic Invertebrates

Ontario Sediment Quality Guidelines			
Lowest Effect Level		Severe Effect Level	
120		**820**	
NOAA Biological Effects of Sediment Sorbed Contaminants			
Effect Range - Low		Effect Range - Median	
120		**270**	
ARCS Sediment Effect Concentrations For *Hyalella azteca* and *Chironomus riparius* (1996)			
Effect Range - Low		Effect Range - Median	
110		**550**	
Freshwater Sediment Quality Assessment Values (Smith et al. 1996)			
Threshold Effect Level		Probable Effect Level	
123		**315**	
Draft Criteria for Managing Contaminated Sediment In British Columbia (1999)			
Level I Criteria (Unlikely to cause unacceptable impacts to benthic orgainisms)		Level II (Likely to cause minor impacts to benthic organisms)	
Sediment	Pore Water (ug/L)	Sediment	Pore Water (ug/L)
220	30	**320**	60
Canadian Sediment Quality Guidelines (1999)			
Interim Sediment Quality Guidelines (TEL)		Probable Effect Level	
123		**315**	
Sediment Guidelines for Marine and Estuarine Sediments (Long et al. 1995)			
Effect Range - Low		Effect Range - Median	
150		**410**	
Summary of Lower and Upper Effect-Based Guideline Concentrations			
Minimum / Low / Threshold Effect Level		Toxic /Probable / Severe Effect Level	
Average	**138**	Average	**428.6**
Minimum	**110**	Minimum	**270**
Maximum	**220**	Maximum	**820**
LOWEST EFFECT LEVEL 138		**HIGHEST EFFECT LEVEL 428**	

Superior Gas Plant
Sediment Sampling

09/19/2000