Final Report

An Assessment of Sediment Quality in Presque Isle Bay Erie, Pennsylvania

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A. Background

A1. Introduction

The harbor at Erie, Pennsylvania, is formed naturally by a re-curved sand spit named Presque Isle, now the location of a Pennsylvania State Park. The sand spit forms a harbor, known as Presque Isle Bay (the Bay), which is approximately 4.5 miles long and with a maximum width of 1.5 miles. The Bay has been designated as the 43rd Great Lakes Area of Concern. The Bay connects to Lake Erie through a narrow channel maintained by the U.S. Army Corp of Engineers.

A2. Goals and Objectives

The restoration of beneficial uses in Presque Isle Bay is the ultimate goal of many interested stakeholders. The impaired beneficial uses currently identified by the Great Lakes Program in the Bay are the high incidence of tumors in Brown Bullheads, and restrictions on dredging of certain areas within the Bay. If it is established that surface sediments in PIB are toxic and a threat to human health or the environment, a remediation plan may be necessary.

The data generated by the current project, in conjunction with data from previous studies, will aid in determining whether the sediments of Presque Isle Bay are contaminated to such an extent as to warrant an active program of capping or removal. If, by weight of evidence provided by coordinated sediment chemical assays, toxicity tests, and benthic community surveys, the sediments are not a threat to human and ecological health, only continued monitoring may be required. It should be noted that an indisputable cause and effect relationship between the presence of certain contaminants and toxicity may be impossible to establish. An insistence on such absolute answers will lead to endless studies and indecision.

Thus, the goal of the current study was to determine if there was sufficient contamination in Presque Isle Bay sediments to present a significant threat to human and/or ecological health.

It was assumed that the previously studied sites adequately represented the variety of habitats within PIB, and provided sufficient coverage to identify "hot spots" if any existed. It was also assumed that the purpose of examining sediment cores was to determine the extent of possible dredging operations, and not to document the historical record of contaminant deposition. It was further assumed that any decision to dredge or cap would be followed by more intensive sampling to better define the exact extent of contaminants exceeding an action level.

Therefore, this study included analysis of sediments from locations identified in previous studies as having high concentrations of contaminants, or having exhibited toxicity in previous testing. The ten sites selected for study (Figure 1)included 6 locations along the city side of the Bay, 2 sites located along the centerline of the Bay, and 2 locations located along the far shore of the Bay (within or near Presque Isle State Park). Evaluation tools used in this study followed the sediment triad approach in which a coordinated array of benthic surveys, sediment toxicity, and chemical analyses were conducted on samples collected at the same time (USEPA, 1994a).

Since toxic sites may become the focus for dredging actions, sediment cores were

obtained. If the feasibility of a dredging operation is to be evaluated, the volume of sediments to be removed and the contaminant status of the sediments thus exposed to the environment would need to be known. If natural capping of the sediments due to influx of new sediments is to be evaluated as a remediation alternative, a sediment transport model based on a mass balance approach will be required. Such a project was beyond the scope of the current study.

Based on previous studies (Batelle 1994a, Batelle 1994b, Batelle 1997, Ganet Fleming 1993, PADEP 1992, PADEP 1993, PADER 1996, Potomac-Hudson Engineering 1991) it was concluded that the contaminants of potential concern included PAHs, and the metals cadmium, nickel and zinc, which, along with copper and lead, are included in the operational grouping referred to as Simultaneously Extracted Metals (SEM). Using USEPA-approved methods, the specific activities conducted in the project were as follows.

1. Surface sediment samples were obtained by Ponar grab samplers at the 10 locations for benthic macroinvertebrate community structure analysis. Other sites were included in hopes of finding a more pristine location for use as a reference. Three (3) replicate samples were obtained at each site. Surface sediment samples were also evaluated for the following constituents: particle size distribution, TOC, oil and grease (Hexane Extractable Material), PAHs (Method 8100 with GC-FID), AVS and SEM (Cd, Cu, Pb, Ni, Zn), and total extractable metals analysis for Cd, Cu, Pb, Ni, Zn.

2. Whole sediment toxicity assays were conducted by the Ecotoxicology Lab of the Department of Biological Sciences at Virginia Tech in Blacksburg, VA, on homogenized surface samples from each of the 10 sites. The toxicology lab supplied a reference sediment from a local pristine stream bed. One of the 10 sites was supplied as a duplicate for QA/QC purposes. The parameters evaluated were survival and reproduction in *Daphnia magna*, growth and survival with *C. tentans*; growth and survival for *H. azteca*.

3. At the 10 sites, 3-ft (~1-m) sediment cores were collected. The cores were sectioned into 2 layers from which samples were taken for chemical analysis. Sediment core layers were analyzed for particle size distribution, TOC, oil and grease (Hexane Extractable Material), PAHs (Method 8100 with GC-FID), and total extractable metals analysis for Cd, Cu, Ni, Pb, and Zn.

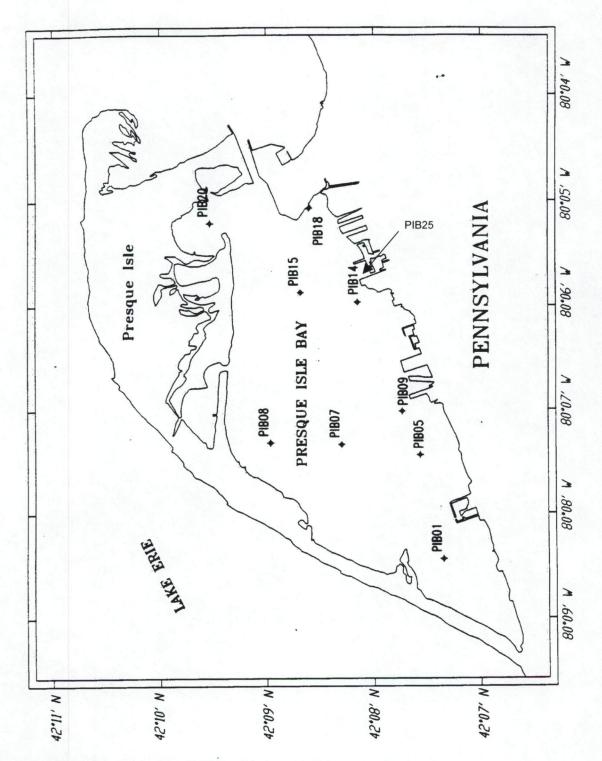


Figure 1. Sites selected for sampling during the study.

B. Sampling and Analytical Methods

B1. Method Selection.

Methods were selected from the Great Lakes Dredged Material Testing & Evaluation Manual (USEPA and USACE, 1998), SW-846 (USEPA, 1990) and the USACE Inland Testing Manual (ITM).

The method specified for measurement of acid volatile sulfides and simultaneously extracted metals (AVS/SEM) is a draft EPA method (Allen et al., 1991).

Analysis of benthic macroinvertebrate community structure was in accordance with the GLNPO's ARCS Assessment Guidance Document (USEPA 1994a) with supporting guidance provided by the Lake and Reservoir Bioassessment and Biocriteria - Technical Guidance Document (USEPA, 1998).

B2. Sampling

Samples were collected over a 10 day period beginning June 5, 2000. Sample processing proceeded immediately after sample collection. Initial sample analysis/extraction was performed within required holding times. Sediment toxicity tests were initiated within 14 days of the collection of the sediments.

The procedures for sample collection, handling, and storage (Table 1) were adapted from the ITM.

B3. Analytical Methods

The methods named below were taken variously from the EPA's SW-846 system and the USACE/EPA's Great Lakes Dredged Material Testing & Evaluation Manual (GLTEM), as revised August, 1999.

B.3.1. Acid Volatile Sulfides and Simultaneously Extracted Metals

The method used for the determination of acid volatile sulfides and simultaneously extracted metals was according to "Draft Method for the Determination of Acid Volatile Sulfides And Simultaneously Extracted Metals" (Allen et al., 1991). The designated metals (Cd, Cu, Pb, Ni, Zn) released in the digestion step were analyzed using a flame atomic absorption spectrophotometer in accordance with the general guidelines specified in SW-846 Method 7000A and specific methods appropriate to each metal (Cd: Method 7130, Cu: Method 7210, Pb: Method 7420, Ni: Method 7520, Zn: Method 7950).

B.3.2. Ammonia

Ammonia in pore-water was analyzed according to the method described in the GLTEM for "Ammonia Nitrogen in Sediments: Colorimetric Manual".

Table 1. Summary of Procedures for Sample Collection, Preservation, and Storage of Sediments.^a

| Analyses | Collection Method ^b | Amount Required | Container ^c | Preservation Technique | Storage Conditions | Holding times ^{<u>d</u>} |
|--|-----------------------------------|--|--|--|-----------------------|--|
| AVS | Grab | 100 g | Pre-washed plastic | Completely fill and refrigerate | ≤ 4 ° C | 14 days |
| SEM Metals | Filtrate from AVS digestion | 120 mL of filtrate | Pre-washed plastic | None necessary | Room temp | 14 days after extraction |
| Total Metals | Grab/Corer | 200 g | Pre-washed plastic | Completely fill and refrigerate | ≤ 4 ° C | 6 mos. |
| Organic compounds (PAHs) | Grab/corer | 250 g | Solvent-rinsed glass jar with Teflon lid | Freeze/ refrigerate | ≤ 4 ° C /dark | 14 days, then 40 days after extraction |
| Particle size | Grab/corer | 100 g | Pre-washed plastic | Refrigerate | ≤ 4 ° C | indefinite |
| Total Organic Carbon | Grab/corer | 50 g | Pre-washed plastic | Freeze/ refrigerate | ≤ 4 ° C | 40 days |
| Oil & Grease | Grab/corer | 100 g | glass jar with Teflon lid | Freeze/ refrigerate | ≤ 4 ° C | 28 days |
| Ammonia | Grab/corer | ~50g | Pre-washed plastic | Refrigerate | ≤ 4 ° C | 28 days |
| Biological Test benthic macro- invertebrates | Grab | A full Ponar grab sample per replicate | Plastic bag or container | Completely fill and refrigerate; sieve | | 14 days |
| Biological Test toxicity assays | Grab | A full Ponar grab sample per site | Plastic bag or container | Completely fill and refrigerate; sieve | | 14 days |

a -- This table is derived from the USACE's Inland Testing Manual, and contains only a summary of collection, preservation, and storage procedures for samples.

B.3.3. Total Extractable Metals (Cu, Cd, Ni, Pb, Zn)

Surficial (grab) samples and core layers were analyzed for cadmium, copper, lead, nickel, and zinc as total extractable metals using the SW-846 digestion Method 3050B, followed by direct aspiration atomic absorption spectrophotometry. This extraction method does not completely digest silicate minerals but, as stated in the method, " is a very strong acid digestion that will dissolve almost all elements that could become environmentally available."

B.3.4. Oil & Grease

The procedure used to estimate oil & grease in the sediments was the SW-846 Method

b -- Collection method should include appropriate liners.

c -- All containers should be certified as clean according to EPA (1990a).

d -- Holding times are from the time of sample collection.

9071B - Hexane Extractable Material.

B.3.5. Particle Size Determinations

The particle size analysis was conducted in accordance with the procedure as specified in the GLTEM which was developed by the US Army Corps of Engineers.

B.3.6. Polycyclic Aromatic Hydrocarbons

Extraction & Clean-up: SW-846 Method 3540C "Soxhlet Extraction" was employed for the extraction of PAHs from the sediment samples. Method 3630 was employed as a silica-gel clean-up step prior to analysis.

Analysis: Method 8100 of the SW-846 system was used for the analysis of PAH compounds. The gas chromatograph with flame ionization detector employed uses a capillary column instead of a packed column, and thus was able to produce satisfactory resolution of the various PAH compounds for the purposes of this study.

B.3.7. Total Organic Carbon (TOC)

Sediments were analyzed in a Shimadzu TOC-5050 Carbon Analyzer according to the TOC method stated in the GLTEM and in accordance with the manufacturer's guidelines.

B.3.8. Whole Sediment Toxicity Testing

Sediment toxicity tests were conducted with three species, *Daphnia magna*, *Chironomus tentans*, and *Hyalella azteca*, following guidelines developed by the USEPA (1994b) and ASTM (1995). The 28-day sediment toxicity test with *Hyallela azteca* was conducted according to Ingersoll et al. (1998), which was used as a revision to the USEPA (1994b) sediment toxicity testing method.

B.3.9. Benthic Macroinvertebrate Community Structure

Analysis of benthic macroinvertebrate community structure was in accordance with the GLNPO's <u>ARCS Assessment Guidance Document</u> (EPA, 1994a), with supporting guidance provided by the <u>Lake and Reservoir Bioassessment and Biocriteria - Technical Guidance</u> <u>Document</u> (USEPA, 1998). Additionally, ten (10) individuals of the Chironimid family from each site were examined for mouthpart deformities, according to the method of Warwick (1989).

C. Results & Discussion

C1. Physical Appearance and Aggregate Characteristics

The sediments were generally black or dark brown in appearance, and were described by research assistants as gooey and sticky in texture. Some grab samples had a reddish-brown surface coating, presumed to be oxidized iron hydroxides. Some samples had a mild sulfide odor, but generally did not have an odor of petroleum. Oily films were not observed on or in the samples.

C.1.1. Particle Size Distributions

The size categories appropriate for this study are sand (2.0 mm to 0.05 mm), silt (0.05 mm to 0.002 mm), and clay (< 0.002 mm). Zebra mussel shells were found in a few of the locations. In order to not distort the size distribution, zebra mussel shells were excluded from the particle size distribution analysis.

Sand was increasingly common for deeper samples. Grab samples averaged 16.5% sand, while the top core layer averaged 20% sand and the bottom core layer averaged 28% sand (Table 2). Silt was the most abundant size category, ranging from a mean of 42.8% (grab) to 49.6% (bottom layer). Clay-sized particles made up 22% of the bottom layer, 44% of the top core layer, and 40.8% of the grab samples.

Table 2. Size distribution for Presque Isle Bay samples.

Percent in each size category **BOTTOM CORE LAYER** GRAB (SURFACE) TOP CORE LAYER Sand Silt Clay Sand Silt Clay Sand Silt Clay Site PIB01 PIB05 PIB07 PIB08 PIB09 PIB14 PIB15 PIB18 PIB₂₀ PIB25 **MEAN** 16.5 42.8 40.8 20.2 35.6 28.3 49.6

C.1.2. Moisture Content

The moisture content of samples generally decreased with depth. Grab (surface) samples had average moisture contents of 68%, while core samples had average moisture contents of 57% (top) and 41% (bottom).

C.1.3. Total Organic Carbon Concentration

Organic carbon content of the sediments generally decreased with depth (Figure 2). Grab samples ranged in value from 2.6 to 5.6% organic carbon dry wt., with a mean of 3.8%. Top core layer samples had a mean organic carbon concentration of 2.5%, with a range of 0.8 to 4.3%. Bottom layer samples had a mean of 1.1%, with a range of 0.3 to 3.5%. Samples in the eastern portions of the bay generally had higher organic carbon contents than those in the western end of the bay, with the exception of site PIB25, which is in an area which is occasionally dredged for navigation purposes.

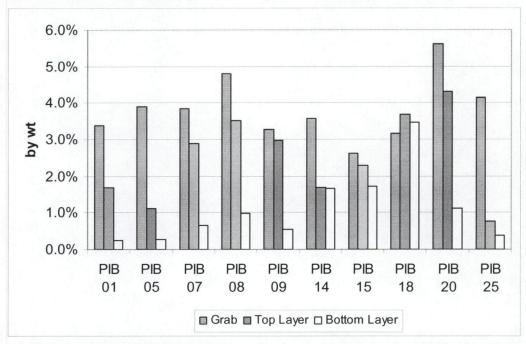


Figure 2. Organic carbon concentration expressed in % dry weight for Presque Isle Bay sites.

C.1.4. Oil & Grease

Oil and grease was determined by means of the Hexane Extractable Material method as previously mentioned. Therefore, the appropriate acronym for these analytical results is HEM, since a different method (Freon) would likely yield a different result.

It was found that at least one sample from each site exceeded the USEPA (1977) Bulk Sediment Chemical Criteria "highly polluted" level for O&G of 2,000 mg/kg dry sediment (Figure 3). In most cases, grab samples had the highest levels of HEM, and in every case but one, the bottom layer samples had the lowest levels of HEM. HEM values ranged from a low of 267 to 12,033 mg/kg dry sediment.

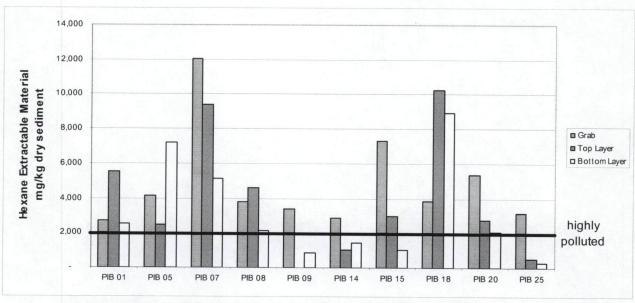


Figure 3. Hexane extractable material in Presque Isle Bay sediment samples. "highly polluted" reference line is from USEPA 1977 Bulk Sediment Chemical Criteria guidelines for oil & grease.

C2. Chemical Analysis

C.2.1. Ammonia

Ammonia is a product of the biological breakdown of proteins. It is highly toxic to most aquatic organisms, but only in the un-ionized form (NH₃). The fraction of the total ammonia nitrogen which is un-ionized is a function of pH. No attempt was made to measure *in situ* pH of sediments, but anaerobic metabolism in anoxic sediments generally leads to a lowering of pH. At pH values below neutral (i.e., pH 6), less than 0.1% of the total ammonia would be un-ionized. Only grab samples were analyzed for ammonia. It was found that the ammonia concentration in sediment samples did not vary significantly from that of the field blanks and reagent blanks.

C.2.2. Heavy Metals

Heavy metals in sediments were assessed by two digestion methods, followed by atomic absorption spectrophotometry. Total extractable metals were measured after aggressive digestion with strong acids and heat and may not normally be available to organisms in the sediments (Hansen et al. 1998). A milder digestion is used in the AVS/SEM method, which is intended to suggest bioavailability. The levels at which heavy metals become toxic to aquatic organisms are controversial. The state of New York has adopted a set of sediment criteria (DEC, 1999) represented by lowest effects level (LEL): that level which "can be tolerated by the majority of benthic organisms, but still causes toxicity to a few species", and severe effect level (SEL): a level such that "pronounced disturbance of the sediment dwelling community can be expected." A widely referenced publication (Ingersoll et al. 2000) advocates the use of a probable

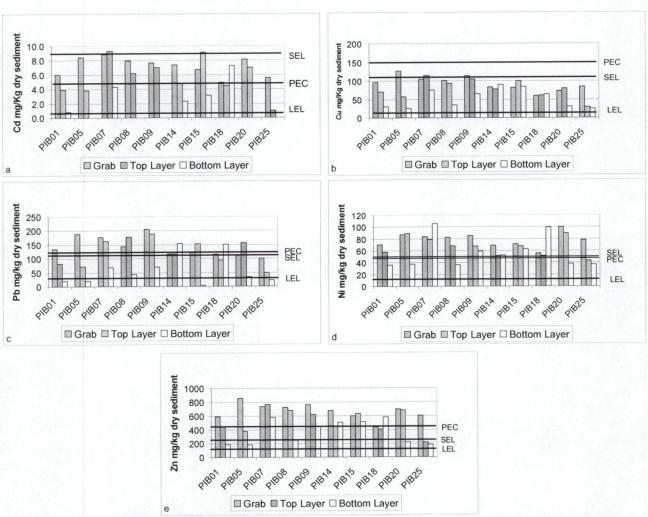


Figure 4 a-e. Heavy metal concentrations (total extractable) in Presque Isle Bay sediments; Fig 5a – cadmium, Fig 5b – copper, Fig 5c – lead, Fig 5d – nickel, Fig 5e – zinc. Lines for LEL= lowest effects level, SEL= severe effects level, and PEC= probable effects concentration; see text for citations.

effects concentration (PEC), developed by reviewing a variety of prior studies of toxic effects of sediments with varying levels of heavy metals.

C.2.2.1. Total

Bay sediments were analyzed for five heavy metals: cadmium, copper, lead, nickel, and zinc. It was found that in samples from every site these heavy metals were present at levels in excess of the LEL, and in many cases were present at concentrations above the SEL and/or PEC. a through e present the findings for grab and core samples at each site.

C.2.2.2. Acid Volatile Sulfide (AVS) and Simultaneously Extracted Metals (SEM)

The most common metal sulfide precipitates in sediments are those of iron and manganese. Most divalent toxic heavy metals also form insoluble precipitates with sulfide. Since the solubilities of most toxic heavy metals are lower than those of ferrous sulfide and manganous sulfide, the toxic heavy metals are unlikely to dissolve so long as there is sufficient sulfide available to form precipitates. Therefore, one hypothesis (Hansen et al. 1998) states that if there is an excess of sulfide compared to toxic heavy metals, the likelihood that these metals would become available to organisms would be low. The analytical protocol for measuring this ratio (which involves a mild acid digestion) and the hypothesis behind it is controversial, and is not endorsed in final form by the EPA (Allen et al., 1991). Thus, the method continues to be in "draft" form. The draft method suggests that if the SEM:AVS ratio is less than one (1), the probability of the toxic heavy metals becoming bioavailable is low.

Samples for this analysis were carefully removed from grab samples without mixing and without long exposure to air. It was thought that these samples would most closely represent the sediment occupied by benthic organisms and most likely to release metals to the overlying water column. For all samples thus analyzed, the SEM:AVS ratio was below one (1) for all sites (Figure 5). This suggests that while heavy metals are present in Bay sediments, there may be sufficient sulfide present to prevent these metals from becoming bioavailable.

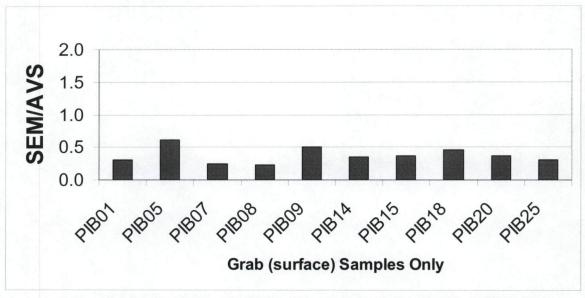


Figure 5. Molar ratio of simultaneously extracted metals (SEM) to acid volatile sulfide (AVS) released during mild digestion as specified in the EPA draft analytical protocol (Allen et al., 1991).

C.2.3. Polycyclic Aromatic Hydrocarbons (PAHs)

Persistent organic compounds which present a risk to aquatic organisms and human health include non-chlorinated fused ring compounds known as PAHs. Guidelines for assessing the toxicity of PAH-contaminated sediments have been provided by Ingersoll, et al. (2000). While individual PAH compounds were quantified, for simplicity this document will report values for total PAHs only (the simple sum of the concentrations of the 16 priority PAHs). The probable effects concentration (PEC) for total PAHs, which is not adjusted for organic carbon content of the sediments, is 22.8 mg/kg dry sediment, and is indicated by a noticeable line in

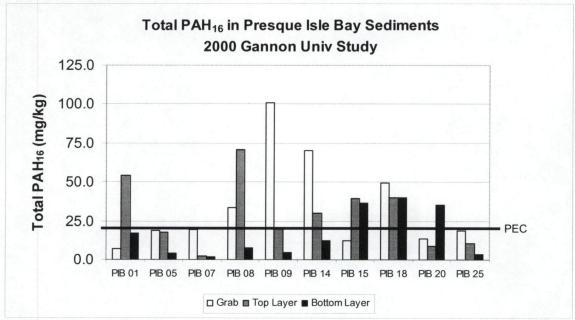


Figure 6. The Ingersoll et al. (2000) report does not advocate normalizing organic contaminants to organic carbon

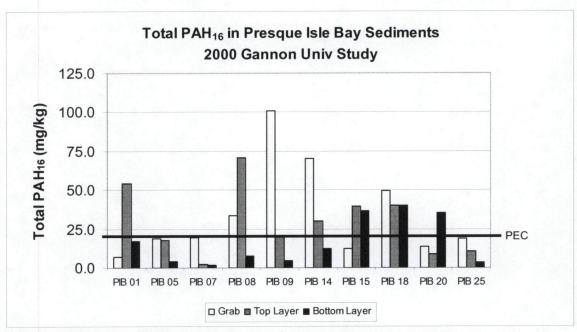


Figure 6. Total PAH concentration in sediment samples from Presque Isle Bay.

content as some prior studies have advocated, because they did not observe a correlation between toxicity and organic matter concentration.

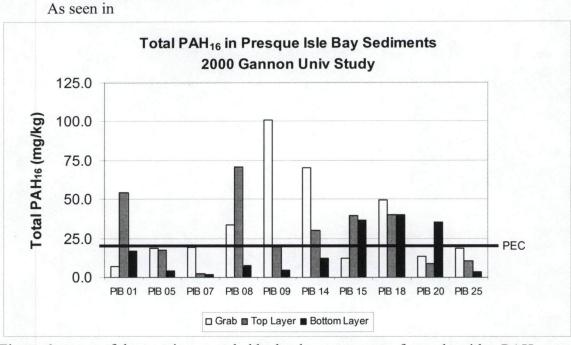
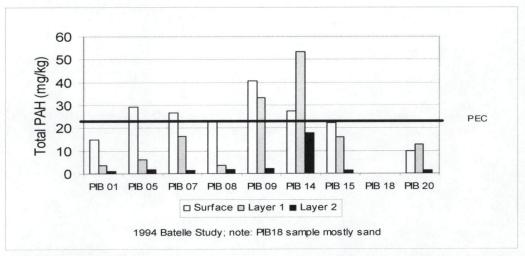


Figure 6, seven of the ten sites sampled had at least one type of sample with a PAH concentration above the PEC. Five of the grab samples exceeded the PEC, while four of



the top layer samples and only two of the bottom layer samples did so. At six sites, the surface sample had a higher concentration than did the deep sample, a pattern similar to that found in the 1994 Batelle study (Figure 7).

Figure 7. Total PAH concentrations found in Presque Isle Bay samples in a prior study. (Batelle, 1994)

C3. Benthic Community Structure

Benthic macroinvertebrate organisms were collected, sorted, and identified in accordance with section B.3.9 of this document. The purpose of benthic macroinvertebrate community analysis was to document the quality of the sediment habitat in terms of biodiversity, abundance, and occurrence/absence of certain pollution tolerant groups.

The number of all organisms found at each site was adjusted to a per square meter basis (m⁻²) and is reported in Figure 8. The organism density was greatest at sites PIB 12, 14, 15, 18, and 25, where more than 3,000 organisms m⁻² were collected. The other sites had about 2,000 m⁻² or less.

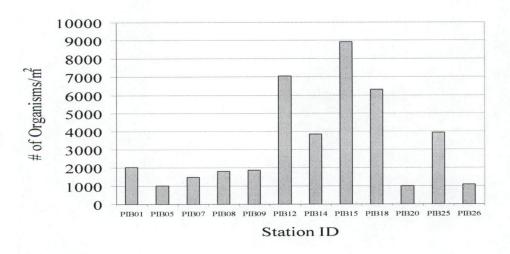


Figure 8. Mean density of benthic organisms at each site (n = 3).

To a large degree, the high density at these sites can be explained by the presence of zebra mussels (*Dreissena*), and two pollution-tolerant types: segmented worms (Oligochaetae), and midges (Chironimidae), and moderately tolerant gastropods and amphipods (Figure 9), although there was considerable variation in the most abundant taxa at each of those sites.

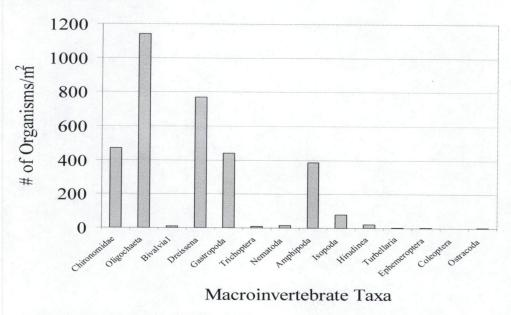


Figure 9. Average density of benthic organisms by taxa at all PIB sites.

Zebra mussels were found to some degree at most sites, but were abundant at PIB 1 and 14, and particularly at PIB 15 where there were more than 4,500 individuals m⁻² (Figure 10).

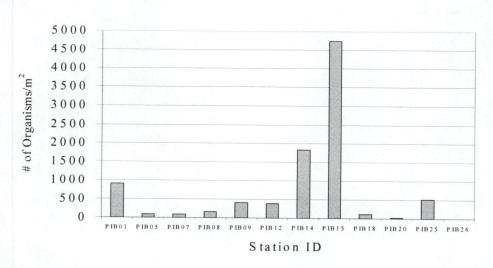


Figure 10. Density of zebra mussels (Dreissena) at each station (mean of 3 samples).

Oligochaetes (segmented worms) were found all sites (Figure 11), but were particularly abundant at sites PIB 12 and 25 which had more than 1,000 individuals m⁻², and PIB 18 which had nearly 6,000 m⁻².

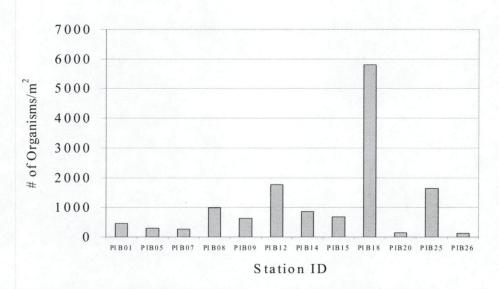


Figure 11. Density of Oligochaetae at each station (mean of 3 samples).

Midges (chironimid larvae) were found at all sites. The density of chironimids ranged from about 150 m⁻² at PIB 12 to over 900 m⁻² at PIB 26 (**Figure 12**).

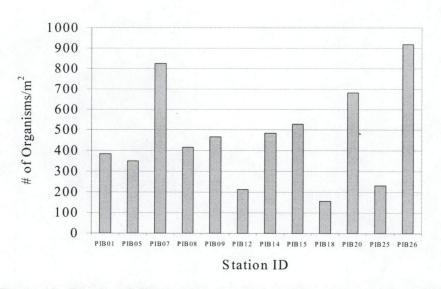


Figure 12. Density of Chironimidae at each station (mean of 3 samples).

More pollution-sensitive taxa include Ephemoptera (mayflies), Plecoptera (stoneflies) and Trichoptera (caddis flies). These taxa were absent or rare in PIB sediments. Notice the vertical axis in Figure 13, indicating that only a few individuals were found at certain sites and none at others. No plecopterans were found at any site.

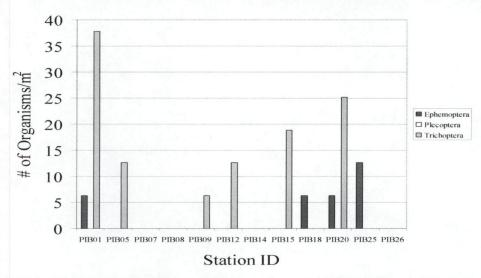


Figure 13. Density of Ephemoptera, Plecoptera, and Trichoptera and at PIB sites.

C4. Sediment Toxicity

C.4.1. Bioassays

Three organisms were used to assess the toxicity of the sediments by means of laboratory bioassays. The end points for these tests were, variously, survival, reproduction, and growth when organisms were exposed to the test sediments. Control sediments were collected from a remote stream considered to be "pristine". The *Daphnia magna* test was a 7-day test, the *Chironimous tentans* test was a 10-day test, while the test with *Hyallela azteca* was a 28-day test. Much of the following is from the report prepared by the testing laboratory (Cherry, et al., 2000) whose report is included in the appendix.

All data were tested for normality (Shapiro Wilks Test for Normality, α =0.05) then analyzed using the appropriate parametric or nonparametric statistical tests (One-Way Parametric ANOVA, NPAR1WAY ANOVA, α =0.05). Multiple Range Tests (MRT) (Tukeys, α =0.05) were used to determine significant differences between sites.

Although survival of *C. tentans* was slightly lower in the PIB sediments than the control, the difference was not significant (Figure 14). Growth of the organisms during the test was both greater and less than the control for various PIB sites, and not significantly different from the control (Figure 15).

Survival and growth of H. azteca in PIB sediments was also not significantly different from the control.

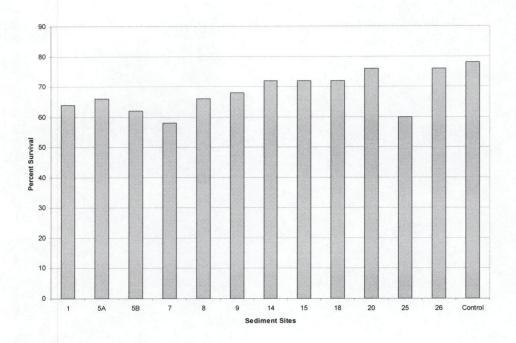


Figure 14. Survival of C. tentans in PIB sediments.

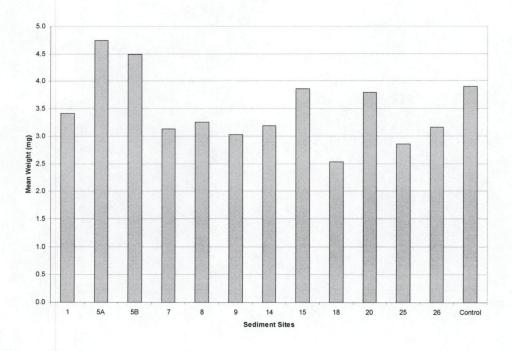


Figure 15. Growth of C. tentans in PIB sediments.

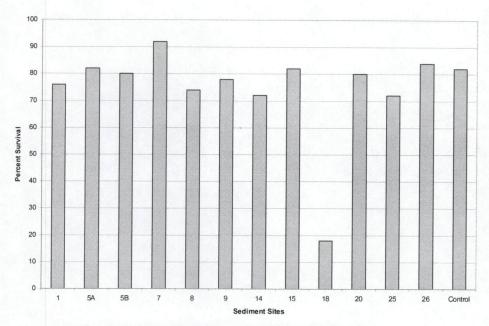


Figure 16. Survival of *H. azteca* in PIB sediments.

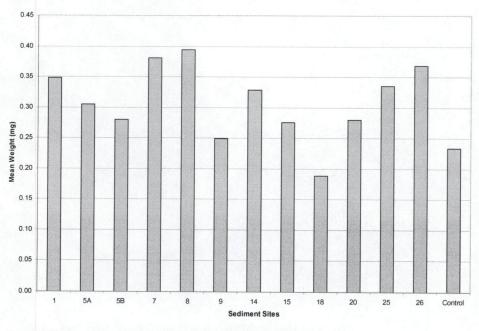


Figure 17. Growth of *H. azteca* in PIB sediments.

The response of *D. magna* was more sensitive to PIB sediments. Survival of the organisms (Figure 18) was not significantly different from the control (although two sites had only 60% survival and one site had 40% survival while the control had 100%

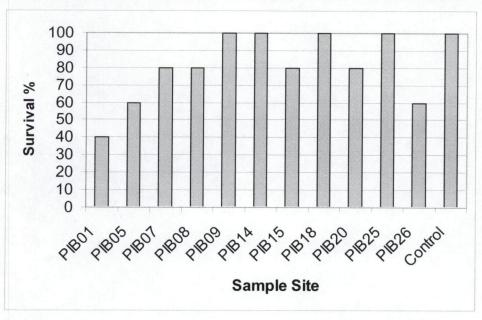


Figure 18. Suvival of D. magna in PIB sediments.

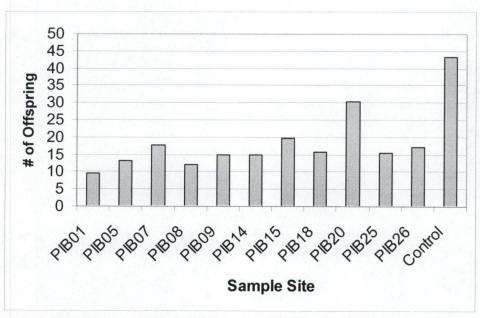


Figure 19. Reproduction of D. magna in PIB sediments.

survival). Reproduction was significantly affected by sediments from seven of the sites compared to the control (Figure 19), and at all of the test sites yielded lower reproductive behavior than was observed in the control sediments

Nebeker et al. (1984) suggested that *Daphnia* appeared to be especially sensitive to metals, while midges (Chironimids), which burrow into the sediment may be more sensitive to toxic organics.

C.4.2. Chironimid Mouthpart Deformities

Another indication of sediment toxicity is the occurrence of deformities in the mouthparts of chironimids (Bird, et al., 1995; Hamilton and Saether, 1971; Warwick, 1985). Guidance for identifying deformities was obtained from Warwick (1989). Ten individuals from each of nine sites were chosen at random from the benthic macroinvertebrate samples collected for community structure analysis, for a total of ninety individuals examined. Only one individual exhibited mouthpart deformities.

C5. Ranking of Sites based on Ratios

Sites were ranked based on the findings for the grab samples obtained by Ponar dredge. Results for each parameter were compared to the appropriate reference value to obtain a ratio, either a toxicity unit ratio or a proportional response ratio. For metals, the PEC value was used; for PAHs, the value for Total PAHs was used since there are no widely accepted values for some of the individual compounds. For toxicity results, responses were compared to those of the control sediments. For the benthos, the percentage contribution of oligochaetes + chironimids was used as an indication of distortion (with a high percentage being taken as undesirable).

A consolidated score was calculated for each of the three components of the Triad (chemistry, toxicity, and benthos). These scores were then combined, and the total combined score ranked to indicate the relative environmental quality of each site. The result of this analysis is presented in Table 3.

Table 3. Ranking of sites based on consolidated findings.

| | Rankings wi | thin Paramete | Combined | Final | |
|--------|-------------|---------------|----------|-------|------|
| Site | Chemistry | Toxicity | Benthos | Score | Rank |
| PIB 15 | 5 | 4 | 1 | 10 | 1 |
| PIB 25 | 2 | 2 | 8 | 12 | 2 |
| PIB 01 | 1 | 10 | 4 | 15 | 3 |
| PIB 07 | 8 | 4 | 3 | 15 | 3 |
| PIB 20 | 6 | 7 | 2 | 15 | 3 |
| PIB 14 | 3 | 9 | 5 | 17 | 6 |
| PIB 18 | 6 | 1 | 10 | 17 | 6 |
| PIB 09 | 9 | 3 | 7 | 19 | 8 |
| PIB 08 | 3 | 8 | 9 | 20 | 9 |
| PIB 05 | 10 | 6 | 6 | 22 | 10 |

note: rankings are from 1 (best) to 10 (worst).

D. Quality Assurance/ Quality Control

Prior to conducting any field or laboratory work, a Quality Assurance Project Plan was developed by the Principal Investigator and approved by the USEPA's GLNPO office. All study activities complied with the requirements of that plan. A summary of the various quality control indicator results is presented in Table 4. Comments on some analyses follow.

Table 4 Summary of Analytical Data Quality Indicators for Sediment Samples

| A 1 - 4 - | Precision 1 | Accuracy (%) | Completeness (%) |
|--------------------|---------------|---------------|------------------|
| Analyte | (Goal) Actual | (Goal) Actual | (Goal = 95) |
| Total Metals | (<20) 11 | (65-125) 82 | 100 |
| SEM | (<20) 2 | (80-120) 88 | 100 |
| AVS | (<20) 10 | (80-120) 74 | 100 |
| Particle Size | (<50) 15 | N/A | 100 |
| HEM (oil & grease) | (<20) 44 | (80-120) 114 | 97 |
| TOC | (<20) 7 | (80-120) 101 | 100 |
| PAHs | (<50) 33 | $(50-130)^2$ | 100 |
| Percent Moisture | (<20) 8 | N/A | 100 |

RPD = Relative Percent Difference

N/A = Not Applicable

The results for AVS indicate good reproducibility but low recovery of sulfide. While undesirable, this would suggest a conservative result, since a higher recovery of sulfide would result in a lower SEM/AVS ratio, which would indicate a less bioavailable reality for these toxic metals.

The oil & grease (HEM) results reflect the extreme variability of the analysis and the difficulty in recovering a small mass of material from relatively small (\sim 10 g) samples. The result is dependant upon small weight changes (a few milligrams) for a rather heavy flask (90 – 100 g) which are then multiplied by a large factor to then express a result in terms of mg kg⁻¹ dry weight. In spite of this, recovery of spiked material was good (114%).

Quantification of PAHs employed the use of one of the surrogates (2-fluorobiphenyl) as an internal calibration standard. The relative response for each analyte compared to 2-fluorobiphenyl was determined. Recovery of analytes was assumed to be similar to recovery of surrogates which were added to each sediment sample prior to extraction. Repeated analysis of the PAH standard solution on each day of GC analysis was used to identify the retention time windows for individual compound identification for that day. Repeated analysis of the same extract (PIB05-Layer 2) yielded good reproducibility (Table 5). The relative standard deviation (RSD) for this set of replicates was 0.354. Similarly, replicates of sample PIB05-Grab yielded an RSD of 16 %, and replicates of PIB25-Layer 2 yielded an RPD of 13%. However, the analysis of field duplicates (samples collected from the same general location at approximately the same time) led to widely differing values: for PIB14, PAH values of 3.4 and 21 mg/kg (RPD =

² see below for discussion of PAH analysis

139%) and for PIB20, PAH values of 13 and 58 mg/kg (RPD = 128%).

Table 5. Replicate PAH analysis of a single extract of PIB sediments.

| PIB05-C-L2-G-C-01 | | Replicate | | |
|------------------------|------|-----------|------|--|
| PAH | No 1 | No 2 | No 3 | |
| naphthalene | nd | nd | nd | |
| acenaphthene | 0.39 | 0.43 | 0.48 | |
| acenaphthylene | 0.39 | 0.43 | 0.48 | |
| fluorene | nd | nd | nd | |
| phenanthrene | 0.30 | 0.41 | 0.72 | |
| anthracene | nd | nd | nd | |
| fluoranthene | 0.38 | 0.37 | 0.74 | |
| pyrene | nd | nd | nd | |
| benzo(a)anthracene | nd | nd | nd | |
| chrysene | 0.46 | 0.27 | 0.91 | |
| benzo()fluoranthene | 2.04 | 1.08 | 2.77 | |
| benzo(a)pyrene | nd | nd | nd | |
| dibenzo(a,h)anthracene | nd | nd | nd | |
| indeno(1,2,3-cd)pyrene | nd | nd | nd | |
| benzo(ghi)perylene | nd | 0.13 | nd | |
| Totals | 3.96 | 3.12 | 6.10 | |

E. Conclusions and Recommendations

The sediments of Presque Isle Bay are contaminated with heavy metals, polycyclic aromatic hydrocarbons (PAHs), and oil & grease. While the metals and PAHs appear to be tightly bound to the sediments, the presence of these contaminants, combined with the very fine particle sizes typically found in the Bay sediments, result in a relatively inhospitable environment for sediment-dwelling organisms, as exhibited by the distorted community structure presented above. The benthic community is clearly dominated by pollution-tolerant organisms, such as worms, midges, and snails, and is relatively lacking in those species which are known to be sensitive to stressful conditions, such as mayflies and caddisflies.

In vitro bioassays yielded mixed results. There was essentially no toxicity observed with the amphipod and midge larvae, but this was not particularly surprising since these types of organisms are found to occur naturally in these sediments. The water flea, Daphnia magna, is considered by many aquatic ecotoxicologists to be one of the most sensitive organisms, and that sensitivity was demonstrated by diminished reproductive success when exposed to PIB sediments. D. magna is a ubiquitous freshwater organism and this toxic effect should not be dismissed.

The impairment of Presque Isle Bay sediments should be considered modest only when it is compared with other Great Lakes sites which have dramatically higher levels of toxic contaminants. Nonetheless, water quality of the Bay appears to be satisfactory, and the fishery appears to be robust (although continued concern for the incidence of

tumors in bottom dwelling fish should be noted).

The management alternatives for Presque Isle Bay include active in-Bay actions such as dredging or capping. Due to the size and depth of the Bay, both of these options appear to be costly and/or impractical. However, the removal of the top 0.5 m of sediments would expose materials with much lower concentrations of all contaminants. A more practical approach may be to focus efforts on improving the release and transport of contaminants from the watershed into the Bay. Eventually, the natural transport of sediments into the Bay will cover the existing sediments and to some degree isolate it from the biotic environment. There is no evidence, however, that sediments currently moving down the Bay's tributaries are less contaminated that those in the Bay, but there is hope that aggressive efforts within the community could result in this desirable environmental goal.

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G. Appendix

G1. Moisture Content

Table 6. Moisture content (expressed as fraction moisture by mass) of PIB sediment samples.

| | Moisture conten | t (fraction by mass) | | |
|-------|-----------------|----------------------|--------------|--|
| Site | GRAB | Top Layer | Bottom Layer | |
| PIB01 | 0.69 | 0.55 | 0.30 | |
| PIB05 | 0.73 | 0.48 | 0.34 | |
| PIB07 | 0.68 | 0.69 | 0.46 | |
| PIB08 | 0.79 | 0.70 | 0.42 | |
| PIB09 | 0.66 | 0.59 | 0.37 | |
| PIB14 | 0.65 | 0.46 | 0.45 | |
| PIB15 | 0.62 | 0.61 | 0.50 | |
| PIB18 | 0.55 | 0.51 | 0.49 | |
| PIB20 | 0.75 | 0.70 | 0.46 | |
| PIB25 | 0.71 | 0.37 | 0.30 | |
| MEAN | 0.68 | 0.57 | 0.41 | |

G2. Total Organic Carbon

Table 7. Total organic carbon content (expressed as percentage by dry mass) of PIB sediment samples.

| | | TOC by mass | |
|--------|-------|-------------|--------------|
| Site | Grab | Top Layer | Bottom Layer |
| PIB 01 | 3.4% | 1.7% | 0.3% |
| PIB 05 | 3.9% | 1.1% | 0.3% |
| PIB 07 | 3.8% | 2.9% | 0.7% |
| PIB 08 | 4.8% | 3.5% | 1.0% |
| PIB 09 | 3.3% | 3.0% | 0.6% |
| PIB 14 | 3.6% | 1.7% | 1.7% |
| PIB 15 | 2.6% | 2.3% | 1.7% |
| PIB 18 | 3.2% | 3.7% | 3.5% |
| PIB 20 | 5.6% | 4.3% | 1.1% |
| PIB 25 | 4.1% | 0.8% | 0.4% |
| mean | 3.84% | 2.49% | 1.10% |

G3. Hexane Extractable Material (oil & grease)

Table 8. Hexane extractable material in PIB sediments.

Hexane Extractable Material (mg/kg dry mass) Site Grab Top Layer **Bottom Layer** PIB 01 2,710 5,538 2,553 **PIB 05** 4,172 2,490 7,187 **PIB 07** 12,033 9,365 5,108 **PIB 08** 3,823 4,589 2,143 **PIB 09** 3,426 X 856 **PIB 14** 2,885 1,063 1,449 **PIB 15** 7,300 2,980 1,051 **PIB 18** 3,882 10,234 8,905 **PIB 20** 5,348 2,771 2,079 **PIB 25** 3,191 514 267 mean 4,877 4,394 3,160

G4. Sediment Ammonia Content

Table 9. Ammonia content of PIB sediments (Ponar grab samples only).

| Site | NH3-N (mg/kg moist sed) |
|---------------|-------------------------|
| PIB01 | 50.3 |
| PIB01 dup | 38.6 |
| PIB05 | 13.1 |
| PIB07 | 39.2 |
| PIB08 | 46.3 |
| PIB09 | 43.1 |
| PIB14 | 35.8 |
| PIB15 | 15.5 |
| PIB18 | 80.5 |
| PIB20 | 53.3 |
| PIB25 | 102.8 |
| PIB25 dup | 74.4 |
| Field Blank 1 | 28.2 |
| Field Blank 2 | 108.6 |
| mean | 49.4 |

G5. Total Extractable Metals

Table 10. Cadmium in PIB sediments.

Cd (mg/kg dry sediment) Site Grab Top Layer **Bottom Layer PIB 01** 6.1 3.9 8.0 **PIB 05** 8.5 3.8 nd **PIB 07** 8.9 9.3 4.3 **PIB 08** 8.0 6.2 nd **PIB 09** 9.0 7.0 nd **PIB 14** 2.2 7.4 4.8 **PIB 15** 6.7 9.4 3.1 **PIB 18** 5.0 4.6 7.3 **PIB 20** 8.1 7.1 nd **PIB 25** 5.6 1.0 nd 5.7 mean 7.3 3.6

Table 11. Copper in PIB sediments.

Cu (mg/kg dry sediment) Site Grab Top Layer **Bottom Layer** PIB 01 97 72 30 **PIB 05** 127 57 26 **PIB 07** 104 116 76 **PIB 08** 101 93 35 **PIB 09** 116 104 38 **PIB 14** 82 78 83 **PIB 15** 82 100 85 **PIB 18** 60 61 64 **PIB 20** 73 80 29 **PIB 25** 84 29 25 93 79 mean 49

Table 12. Lead in PIB sediments.

Pb (mg/kg dry sediment) Site Grab Top Layer **Bottom Layer** PIB 01 **PIB 05 PIB 07 PIB 08 PIB 09 PIB 14 PIB 15 PIB 18 PIB 20 PIB 25** mean

Table 13. Nickel in PIB Sediments.

Ni (mg/kg dry sediment) Grab **Bottom Layer** Site Top Layer **PIB 01 PIB 05 PIB 07 PIB 08 PIB 09 PIB 14 PIB 15 PIB 18 PIB 20 PIB 25** mean

Table 14. Zinc in PIB Sediments.

Zn (mg/kg dry sediment) Site Grab Top Layer **Bottom Layer** PIB 01 **PIB 05 PIB 07 PIB 08 PIB 09 PIB 14 PIB 15 PIB 18 PIB 20 PIB 25** mean

G6. Acid Volatile Sulfide / Simultaneously Extracted Metals

Table 15. Acid volatile sulfide and simultaneously extracted metals in PIB sediments.

| u moles/g Total SEM | | | | | AVS | Ratio | | |
|---------------------|---------|--------|-------|--------|-------|-------|-------|---------|
| Site | Cadmium | Copper | Lead | Nickel | Zinc | u m/g | u m/g | SEM/AVS |
| PIB01 | 0.057 | 0.596 | 0.697 | 0.535 | 7.200 | 9.08 | 29.06 | 0.31 |
| PIB05 | 0.034 | 1.081 | 0.611 | 0.576 | 6.946 | 9.25 | 15.11 | 0.61 |
| PIB07 | 0.085 | 0.963 | 0.604 | 0.423 | 6.506 | 8.58 | 34.74 | 0.25 |
| PIB08 | 0.005 | 0.017 | 0.211 | 0.159 | 2.622 | 3.02 | 13.15 | 0.23 |
| PIB09 | 0.020 | 0.543 | 0.659 | 0.358 | 5.829 | 7.41 | 12.28 | 0.60 |
| PIB09 dup | 0.022 | 0.478 | 0.670 | 0.377 | 6.103 | 7.65 | 18.62 | 0.41 |
| PIB14 | 0.022 | 0.280 | 0.461 | 0.303 | 5.374 | 6.44 | 18.05 | 0.36 |
| PIB15 | 0.000 | 0.180 | 0.364 | 0.244 | 3.903 | 4.69 | 12.76 | 0.37 |
| PIB18 | 0.045 | 0.453 | 0.543 | 0.330 | 5.740 | 7.11 | 15.79 | 0.45 |
| PIB20 | 0.045 | 0.237 | 0.448 | 0.342 | 5.493 | 6.57 | 17.89 | 0.37 |
| PIB25 | 0.017 | 0.470 | 0.358 | 0.365 | 5.322 | 6.53 | 21.84 | 0.30 |
| PIB25 dup | 0.071 | 0.070 | 0.450 | 0.332 | 5.589 | 6.51 | 20.39 | 0.32 |

G7. PAHs in PIB Sediments.

Table 16. PAH concentrations in Ponar grab samples.

| | | Con | centration | of Compo | ound (mg/l | (g dry wt) | In Ponar G | rab Samp | les | |
|------------------------|-------|-------|------------|----------|------------|------------|------------|----------|-------|-------|
| | PIB01 | PIB05 | PIB07 | PIB08 | PIB09 | PIB14 | PIB15 | PIB18 | PIB20 | PIB25 |
| napthalene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| acenaphthene | 2.5 | 1.3 | 0.3 | nd | nd | nd | nd | nd | nd | nd |
| acenaphthylene | nd | nd | 0.4 | 2.0 | nd | 1.8 | 0.9 | nd | 1.8 | 0.8 |
| fluorene | nd | 0.9 | nd | nd | nd | nd | nd | nd | nd | nd |
| phenanthrene | nd | 2.7 | 0.9 | 2.4 | 3.2 | nd | 0.7 | 4.3 | nd | 1.6 |
| anthracene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| fluoranthene | 1.9 | 4.3 | 3.2 | 6.0 | 8.1 | 11.4 | 1.2 | 9.2 | 3.5 | 3.4 |
| pyrene | 1.2 | 4.4 | 3.5 | 5.7 | 8.2 | 12.4 | 1.2 | 9.4 | nd | 3.6 |
| benzo(a)anthracene | nd | nd | nd | nd | 10.1 | 10.1 | nd | nd | nd | 2.0 |
| chrysene | nd | 2.2 | 4.7 | nd | 10.6 | 9.6 | 0.6 | 7.4 | nd | 2.2 |
| benzo()fluoranthene | 1.5 | 3.7 | 6.2 | 17.6 | 40.8 | 16.8 | 5.3 | 10.2 | 8.4 | 5.1 |
| benzo(a)pyrene | nd | 0.7 | nd | nd | 20.0 | 8.1 | 0.8 | 3.5 | nd | nd |
| dibenzo(a,h)anthracene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| indeno(1,2,3-cd)pyrene | nd | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| benzo(ghi)perylene | nd | nd | nd | nd | nd | nd | 1.6 | 5.5 | nd | nd |
| TOTAL PAHs | 7.1 | 20.2 | 19.2 | 33.7 | 101.0 | 70.2 | 12.3 | 49.5 | 13.7 | 18.7 |

Table 17. PAH concentrations in top core layer samples.

| | | 0 | oncentrat | ion of Con | npound (m | g/kg dry | wt) In Top (| Core Laver | | |
|------------------------|-------|-------|-----------|------------|-----------|----------|--------------|------------|-------|-------|
| | PIB01 | PIB05 | PIB07 | PIB08 | PIB09 | PIB14 | PIB15 | PIB18 | PIB20 | PIB25 |
| napthalene | nd | nd | nd | nd | nd | | nd | nd | nd | nd |
| acenaphthene | nd | 0.6 | nd | nd | 4.5 | | nd | 2.0 | nd | nd |
| acenaphthylene | nd | 0.7 | 2.1 | nd | 1.8 | | 11.9 | 2.5 | nd | 0.7 |
| fluorene | nd | nd | nd | 11.2 | 0.7 | | nd | nd | nd | nd |
| phenanthrene | nd | 0.9 | nd | nd | 3.5 | | 6.8 | 6.6 | nd | 1.0 |
| anthracene | nd | nd | nd | nd | nd | | nd | nd | nd | nd |
| fluoranthene | nd | 1.7 | nd | nd | 1.9 | | 6.0 | 14.0 | 2.1 | nd |
| pyrene | nd | 2.8 | nd | nd | 0.7 | | 1.6 | 15.1 | 2.4 | 1.9 |
| benzo(a)anthracene | nd | nd | nd | nd | nd | | nd | nd | nd | 0.7 |
| chrysene | 6.3 | 2.4 | nd | nd | 2.3 | | nd | nd | nd | 0.6 |
| benzo()fluoranthene | 36.6 | 7.6 | nd | 59.7 | 3.9 | | 8.9 | nd | 4.3 | 4.8 |
| benzo(a)pyrene | nd | nd | nd | nd | nd | | nd | nd | nd | 0.8 |
| dibenzo(a,h)anthracene | nd | nd | nd | nd | nd | | nd | nd | nd | nd |
| indeno(1,2,3-cd)pyrene | nd | nd | nd | nd | nd | | nd | nd | nd | nd |
| benzo(ghi)perylene | 11.6 | 0.6 | nd | nd | 1.5 | | 4.6 | nd | nd | nd |
| TOTAL PAHs | 54.5 | 17.3 | 2.1 | 70.9 | 20.8 | | 39.8 | 40.2 | 8.8 | 10.5 |

Table 18. PAH concentrations in bottom core layer samples.

| | | | | | | | | Core Lay | er | |
|------------------------|-------|-------|-------|-------|-------|-------|-------|----------|-------|-------|
| | PIB01 | PIB05 | PIB07 | PIB08 | PIB09 | PIB14 | PIB15 | PIB18 | PIB20 | PIB25 |
| napthalene | nd | nd | nd |
| acenaphthene | 0.6 | 0.4 | 0.3 | 0.3 | nd | nd | 6.8 | nd | 0.4 | nd |
| acenaphthylene | nd | 0.4 | 0.3 | 0.3 | 0.4 | 1.9 | 1.8 | 3.0 | 5.3 | nd |
| fluorene | nd | nd | nd | nd | nd | 1.0 | nd | nd | nd | nd |
| phenanthrene | nd | 0.5 | 0.2 | 0.7 | nd | 1.8 | 5.9 | 8.6 | 2.8 | 0.8 |
| anthracene | nd | nd | nd | nd | 0.1 | 1.0 | nd | nd | 0.5 | nd |
| fluoranthene | 0.2 | 0.5 | 0.6 | 1.5 | 0.5 | 3.2 | 6.9 | 11.8 | 5.4 | 0.9 |
| pyrene | nd | nd | nd | 1.5 | nd | 2.0 | 5.0 | 10.1 | 1.9 | 1.0 |
| benzo(a)anthracene | 3.7 | nd | nd | 1.3 | 0.7 | 1.8 | nd | nd | nd | 0.4 |
| chrysene | nd | 0.6 | 0.6 | nd | nd | 2.2 | nd | nd | 7.3 | 0.3 |
| benzo()fluoranthene | 9.3 | 2.0 | nd | 2.0 | 3.1 | 2.8 | 6.5 | 6.3 | 15.7 | 0.3 |
| benzo(a)pyrene | nd | nd | nd | nd | nd | 1.1 | nd | nd | nd | nd |
| dibenzo(a,h)anthracene | nd | nd | nd |
| indeno(1,2,3-cd)pyrene | nd | nd | nd |
| benzo(ghi)perylene | 3.0 | nd | nd | nd | nd | nd | 3.4 | nd | 7.6 | nd |
| TOTAL PAHs | 16.8 | 4.4 | 2.0 | 7.6 | 4.8 | 18.7 | 36.3 | 39.8 | 46.8 | 3.7 |

G8. Benthic Community Structure

Table 19. Mean organism density (individuals m⁻²) in PIB sediments; n=3. Taxa are ordered by descending abundance.

| | | | | | PIB | Site | | | | | |
|-----------------------|-------|-------|-------|-------|-------|--------|--------|--------|-------|--------|--------|
| Taxon | PIB01 | PIB05 | PIB07 | PIB08 | PIB09 | PIB12 | PIB15 | PIB18 | PIB20 | PIB25 | Mean |
| Oligochaeta | 460.0 | 296.2 | 277.3 | 995.6 | 642.7 | 1777.0 | 680.5 | 5809.8 | 151.2 | 1638.4 | 1272.9 |
| Dreissena | 907.4 | 94.5 | 94.5 | 157.5 | 409.6 | 390.7 | 4738.6 | 113.4 | 18.9 | 508.0 | 743.3 |
| Gastropoda | 56.7 | 201.6 | 132.3 | 31.5 | 189.0 | 113.4 | 2602.4 | 170.1 | 31.5 | 1291.8 | 482.0 |
| Amphipoda | 81.9 | 50.4 | 37.8 | 63.0 | 132.3 | 3913.2 | 296.2 | 6.3 | 37.8 | 12.6 | 463.2 |
| Chironomidae | 384.4 | 349.9 | 825.5 | 416.9 | 467.6 | 214.2 | 529.3 | 157.5 | 680.5 | 233.2 | 425.9 |
| Isopoda | 0.0 | 12.6 | 0.0 | 0.0 | 0.0 | 497.8 | 44.1 | 0.0 | 12.6 | 226.8 | 79.4 |
| Hirudinea | 25.2 | 0.0 | 50.4 | 82.6 | 0.0 | 88.2 | 18.9 | 0.0 | 0.0 | 0.0 | 26.5 |
| Nematoda | 63.0 | 6.3 | 0.0 | 37.8 | 25.2 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 13.2 |
| Bivalvia ¹ | 0.0 | 0.0 | 56.7 | 12.6 | 0.0 | 0.0 | 0.0 | 44.1 | 0.0 | 12.6 | 12.6 |
| Trichoptera | 37.8 | 12.6 | 0.0 | 0.0 | 6.3 | 12.6 | 18.9 | 0.0 | 25.2 | 0.0 | 11.3 |
| Turbellaria | 6.3 | 0.0 | 0.0 | 0.0 | 0.0 | 44.1 | 0.0 | 0.0 | 0.0 | 0.0 | 5.0 |
| Ephemeroptera | 6.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.3 | 6.3 | 12.6 | 3.2 |
| Ostracoda | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 31.5 | 0.0 | 3.2 |
| Coleoptera | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 6.3 | 0.0 | 0.0 | 0.6 |
| Plecoptera | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Total | 2029 | 1024 | 1475 | 1798 | 1873 | 7051 | 8929 | 6314 | 996 | 3936 | 3542 |

¹ Bivalvia other than Dreissena

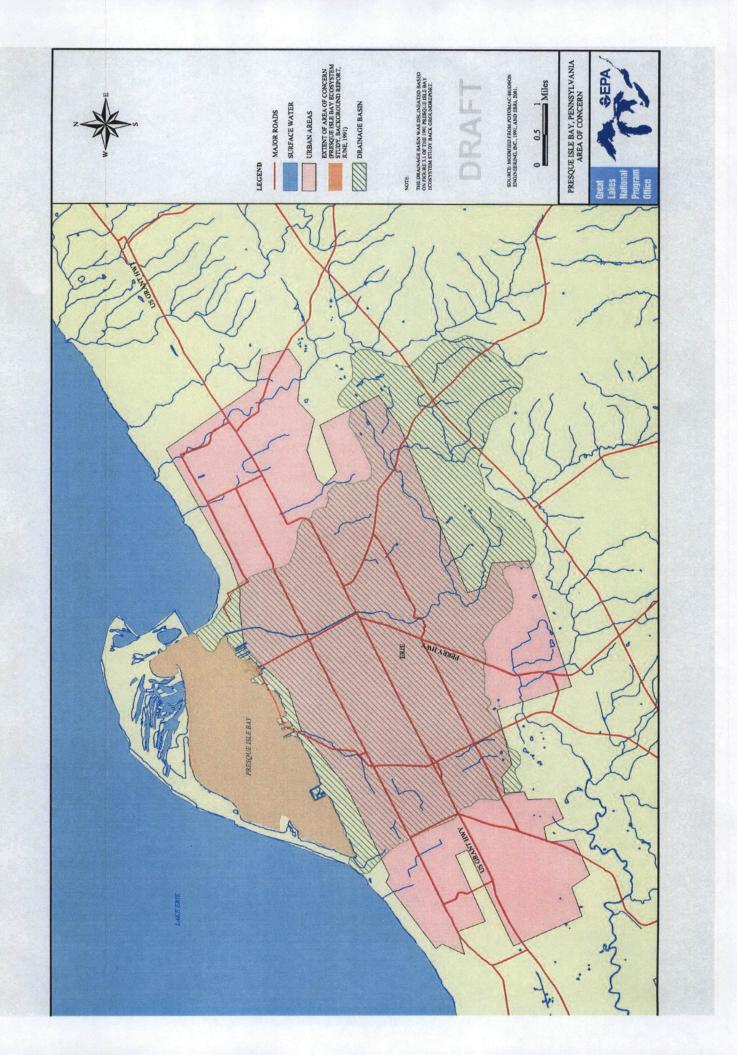
Table 20. Percent contribution to total organism density by each taxon in PIB sediments; taxa are ordered by descending mean percentage.

| | | | Percent | contributio | on by each | taxa to tot | al organis | m density | A 1 Short | | |
|-----------------------|-------|-------|---------|-------------|------------|-------------|------------|-----------|-----------|-------|------|
| Taxon | PIB01 | PIB05 | PIB07 | PIB08 | PIB09 | PIB12 | PIB15 | PIB18 | PIB20 | PIB25 | mean |
| Oligochaeta | 22.7 | 28.9 | 18.8 | 55.4 | 34.3 | 25.2 | 7.6 | 92.0 | 15.2 | 41.6 | 34.2 |
| Chironomidae | 18.9 | 34.2 | 56.0 | 23.2 | 25.0 | 3.0 | 5.9 | 2.5 | 68.4 | 5.9 | 24.3 |
| Dreissena | 44.7 | 9.2 | 6.4 | 8.8 | 21.9 | 5.5 | 53.1 | 1.8 | 1.9 | 12.9 | 16.6 |
| Gastropoda | 2.8 | 19.7 | 9.0 | 1.8 | 10.1 | 1.6 | 29.1 | 2.7 | 3.2 | 32.8 | 11.3 |
| Amphipoda | 4.0 | 4.9 | 2.6 | 3.5 | 7.1 | 55.5 | 3.3 | 0.1 | 3.8 | 0.3 | 8.5 |
| Isopoda | 0.0 | 1.2 | 0.0 | 0.0 | 0.0 | 7.1 | 0.5 | 0.0 | | | 1.6 |
| Hirudinea | 1.2 | 0.0 | 3.4 | 4.6 | 0.0 | 1.3 | 0.2 | 0.0 | 0.0 | | 1.1 |
| Nematoda | 3.1 | 0.6 | 0.0 | 2.1 | 1.3 | 0.0 | 0.0 | 0.0 | 0.0 | | 0.7 |
| Trichoptera | 1.9 | 1.2 | 0.0 | 0.0 | 0.3 | 0.2 | 0.2 | 0.0 | 2.5 | 0.0 | 0.6 |
| Bivalvia ¹ | 0.0 | 0.0 | 3.8 | 0.7 | 0.0 | 0.0 | 0.0 | 0.7 | 0.0 | | 0.6 |
| Ostracoda | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | | 0.3 |
| Ephemeroptera | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.1 | 0.6 | | 0.1 |
| Turbellaria | 0.3 | 0.0 | 0.0 | 0.0 | 0.0 | 0.6 | 0.0 | 0.0 | | | 0.1 |
| Coleoptera | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | | 0.1 | 0.0 | | 0.0 |
| Plecoptera | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |

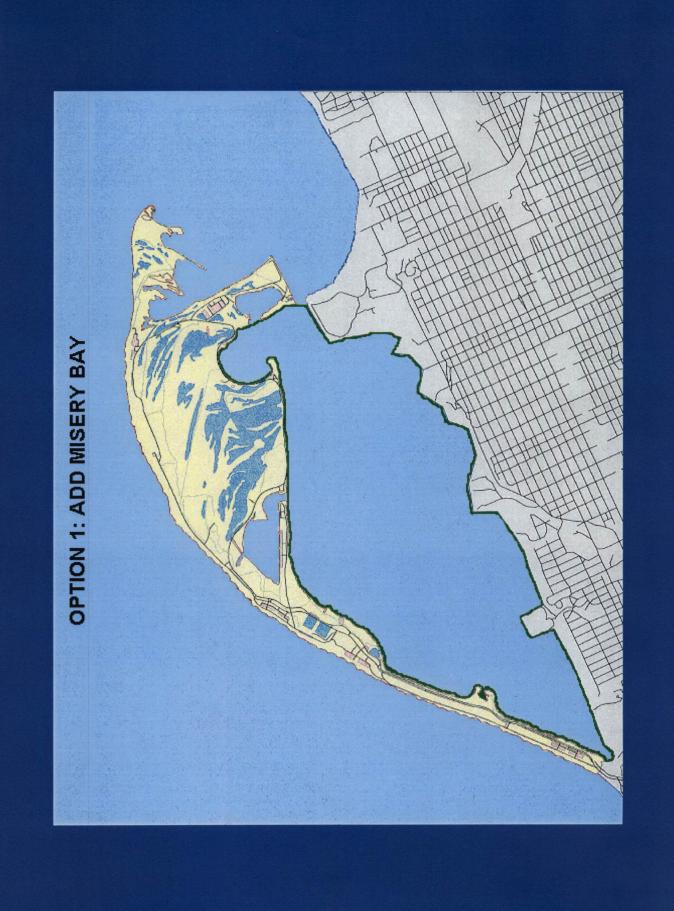
G9. Whole Sediment Toxicity by Bioassay

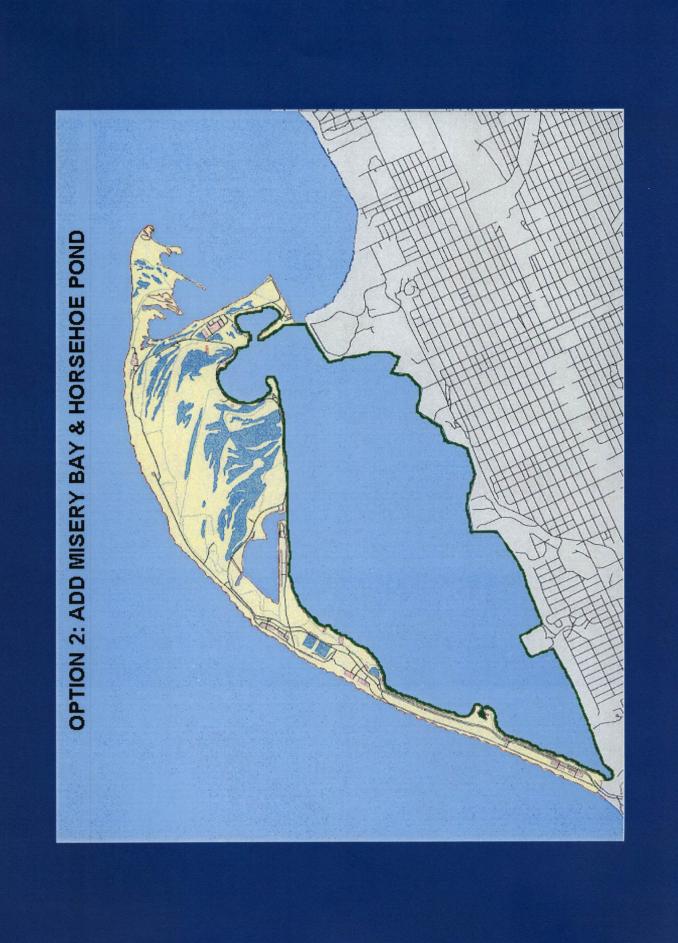
Table 21. Bioassay results for three organisms exposed to PIB sediments and control sediments; endpoints include survival, growth, and reproductive success; mean of 5 replicates.

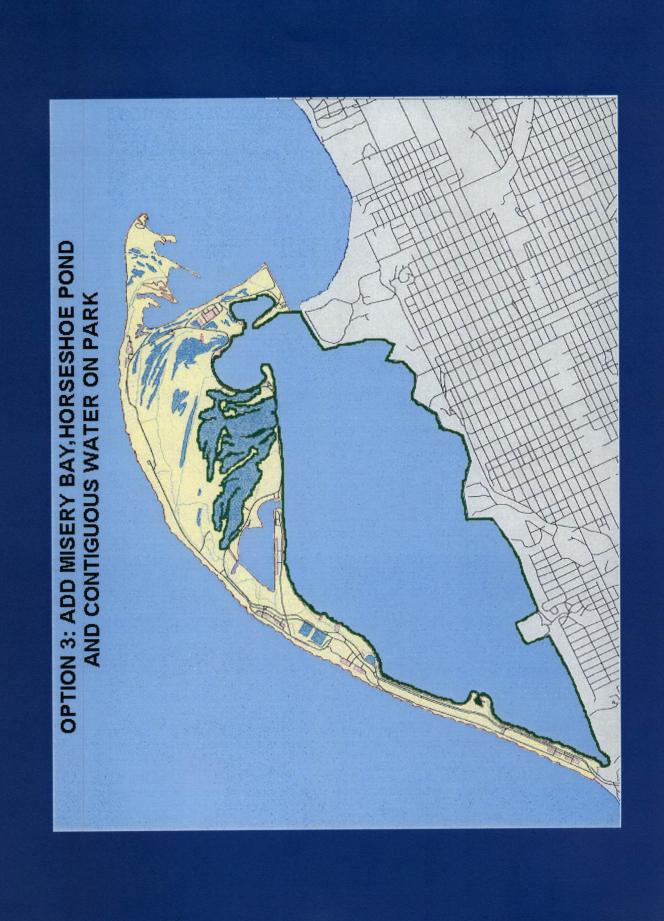
| | Or | ganism Surviv | al | Repro | oduction or Grov | vth |
|---------|----------|---------------|-----------|---------------|------------------|-------------|
| | D. magna | C. tentans | H. azteca | D. magna | C. tentans | H. azteca |
| Site | % | % | % | Mean Neonates | Weight (mg) | Weight (mg) |
| PIB01 | 40 | 64 | 76 | 9.6 | 3.42 | 0.349 |
| PIB05A | 60 | 66 | 82 | 13.2 | 4.75 | 0.305 |
| PIB05B | | 62 | 80 | | 4.49 | 0.280 |
| PIB07 | 80 | 58 | 92 | 17.6 | 3.13 | 0.381 |
| PIB08 | 80 | 66 | 74 | 12 | 3.25 | 0.394 |
| PIB09 | 100 | 68 | 78 | 15 | 3.03 | 0.249 |
| PIB14 | 100 | 72 | 72 | 14.8 | 3.19 | 0.328 |
| PIB15 | 80 | 72 | 82 | 19.8 | 3.86 | 0.276 |
| PIB18 | 100 | 72 | 18 | 15.8 | 3.79 | 0.189 |
| PIB20 | 80 | 76 | 80 | 30.4 | 2.53 | 0.280 |
| PIB25 | 100 | 60 | 72 | 15.4 | 2.85 | 0.335 |
| Control | 100 | 78 | 82 | 43.2 | 3.90 | 0.234 |

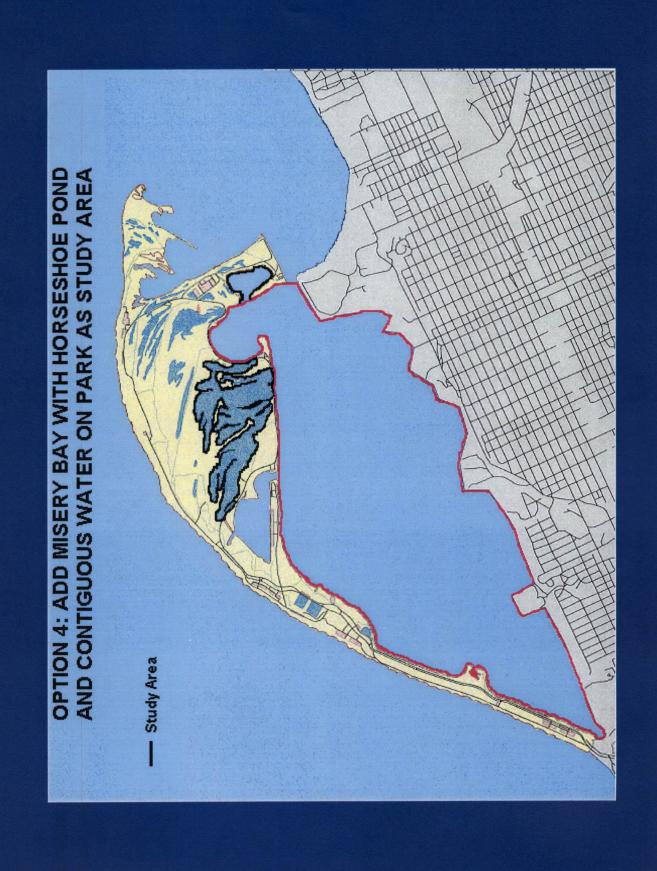












OPTION 4: ADD MISERY BAY WITH HORSESHOE POND AND CONTIGUOUS WATER ON PARK AS STUDY AREA - Study Area

| | Cadı | mium | Coppe | Copper | | | |
|--------|--------------------|-------------|--------------|----------|--|--|--|
| Site | Grab T Lay | yer B Layer | Grab T Layer | B Layer | | | |
| PIB 01 | 6.1 3 | .9 0.8 | 97.3 | 1.5 30.2 | | | |
| PIB 05 | 8.5 | nd nd | 127.2 5 | 7.3 26.3 | | | |
| PIB 07 | 8.9 | .3 4.3 | 104.0 118 | 5.7 75.6 | | | |
| PIB 08 | 8.0 | i.2 nd | 101.1 93 | 3.1 35.1 | | | |
| PIB 09 | 9.0 | .0 nd | 116.3 104 | 4.0 38.2 | | | |
| PIB 14 | 7.4 4 | .8 2.2 | 82.3 | 7.6 82.5 | | | |
| PIB 15 | 6.7 9 | .4 3.1 | 82.0 100 | 0.4 84.8 | | | |
| PIB 18 | 5.0 4 | .6 7.3 | 59.6 | 1.2 63.6 | | | |
| PIB 20 | <mark>8.1</mark> 7 | .1 nd | 73.1 79 | 9.9 29.1 | | | |
| PIB 25 | <u>5.6</u> 1 | .0 nd | 83.8 29 | 9.2 24.5 | | | |
| mean | 7.3 | 5.7 3.6 | 92.7 79 | 9.0 49.0 | | | |

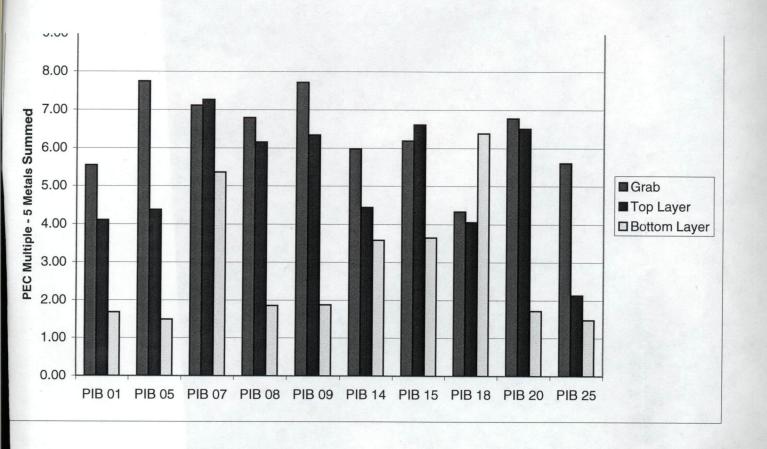
| | | | | To | tal Extrac | table Metal | (mg kg-1 | dry sedime | nt) |
|---------|--------------|--------|--------|--------|------------|-------------|----------|------------|-----|
| | | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 | P |
| Cadmium | Grab | 6.1 | 8.5 | 8.9 | 8.0 | 9.0 | 7.4 | 6.7 | |
| | Top Layer | 3.9 | 3.8 | 9.3 | 6.2 | 7.0 | 4.8 | 9.4 | |
| | Bottom Layer | 0.8 | nd | 4.3 | nd | nd | 2.2 | 3.1 | |
| Copper | Grab | 97 | 127 | 104 | 101 | 116 | 82 | 82 | |
| | Top Layer | 72 | 57 | 116 | 93 | 104 | 78 | 100 | |
| | Bottom Layer | 30 | 26 | 76 | 35 | 38 | 83 | 85 | |
| Lead | Grab | 116 | 192 | 166 | 157 | 227 | 133 | 194 | |
| | Top Layer | 83 | 71 | 166 | 178 | 189 | 116 | 154 | |
| | Bottom Layer | 20 | 20 | 69 | 44 | 42 | 75 | 4 | |
| Nickel | Grab | 71 | 88 | 84 | 83 | 84 | 69 | 71 | |
| | Top Layer | 59 | 89 | 80 | 68 | 68 | 51 | 68 | |
| | Bottom Layer | 36 | 37 | 106 | 36 | 35 | 48 | 63 | |
| Zinc | Grab | 600 | 862 | 739 | 729 | 747 | 679 | 602 | |
| inc | Top Layer | 457 | 383 | 776 | 685 | 626 | 451 | 664 | |
| | Bottom Layer | 187 | 183 | 585 | 247 | 266 | 470 | 517 | |

| | | | | | | | PEC | Multiple | | |
|---------|---|--------------|--------|--------|--------|--------|--------|----------|--------|-------|
| | | | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 | PIB 1 |
| Cadmium | | Grab | 1.22 | 1.71 | 1.78 | 1.60 | 1.81 | 1.48 | 1.35 | |
| | | Top Layer | 0.78 | 0.77 | 1.86 | 1.25 | 1.41 | 0.97 | 1.89 | |
| | , | Bottom Layer | 0.17 | | 0.87 | | | 0.44 | 0.63 | |
| Copper | | Grab | 0.65 | 0.85 | 0.70 | 0.68 | 0.78 | 0.55 | 0.55 | |

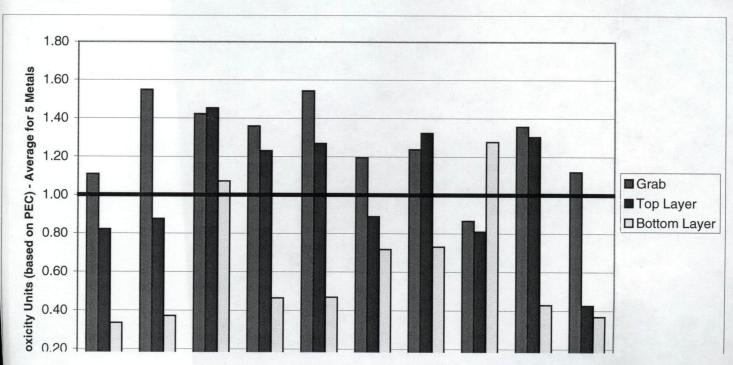
| | Lead | | | Nickel | | | Zinc | |
|-------|---------|---------|--------|---------|---------|------|-----------|------------|
| Grab | T Layer | B Layer | Grab | T Layer | B Layer | Grab | Top Layer | Bottom Lay |
| 115.5 | 83.20 | 20.10 | 70.90 | 58.50 | 36.10 | 600 | 457 | 187 |
| 192.3 | 71.30 | 19.70 | 87.60 | 89.10 | 37.00 | 862 | 383 | 183 |
| 166.0 | 165.80 | 69.10 | 84.10 | 79.80 | 105.80 | 739 | 776 | 585 |
| 157.0 | 177.80 | 43.60 | 82.50 | 68.24 | 36.15 | 729 | 685 | 247 |
| 227.2 | 189.30 | 41.70 | 83.80 | 67.80 | 34.70 | 747 | 626 | 266 |
| 132.8 | 116.40 | 74.50 | 69.40 | 51.40 | 47.80 | 679 | 451 | 470 |
| 193.6 | 153.50 | 4.20 | 71.30 | 68.40 | 62.80 | 602 | 664 | 517 |
| 106.9 | 95.10 | 150.70 | 55.92 | 52.10 | 99.87 | 434 | 414 | 582 |
| 138.1 | 157.50 | 34.90 | 100.20 | 89.40 | 37.80 | 697 | 684 | 216 |
| 126.6 | 49.70 | 21.90 | 78.22 | 42.89 | 36.43 | 607 | 216 | 180 |
| 155.6 | 126.0 | 48.0 | 78.4 | 66.8 | 53.4 | 670 | 536 | 343 |

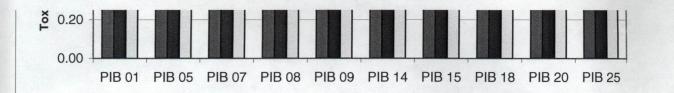
| 18 | PIB 20 | PIB 25 |
|-----|--------|--------|
| 5.0 | 8.1 | 5.6 |
| 4.6 | 7.1 | 1.0 |
| 7.3 | nd | nd |
| 60 | 73 | 84 |
| 61 | 80 | 29 |
| 64 | 29 | 25 |
| 107 | 138 | 127 |
| 95 | 158 | 50 |
| 151 | 35 | 22 |
| 56 | 100 | 78 |
| 52 | 89 | 43 |
| 100 | 38 | 36 |
| 434 | 697 | 607 |
| 414 | 684 | 216 |
| 582 | 216 | 180 |

| 3 | PIB 20 | PIB 25 |
|------|--------|--------|
| 1.00 | 1.63 | 1.12 |
| 0.92 | 1.42 | 0.20 |
| 1.46 | | |
| 0.40 | 0.49 | 0.56 |



| - | - 8 | | | | Average PE | C Multiple | | | | |
|--------------|--------|--------|--------|--------|------------|------------|--------|--------|--------|--------|
| _ | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 | PIB 18 | PIB 20 | PIB 25 |
| Grab | 1.11 | 1.55 | 1.42 | 1.36 | 1.54 | 1.20 | 1.24 | 0.87 | 1.36 | 1.12 |
| Top Layer | 0.82 | 0.88 | 1.45 | 1.23 | 1.27 | 0.89 | 1.32 | 0.81 | 1.30 | 0.43 |
| Bottom Layer | 0.34 | 0.37 | 1.07 | 0.46 | 0.47 | 0.72 | 0.73 | 1.28 | 0.43 | 0.37 |





| | Top Layer | 0.48 | 0.38 | 0.78 | 0.62 | 0.70 | 0.52 | 0.67 |
|----------------------|------------------------------|--------|--------|--------|--------|--------|---------|--------|
| | Bottom Layer | 0.20 | 0.18 | 0.51 | 0.24 | 0.26 | 0.55 | 0.57 |
| | | | | | | | | |
| Lead | Grab | 0.90 | 1.50 | 1.30 | 1.23 | 1.78 | 1.04 | 1.51 |
| | Top Layer | 0.65 | 0.56 | 1.30 | 1.39 | 1.48 | 0.91 | 1.20 |
| | Bottom Layer | 0.16 | 0.15 | 0.54 | 0.34 | 0.33 | 0.58 | 0.03 |
| | zonom zayo. | | | | | | | |
| Nickel | Grab | 1.46 | 1.80 | 1.73 | 1.70 | 1.72 | 1.43 | 1.47 |
| | Top Layer | 1.20 | 1.83 | 1.64 | 1.40 | 1.40 | 1.06 | 1.41 |
| | Bottom Layer | 0.74 | 0.76 | 2.18 | 0.74 | 0.71 | 0.98 | 1.29 |
| <u>_</u> | | | | | | | | |
| Zinc | Grab | 1.31 | 1.88 | 1.61 | 1.59 | 1.63 | 1.48 | 1.31 |
| | Top Layer | 1.00 | 0.83 | 1.69 | 1.49 | 1.36 | 0.98 | 1.45 |
| | Bottom Layer | 0.41 | 0.40 | 1.27 | 0.54 | 0.58 | 1.02 | 1.13 |
| | | | | | | PEC M | ultiple | |
| | • | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 |
| Cadmium | Grab | 1.22 | 1.71 | 1.78 | 1.60 | 1.81 | 1.48 | 1.35 |
| Copper | Grab | 0.65 | 0.85 | 0.70 | 0.68 | 0.78 | 0.55 | 0.55 |
| Lead | Grab | 0.90 | 1.50 | 1.30 | 1.23 | 1.78 | 1.04 | 1.51 |
| Nickel | Grab | 1.46 | 1.80 | 1.73 | 1.70 | 1.72 | 1.43 | 1.47 |
| Zinc | Grab | 1.31 | 1.88 | 1.61 | 1.59 | 1.63 | 1.48 | 1.31 |
| Total PEC Mul | | 5.55 | 7.74 | 7.11 | 6.79 | 7.71 | 5.98 | 6.19 |
| Average PEC Multiple | | 1.11 | 1.55 | 1.42 | 1.36 | 1.54 | 1.20 | 1.24 |
| | | | | | | | | |
| | | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 |
| Cadmium | Top Layer | 0.78 | 0.77 | 1.86 | 1.25 | 1.41 | 0.97 | 1.89 |
| Copper | Top Layer | 0.48 | 0.38 | 0.78 | 0.62 | 0.70 | 0.52 | 0.67 |
| Lead | Top Layer | 0.65 | 0.56 | 1.30 | 1.39 | 1.48 | 0.91 | 1.20 |
| Nickel | Top Layer | 1.20 | 1.83 | 1.64 | 1.40 | 1.40 | 1.06 | 1.41 |
| Zinc | Top Layer | 1.00 | 0.83 | 1.69 | 1.49 | 1.36 | 0.98 | 1.45 |
| Total PEC Mul | tiple | 4.11 | 4.38 | 7.27 | 6.16 | 6.34 | 4.44 | 6.61 |
| Average PEC Multiple | | 0.82 | 0.88 | 1.45 | 1.23 | 1.27 | 0.89 | 1.32 |
| | | PIB 01 | DID OF | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 |
| Cadmium | Bottom Layer | 0.17 | PIB 05 | 0.87 | FID U8 | FID U9 | 0.44 | 0.63 |
| | | 0.17 | 0.18 | 0.51 | 0.24 | 0.26 | 0.55 | 0.57 |
| Copper Lead | Bottom Layer Bottom Layer | 0.20 | 0.15 | 0.54 | 0.24 | 0.33 | 0.58 | 0.03 |
| | | | 0.15 | 2.18 | 0.34 | 0.33 | 0.58 | 1.29 |
| Nickel | Bottom Layer | 0.74 | | | | | | |
| Zinc | Bottom Layer | 0.41 | 0.40 | 1.27 | 0.54 | 0.58 | 1.02 | 1.13 |
| Total PEC Mul | | 1.68 | 1.49 | 5.36 | 1.86 | 1.88 | 3.58 | 3.65 |
| Average PEC | iviuitipie | 0.34 | 0.37 | 1.07 | 0.46 | 0.47 | 0.72 | 0.73 |
| | | | | | | | | |
| | - | | | | | PEC M | ultiple | |
| | | PIB 01 | PIB 05 | PIB 07 | PIB 08 | PIB 09 | PIB 14 | PIB 15 |
| | Grab | 5.55 | 7.74 | 7.11 | 6.79 | 7.71 | 5.98 | 6.19 |
| | Top Layer | 4.11 | 4.38 | 7.27 | 6.16 | 6.34 | 4.44 | 6.61 |
| | Bottom Layer | 1.68 | 1.49 | 5.36 | 1.86 | 1.88 | 3.58 | 3.65 |
| | | | | | | | | |

| 0.41 0.43 | 0.54 0.20 | 0.20 0.16 |
|----------------------|----------------------|----------------------|
| 0.84 0.74 1.18 | 1.08 1.23 0.27 | 0.99 0.39 0.17 |
| 1.15 1.07 2.06 | 2.06 1.84 0.78 | 1.61 0.88 0.75 |
| 0.95 0.90 1.27 | 1.52 1.49 0.47 | 1.32 0.47 0.39 |
| PIB 18 | PIB 20 | PIB 25 |
| 1.00 | 1.63 | 1.12 |
| 0.40 | 0.49 | 0.56 |
| 0.84 | 1.08 | 0.99 |
| 1.15 | 2.06 | 1.61 |
| 0.95 | 1.52 | 1.32 |
| 4.33 | 6.78 | 5.61 |
| 0.87 | 1.36 | 1.12 |
| PIB 18 | PIB 20 | PIB 25 |
| 0.92 | 1.42 | 0.20 |
| 0.41 | 0.54 | 0.20 |
| 0.74 | 1.23 | 0.39 |
| 1.07 | 1.84 | 0.88 |
| 0.90 | 1.49 | 0.47 |
| 4.05 | 6.51 | 2.13 |
| 0.81 | 1.30 | 0.43 |
| PIB 18 | PIB 20 | PIB 25 |
| 1.46 | | |
| 0.43 | 0.20 | 0.16 |
| 1.18 | 0.27 | 0.17 |
| 2.06 | 0.78 | 0.75 |
| 1.27 | 0.47 | 0.39 |
| 6.39 | 1.72 | 1.48 |
| 1.28 | 0.43 | 0.37 |
| PIB 18 | PIB 20 | DID OF |
| | | PIB 25 |
| 4.33 4.05 | 6.78 | 5.61 |
| 6.39 | 6.51 1.72 | 2.13 1.48 |
| 0.39 | 1.72 | 1.48 |
| | | |