♻EPA **Sediment Remediation Scoping Project in Minnesota Slip, Duluth Harbor**

SEDIMENT REMEDIATION SCOPING PROJECT IN

MINNESOTA SLIP, DULUTH HARBOR

Final Report

Submitted by:

Judy L. Crane[1], Dawn E. Smorong[2], David A. Pillard[3], and Donald D. MacDonald[2]

[1]Minnesota Pollution Control Agency
Environmental Outcomes Division
520 Lafayette Road North
St. Paul, Minnesota 55155-4194
Email: judy.crane@pca.state.mn.us

[2]MacDonald Environmental Sciences Ltd.
#24 – 4800 Island Highway North
Nanaimo, British Columbia V9T 1W6 Canada

[3]ENSR International
Fort Collins Environmental Toxicology Laboratory
4303 West LaPorte Avenue
Fort Collins, CO 80521

DISCLAIMER

The information in this document has been funded by the U.S. Environmental Protection Agency's (EPA) Great Lakes National Program Office. It has been subject to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Continued)

LIST OF ACRONYMS AND ABBREVIATIONS

2Metnap	2-Methylnaphthalene
AC	Alternating Current
Acene	Acenaphthene
Aceny	Acenaphthylene
AFDW	Ash Free Dry Weight
Anth	Anthracene
AOC	Area of Concern
ARCS	Assessment and Remediation of Contaminated Sediments
ASTM	American Society of Testing and Materials
AVS	Acid Volatile Sulfide
Bena	Benzo[a]anthracene
Benap	Benzo[a]pyrene
Benb	Benzo[b&j]fluoranthene
Bene	Benzo[e]pyrene
Beng	Benzo[g,h,i]perylene
Benk	Benzo[k]fluoranthene
BMP	Best Management Practice
CAC	Citizen's Action Committee
CDF	Cumulative Distribution Frequency
Chry	Chrysene
cm	Centimeter
CO	Colorado
Corp.	Corporation
CV	Coefficient of Variation
d	Day
DC	Direct Current
DDD	Metabolite of DDT
DDT	Dichloro-diphenyl-trichloroethane
DECC	Duluth Entertainment and Convention Center
DI	Deionized (as in deionized water)
Diben	Dibenzo[a,h]anthracene
ECGO	Electrochemical Geooxidation
ECRTs	Electrochemical Remediation Technologies
EPA	Environmental Protection Agency
FCETL	Fort Collins Environmental Toxicology Laboratory
FIELDS	Fully Integrated Environmental Location Decision Support System
Fluo	Fluorene
Flut	Fluoranthene
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/MS SIM	Gas Chromatography/Mass Spectrometry Selected Ion Monitoring
GFT	Glass Furnace Technology
GIS	Geographic Information System
GLNPO	Great Lakes National Program Office

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

GPS	Global Positioning System
HCl	Hydrochloric Acid
HMW	High Molecular Weight
IC	Induced Complexation
ID	Identifier Code
IDW	Inverse Distance Weighted
IJC	International Joint Commission
IL	Illinois
IN	Indiana
Indp	Indeno[1,2,3-cd]pyrene
IT Corp.	International Technology Corporation
KCl	Potassium Chloride
kg	Kilogram
l	Liter
lb	Pound
LMW	Low Molecular Weight
m	Meter
MDH	Minnesota Department of Health
MESL	MacDonald Environmental Sciences Ltd.
mg	Milligram
MI	Michigan
mm	Millimeter
MN	Minnesota
MNS	Minnesota Slip
mo	Month
MO	Missouri
MPCA	Minnesota Pollution Control Agency
n	Number
Naph	Naphthalene
NT	Not Toxic
NY	New York
OH	Ohio
ON	Ontario
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PEC	Probable Effect Concentration
PEC-Q	Probable Effect Concentration Quotient
Phen	Phenanthrene
PRP	Potentially Responsible Party
Pyrn	Pyrene
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
QC	Quality Control

r^2	Coefficient of Determination
R	Field Replicate
R/V	Research Vessel
RAP	Remedial Action Plan
R-EMAP	Regional Environmental Monitoring and Assessment Program
RPD	Relative Percent Difference
SADA	Spatial Analysis and Decision Assistance
SD	Standard Deviation
SEM	Simultaneously Extractable Metals
SLRAOC	St. Louis River Area of Concern
SOP	Standard Operating Procedure
SQG	Sediment Quality Guideline
SQT	Sediment Quality Target
S.S.	Steam Ship
T	Toxic
TIF	Tag Image File format
TMA	Thermo Analytical
TOC	Total Organic Carbon
μg	Microgram
μm	Micrometer (also termed micron)
UMD	University of Minnesota--Duluth
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
WA	Washington
WDNR	Wisconsin Department of Natural Resources
WI	Wisconsin
WLSSD	Western Lake Superior Sanitary District
wt.	Weight
WWI	World War I
WWII	World War II
yd	Yard
yr	Year

ACKNOWLEDGMENTS

This report should be cited as:

Crane, J.L., D.E. Smorong, D.A. Pillard, and D.D. MacDonald. 2002. Sediment remediation scoping project in Minnesota Slip, Duluth Harbor. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA-905-R02-002.

ABSTRACT

A sediment remediation scoping project was conducted in Minnesota Slip in the Duluth, MN Harbor. Previous investigations of this boat slip indicated that elevated levels of polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), DDT metabolites, toxaphene, mercury, cadmium, chromium, copper, lead, nickel, and zinc were present in the sediments. Minnesota Slip appears to be an orphan site since this contamination has not been attributed to any potentially responsible parties. A sediment survey was conducted in August 1998 and September 1999 to collect additional sediment samples to further delineate the vertical and horizontal distribution of a short-list of chemicals of potential concern (i.e., PAHs, PCBs, lead, mercury, and zinc), as well as the distribution of total organic carbon (TOC) and particle size classes. In addition, acid volatile sulfides (AVS), simultaneously extractable metals (SEM), ammonia, cadmium, chromium, copper, nickel, and selenium were measured in six surficial (0-5 cm) sediment samples in which matching sediment toxicity tests were run. For 10-d sediment toxicity tests run using the midge, *Chironomus tentans*, comparison of treatment survival to the control was made by observation since control survival was less than in any of the treatments. For 28- to 42-d sediment toxicity tests run using the amphipod, *Hyalella azteca*, survival in two of six samples was significantly lower than in the respective controls. This toxicity was associated with [SEM] – [AVS] > 5 in the corresponding sediment chemistry samples, although the specific cause of toxicity could not be determined. Isopleth figures of sediment quality data were assembled for various depth intervals for the following parameters: percentage of sand, silt, and clay, TOC, total PCBs, total PAHs, mercury, lead, and zinc. Contamination in the slip is heterogeneous, and several sites either exceeded the corresponding Level I or Level II sediment quality targets (SQTs). The greatest exceedances of the Level II SQTs occurred with PAHs. Mean probable effect concentration quotients (PEC-Qs) were calculated for surficial sediments in Minnesota Slip and compared to other surficial sites within the St. Louis River Area of Concern (AOC), as well as other Great Lakes AOCs. Minnesota Slip is much less contaminated than one of the Superfund sites in the Duluth Harbor, but more contaminated than other areas in the St. Louis River AOC. In addition, the Oswego River, NY AOC and the Cuyahoga River, OH AOC had similar mean PEC-Qs as Minnesota Slip. The volume of contaminated sediments was estimated in only the upper depth segments of Minnesota Slip in which sediment quality data were available for the entire slip. A short-list of sediment remediation options, including dredging, is presented for further consideration. However, before any of these remediation options can be seriously evaluated, best management practices need to be implemented to reduce contaminant inputs from five storm water outfalls in Minnesota Slip.

CHAPTER 1

INTRODUCTION

The St. Louis River is an important transboundary waterway, located in northeastern Minnesota and northwestern Wisconsin, which culminates in the Duluth-Superior Harbor (Figure 1). In 1987, the International Joint Commission (IJC) designated the lower St. Louis River as one of 43 Areas of Concern (AOCs) in the Great Lakes basin (IJC 1989). The St. Louis River AOC includes several sites where concentrations of metals, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and/or dioxins and furans are elevated in the sediments (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997; Breneman *et al*. 2000). In areas where these chemical substances occur at concentrations that pose a known or suspected threat to environmental or human health, the sediments are designated as contaminated. Contaminated sediments contribute to several use impairments in the St. Louis River AOC, including the issuance of fish advisories, restrictions on dredging, and habitat impairments to bottom feeding organisms (MPCA and WDNR 1992, 1995).

The Minnesota Pollution Control Agency (MPCA), and its collaborators, have conducted a number of sediment assessment studies in the St. Louis River AOC, particularly in the Duluth-Superior Harbor and in the impounded reservoirs of the river near Cloquet, MN (Schubauer-Berigan and Crane 1996, 1997; Crane *et al*. 1997; AScI Corporation 1999; Crane 1999a,b; Breneman *et al*. 2000; King 2001). The MPCA utilizes a number of sediment quality assessment tools to characterize the sediments, including sediment chemistry measurements, physical measurements (e.g., particle size), sediment toxicity tests (acute and chronic tests), benthic community surveys, and bioaccumulation studies (Crane *et al*. 2000). The information gained from these studies is evaluated, using a weight-of-evidence approach, for making management decisions about contaminated areas. The Wisconsin Department of Natural Resources (WDNR), Fond du Lac Band, U.S. Army Corps of Engineers, and consultants for industries and potentially responsible parties have also used a similar set of sediment assessment tools in studies they have conducted in the St. Louis River AOC (Redman and Janisch 1995; Wenck Associates 1995; ENSR 1996; TMA 1996; IT Corporation 1997; Glass *et al*. 1998).

Successful remediation of contaminated sediments is essential for restoring impaired uses and contributing to the de-listing of the St. Louis River AOC. Several hot spot areas of elevated contamination occur in the Duluth-Superior Harbor, including the Interlake/Duluth Tar and USX

Superfund sites, Hog Island Inlet/Newton Creek, several boat slips (e.g., Minnesota Slip, Slip C), Howard's Bay, in the vicinity of historical and current wastewater treatment plants, and other areas with historical sources of contamination (e.g., Grassy Point) (Figure 2). Additional background information on the extent of sediment contamination in the St. Louis River AOC is given in the Stage I and II Remedial Action Plans (RAPs) (MPCA and WDNR 1992, 1995) and in Crane *et al*. (2000).

During 1996, the MPCA solicited input from the Sediment Contamination Work Group of the St. Louis River Citizen's Action Committee (CAC) to assist them in selecting an appropriate site for a sediment remediation scoping project. The group selected Slip C, followed by Minnesota Slip, as the best candidate sites. The reasons for selecting these sites were because the contamination appeared to be well-contained within the slips; several surficial contaminants exceeded benchmark sediment quality guidelines (Persaud *et al*. 1993); the sediments contained bioaccumulative contaminants (e.g., PCBs, PAHs, mercury) in the surficial and deeper sediment layers; significant sediment toxicity had been observed at both sites in the past, and the benthic community was composed of organisms associated with degraded environments (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997; AScI Corporation 1999; Breneman *et al*. 2000). The level of contamination in Minnesota Slip is of additional concern because of the close proximity of the slip to the Duluth entry of Lake Superior. The group felt these sites had a high potential for being effectively remediated in the future. A sediment remediation scoping project was initiated in Slip C in 1996; however, the project was scaled down to an assessment of chemical contamination in the sediments of Slip C (Crane 1999a). The MPCA obtained a grant from the U.S. Environmental Protection Agency's (EPA) Great Lakes National Program Office (GLNPO) in 1998 to conduct a sediment remediation scoping project in Minnesota Slip. This sediment remediation scoping project was designed to fill data gaps from previous sediment investigations in order to characterize site conditions and to develop some preliminary remediation options for further consideration. This scoping project did not include an ecological or human health risk assessment as would be required at Superfund sites through the completion of a remedial investigation/feasibility study.

The objectives of this project were to:

- Delineate the extent and depth of selected contaminants of concern in the sediments of Minnesota Slip;
- Determine the acute and chronic toxicity of surficial sediments to selected benthic invertebrates;

- Estimate the volume of contaminated sediments in the inner 75% of the slip, because a previous sediment investigation indicated the inner slip was more contaminated than the outer slip (Crane *et al*. 1997); and
- Develop a short list of sediment remediation options for further consideration.

The chemicals of potential concern included in this study were: eighteen PAH compounds, congener-specific PCBs, mercury, lead, and zinc. Total organic carbon (TOC) and particle size classes (sand, silt, and clay) were also measured in selected depth intervals. In addition, acid volatile sulfides (AVS), simultaneously extractable metals (SEM), ammonia, cadmium, chromium, copper, nickel, and selenium were measured in six surficial (0-5 cm) sediment samples in which corresponding sediment toxicity tests were conducted. This expanded list of chemicals was included to widen the MPCA's database of matching sediment chemistry and bioeffects data. Selenium was included in the list because this metal had not previously been measured in Minnesota Slip, and the MPCA had some unpublished data that indicated selenium was elevated in soil samples collected from nearby sites in the Canal Park area of Duluth. Although elevated concentrations of DDT metabolites and toxaphene have been detected in sediments collected from Minnesota Slip (Crane *et al*. 1997), the high costs associated with these analyses could not be accommodated in the project budget. Since previous studies showed PAHs to be a primary contaminant of concern in Minnesota Slip (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997; Breneman *et al*. 2000), an assumption was made that any future remediation of this slip to address PAH contamination would probably also take care of elevated concentrations of DDT metabolites and toxaphene.

Two types of sediment toxicity tests were performed on six surficial sediment samples. Ten-day sediment toxicity tests with the midge, *Chironomus tentans*, were conducted in order to measure the biological responses of death and growth. Twenty-eight to 42-d sediment toxicity tests with the amphipod, *Hyalella azteca*, were conducted to measure the biological responses of death, reproduction, and growth.

Isopleth figures of sediment quality data were made to visualize the two-dimensional extent of contamination in Minnesota Slip for selected depth intervals. This information was also used to estimate the volume of contaminants in Minnesota Slip. A comparison of the degree of chemical contamination measured in surficial sediments in Minnesota Slip was made with other sites within the St. Louis River AOC, as well as at other Great Lakes AOCs. A preliminary list of sediment remediation options was also developed for further consideration by the MPCA and stakeholders.

CHAPTER 2

DESCRIPTION OF STUDY SITE

2.1 SITE DESCRIPTION

Minnesota Slip is located in the northern section of the Duluth Harbor basin between Canal Park and the Duluth Entertainment and Convention Center (DECC) (Figure 3). Canal Park is a popular tourist destination in the Duluth-Superior area. The northeast side of the slip is bounded by a parking lot and commercial businesses in Canal Park (e.g., restaurants, hotels, and small retail stores), whereas the southwest side of the slip is bounded by Harbor Avenue and the DECC. The slip itself is used to permanently dock the S.S. William A. Irvin, a former flagship of U.S. Steel's fleet of ore carriers. Since 1986, it has been used as a floating museum administered by the DECC. The Irvin takes up about one-third of the slip as shown in Figure 4. The rest of the slip houses a marina for commercial and private boat owners. In addition, one of the Vista fleet boats is docked in the outer part of the slip; the Vista fleet boats offer harbor and dinner cruises. Entry into the slip is restricted by a drawbridge. The bridge acts as a wave retention wall that decreases washout of the slip.

Three known storm sewers, and two unknown storm sewers, drain into Minnesota Slip. Two other storm sewers discharge from the breakwall immediately outside of the slip. Most of the drainage area borders the downtown business area of Duluth and adjacent residential neighborhoods; this area extends from 2nd Avenue West to 1st Avenue East up to 14th Street. Storm sewers that drain Canal Park and Commerce Street also discharge into the slip.

Local charter boat operators have called the U.S. Coast Guard on several occasions to report oil slicks on the water in Minnesota Slip after rainstorm events. Oil and grease, as well as garbage, appear to be flushed into the slip primarily from the most inland storm sewers. The city of Duluth has created a Storm Water Utility that will seek out funding to update the maps of the storm water system and make improvements to the system. This would include the implementation of best management practices (BMPs) such as the use of sediment traps, retention ponds, and filters. A preproposal submitted to GLNPO in 1999, by the city of Duluth, was unsuccessful in obtaining funding for a contaminant loading study in Minnesota Slip. This type of study would have helped to determine the direction and types of emphasis required for the selection of BMPs to reduce contaminants entering Minnesota Slip from the storm sewers.

Historically, Minnesota Slip has undergone several physical modifications since European settlement of the area. The area encompassing the northern section of the Duluth Harbor was initially swampland. Modern development of the harbor began after 1861 (Walker and Hall 1976). Construction of the Duluth Ship Canal was started in 1870, thereby providing a Duluth entry into the harbor from Lake Superior. A map of the harbor, circa 1887, shows that a portion of the current Minnesota Slip had already been formed through dredging operations (Figure 5). The slip used to be called the Marshall Wells slip, and there was a Marshall Wells building adjacent to it; part of this building is now called the Meyerhoff building.

Several historical photos of the slip are retained at the U.S. Army Corps of Engineers Maritime Museum in Duluth. A photo taken in 1904 shows a coal yard west of Minnesota Slip that was eventually replaced by a scrap yard. A double train freight shed used to be located just west of the slip. A May 1, 1929 photo of the slip shows a pile of material to the north of the slip that appears to be coal. Another historical photo shows workers dumping wheelbarrows full of material into the slip, approximately half-way down the east side of the slip. As of 1931, there was another slip just west of Minnesota Slip; this area is now filled in. Over time, parts of Minnesota Slip have been dredged out and filled in. Additional historical information about surrounding land uses in the vicinity of Minnesota Slip is given in Table 1 (Kellner *et al.* 1999). However, none of these historical businesses have been determined to be responsible for sediment contamination in Minnesota Slip.

2.2 PREVIOUS SEDIMENT INVESTIGATIONS IN MINNESOTA SLIP

Minnesota Slip has been included in the following MPCA sediment assessment studies for the St. Louis River AOC:

- Survey of sediment quality in the Duluth-Superior Harbor: 1993 sampling results (Schubauer-Berigan and Crane 1997) (one core site in Minnesota Slip);
- Sediment assessment of hot spot areas in the Duluth-Superior Harbor (Crane *et al.* 1997) (five core sites in Minnesota Slip);
- Regional Environmental Monitoring and Assessment Program (R-EMAP) surveying, sampling and testing: 1995 and 1996 sampling results (Breneman *et al.* 2000 and unpublished data) [one surficial (0-5 cm) site sampled in 1995 and resampled in 1996 in Minnesota Slip];

- Minnesota Slip sampling to assess PAH analytical techniques (unpublished MPCA data 1998) (two core sites and three surficial sites); and
- Bioaccumulation of contaminants in the Duluth-Superior Harbor (AScI Corporation 1999) (four surficial sites in Minnesota Slip).

The aforementioned studies have provided information about: chemicals of potential concern, contaminants of concern, potential for short-term and long-term toxicity to bottom feeding (i.e., benthic) organisms living in the sediments, potential for changes in the community structure of naturally occurring benthic organisms, and potential for bioaccumulation of certain contaminants (like PAHs) in the base of the aquatic food chain in Minnesota Slip.

These studies have given rise to concerns of extensive contamination in Minnesota Slip sediments. Based on these previous studies, the most contaminated sediments appear to be located in the inner portion of the slip. Some sites are contaminated with oil to as deep as 1.6 m (Crane *et al*. 1997). Chemicals of potential concern include: PAHs, PCBs, mercury, cadmium, chromium, copper, lead, nickel, zinc, AVS, SEM, toxaphene, p,p'-DDD and o,p'-DDT, and KCI-extractable ammonia (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997; AScI Corporation 1999; Breneman *et al*. 2000; unpublished R-EMAP and MPCA data). Since Minnesota did not have its own sediment quality guidelines (SQGs) at the time these studies were conducted, the Ontario low effect level and severe effect level SQGs (Persaud *et al*. 1993) were used as benchmark values to compare the sediment quality data to. Chemicals that exceeded the Ontario low effect level SQGs were designated as chemicals of potential concern. The concentration ranges of chemicals of potential concern, and other parameters, are given in Table 2.

A limited number of 10-d sediment toxicity tests, using *Hyalella azteca* and *Chironomus tentans*, have not revealed significant acute toxicity to the sediments, although sediments from the most contaminated area of the slip have not been tested (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997). The results of one Mutatox[®] test of a Minnesota Slip sample in 1993 indicated the sample was genotoxic (Schubauer-Berigan and Crane 1997). A previous benthic survey showed the slip is consistently dominated with pollutant tolerant worms [e.g., Tubificids and naidid oligochaetes (Crane *et al*. 1997)]. The results of some bioaccumulation studies indicated that benthic worms, *Lumbriculus variegatus*, accumulated PAH compounds in their tissues, but little PCBs or mercury were accumulated (AScI Corporation 1999). Based on this sediment quality information, the MPCA has designated Minnesota Slip as a hot spot area of elevated contamination where there is the potential for biological impairments to the benthic community.

CHAPTER 3

METHODS

3.1 FIELD SAMPLING PROTOCOLS

3.1.1 Field Sampling Conducted During 1998

Before the GLNPO-sponsored study was implemented in Minnesota Slip, state funds were used to analyze a small number of sediment samples from the slip so that the Minnesota Department of Health (MDH) could evaluate the adequacy of their analytical techniques for extracting PAHs from these contaminated sediments. Sediment samples were collected by MPCA staff on May 26, 1998 (sample 98-MNS-01) and during August 12-13, 1998 (samples 98-MNS-02, 98-MNS-03, and 98-MNS-04). The surficial (0-5 cm) sample from 98-MNS-01 was not analyzed. The field sampling information for the other sites are described in Tables 3 and 4. The site locations were marked on an aerial photograph of the slip.

Sediment samples were analyzed for 18 PAH compounds, mercury, lead, and TOC as described in Crane (1999 a,b). The MDH met the quality control (QC) requirements for PAH compounds. Thus, MDH was used to analyze PAHs from sediment samples collected in Minnesota Slip during September 1999.

3.1.2 Field Sampling Conducted During 1999

Sediment samples were collected during September 22-29, 1999 according to the procedures specified in the quality assurance project plan (QAPP) (Crane 1999b) and Smith and Rood (1994). Health and safety measures complied with GLNPO (1997). The field crew consisted of staff provided by GLNPO, Deep Ocean Navigation, and the MPCA. The full field crew was used to sample a portion of the sediment sites, using GLNPO's specially designed research vessel, the R/V Mudpuppy. A contractor to GLNPO took air measurements while people were working on the R/V Mudpuppy to ensure that personal exposure to mercury and volatile organic compounds did not exceed OSHA standards. The other sediment sites were sampled by Judy Crane and Harold Wiegner (MPCA) either from shore or boat piers, or by using the MPCA's R/V Naiad.

8

A nonrandom sampling plan was used to select sites to delineate the vertical and horizontal distribution of selected contaminants, especially in the inner 75% of the slip. Sediment sampling in the outer 25% of the slip was done to confirm the sediments had a lower level of contamination, as indicated in earlier sediment sampling surveys of this slip (Crane *et al*. 1997). A total of eighteen sampling sites were selected. The sampling design in Minnesota Slip was best represented by a rectangular grid pattern for an elliptical-shaped hot spot area (Lubin *et al*. 1995).

A sediment sounding was taken at each site to determine the approximate depth of the soft sediment layer. This was done using a long metal rod of known length, in which the pole was lowered into the sediment and pushed in until the point of refusal (WDNR 1995). A real-time, differential global positioning system (GPS) unit was used to determine station positions by receiving digital codes from three or more satellite systems, computing time and distance, and then calculating an earth-based position. The positional accuracy of the GPS measurements was between 0.5-5 m. The GPS measurements were made in degree/minute format. It was anticipated that problems might be encountered with taking GPS measurements in this boat slip due to potential interference caused by the S.S. William A. Irvin. Thus, all sites were also marked on an aerial photograph of the slip. When the GPS measurements were used to generate a map of the sampling sites in ArcView, several sites appeared in the wrong location. The site locations were corrected to match the sites marked on an aerial photograph of the slip.

The sampling sites were georeferenced using a digital file (TIF image) of a rectified aerial photograph in ArcView (Figure 6). Charles Burg (U.S. Army Corps of Engineers—Detroit District) prepared this digital file by rectifying a GeoTIF image supplied by the MPCA to an existing U.S. Geological Survey (USGS) digital orthophoto quadrangle image.

Three different sediment sampling devices were used in this study (Table 3). A shipek grab sampler, from the MPCA's R/V Naiad, was used to collect composite grab samples of surficial sediments at six sites. The approximate upper 5 cm layer of sediment was removed using a Teflon®-lined spatula. Samples were placed into a 4-L acid and solvent-rinsed Pyrex® measuring cup and homogenized by stirring. Each composited sample was split for synoptic sediment chemistry and toxicity testing analyses. A Livingston corer was used to sample sediments from shore in the approximate one meter band of water between the west wall of Minnesota Slip and the S.S. William A. Irvin. As cohesive sediment core sections were extruded from the core, the outer 1-2 mm of sediment was scraped off, using a Teflon®-lined spatula. The sample was transferred into a 4-L acid and solvent-rinsed Pyrex® measuring cup. Observations

were made, the sediments were mixed, and subsamples were put into pre-cleaned analytical jars per the specifications given in the QAPP (Crane 1999b). GLNPO's R/V Mudpuppy was used to sample 14 sites in Minnesota Slip. The R/V Mudpuppy was either tied off to the boat docks, triple-anchored, or else the crew stabilized the boat against the S.S. William A. Irvin for sites MNS-99-02, MNS-99-03, and MNS-99-14. A Vibrocorer system, composed of lexan plastic, was used to collect sediment cores down to 2.1 m. GLNPO staff pre-cut most of the core tubes to 1.6 m for use in this investigation. The cores were processed on-board the R/V Mudpuppy immediately after collection. Each core was sectioned by sawing off the top section (0-15 cm) and subsequent sections according to the sample scheme given in Table 5. After sectioning the cores, the Vibrocorer samples were decontaminated by scraping the outer 1-2 mm of sediment from the core section with an acid- and solvent-rinsed spatula, and discarding it prior to sample homogenization. Samples were placed into a 4-L acid and solvent-rinsed Pyrex® measuring cup and homogenized by stirring. Homogenized samples were apportioned into pre-cleaned sample jars for delivery to the appropriate analytical laboratory (Crane 1999b).

All samples were stored on ice in a cooler during the day of sampling. At the end of each day, the sediment samples were stored at 4 °C in the dark at the MPCA regional office in Duluth. Samples were delivered to the contract laboratories for chemical analyses within one week of collection. As shown in Table 5, selected sediment core sections were analyzed for either all or a portion of the following chemical/physical measurements: eighteen PAH compounds, 107 PCB congeners, mercury, cadmium, chromium, copper, lead, nickel, selenium, zinc, ammonia, SEM, AVS, TOC, and particle size classes (percentage of sand, silt, and clay). Due to cost constraints, the aforementioned chemical and physical parameters could not be measured in all samples. An emphasis was placed on assessing sediments in the inner 75% of the slip where previous studies have indicated the sediments to be more contaminated (Schubauer-Berigan and Crane 1997; Crane *et al*. 1997).

3.2 SEDIMENT TOXICITY TEST PROCEDURES

Six surficial (0-5 cm) sediment samples (i.e., 99-MNS-01 through 99-MNS-06) were received on October 5, 1999 at the ENSR Fort Collins Environmental Toxicology Laboratory (FCETL) in Fort Collins, CO (Appendices A and B). Sediment samples were stored at 4 ºC in the dark until test setup. Each sediment sample was homogenized prior to use. Homogenization consisted of transferring sediment to a clean Nalgene® container and thoroughly mixing the sediment with a stainless steel auger attached to an electric drill for not less than three minutes. The auger and container were thoroughly cleaned and decontaminated (i.e., soap, tap water rinse, acetone, tap

10

water rinse, HCl, tap water rinse, DI rinse) between homogenization of each sediment. A control sediment (Florissant reference soil obtained from USGS-Biological Resources Division in Columbia, MO) was tested concurrently.

3.2.1 10-d *Chironomus tentans* Toxicity Tests

A portion of the six sediment samples were used for 10-d static-renewal toxicity tests using the midge, *Chironomus tentans*. The tests were conducted according to USEPA (1994) and ASTM Method E 1706-95b (ASTM 1997) guidelines. The test was modified to include ash free dry weight (AFDW) as a growth endpoint, per the draft (unpublished) ASTM and USEPA guidelines that have since then been published as ASTM (2001) and USEPA (2000a). The biological responses measured were death (defined as no visible movement or any response to gentle prodding with a blunt probe) and growth (mean dry weight and AFDW per surviving organism). The complete test protocol is included in ENSR's sediment toxicity test report given in Appendix A.

On day 1, dissolved oxygen in the MNS-99-03 and MNS-99-04 test chambers was at or less than 2.5 mg/L (Appendix A). Therefore, aeration was initiated on day 1 in all test chambers, including the control. The aeration apparatus consisted of a Pasteur pipette (connected to the laboratory air supply), the tip of which was positioned so as not to disturb the sediment. All test chambers were aerated for the remainder of the test.

Acute reference toxicant tests were initiated from the lot of *C. tentans* obtained for this study. Sodium chloride was the reference toxicant with moderately hard water as the dilution water. The tests were 96 hours in length; 24-hour data were also collected, where possible, from the tests for use with ENSR's historical 24-hour reference toxicant database.

3.2.2 28- to 42-d *Hyalella azteca* Toxicity Tests

A portion of the six sediment samples were used for 28- to 42-d static-renewal toxicity tests using the amphipod, *Hyalella azteca*. At the time the tests were conducted, methods had not yet been published, but were available in the draft USEPA and ASTM guidelines for conducting sediment toxicity tests which have since been published as USEPA (2000a) and ASTM (2001). The biological responses measured were death (defined as no visible movement or any response to gentle prodding with a blunt probe), reproduction (number of young produced per female), and growth (mean dry weight per surviving organism). At the time the tests were conducted, the 42-d

reproduction study was new and little historical data existed for it. The ENSR Study Director decided to include six control sediment treatments, one with each test sediment.

On days 0 through 28, the organisms were exposed to the test sediments with overlying water. On day 28, all organisms were removed from the test chambers. Live organisms were counted and organisms from replicates A through D were removed for determination of dry weight. Organisms from replicates E through L were placed back in test chambers that contained overlying water only (and a small piece of Nitex netting). On day 35, the number of surviving adults and young were counted; young were removed from the test chambers. On day 42, the number of surviving adults and young were counted and the surviving adults were removed for determination of dry weight and identification of males and females. Adult *H. azteca* from each replicate were placed in 10% sugar formalin. Under a compound microscope, males were identified by the enlarged second gnathopod. Organisms were then rinsed with deionized water, dried at 60-90 °C, and weighed. Reproduction for each replicate was determined by summing the number of young produced on days 35 and 42 and dividing by the number of females in the test chamber at test termination. Additional information about the test procedures are provided in the toxicity test report produced by ENSR in Appendix B.

Acute reference toxicant tests were initiated using the lots of *H. azteca* obtained for this study. Sodium chloride was the reference toxicant with moderately hard water as the dilution water. Tests were 96 hours in length; 24-hour data were also collected for use with ENSR's historical 24-hour reference toxicant database.

3.3 LABORATORY ANALYTICAL PROCEDURES

Sediment samples were analyzed by three different analytical laboratories. PCB congeners, AVS, and SEM (cadmium, copper, mercury, lead, nickel, and zinc) were analyzed by En Chem (Madison, WI), whereas particle size was analyzed by the University of Minnesota-Duluth (UMD). PAH compounds, mercury, cadmium, chromium, copper, lead, nickel, selenium, zinc, ammonia, and TOC were analyzed by MDH. Each laboratory did its own determination of percent moisture. Most of the sediment samples were either analyzed or extracted (for organics) within the holding times specified in the QAPP (Crane 1999b). However, the sediment samples analyzed by MDH for metals and TOC exceeded the holding times specified in the QAPP (Crane 1999b). The sediment samples for conventional metals were digested within 34 days to 2.5 months instead of 30 days, and TOC was analyzed within 7 months instead of 40 days. The quality of the data was acceptable for samples that exceeded the holding times.

A subset of 107 PCB congeners were analyzed by capillary column GC/ECD according to En Chem's standard operating procedures (SOPs) (En Chem 1999a). Eighteen target PAH compounds were measured by capillary column GC/MS SIM using MDH Method 513 (MDH 1997). Mercury was measured using flow injection atomic absorption spectrometry--cold vapor technique according to EPA Method 245.1 A (USEPA 1983). The extraction of sediment samples for total metals was based on EPA Method 200.7 (USEPA 1991); the metals were analyzed using stabilized temperature graphite furnace atomic absorption spectroscopy (MDH 1993). Ammonia was determined using QuickChem method 12-107-06-1-A (Lachat Instruments 1994). AVS and SEM were determined based on En Chem's SOP WCM-63 (En Chem 1999b). AVS was measured using a spectrophotometer, whereas SEM was measured using an inductively coupled plasma emission spectrophotometer and cold vapor atomic absorption spectrophotometer (for mercury only). TOC was measured on a Dohrmann DC-80 TOC analyzer (Rosemount Analytical 1990a,b; 1991). Percent moisture of samples run by MDH was done according to MDH Method 261 (MDH 1995). Particle size was measured using an Horiba LA-900 analyzer (Lodge 1996). The particle size results were reported as percentages of the following classes: sand and gravel (>53 μm), coarse silt (53 - 20 μm), medium silt (20 - 5 μm), fine silt (5 - 2 μm), coarse clay (2 - 0.2 μm), medium clay (0.2 - 0.08 μm), and fine clay (<0.08 μm).

3.4 QUALITY ASSURANCE/QUALITY CONTROL

The Quality Assurance/Quality Control (QA/QC) procedures followed in this study adhered to the site-specific QAPP (Crane 1999b) which was based on guidance given in USEPA (1995). Two field replicate samples were collected to assess field precision. Analytical data quality objectives were made to assess analytical precision, accuracy, and completeness. The sampling strategy was designed to generate representative data for Minnesota Slip. The analytical methods utilized in this study were similar to methods used in previous investigations so that the data would be directly comparable to them.

A summary of the analytical quality control checks for chemical and physical parameters, as well as the test acceptability requirements for sediment toxicity tests are given in the QAPP (Crane 1999b).

3.5 DATA ANALYSIS

The analytical data were obtained electronically from each laboratory as either Excel™ or Lotus™ spreadsheets. The results of analytical duplicates were averaged with the field sample results, providing all data quality objectives had been met as specified in the QAPP (Crane 1999b). All manipulations of the data sets were double-checked to ensure that no errors had occurred. Electronic copies of the sediment toxicity test reports (Appendices A and B) were obtained from ENSR.

3.5.1   Comparison of Sediment Chemistry Data to Sediment Quality Targets

Sediment chemistry data were compared to Level I and Level II sediment quality targets (SQTs) adopted for the St. Louis River AOC (Crane *et al*. 2000) in which:

- Level I SQTs are intended to identify contaminant concentrations below which harmful effects on sediment-dwelling organisms are unlikely to be observed; and
- Level II SQTs are intended to identify contaminant concentrations above which harmful effects on sediment-dwelling organisms are likely to be frequently or always observed.

The SQTs were used as a benchmark tool by which to assess the severity of sediment contamination in Minnesota Slip, and to predict the incidence of toxicity in sediment samples collected from this slip. For most chemicals, the SQTs are the same as the consensus-based sediment quality guidelines (SQGs) that were developed by Ingersoll and MacDonald (1999) and MacDonald *et al*. (2000a) for evaluating whole sediment chemistry data. As the term implies, consensus-based SQGs reflect the agreement among the various SQGs by providing an estimate of their central tendency for SQGs of similar narrative intent. Importantly, the consensus-based SQGs are considered to provide a unifying synthesis of the existing SQGs, reflect causal rather than correlative effects, and account for the effects of contaminant mixtures in sediment (Swartz 1999; MacDonald *et al*. 2000a,b; Di Toro and McGrath 2000).

3.5.2   Calculation of Mean Probable Effect Concentration Quotients

Most of the Level II SQTs were adopted from consensus-based probable effect concentration (PEC) values (USEPA 2000b). Mean PEC quotients (PEC-Qs), for chemicals with reliable PECs, were calculated using the methods recommended by USEPA (2000b) and outlined in the box on the following page. Mean PEC-Qs were calculated using dry weight concentrations of chemical

contaminants, and values representing one-half the detection limit were used in instances where substances were not detected.

Procedure for Calculating Mean PEC-Qs for Chemicals with Reliable PECs (USEPA 2000b)

Step 1. Calculate the individual PEC-Qs for chemicals with reliable PECs (i.e., metals, total PAHs, and total PCBs). Note: the PEC for total PAHs (instead of the PECs for individual PAHs) was used in the calculation to avoid double counting the PAH concentration data.

$$\text{PEC-Q} = \frac{\text{chemical concentration (in dry wt.)}}{\text{corresponding PEC value}}$$

Step 2. Calculate the mean PEC-Q for the metals with reliable PECs (i.e., arsenic, cadmium, chromium, copper, lead, nickel, and zinc).

$$\text{mean PEC-Q}_{metals} = \frac{\Sigma \text{ individual metal PEC-Qs}}{n}$$

where n = number of metals with reliable PECs for which sediment chemistry data were available (i.e., 1 to 7).

Step 3. Calculate the mean PEC-Q for the three main classes of chemicals with reliable PECs. Note: the average PEC-Q for pesticides was not used in this calculation because no matching sediment chemistry and toxicity data were available for this class of contaminants in Minnesota Slip.

$$\text{mean PEC-Q} = \frac{(\text{mean PEC-Q}_{metals} + \text{PEC-Q}_{T.\,PAHs} + \text{PEC-Q}_{T.\,PCBs})}{n}$$

where n = number of classes of chemicals for which sediment chemistry data were available (i.e., 1 to 3).

3.5.3 Development of Isopleth Figures for Sediment Quality Parameters

Electronic sediment quality data obtained from field sampling conducted in 1998 and 1999 were merged together in order to examine spatial trends in the data. Isopleth figures, for selected depth intervals, were generated for the percentage of sand, silt, and clay, TOC, total PAHs [based on the addition of the 13 low molecular weight (LMW) and high molecular weight (HMW) PAHs], total PCBs, mercury, lead, and zinc.

The steps involved in generating isopleth figures for sediment quality parameters in Minnesota Slip were as follows:

1. Several different interpolation techniques were evaluated to determine which one was most appropriate to apply to the Minnesota Slip data set, and also provided flexibility in terms of modifying and working with the resulting maps. The techniques that were evaluated included:

   - The Inverse Distance Weighted (IDW) interpolator in ArcView Version 3.2, ESRI's Geographic Information System (GIS) software. This interpolator assumes that each input point has a local influence that diminishes with distance. It weights the points closer to the processing cell greater than those farther away.

   - The Spline interpolator in ArcView Version 3.2. This is a general purpose interpolation method that fits a minimum curvature surface through the input points. This method is best for gently varying surfaces such as elevation, water table heights, or pollutant concentrations.

   - The Natural Neighbor interpolator employed by the U.S. EPA's Fully Integrated Environmental Location Decision Support (FIELDS) system. This interpolator is a weighted moving average technique that uses geometric relationships in order to choose and weight nearby points. It is capable of generating estimates above and below the maximum and minimum of the original data (i.e., parameter value extrapolation).

   - The Natural Neighbor interpolator employed by the University of Tennessee Research Corporation's Spatial Analysis and Decision Assistance (SADA) computer software (SADA Version 2.0.108).

The maps were produced using the FIELDS natural neighbor interpolator within ArcView. The FIELDS interpolator is added into ArcView as an extension, which is an add-on program. The interpolation extension was downloaded from the FIELDS system web page (http://www.epa.gov/region5fields/static/pages/index.html). This interpolation method was deemed to be the most appropriate option for this data set, for the following reasons:

- Natural Neighbor interpolation provides more precise results than IDW interpolation;
- Natural Neighbor interpolation calculates weights depending on the area about each of the data points (Voronoi polygons) instead of the distance between data points, as with IDW;
- The ArcView software provides the most flexibility for modifying and presenting the results; and,

- Dr. Robert Stewart, University of Tennessee and creator of SADA, recommended that Natural Neighbor interpolation be used for this site based on discussions held with Dr. Judy Crane during a SADA training workshop (March 8, 2001).

The isopleth figures were generated in color using a maximum of six isopleth ranges. The rationale for the selection of isopleth ranges was as follows:

- For particle size and TOC, the isopleth ranges were denoted at even intervals that took into consideration the range of values observed for each parameter;
- For total PCBs, total PAHs, mercury, lead, zinc, and mean PEC-Qs, the number of ranges was partly dependent on the distribution of the sediment chemistry data. As a minimum, the following ranges were included in the isopleth figures:
  - 0 to < Level I SQT,
  - ≥ Level I SQT to < ½ Level II SQT,
  - ≥ ½ Level II SQT to < Level II SQT, and
  - ≥ Level II SQT.

  If many low level samples were measured, then the lowest range was subdivided as follows:
  - 0 to < ½ Level I SQT, and
  - ≥ ½ Level I SQT to < Level I SQT.

  If many high level samples were measured, then the upper level range was further subdivided to make it easier to view the most contaminated areas of the slip. By dividing the isopleth ranges in this manner, it was easier to discern possible inputs of contaminants into the slip (e.g., through storm water outfalls) and to identify areas that may require remediation.

3.5.4 Comparison of Mean PEC-Qs

A step-wise approach was used to compare sediment chemistry data in surficial sediment samples from Minnesota Slip with that in surficial sediments from other sites within the St. Louis River AOC and other Great Lakes AOCs. The five main steps in this process included:

- Collection, evaluation, and compilation of the existing information on sediment quality conditions in Minnesota Slip, the St. Louis River AOC, and other Great Lakes AOCs;
- Identification of appropriate sites within the St. Louis River AOC to include in the comparison;
- Identification of appropriate Great Lakes AOCs to include in the comparison;

- Determination of mean PEC-Qs for sediment samples from Minnesota Slip, other areas within the St. Louis River AOC, and selected Great Lakes AOCs, and;
- Production of box and whisker plots and cumulative distribution frequency (CDF) plots to graphically present the distribution of mean PEC-Qs within the selected areas.

Each of these steps is described in the following subsections.

3.5.4.1 *Collection, Evaluation, and Compilation of Sediment Quality Data*

The information used in this comparison was acquired from four different sources. The information on sediment quality conditions in the St. Louis River AOC (including a small number of Minnesota Slip sites) was obtained from the existing matching sediment chemistry and toxicity database developed for the purpose of evaluating numerical SQTs and sediment contamination in the St. Louis River AOC (Crane *et al.* 2000). The information on sediment quality conditions in other Great Lakes AOCs was obtained from the matching sediment chemistry and toxicity database maintained by MacDonald Environmental Sciences Ltd. (MESL). Sediment quality data specific to the Indiana Harbor AOC was obtained from the MESL project database, which included both matching and non-matching sediment chemistry and toxicity data. All of the data sets that were included in these databases were critically reviewed and verified to ensure that only high quality data sets were used in the assessment. The screening criteria that were used to critically review the data provided a means of consistently evaluating the methods that were used in each study, including the procedures that were used to collect, handle, and transport sediment samples, the protocols that were applied to conduct sediment toxicity tests, the methods that were used to determine the concentrations of contaminants in sediments, and the statistical tests that were applied to the study results (MacDonald *et al.* 2000a; Crane *et al.* 2000). The Minnesota Slip data set was acquired in electronic format from MPCA files for this site. Only data obtained from surficial sediment samples were included in the analysis, which were considered to be any samples with an upper sampling depth of zero.

3.5.4.2 *Identification of Appropriate Sites Within the St. Louis River AOC*

The matching sediment chemistry and toxicity database that was developed for the St. Louis River AOC as part of a previous project (Crane *et al.* 2000) was augmented with all the sediment chemistry and toxicity data from this project (i.e., including sites that only had sediment chemistry data available) to yield 198 data records. This database included samples from

approximately 30 different reaches within the AOC. The sites selected for this analysis, besides Minnesota Slip, included: Interlake/Duluth Tar Superfund site, Howards Bay, the embayment around the Western Lake Superior Sanitary District (WLSSD) and the confluence of Miller and Coffee Creeks (i.e., the embayment encompassed one hot spot site), and the matching sediment chemistry and toxicity samples collected for an assessment of contaminated areas in the Duluth-Superior Harbor, as well as a reference area (Crane *et al*. 1997). These sites were selected based on the criteria that data were available for ten or greater surficial sediment samples. In addition, the entire St. Louis River AOC was included as an area (both including and excluding the 33 samples collected from Minnesota Slip). The sediment quality data included in the entire St. Louis River AOC ranged from reference areas to Superfund sites.

3.5.4.3 *Identification of Appropriate Great Lakes AOCs*

The matching sediment chemistry and toxicity database maintained by MESL contains information on sediment quality conditions in a total of 21 Great Lakes AOCs. Figure 7 shows the locations of all Great Lakes AOCs. The other AOCs, besides the St. Louis River, that were selected for this analysis included: Indiana Harbor, IN; Sheboygan Harbor, WI; Maumee River, OH; St. Mary's River, ON and MI; Waukegan Harbor, IL; Cuyahoga River, OH; Oswego River, NY; and the St. Clair River, ON and MI. These areas were selected based on three criteria:

- Availability of data for twenty or greater surficial sediment samples;
- Provision of broad geographic coverage within the Great Lakes; and
- Similar patterns of contamination in Minnesota Slip (i.e., a mixture of PAHs, PCBs, and metals in the sediments).

3.5.4.4 *Determination of Mean PEC-Q Distribution*

The extent of chemical contamination in each sediment sample was determined by calculating mean PEC-Qs as described in Section 3.5.2. Mean PEC-Qs were determined two different ways, both including and excluding mercury. This approach was selected because, although mercury is an important chemical of potential concern in the St. Louis River AOC, a reliable PEC is not available for mercury. USEPA (2000b) indicated that the reason reliable SQGs do not exist for mercury is because of mercury speciation in sediments and the fact that methyl mercury tends to bioaccumulate in organisms rather than resulting in direct toxicity.

The distribution of mean PEC-Qs in Minnesota Slip, other sites within the St. Louis River AOC, and selected areas in the Great Lakes was determined by calculating summary statistics for each of the selected areas, using Microsoft Excel™ software, including:

- Measures of central tendency (mean, median);
- Measures of variation (range, standard deviation); and,
- Measures of position (10th and 90th percentile).

3.5.4.5 *Production of Box and Whisker Plots and Cumulative Distribution Frequency Plots*

Box and whisker plots were generated within the graphical software program SigmaPlot Version 6.0. Box and whisker plots graph data as a box representing statistical values. The boundary of the box closest to zero indicates the 25th percentile, a line within the box marks the median, and the boundary of the box farthest from zero indicates the 75th percentile. Whiskers above and below the box indicate the 90th and 10th percentiles, respectively.

Cumulative distribution frequency (CDF) plots were also generated using SigmaPlot Version 6.0. The design is such that the mean PEC-Q values are the independent variable (x-axis), and the number of stations for each area are normalized to 100 (% stations) and represented on the y-axis. These plots display exactly the same information as do histograms, except histogram values are summed as the independent (x axis) variable increases, while the CDF plot begins at 0% (left axis) and ends at 100% (right axis). These plots are extremely useful for quickly finding the mean PEC-Q of a distribution corresponding to any given percentile (such as the median).

3.5.5 Calculation of Sediment Contaminant Volume Estimates

The FIELDS software was used to estimate the volume of total PAHs within each sediment depth interval (i.e., length x width x depth) and the proportion of that depth interval that exceeded a mean PEC-Q of 0.6. At mean PEC-Qs of >0.6, the probability of observing chronic sediment toxicity is higher (i.e., >50%), indicating that sediment-dwelling organisms would be afforded a lower level of protection (USEPA 2000b). The density of silty sand (i.e., 3257 lb yd^{-3}) was used as a default parameter in the calculations.

3.6 DATA ARCHIVAL

The sediment quality data obtained from this study will be entered into a new GIS-based sediment quality database for the St. Louis River (GLNPO grant number GL975363-01). Hard copies of the data will be archived at the MPCA for five years, upon which time it will be moved off site to the Minnesota Records Center for 30 years. After that time period, the files will either be returned to the MPCA, archived at the Minnesota Historical Society, or recycled.

CHAPTER 4

RESULTS

4.1 FIELD SAMPLING INFORMATION

The field sampling information for sediment samples collected from Minnesota Slip is given in Table 3. Alterations in the field sampling plan given in the QAPP (Crane 1999b) were made as necessary. Plans to sample below two storm water outfalls in the inner slip had to be adjusted because the sediments contained too much gravel to obtain a cohesive sediment core. Coarse sediments were also encountered in some areas between the wall of the slip and the S.S. William A. Irvin. In addition, some alterations in sample sites had to be made because several boats were still in the marina at the end of September 1999 when most of the field sampling was conducted.

During the 1998 field sampling trip, gas bubbles were observed throughout the sediment cores collected at 98-MNS-02 and 98-MNS-03, using the Livingston corer. The gas bubbles probably resulted from the generation of methane gas in the sediments. Gas bubbles were also observed on the surface of the water where the sediments were collected. During the 1999 field sampling trip, gas bubbles were also observed throughout the sediment cores collected with a Livingston corer at: MNS-99-07, MNS-99-09, and MNS-99-10. A few gas bubbles were observed in the sediment core for MNS-99-08. Gas bubbles were not so easily observed in samples collected using the Vibrocorer, possibly because the samples were processed more rapidly and the lexan core tubes were cut into sections to extract the sediments. With the Livingston corer, the sediments were extruded out of the top of the clear core tube which allowed more time for observation of the sediments.

Pieces of trash, detritus, and oil were observed in many sediment samples collected from Minnesota Slip (Table 3). Garbage was removed from each sample prior to homogenizing the sediment.

4.2 SEDIMENT TOXICITY TESTS

4.2.1 10-d *C. tentans* Sediment Toxicity Tests

Water quality parameters measured during the test are included in Appendix A. On day 1, dissolved oxygen concentrations in MNS-99-03 and MNS-99-04 fell to 2.4 and 2.5 mg/L,

respectively. Aeration was initiated on day 1 in all test chambers and dissolved oxygen concentrations remained above 5.0 mg/L for the remainder of the study. Test temperature, as measured in the test solutions, remained at 23 °C throughout the test. The pH of the test solutions ranged from 7.0 to 8.5. Ammonia was detectable in the overlying water of all treatments on day 0. Ammonia concentrations decreased after aeration was initiated. In the ENSR study director's judgment, these protocol deviations to dissolved oxygen and ammonia did not impact the test outcome. The physical and chemical data of the overlying water are provided in the toxicity test report (Appendix A).

At test takedown, it was discovered that four replicates contained no live or dead organisms. Those replicates were Control B, MNS-99-04 H, MNS-99-05 H, and MNS-99-06 F. Since there were organisms in all other replicates and these four replicates were in a row after test chamber randomization (Appendix A), it was the study director's judgment at ENSR that these test chambers were not seeded with test organisms at test initiation. These four test chambers were, therefore, not included in the analysis of the data. In addition, 12 organisms were found in MNS-99-01 replicate H and 19 organisms were found in MNS-00-02 replicate E. It is likely that replicate E of MNS-99-02 was double-seeded so it was assumed that 20 organisms were put into the test chamber at test initiation. The number of organisms placed into replicate H of MNS-99-01 is not known. However, due to the good survival of all other MNS-99-01 replicates (not less than 90% survival in any replicate) it was assumed by the ENSR study director that 12 organisms were placed in this chamber at test initiation. Both of these test chambers were included in the statistical analysis of the data.

Percent survival and growth of test organisms were determined after ten days of exposure. Growth was measured both as AFDW and as dry weight. The results are presented in Table 6.

Significant differences were identified with Toxstat Version 3.4 (West, Inc. and Gulley 1994). Survival data were transformed using arcsine square root. Data normality was evaluated with the Chi-square goodness of fit test ($\alpha = 0.01$) due to the large number of treatments and replicates; homogeneity of variance was evaluated with Bartlett's test ($\alpha = 0.01$). All data were found to meet the requirements for parametric analysis; where necessary, data were analyzed using a T-test with Bonferroni adjustment ($\alpha = 0.05$) because of unequal numbers of replicates in the treatments.

Comparison of treatment survival to the control was completed by observation since control survival (71.4%) was less than in any of the treatments (i.e., 81.4% to 95%). Dry weight and

23

AFDW were compared to the control using Toxstat. Dry weight and AFDW in the test treatments were not significantly reduced relative to the control.

At the time the statistical analysis of the sediment toxicity data for *C. tentans* was conducted, the corresponding sediment chemistry data were not yet available. Since there was a gradient of higher survival (i.e., 95%) to lower survival (i.e., 81.4%) from the outer slip to the inner slip in the 10-d *C. tentans* toxicity test results (Table 6), the ENSR study director was asked to compare the survival, dry weight, and AFDW from sediments MNS-99-02 through MNS-99-06 to sediment MNS-99-01 using Toxstat (Appendix A). MNS-99-01 was suspected of being less contaminated than the other Minnesota Slip sites in which sediment toxicity tests were conducted, and could possibly be used as a reference site for the other samples. Survival in sediment MNS-99-05 (81.4%) was significantly reduced relative to survival in sediment MNS-99-01 (95%). There was no significant reduction in dry weight or AFDW in sediments MNS-99-02, MNS-99-03, MNS-99-04, or MNS-99-06 relative to sediment MNS-99-01.

Three reference toxicant tests were conducted using *C. tentans* from one lot number. Twenty-four hour reference toxicant data from all three tests were included in ENSR's historical reference toxicant database. Two tests also had acceptable 96-hour data. Because previous reference toxicant tests conducted at FCETL with this species were only 24 hours in duration, and only three 96-hour tests have been conducted, insufficient data have been generated to calculate historical 95% control limits for the 96-hour endpoint. The *C. tentans* reference toxicant data sheets and 24-hour reference toxicant control chart are included in Appendix A.

Judy Crane (MPCA) conducted an external QA/QC review of ENSR's sediment toxicity test report given in Appendix A to verify the data, including checks on transcriptions of the data from laboratory sheets to the report, calculations, and statistical procedures that were used. The data passed this QA/QC evaluation.

4.2.2 28- to 42-d *H. azteca* Toxicity Tests

Water quality parameters measured during the test are included in Appendix B. Aeration was initiated on day 0 in all test chambers, because previous testing with *C. tentans* under the same test conditions indicated that dissolved oxygen in some of the test sediments might drop below 2.5 mg/L. On day 0 (before organisms were added and aeration initiated), dissolved oxygen concentrations in sediments MNS-99-01, MNS-99-02, and MNS-99-03 were ≤4.2 mg/L. All other dissolved oxygen measurements were ≥5.0 in all treatments for the remainder of the test. Aeration

was terminated on day 28 at the end of the sediment exposure. Test chambers were not aerated during the water-only exposure phase of the test and dissolved oxygen concentrations remained greater than 5.3 mg/L for the remainder of the test. On day 11, test temperature in Controls 1, 2, and 3 and sediments MNS-99-01, MNS-99-02, and MNS-99-03 was 17 ˚C. This decrease in temperature was due to a malfunctioning refrigeration/heating unit (Remcor™). The unit was repaired and test temperatures remained between 22 and 24 ˚C for the remainder of the test. In the ENSR study director's judgment, this temperature deviation did not impact the study results. The pH of the overlying water in the test sediment beakers ranged from 7.3 to 8.6. Ammonia was detectable in all test sediments, except MNS-99-06, on day 0. Ammonia concentrations decreased after aeration was initiated. The highest ammonia concentration (38 mg/L) was measured on day 0 in MNS-99-03. Because the test included a "with-sediment" period (days 0-28) and a "without-sediment" period (days 28-42), water quality data are presented for these separate time periods in the toxicity test report (Appendix B).

Percent survival and growth of test organisms were determined after 28 days of sediment exposure. Survival and number of young produced on day 35 was determined. Survival, growth, and reproduction at test termination (day 42) were also measured. The raw test data are presented in Appendix B. Survival results are presented in Table 7. Dry weight (per surviving organism) results are presented in Table 8. Reproduction results are presented in Table 9.

Controls 1, 2, and 3 all met the acceptability criterion of 80% survival on day 28. All endpoints (survival, reproduction, and dry weight) for these treatments were statistically compared and were not found to be significantly different. Therefore, data from all three of these controls were combined and used as the control for comparison to MNS-99-01, MNS-99-02, and MNS-99-03. Controls 4 and 5 had less than 80% survival on day 28. These controls were not used for comparison to treatments MNS-99-04, MNS-99-05, and MNS-99-06; only Control 6 was used. The poor survival in Controls 4 and 5 may have been due to the use of reconstituted water as the overlying water in these tests. The U.S. EPA guidelines for the 28- to 42-d *H. azteca* toxicity test (USEPA 2000a) recommend using either culture water, well water, surface water, or site water as the overlying water; the use of reconstituted water is specifically not recommended. However, this toxicity test was not invalidated by using reconstituted water, and the results of this amphipod test are useable for this study.

Significant differences were identified with Toxstat Version 3.4 (West, Inc. and Gulley 1994). Survival data were transformed using arcsine square root. Normality was evaluated with the Chi-Square or Shapiro-Wilks test ($\alpha = 0.01$); homogeneity of variance was evaluated with Bartlett's

test ($\alpha = 0.01$). Where data met the requirements for parametric analysis; data were analyzed using analysis of variance with Dunnett's test or (for unequal replicates) a T-test with Bonferroni adjustment ($\alpha = 0.05$). Where parametric requirements were not met, data were analyzed with Steel's Many-One Rank test.

Survival in MNS-99-03 and MNS-99-05 was significantly lower than in the respective controls. Because survival was significantly lower in these two sediments, they were excluded from analysis of sublethal endpoints. Neither reproduction nor dry weight of any of the remaining test treatments were significantly less than in the respective controls.

Three reference toxicant tests were conducted using *H. azteca* from two different lot numbers (Appendix B). Twenty-four hour reference toxicant data from all three tests were included in ENSR's historical reference toxicant database. All three tests had acceptable 96-hour data. Because previous reference toxicant tests conducted at the FCETL with this species were only 24 hours in duration, and only three 96-hour tests have been conducted, insufficient data have been generated to calculate reliable historical 95% control limits for the 96-hour endpoint. The *H. azteca* reference toxicant data sheets and 24-hour reference toxicant control chart are included in Appendix B.

Judy Crane (MPCA) conducted an external QA/QC review of ENSR's sediment toxicity test report given in Appendix B to verify the data, including checks on transcriptions of the data from laboratory sheets to the report, calculations, and statistical procedures that were used. The data passed this QA/QC evaluation.

4.3 SEDIMENT CHEMISTRY RESULTS

The sediment quality data assembled for this study met the data quality objectives of the QAPP (Crane 1999b), except for a few quality control deviations noted in the following sections.

4.3.1 Particle Size

The particle size distribution in Minnesota Slip is presented in Table 10. The composition of the sediments in Minnesota Slip is heterogeneous in regards to particle size. The percentage of sand and gravel (>53 μm), silt (53 – 2 μm), and clay (2 – 0 μm) ranged from 15.6 – 98.3%, 1.4 – 73.9%, and 0.3 – 13.4% by volume, respectively. A detailed analysis of the three different silt and clay fractions is given in Table 10, with the medium silt (20-5 μm) and coarse clay (2 – 0.2 μm)

26

fractions comprising the largest percentage of the respective silt and clay fractions. Very little medium (0.2 – 0.08 µm) or fine (<0.08 µm) clay fractions were measured in the sediments. The median particle size diameter was calculated for samples with <50% sand and was estimated for samples with >50% sand (Table 10). The surface area of particles in the sediment samples ranged from 254 – 16,002 cm^2/cm^3, with very sandy sediments comprising the smallest surface area (Table 10).

Enough particle size data were available to generate isopleth graphics for the 0-15 cm and 15-30 cm depth segments for the entire slip, and for the 30-45 cm and 45-60 cm depth segments for the inner slip. The particle size isopleth figures for sand (>53 µm), silt (53-2 µm), and clay (2-0 µm) visibly show the heterogeneity of the sediments between sites and within the same site at different depth intervals (Figures 8 to 10, respectively). A few areas of the slip that appeared to be physically scoured (i.e., MNS-99-06, MNS-99-07 and MNS-99-11) had a very high percentage of sand (Figure 8) down to 30 cm for which data were available.

4.3.2 TOC

The range of TOC values in the 0-5 cm surficial sediments, in which matching sediment toxicity tests were run, is given in Table 11. The distribution of TOC throughout Minnesota Slip for the 0-15, 15-30, and 30-45 cm depth intervals is shown in the isopleth plots in Figure 11. TOC data for the inner half of the slip is shown in Figure 11 for isopleth plots down to 150 cm. TOC ranged from 0.56 – 21% in the slip. Detrital matter, wood fibers, and oil were observed in several sediment samples collected from Minnesota Slip (Table 3) which contributed to the TOC measurements. The highest percentage of TOC (14 – 21%) was observed at MNS-99-04 between the 60-75, 75-90, and 90-120 cm depth segments.

4.3.3 Total PCBs

Total PCBs were determined by adding up the individual or coeluting congeners in each sample. A value of one-half the detection limit was used for nondetectable PCB congener data. The range of total PCB concentrations in the 0-5 cm surficial sediments, in which matching sediment toxicity tests were run, is shown in Table 11. Total PCB concentrations were between the Level I and Level II SQT values in the 0-15 cm isopleth figure (Figure 12). The highest total PCB concentrations were present in the middle part of the slip. The lowest PCB concentrations were observed at two sites with very sandy sediments (MNS-99-06 and MNS-99-11; Table 11 and Figure 12).

The most predominant PCB congeners included BZ numbers (Ballschmiter and Zell 1980):

- 110/77: 2,3,3'4',6-pentachlorobiphenyl / 3,3',4,4'-tetrachlorobiphenyl;
- 47: 2,2',4,4'-tetrachlorobiphenyl;
- 138/163: 2,2',3,4,4',5'-hexachlorobiphenyl / 2,3,3',4',5,6-hexachlorobiphenyl;
- 101/90: 2,2',4,5,5'-pentachlorobiphenyl / 2,2',3,4',5-pentachlorobiphenyl; and
- 66/95: 2,3',4,4'-tetrachlorobiphenyl / 2,2',3,5',6-pentachlorobiphenyl.

Congeners listed together indicate co-eluting congeners that cannot be separated using GC/ECD. The full assemblage of PCB congener data from this study will be entered into a new GIS-based sediment quality database for the St. Louis River AOC.

4.3.4 PAHs

A summary of the results for individual PAH compounds is given in Table 12. The relative percent difference (RPD) was calculated for field replicate samples. The RPD was within the 50% QC limit for most of the replicates, except for several PAHs in MNS-99-13R (15-30 cm) and MNS-99-04R (45-60 cm).   This exceedance of the QC limit for RPD was most likely due to the heterogeneous distribution of PAH compounds between field samples and replicates, rather than due to a problem with the analytical precision of the PAH method. Therefore, these field replicate samples were treated as separate samples, except that they were averaged for the purpose of creating contaminant isopleth figures.

Of the 18 PAH compounds, Level I and Level II SQT values were available for 13 compounds corresponding to 7 LMW PAHs (2-methylnaphthalene, acenapthene, acenapthylene, anthracene, fluorene, naphthalene, and phenanthrene) and 6 HMW PAHs (benz[a]anthracene, benzo[a]pyrene, chrysene, dibenzo[a,h]anthracene, fluoranthene, and pyrene). Of these 13 compounds, most of them exceeded the corresponding Level II SQT value in most depth intervals, except for 2-methylnaphthalene, acenapthylene, and naphthalene which exceeded the corresponding Level II SQT value mostly in deeper sediments (i.e., below 60 cm).

The percentage of PAH compounds comprising the LMW and HMW PAHs is given in Table 13. Phenanthrene made up over 66% of the mean LMW PAHs, whereas acenapthene comprised the lowest percentage (0.65%) of LMW PAHs. The mix of HMW PAHs was more widely distributed with fluoranthene (29.5%), pyrene (27.3%), chrysene (14.7%), benz[a]anthracene (13.3%), and

benzo[a]pyrene (12.5%) comprising the majority of the mean HMW PAH concentrations for all sites and depth intervals for which PAH data were collected.

A summary of the concentrations of LMW, HMW, and total PAHs (based on the addition of the 13 LMW and HMW compounds) is presented in Table 14. Total PAHs ranged from 7.07 – 1,188 mg/kg dry wt., with sites MNS-99-11 (0-15 cm) and MNS-99-04 (75-90 cm) containing the lowest and highest total PAH concentrations, respectively. Nearly all sites exceeded the Level II SQT value. The HMW PAHs comprised, on average, 74.5% (±5.8 %) of total PAHs (Table 15). The percentage composition of HMW and LMW PAHs was fairly consistent in Minnesota Slip, and the concentration of HMW PAHs can be predicted from the concentration of LMW PAHs based on the following regression equation:

HMW PAHs (mg/kg dry wt.) = 1.43[LMW PAHs (mg/kg dry wt.)] + 20.7 $r^2 = 0.9876$ (n = 64)

Total PAH data were available to generate isopleth figures for the entire slip for the 0-15 and 15-30 cm depth segments (Figure 13). For the other depth intervals down to 120 cm, isopleth figures were generated for the inner half of the slip (Figure 13). The distribution of total PAHs was heterogeneous with hot spots of contamination at depth (i.e., MNS-99-14 in the 30-45 cm segment and MNS-99-04 in the 60-75 and 75-90 cm depth segments). The 15-30 cm isopleth figure showed an odd distribution of total PAHs in the 50 to <100 mg/kg range, probably due to the forcing of the data through a data point of 50 mg/kg (Figure 13). The distribution of the ≥100 mg/kg range in the 30-45 cm isopleth figure may be a more isolated hot spot than shown, but the interpolation is done based on the available data (Figure 13).

Several long cores were collected from Minnesota Slip in order to look at the historical distribution of contaminants. Although radioisotope dating was not done, data from the cores can still be used to discern patterns of contamination in the slip (e.g., are newer surficial sediments cleaner than historical sediments?). Figures 14-17 show the historical distribution of total PAHs in sediment cores collected from MNS-99-15, MNS-99-04, MNS-99-03, and MNS-99-13, respectively. The position of these cores represents a transect of sites from the inner slip to near the middle of the slip. Similar figures for MNS-99-04R and MNS-99-13R are shown in Appendix C. The most contaminated sediments were located in the 60-75 cm and 75-90 cm segments of MNS-99-04 (Figure 15). The Level II SQT was exceeded in each depth interval analyzed for PAHs at these sites (Figures 14-17). For each of these sites, the surficial (0-15 cm) sediments were either similar or somewhat exceeded the concentration of total PAHs in the 15-30 cm segment (Figures 14-17). The deepest sediment core collected was at MNS-99-15; total PAHs were still very high (168

mg/kg dry wt.) in the bottom (1.8–2.1 m) segment of this core. Deeper sediment cores could not be collected with the Vibrocorer, because the Vibrocorer could not penetrate through dense sand. Thus, we were not able to determine the depth at which pre-industrial concentrations of total PAHs could be found in Minnesota Slip.

4.3.5   Ammonia Nitrogen

Ammonia nitrogen was only measured in surficial (0-5 cm) sediments in which matching sediment toxicity tests were run (i.e., MNS-99-01 though MNS-99-06). Ammonia nitrogen ranged from 7.8 – 71.4 mg/kg dry wt., with sites MNS-99-06 and MNS-99-02 containing the lowest and highest ammonia nitrogen concentrations, respectively (Table 11).

4.3.6   Total Metals: Cadmium, Chromium, Copper, Nickel, and Selenium

Cadmium, chromium, copper, nickel, and selenium were only measured in six surficial (0-5 cm) sediments in which matching sediment toxicity tests were run (i.e., MNS-99-01 though MNS-99-06). Cadmium was not detected in any of these samples, so one-half the reporting level was reported in Table 11. Selenium was also not detected in MNS-99-02 through MNS-99-06; one-half the reporting level was reported for these samples (Table 11). MNS-99-06 had the lowest concentrations of chromium, copper, and nickel in the surficial (0-5 cm) sediments (Table 11), whereas MNS-99-02 had the highest concentrations of these metals. While exceedances of the Level I SQTs were observed for metals at some of these sites, the corresponding Level II SQTs were not exceeded (Table 11). The interpretation of cadmium concentrations should be made with caution since one-half of the cadmium reporting limit for samples MNS-99-01 through MNS-99-06 exceeded the corresponding Level I SQT value.

4.3.7   AVS and SEM

AVS and SEM were only measured in surficial (0-5 cm) sediments in which matching sediment toxicity tests were run (i.e., MNS-99-01 through MNS-99-06).   AVS ranged from 0.245 – 5.15 µmole/g dry wt., with sites MNS-99-06 and MNS-99-01 containing the lowest and highest AVS concentrations, respectively (Table 11). MNS-99-04 and MNS-99-06 also had the lowest total SEM concentrations (2.92 µmole/g dry wt.), whereas MNS-99-05 had the highest total SEM concentration (8.47 µmole/g dry wt.) (Table 11). The only site in which SEM did not exceed AVS was MNS-99-01 (Table 11). MNS-99-05 and MNS-99-03 had the greatest exceedances of SEM over AVS.

4.3.8 Mercury

The range of mercury concentrations in the 0-5 cm surficial sediments, in which matching sediment toxicity tests were run (i.e., MNS-99-01 through MNS-99-06), is shown in Table 11. Mercury data were available to generate isopleth plots for the full slip down to 60 cm, and in the inner half of the slip down to 120-150 cm (Figure 18). Mercury ranged from 0.016 - 2.2 mg/kg dry wt., with sites MNS-99-06 (0-5 cm) and MNS-99-15 (1.5-1.8 m) containing the lowest and highest mercury concentrations, respectively. The corresponding Level I SQT was exceeded in all depth intervals, and the Level II SQT was exceeded in the 15-30, 60-75, 75-90, 90-120, and 120-150 cm depth segments (Figure 18), as well as in the 1.5-1.8 and 1.8-2.1 m segments of MNS-99-15 (Figure 19). Most mercury concentrations ranged between 0.18 - 0.55 mg/kg dry wt. A hot spot of mercury contamination occurred in the 15-30 cm segment in the inner quarter of the slip (MNS-99-03), but the source of this contamination was not known. The extent of mercury contamination also increased in the 60-75 and 75-90 cm segments in the inner slip (Figure 18), and higher mercury concentrations were observed in deeper core segments of MNS-99-15 (Figure 19), MNS-99-04 (Figure 20), MNS-99-03 (Figure 21), and MNS-99-13 (Figure 22). Refer to Appendix C for depth profiles of mercury at MNS-99-04R and MNS-99-13R.

4.3.9 Lead

The range of lead concentrations in the 0-5 cm surficial sediments, in which matching sediment toxicity tests were run (i.e., MNS-99-01 through MNS-99-06), is shown in Table 11. Lead data were available to generate isopleth plots for the full slip down to 60 cm, and in the inner slip down to the 120-150 cm depth segment (Figure 23). The concentration of lead exceeded the Level II SQT in each of these depth segments (Figure 23), as well as in the 1.5-1.8 and 1.8-2.1 m depth segments of MNS-99-15 (Figure 24). Less than detectable concentrations of lead (20 mg/kg dry wt.) were observed at MNS-99-06 (0-5 cm; Table 11) and MNS-99-11 (0-15 cm); one-half the detection limit (10 mg/kg dry wt.) was used for these sites. The highest concentration of lead (880 mg/kg dry wt.) was observed at MNS-99-09 (15-30 cm). The 0-15 cm depth segment was generally less contaminated than the deeper sections (Figure 23). In addition, the outer slip and MNS-99-07 (in the inner slip) were less contaminated than other areas of the slip (Figure 23). The distribution of lead was heterogeneous throughout the slip and core segments (Figures 23-27). Refer to Appendix C for depth profiles of lead at MNS-99-04R and MNS-99-13R.

4.3.10 Zinc

The range of zinc concentrations in the 0-5 cm surficial sediments, in which matching sediment toxicity tests were run (i.e., MNS-99-01 through MNS-99-06), is shown in Table 11. Zinc data were available to generate isopleth plots for the full slip down to 60 cm, and in the inner slip down to 120-150 cm (Figure 28). Zinc ranged from 41 to 1,110 mg/kg dry wt., with sites MNS-99-11 (0-15 cm) and MNS-99-04R (1.2-1.5 m), containing the lowest and highest zinc concentrations, respectively. The corresponding Level I SQT (120 mg/kg dry wt.) was exceeded in each depth interval (Figure 28). The Level II SQT (460 mg/kg dry wt.) was exceeded in the 30-45, 60-75, 75-90, 90-120, and 120-150 cm depth segments (Figure 28), as well as in the 1.5-1.8 and 1.8-2.1 m depth segments of MNS-99-15 (Figure 29). The distribution of zinc was heterogeneous in the 0-15, 15-30, and 30-45 cm depth segments (Figures 28-32), and the distribution of zinc appeared to follow more of a gradient of decreasing zinc concentrations from the inner slip to the middle of the slip in deeper core segments (Figure 28). Refer to Appendix C for depth profiles of zinc at MNS-99-04R and MNS-99-13R.

4.3.11 Mean PEC-Qs

Mean PEC-Qs were calculated for each site in Minnesota Slip (Table 16), although the number of chemicals included in the mean PEC-Q calculations varied due to the availability of chemistry data. For example, PCBs were only measured in the 0-5 cm and 0-15 cm depth segments and were thus only included in the mean PEC-Q calculations for these depth segments. Mercury was not included in the calculations given in Table 16, because this chemical does not have a reliable PEC value (MacDonald *et al.* 2000a). Mean PEC-Qs ranged from 0.15 to 26.9, with sites MNS-99-11 (0-15 cm) and MNS-99-04 (mean value for 75-90 cm) containing the lowest and highest mean PEC-Q values, respectively.

Isopleth figures for the entire slip were made for core sections down to 60 cm, and for the inner slip down to 90-120 cm (Figure 33). The mean PEC-Qs exceeded 0.1 (equivalent to the Level I SQT) at all sites and depth intervals, and exceeded 0.6 (equivalent to the Level II SQT) in portions of all depth intervals. The highest mean PEC-Q values were observed at MNS-99-04 (mean values) in the 60-75, 75-90, and 90-120 cm segments.

CHAPTER 5

DISCUSSION

5.1 PATTERN OF CONTAMINATION IN MINNESOTA SLIP

The results of this investigation provided a more representative data set of sediment chemistry and physical data in Minnesota Slip than had been collected in previous studies (Table 2). The isopleth plots of sediment quality data demonstrate the heterogeneous pattern of particle size (Figures 8-10), TOC (Figure 11), total PCBs (Figure 12), total PAHs (Figure 13), mercury (Figure 18), lead (Figure 23), and zinc (Figure 28), both spatially and temporally (i.e., with depth), in Minnesota Slip. This lack of a well-defined pattern of contamination is indicative of multiple sources of contaminants to the slip, such as from: storm water outfalls, unknown fill material that was used to fill in part of the inner slip, historical dumping of material into the slip, probable sediment mixing caused by bioturbation, wind-induced waves, and movement of the S.S. William A. Irvin during storms, possible advective transport and deposition of contaminated suspended sediment particles from other areas of the harbor into Minnesota Slip, possible land runoff of contaminants directly into the slip, possible inputs of contaminants (e.g., oil, gasoline) into the water column from boat operations in the slip, and possible groundwater transport of contaminants into the slip. Due to the small size of Minnesota Slip, current and historical air deposition of contaminants directly into the slip would probably comprise a small proportion of the contaminant load to the slip; air deposition of contaminants in the St. Louis River watershed that ultimately deposit in Minnesota Slip would probably be represented by water-borne transport of contaminants into the slip.

Gas bubbles were observed in several sediment samples collected from Minnesota Slip, and bubbles were observed breaking at the surface of the water. We do not know if gas formation may promote mixing in the sediment at Minnesota Slip or serve as a transport mechanism for contaminants that partition to bubbles during transport through the sediments to the water column and overlying air. Adams *et al*. (1990 as reported in Jepsen *et al*. 2000) found that gas generation in fine-grained sediments significantly affected the flux of organic chemicals from sediments. High concentrations of gas, up to 5% by volume, have been noted at another Great Lakes site (Grand River, MI). Jepsen *et al*. (2000) determined that for reconstructed Grand River sediments at approximately 20 ˚C, the effects of gas were to decrease the sediment densities by up to 10%, to increase the erosion rates by as much as a factor of sixty, and to decrease the

critical shear stress for erosion by as much as a factor of twenty compared to sediments with no gas present. At lower temperatures, these effects decreased significantly. If the generation of gas in Minnesota Slip sediments happened to increase erosion rates, then this might hasten the effects of bioturbation as a sediment and contaminant transport mechanism. Mean densities of Tubificidae in Minnesota Slip have been found on the order of 9,220 to 50,700 organisms/m^2 (Crane *et al*. 1997). Thibodeaux *et al*. (2001) have observed that compared to molecular diffusion, the bioturbation-driven soluble fraction transport of hydrophobic organic chemicals from bed sediment is rapid, and it increases with increasing partitioning on the particle phase. Thus, there may be a greater potential for the transport of hydrophobic organic contaminants (e.g., PCBs, PAHs) from the sediments to the overlying water in Minnesota Slip during the summer when the water temperature is warmer and benthic abundance is probably higher. Gas bubble formation is currently being studied at the Interlake/Duluth Tar Superfund site in the Duluth Harbor to assess whether it would adversely impact the integrity of a proposed sediment cap.

The deepest sediment core sample obtained in this study was 2.15 m long at MNS-99-15. It was not possible to obtain deeper sediment cores because the Vibrocorer could not penetrate through the dense sand. Thus, in this study, we were not able to determine the sediment depth at which cleaner (i.e., mean PEC-Q <0.1) sediments were present under contaminated sediments in Minnesota Slip. Since fill material of an unknown origin has been dumped in the slip in the past, there could possibly be more contaminated material under the sand layer that stopped the Vibrocorer. Scott Cieniawski (GLNPO, personal communication, 1999) has suggested that a Russian peat corer would probably be able to penetrate through the sand to obtain a deeper core segment. The water depth in the navigation channels in the Duluth-Superior Harbor is maintained at 27 feet; it would be prudent to sample the sediments in Minnesota Slip down to a combined water column and sediment depth of 27 feet. Given that the percentage composition of PAH compounds was fairly consistent throughout the slip, a PAH fluorescence screening technique (calibrated to the mix of PAHs observed in Minnesota Slip) could provide an effective screening tool for quickly assessing deeper sediment core sections for contamination.

Particle size was not a good predictor of contamination in Minnesota Slip, either of total PAHs or of mean PEC-Qs. There was no relationship (i.e., r^2 <0.004) between single regression analyses of either total PAHs, LMW PAHs, HMW PAHs, or mean PEC-Q with the percentage of sand and gravel, silt, or clay. In contrast, a linear relationship between total PAHs and the percentage of silt ($r^2 = 0.802$) was found in nearby Slip C (Crane 1999a). The lack of a relationship between these parameters in Minnesota Slip may be due to oily sediments. Thus,

some samples that had very sandy sediments were still contaminated with PAHs due to oil coating the sand. In addition, very high mean PEC-Q values (i.e., >5) were observed in 7 sediment samples in which the percentage of silt ranged from 25-55%, thus leading to a scattered distribution of the data.

PAHs are a principal contaminant of concern in Minnesota Slip due to the degree of their exceedance of corresponding Level II SQT values for individual PAHs and total PAHs (Tables 12 and 14). The sediments in Minnesota Slip were more contaminated with PAHs than the sediments in nearby Slip C. The ratio of either LMW or HMW PAHs to total PAHs was calculated from sediment quality data collected in 1997 from Slip C (Crane 1999a). A similar percentage and range of dominant LMW and HMW PAHs were observed in Slip C (Table 17) as for Minnesota Slip. In addition, the composition of LMW and HMW PAHs was similar at both sites, with a slightly higher percent composition of the more volatile 2-methylnaphthalene and naphthalene in Slip C (Table 17) than Minnesota Slip (Table 13). A leaking underground oil line contaminated the soil and groundwater by Slip C during 1990 and 1991 (Crane 1999a); this leakage could have contributed to the more volatile PAHs observed in Slip C.

There may be a common source material of PAHs, such as from coal combustion products, that may have contaminated both slips. The Duluth/Superior Harbor area had a high historical use of coal during the past 100 years through the storage and transport of coal along the waterfront, the presence of several coal gasification plants, and the manufacture of coal-powered ships, especially during WWI. Throughout the United States, loading of PAHs to the atmosphere increased during the WWII era due to an increase in coal consumption; this increase was accentuated in the Great Lakes due to their proximity to the industrial centers (Schneider *et al.* 2001). The MPCA has found coal tar in the soils of Canal Park, including some areas that have been paved over and made into parking lots. Further upstream, the U.S. Steel Company ran a steel smelting operation from 1915-1973, in which the plant also produced coke for use in steel making. This site is now a Superfund site. Another Superfund site, the Interlake/Duluth Tar Superfund site, is located along the St. Louis River and includes Stryker Bay and two nearby boat slips. The MPCA named four companies, including the Interlake Iron Company, as being responsible for the investigation and clean-up of contaminated sediments at this Superfund site. The Interlake portion of the site was used for manufacturing purposes from the later 1800s to the early 1960s, including coking and by-product recovery, iron smelting and manufactured gas production (Service Environmental and Engineering 2001). The last coke plant ceased operation in 1961. Some of the rest of the site was used for coal tar refining and tar product manufacturing until 1948. Coke emissions are typically enriched in HMW PAH compounds, whereas lower

temperature combustion is dominated by the LMW PAHs. Therefore, the preponderance of HMW PAHs in the sediments of Minnesota Slip and Slip C are consistent with coke-type material that may have been used or disposed of in the vicinity of both slips. The preponderance of HMW PAHs at both slips is also influenced by the physical-chemical properties of PAHs. LMW PAHs are more volatile and would partition more readily to pore water and the overlying water.

Another source of PAHs and PCBs may come from street dust that is washed into the storm sewers draining into Minnesota Slip. For example, Tokyo street dust, containing PAHs from asphalt, automobile exhaust, and tire wear residue, with contributions from used motor oil and gasoline spills, was a rich (mg/kg by weight) source of PAHs (Takada *et al*. 1991 as cited by Van Metre *et al*. 2001). Elevated concentrations of PCB congeners have been found in combined sewer overflows (CSOs) draining into the Buffalo River, NY as a result of street dust and dirt washing off into the CSOs (Loganathan *et al*. 1997).

Mercury, lead, and zinc also result from the combustion of fossil fuels and can be found in street dust. Zinc is added during the manufacture of automobile tires in the form of zinc oxide, as an accelerator in the vulcanization process (Christensen and Guinn 1979 as cited in Callender and Rice 2000). Thus, as tires abrade during road travel, zinc and PAHs contained in the abraded rubber contribute to street dust. Automobile exhaust emissions of tetraethyl lead contributed to major sources of lead to the environment from 1950 to the 1970s (USEPA 1993 as cited in Callender and Rice 2000). Lead and zinc are also a significant component of coal fly ash emissions (Thornton 1995 as cited in Callender and Rice 2000). Surficial concentrations of lead in Minnesota Slip have decreased compared to deeper sediment cores, probably in part due to the phase-out of leaded gasoline in the 1970s. However, concentrations of lead still exceed the Level II SQT in much of the surficial sediments, possibly due to fossil fuel-derived sources.

Zinc has remained elevated in the surficial sediments of Minnesota Slip, possibly due to increased motor vehicle traffic in the central hillside area of Duluth, including a portion of Interstate 35. The storm water system draining the central hillside area flows into Minnesota Slip, mainly through two storm water outfalls. Tourism and population levels have also increased in the Duluth and North Shore area of Lake Superior, especially during the past 15 years, which has resulted in increased traffic along Interstate 35 and the Canal Park area by Minnesota Slip. Callender and Rice (2000) found that population density in the southeast U.S. was strongly related to traffic density and was a predictor of lead and zinc concentrations in the environment derived from anthropogenic sources. A similar scenario may be taking place in

other urban areas of the country. Although a contaminant loading study has not been done for storm water draining into Minnesota Slip, anecdotal observations suggest water quality may be degraded by oil and grease, mud, and garbage that enters the slip from storm water outfalls during rain events. For Minnesota Slip, it would be beneficial to implement BMPs to pretreat storm water to reduce potential contaminant inputs to the slip.

A railroad yard was historically located on the west side of Minnesota Slip, and it was used for loading and unloading cargo to and from ships moored in the slip. Some cargo could have been spilled or accidentally dropped into Minnesota Slip, thus contributing pollutants to the slip. At the USX Superfund site in Duluth, mercury was regularly replaced in the nearby rail yard switches and disposed of in a pit on the site. It is not know if a similar practice could have taken place at the railroad yard by Minnesota Slip and if any mercury was directly disposed of in the slip.

The sediments in Minnesota Slip were most likely contaminated from several different sources, including nonpoint runoff. A potentially responsible party (PRP) is not immediately apparent for this site. However, the MPCA's Northern Assessment and Response Unit in Duluth should look into this issue further to determine if there are any historical businesses that could be designated as PRPs for Minnesota Slip.

5.2   INTEGRATION OF SEDIMENT CHEMISTRY AND TOXICITY RESULTS

Sublethal effects to growth and/or reproduction were not found in the sediment toxicity tests conducted for this study. However, in terms of survival, the 28- to 42-d sediment toxicity tests with *H. azteca* provided a more sensitive test than the 10-d *C. tentans* toxicity test. Significant toxicity was observed at sites MNS-99-03 and MNS-99-05 for the amphipod test (Table 18). Based on a North American data set, the 28- to 42-d amphipod test has also been found to be more sensitive than either the 10-d amphipod or midge tests (Ingersoll *et al.* 2001), and use of it would reduce the potential for false negatives at low mean PEC-Qs. In addition, use of these chronic amphipod tests increases the potential for detecting toxicity at moderate mean PEC-Qs (Ingersoll *et al.* 2001).

The corresponding mean PEC-Q values for sediment samples in which toxicity tests were conducted (i.e., MNS-99-01 to MNS-99-06) ranged from 0.68 – 1.1 (Table 18). A previous study of the predictive ability of mean PEC-Qs, based on the results of 10-d *C. tentans* tests in the St. Louis River AOC, corresponded to 20% toxicity (n = 20) at mean PEC-Q ranges of >0.5

to ≤1.0 (Crane *et al.* 2000). Although no significant toxicity was observed in the 10-d *C. tentans* sediment toxicity tests conducted for this study when compared to the control, the control survival (although acceptable) was much lower (71.4%) than the sample treatment survival, especially in sample MNS-99-01 (95% survival).

As mentioned in Section 4.2.1, the corresponding sediment chemistry data were not yet available at the time the statistical analysis of the sediment toxicity data for *C. tentans* was conducted. Since there was a gradient of higher survival (95%) to lower survival (81.4%) from the outer slip to the inner slip in the 10-d *C. tentans* test results (Table 6), the ENSR study director was also asked to compare the survival and growth results of MNS-99-02 through MNS-99-06 to MNS-99-01 (i.e., outer slip sample). MNS-99-01 was suspected of being less contaminated than the other Minnesota Slip sites in which sediment toxicity tests were conducted. Survival in MNS-99-05 was significantly reduced relative to survival in MNS-99-01 (this would result in 20% toxicity for a mean PEC-Q range of >0.5 to ≤1.0). There was no significant reduction in dry weight or AFDW in MNS-99-02 through MNS-99-06 relative to MNS-99-01. However, when the sediment chemistry data became available for these sites, MNS-99-01 was found to have a mean PEC-Q value similar to most of the other sediment toxicity sites (Table 18). Therefore, MNS-99-01 could not be used as an internal reference site. These statistical comparisons should be used in an anecdotal way that if the control survival had been >95%, then sample MNS-99-05 would have been designated as toxic for the 10-d *C. tentans* test.

In examining the surficial sediment chemistry results for MNS-99-01, MNS-99-03, and MNS-99-05, all three sites had a similar percentage of sand, silt, and clay, as well as TOC and ammonia nitrogen (Table 11). Concentrations of total metals, PCBs, and PAHs (Tables 11 and 14) were also similar for these three sites. The main differences in these sites were with the AVS and total SEM concentrations. MNS-99-01 was the only one of the six sites that had a higher concentration of AVS than total SEM (Table 11). MNS-99-05 and MNS-99-03 had the greatest exceedance of total SEM compared to AVS (i.e., >5 μmole/g dry wt.; Table 11). Assuming that AVS binds a molar equivalent of SEM metal (Di Toro *et al.* 1990), the fraction of SEM metals in excess of AVS concentrations may be available for uptake by benthic biota. Most benthic organisms, including those used in toxicity tests, survive in sediments that have a thin oxidized surface layer and then an anoxic layer. The anoxic layer can have higher AVS concentrations that would reduce the metal activity to which these organisms are exposed (Di Toro *et al.* 1992). When SEM exceeds AVS by a factor of 5 (on a molar basis), a higher incidence of toxicity (80% to 90%) has been observed in freshwater and saltwater sediment amphipod tests (USEPA 1997). Thus, [SEM] – [AVS] ≥5 is a better predictor of sediment toxicity to amphipods. A sediment

toxicity identification evaluation procedure could be used to determine the classes of chemicals responsible for toxicity in Minnesota Slip.

The 28- to 42-d sediment toxicity tests with *H. azteca* were the first tests of this kind conducted in the St. Louis River AOC. In the future, reconstituted water should not be used as the overlying water in this sediment toxicity test. For samples corresponding to mean PEC-Qs of >0.5 to ≤1.0, two of five sites (40%; MNS-99-03 and MNS-99-05) were toxic to amphipods at α = 0.05 (Table 18). In comparison, the incidence of toxicity in the same type of toxicity test and mean PEC-Q range was 56% (n = 27) in samples collected from North America (USEPA 2000b). The lower toxicity observed in the Minnesota Slip sediments may be due to a lower percentage of LMW PAHs observed in these samples compared to the North American data set (USEPA 2000b). Preliminary analyses of the USEPA (2000b) database indicate a trend of lower correct classification of the toxicity attributed to PAHs in samples with a lower percentage of LMW PAHs (<40%) compared to samples with a higher percentage of LMW PAHs (>40%; Chris Ingersoll, U.S. Geological Survey, personal communication, 2002). Therefore, the mean PEC-Qs described in MacDonald *et al*. (2000a) may over predict the toxicity of samples with PAHs primarily from combustion sources (i.e., with PAHs dominated by HMW PAHs).

Mercury exceeded the Level I SQT in a large portion of the surficial sediments of Minnesota Slip (Figure 18). The ecological and toxicological effects of mercury are strongly dependent on the chemical species present. High concentrations of inorganic mercury may depress methylmercury production or may favor demethylation; methymercury levels in sediments rarely exceed a threshold value of 1% (Ullrich *et al*. 2001). No bioaccumulation of mercury was found in 28-d bioaccumulation tests with *Lumbriculus variegatus* that used surficial sediments from Minnesota Slip (AScI Corporation 1999). However, fish consumption advisories are in effect for selected fish species in the St. Louis River AOC because of elevated concentrations of mercury found in the tissue of the fish (MDH 2000).

Although total PAH concentrations exceeded the corresponding PEC value (i.e., 23 mg/kg dry wt.) in the six sediment samples in which sediment toxicity tests were conducted (Table 18), significant toxicity was not always observed. Given the historical usage of coal-derived products along the Duluth waterfront, some PAHs in Minnesota Slip may be associated with soot-type particles, whereas other PAHs are most likely associated with sand, silt, and clay particles. Heterogeneous particle types in sediment exhibit much different amounts and binding of PAHs. Room-temperature PAH desorption kinetic studies on separated sediment fractions from Milwaukee Harbor, WI revealed slow desorption rates for coal-derived particles and fast

desorption rates for clay/silt particles (Ghosh *et al.* 2001). These studies reveal that PAHs associated with coal-derived particles aged over several decades in the field appear to be far from reaching an equilibrium sorption state due to the extremely slow diffusivities through the polymer-like coal matrix (Ghosh *et al.* 2001).

Some PAHs may contribute to dioxin-like activity in sediments, and Eljarrat *et al.* (2001) found benzo[k]fluoranthene to be the most potent PAH in their study to calculate total toxicity equivalent values for PAHs using the toxicity equivalent factors proposed by the literature. Benzo[k]fluoranthene was measured in this study (Table 12), although not all of this compound may be bioavailable to organisms. For example, humic substances make PAHs less bioavailable for aquatic biota, particularly in the pore water and water column. Perminova *et al.* (2001) found that the aromatics enriched humic materials are the most efficient detoxifying agents in relation to PAHs. The most abundant source of such material is brown coal which contains up to 70-80% of humic acids (Perminova *et al.* 2001). Black coal has probably been more heavily used in the Duluth-Superior area because it contains much less water than brown coal.

5.3 COMPARISON OF MEAN PEC-Qs IN MINNESOTA SLIP WITH OTHER SITES

The distribution of mean PEC-Qs in surficial sediments of Minnesota Slip was compared to other sites in the St. Louis River AOC for which more than ten data points were available in the St. Louis River AOC matching sediment chemistry and toxicity database (Crane *et al.* 2001; Table 19). Other contaminated areas, such as the USX Superfund site and Hog Island Inlet/Newton Creek, were excluded from this comparison because there were not more than ten data points of matching sediment chemistry and toxicity data available for these sites. The results of Table 19 are presented graphically in Figure 34 as box and whisker plots. The Interlake/Duluth Tar Superfund site had, by far, the highest mean PEC-Q values in the St. Louis River AOC. The average mean PEC-Q values for Minnesota Slip were slightly less than for the entire St. Louis River AOC, which included sediment quality data ranging from reference areas to Superfund sites. Howards Bay, and the embayment by WLSSD and the confluence of Miller and Coffee Creeks, had similar average mean PEC-Qs that were over half the average of Minnesota Slip. The results of a hot spot investigation in the Duluth-Superior Harbor conducted in 1994 (Crane *et al.* 1997), which excluded the Minnesota Slip results, comprised the lower mean PEC-Qs of this comparison. This hot spot study (Crane *et al.* 1997) did not include highly contaminated areas like the Interlake/Duluth Tar and USX Superfund sites, or Hog Island Inlet/Newton Creek. In addition, a reference area in Kimball's Bay was included in this hot spot study (Crane *et al.* 1997).

Figure 35 shows the CDF plots for surficial sediment samples collected in the St. Louis River AOC that were presently available in a database format. It should be noted that additional sediment chemistry data is available for the St. Louis River AOC, but it has not been entered into a database yet. These data will be entered into a new GIS-based sediment quality database for the St. Louis River AOC. Therefore, similar types of box and whisker plots and CDF plots will be generated after the completion of the GIS-based database. From Figure 35, the broad range of mean PEC-Q values for the St. Louis River (both including and excluding Minnesota Slip) is evident, partly due to the high mean PEC-Q values present at the Interlake/Duluth Tar Superfund site.

A similar exercise was carried out for the St. Louis River AOC, except mercury was included in the calculation of mean PEC-Qs. The inclusion of mercury did not result in substantial changes in the distribution of mean PEC-Qs for selected areas in the St. Louis River AOC (Table 20 and Figures 36-38).

The distribution of mean PEC-Qs for surficial sediment samples collected from selected Great Lakes AOCs is given in Table 21. Based on average values, Minnesota Slip had a similar level of contamination as the St. Louis River AOC (excluding Minnesota Slip data), Cuyahoga River AOC, and the Oswego River AOC. The average mean PEC-Qs in Minnesota Slip were about twice those values in the St. Clair River AOC. The level of mean PEC-Qs were much less in Minnesota Slip compared to the Indiana Harbor AOC, Sheboygan Harbor AOC, Maumee River AOC, St. Mary's River AOC, and Waukegan Harbor AOC.

Because some of the average values were skewed by high maximum mean PEC-Q values at other Great Lakes AOCs, summary statistics for the 10th percentile, median, and 90th percentile provided a more well-rounded picture of the distribution of mean PEC-Qs (Table 21). Based on median values, the mean PEC-Qs in Minnesota Slip (0.97) were only exceeded by the Oswego River AOC (0.9855), Indiana Harbor AOC (2.49), and Waukegan Harbor AOC (2.85). Minnesota Slip had the fourth highest minimum value, the highest 10th percentile mean PEC-Q values, the seventh highest 90th percentile mean PEC-Q values, and the lowest maximum value.

The summary statistics of Table 21 are plotted in Figure 39 as box and whisker plots. The CDF plot shown in Figure 40 demonstrates the range of mean PEC-Q values, which are especially wide for the Indiana Harbor AOC. Minnesota Slip has a narrow, fairly consistent range of mean PEC-Q values compared to the other Great Lakes AOC sites.

5.4 VOLUME OF CONTAMINATED SEDIMENTS

The FIELDS software was used to calculate the volume of sediments exceeding a total PAH concentration of 23 mg/kg dry wt. (i.e., Level II SQT) and a mean PEC-Q of 0.6. The output from FIELDS seemed to be most reliable for sediment sections in which sediment quality data were available for the entire slip. Technical assistance from the FIELDS group in U.S. EPA Region 5 may be needed to learn how volume estimates can be made for depth intervals in which only a portion of the slip contained data (i.e., inner half of Minnesota Slip).

For total PAHs (comprised of the 13 LMW and HMW PAHs), approximately 4,900 yd^3 of sediments in the upper 30 cm exceeded the Level II SQT value of 23 mg/kg dry wt. (Table 22). This volume corresponded to approximately 630 pounds of total PAHs. Mean PEC-Q values were available for the entire slip for the upper four depth intervals (i.e., 0-15, 15-30, 30-45, and 45-60 cm). The volume of sediments exceeding a mean PEC-Q of 0.6 corresponded to approximately 9,600 yd^3 (Table 23). A better estimate of the volume of contaminated sediments will need to be determined before any remediation options can be selected for Minnesota Slip. The MPCA should consider conducting a feasibility study as the principal mechanism for the development, screening, and detailed evaluation of alternative remedial actions for Minnesota Slip.

5.5 CONSIDERATION OF PRELIMINARY REMEDIATION OPTIONS

Based on the sediment quality data that has been collected for Minnesota Slip, additional steps should be taken to conduct a feasibility study of remediation options for this site. Options for dealing with contaminated sediments (Feyerherm and Wardlaw 2001) generally include:

- Natural recovery (also termed natural attenuation) by which contaminated sediments are left in place, and depositional processes cover them with clean material;
- Capping them with clean sediments, sand, gravel, geotextiles, or armored caps;
- *In situ* treatment using technologies that treat contaminants in place including chemical, biological (i.e., bioremediation), and immobilization techniques;
- Dredging them to remove contaminated sediments from Minnesota Slip for:
  - Disposal in the Erie Pier confined disposal facility,
  - Using soil washing techniques of the dredged material to extract "clean" sand for beneficial reuses (such as the creation of wetlands), and

- Using treatment technologies on the dredged sediments such as biological treatment, phytoremediation, metal extraction, chemical treatment of organics, thermal treatment, separation of particle size using hydrocyclones, and immobilization.
- A combination of the sediment management options described above (e.g., limited dredging plus capping, *in situ* treatment plus natural recovery, etc.).

There are often wide variations in cost, technical uncertainty, and environmental risk among these options.

> **Before any sediment remediation options can be seriously considered in Minnesota Slip, steps need to be taken to implement source control measures to reduce contaminant loads into the slip.**

One probable source of contaminants into the slip is from storm water discharges from five storm sewers. The City of Duluth Storm Water Utility is currently targeting the storm sewers in this slip for an evaluation of best management practices (BMPs) during the next year (Marnie Lonsdale, City of Duluth Public Works Department, personal communication, 2001). Due to complexities associated with the water table being below the St. Louis River at this site, more expensive BMPs (e.g., Vortex apparatus) will probably need to be considered.

Other issues that need to be considered as part of an evaluation of remediation options include:

- Direction of ground water flow either into or out of the slip from the surrounding land and from under the sediments. Soils in nearby areas in Canal Park are contaminated with coal tar, and groundwater traveling through these soils may provide a mechanism for the transport of PAHs and other contaminants associated with coal tar to the slip.
- Sedimentation rate in Minnesota Slip. The clearance between the bottom of the S.S. William A. Irvin and the surface of the sediments is approximately 2 m. As sediment accumulates, it will eventually be necessary to dredge the sediments to maintain an adequate water depth for the 3 m draft of the Irvin.
- Short-term and long-term water uses in Minnesota Slip. Minnesota Slip is actively used to support several tourist-related operations. These uses are subject to change over time. For example, several efforts have been made during the last four years to bring other historical

ships (e.g., warships) to Duluth for use as a tourist venue (i.e., conduct tours of the ship). To date, these efforts have been rejected by the community. However, if the S.S. William. A. Irvin is ever replaced with another ship for tourism-related purposes, or another ship is added to Minnesota Slip, in addition to the Irvin, then there may be the need to dredge sediments from the slip to ensure an adequate water depth is maintained.

- Fluctuating water levels in the Great Lakes. Water levels in the Great Lakes normally experience a seasonal decline in the fall due to lower rainfall, reduced inflows from rivers and streams, and from increased evaporation. However, over the past four years, a dramatic decrease in water levels in all of the Great Lakes have been observed. Between 1997 and 2001 (through April), water levels on Lake Superior dropped from within inches of the record high to within inches of the record low (U.S. Army Corps of Engineers 2001). As of February 15, 2002, Lake Superior's water level is currently 6 inches below its long-term average and 8 inches above this time last year; the water level of Lake Superior is expected to decline 2 inches over the next month (http://huron.lre.usace.army.mil/levels/weekly.html). Low water levels have also occurred in the Great Lakes during the mid-1930s and mid-1960s. The current low levels appear to exhibit a natural variability in water level trends. This type of variability, then, needs to be taken into consideration with any selection of sediment remediation options.

- The stability of the sediments in Minnesota Slip. How much the sediments of Minnesota Slip are subject to mixing and movement from hydrodynamic processes (e.g., wind-induced resuspension) and bioturbation can affect the selection of remediation alternatives. Anecdotal descriptions from marina boat owners that the water level in the slip can vary several feet depending on wind and seiche actions will affect sediment transport in the slip. In addition, the close proximity of the bottom of the Irvin to the surficial sediments may create micro-currents from movement of the Irvin during high wind events to result in increased sediment transport.

- Economic value of Minnesota Slip to tourism. The implementation of any remediation actions should be done during a time period that will allow the least disruption to tourist-related activities in the slip. This would roughly correspond to the period from October through early May. Depending on the remediation option selected, the Irvin may have to be moved to another secured slip during a remediation action.

GLNPO has funded two experimental remediation technologies that, if successful, could be considered for Minnesota Slip. The U.S. Army Corps of Engineers is conducting a project to test a sediment treatment technology with sediments dredged from Minnesota Slip. The study is designed to determine the viability of one type of electrochemical remediation technology (ECRT) to reduce PAH contamination in dredged sediments placed in a special containment cell at the Erie Pier confined disposal facility. The ECRT to be used is electrochemical geooxidation (ECGO), in

which an electrical current passing through the sediments is used to mobilize or break down organic contaminants. ECGO operates by imposing an electric current between electrodes (cathodes and anodes) installed in the sediments to be remediated. Electric power is passed through a proprietary direct current (DC)/alternating current (AC) converter that produces a low-voltage and low-amperage DC/AC current. When this modified electrical current is passed through the sediment through the electrodes, the sediment particles become polarized and are purported to develop electrical properties similar to a capacitor. According to the technology developer, when the polarized particles discharge electricity in the ECGO, the energy given off induces chemical reactions (redox reactions), which are purported to decompose organic contaminants. A pilot project has recently been initiated at a marine site at the Georgia-Pacific Log Pond in Bellingham Bay, WA (Washington Department of Ecology 2001) to test the effectiveness of both ECGO and induced complexation (IC) ECRT technologies. The remediation of metals has been reported with IC technology, which relies on ECGO to convert metals to mobile ions that then migrate to the electrodes where they accumulate and are removed. The results of this project in Bellingham Bay will provide additional information on the effectiveness of these ECRT technologies that can be compared to the Corps of Engineers use of ECGO on sediments dredged from Minnesota Slip.

The Wisconsin Department of Natural Resources (WDNR), through its contractor Minergy Corp., is involved in an evaluation of a feasibility study of a vitrification (melting) technology to destroy organic contaminants (primarily PCBs) and immobilize inorganic contaminants (primarily heavy metals) (WDNR 2001). The primary objectives of the study are:

- To determine the treatment efficiency of PCBs in dredged-and-dewatered river sediment when processed in the Minergy Glass Furnace Technology (GFT); and
- To determine whether GFT glass aggregate product meets the criteria for beneficial reuse under relevant federal and state regulations.

In addition, this project will also address the following secondary objectives:

- Determine the unit cost of operating the GFT on dewatered dredged river sediment;
- Quantify the organic and inorganic contaminant losses resulting from the existing or alternative drying process used for the dredged-and-dewatered river sediment; and
- Characterize organic and inorganic constituents in all GFT process input and output streams. Of principal concern is the formation of dioxin and furan during the vitrification step.

This project is being applied to sediments in the Lower Fox River, WI. If it is successful, a full-scale facility will be built that will perhaps be of use to process Minnesota Slip sediments, too.

Neither natural recovery nor capping, when considered alone, are viable remediation alternatives for Minnesota Slip because:

- The surficial sediments are contaminated. At sites MNS-99-01 through MNS-99-06, the 0-5 cm depth segment exceeded a mean PEC-Q of 0.6 at each site. Thus, clean sediments are not being deposited in the slip to allow natural recovery to work. Source control measures (e.g., BMPs) need to be implemented to reduce contaminant inputs into Minnesota Slip.
- The water depth is not sufficient to allow the sediments to be capped and to still maintain existing water uses of the slip. The water depth in Minnesota Slip ranged from 3.2-6.7 m in this study (Table 3). Since the draft of the S.S. William A. Irvin is 3 m, there is not enough room to cap the sediments. The hydrodynamics of water motions in the slip are also not likely to be quiescent enough to allow a cap to remain in place. An additional consideration with capping is that capping efficiency is reduced if there is advective flow through the sediment and capping material as a result of upward moving groundwater flow (Liu *et al.* 2001). The direction of groundwater flow in Minnesota Slip sediments has not been determined.

Bioremediation of either *in situ* or field-applied sediments would also not be an effective remediation technique for treating the mixture of contaminants in Minnesota Slip sediments, particularly with metals, mercury, and higher chlorinated organic compounds. The majority of bioremediation studies are conducted under aerobic conditions and, therefore, offer the possibility of vaporizing PAHs during treatment. Recent studies suggest that vaporization of PAHs (as large as 4 rings) can be emitted from field treated soils and sediments before microbiological activity becomes significant, thus contributing significantly to the reductions in PAH concentrations that are reported for biological treatment (Hawthorne and Grabanski 2000).

After BMPs are implemented for the storm water outfalls draining into Minnesota Slip, the MPCA should consider dredging contaminated sediments from Minnesota Slip and either containing the dredged material at the Erie Pier confined disposal facility or treating the dredged material to reduce the mixture of contaminants to acceptable levels. Since Minnesota Slip is small, and has a drawbridge at the outlet, it would be a fairly straight forward operation to seal the outlet and dredge the sediments (after all boats and docks have been removed from the slip). The slip could possibly be drained prior to dredging. In this case, the overlying water would probably need to be treated by the nearby Western Lake Superior Sanitary District to meet water quality standards. Additional

steps would be needed to divert storm water from the slip during the period of work and to further enforce the walls of the slip. A special contaminated cell would need to be built at the Erie Pier confined disposal facility for disposing or treating the dredged sediments. Since even sandy sediments were contaminated with oil from this slip, soil washing techniques may not work well to separate out clean sand from the slip for beneficial uses.

CHAPTER 6

RECOMMENDATIONS

Recommendations for next steps to be taken at Minnesota Slip include:

- Implement BMPs for the five storm water outfalls draining into Minnesota Slip (through the city of Duluth Storm Water Utility);
- Determine the direction of groundwater flow in the vicinity of Minnesota Slip to assess whether it contributes to advective flow up through the sediments to the water column or passes through contaminated soils in Canal Park to Minnesota Slip;
- Educate stakeholders and tourists visiting Minnesota Slip about the extent of sediment contamination found in Minnesota Slip, what preventative measures they can take to reduce contaminant inputs into the slip (e.g., keep motor boat engines in good working order to reduce oil leakage into the water column), and what remediation options the MPCA may consider in the future for this slip;
- Verify that no potentially responsible parties are available to contribute to clean-up costs at this site;
- Develop narrative use protection objectives for the site, and
- Conduct a feasibility study of remediation options, including cost estimates.

The Northern Assessment and Response Unit in the MPCA's regional office in Duluth will be in charge of future work at Minnesota Slip, including the acquisition of funds to carry-out this work. As with any remediation effort, public input will be needed before a remediation option is selected for Minnesota Slip. Due to the small size of the hot spot area, an ecological and human health risk assessment may not be needed for this site. Sediment quality remediation targets could be based on chemical SQTs, as well as biological effects data. Social and economic factors, in addition to the technical feasibility and cost estimates of various remediation options, will be taken into consideration when securing funds for a remediation action in Minnesota Slip.

REFERENCES

AScI Corporation. 1999. Summary of test results determining potential mercury, PAH and PCB bioaccumulation by *Lumbriculus variegatus* exposed to St. Louis Bay sediment samples. AScI Corporation, Duluth, MN.

ASTM (American Society of Testing and Materials). 1997. Standard test methods for measuring the toxicity of sediment-associated contaminants with fresh water invertebrates. Method E 1706-95b in 1997 Annual Book of ASTM Standards, Volume 11.05, Biological Effects and Environmental Fate; Biotechnology; Pesticides. American Society of Testing and Materials, West Conshohocken, PA.

ASTM. 2001. Test method for measuring the toxicity of sediment-associated contaminants with freshwater invertebrates. Method E 1706-00 in Annual Book of ASTM Standards, Volume 11.05, Biological Effects and Environmental Fate; Biotechnology; Pesticides. American Society of Testing and Materials, West Conshohocken, PA.

Ballschmiter, K. and M. Zell. 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. Fresenius Z. Anal. Chem. 302:20-31.

Breneman, D., C. Richards and S. Lozano. 2000. Environmental influences on benthic community structure in a Great Lakes embayment. J. Great Lakes Res. 26:287-304.

Callender, E. and K.C. Rice. 2000. The urban environmental gradient: Anthropogenic influences on the spatial and temporal distributions of lead and zinc in sediments. Environ. Sci. Technol. 34:232-238.

Crane, J.L. 1999a. Assessment of contaminated sediments in Slip C, Duluth Harbor, Minnesota. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA-905-R-99-007

Crane, J.L. 1999b. Quality assurance project plan (QAPP): Sediment remediation scoping project for Minnesota Slip, Duluth Harbor. Revision: 0. Environmental Outcomes Division, Minnesota Pollution Control Agency, St. Paul, MN.

Crane, J.L., M. Schubauer-Berigan, and K. Schmude. 1997. Sediment assessment of hotspot areas in the Duluth/Superior Harbor. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA-905-R97-020.

Crane, J.L., D.D. MacDonald, C.G. Ingersoll, D.E. Smorong, R.A. Lindskoog, C.G. Severn, T.A. Berger, and L.J. Field. 2000. Development of a framework for evaluating numerical sediment quality targets and sediment contamination in the St. Louis River Area of Concern. Great Lakes National Program Office, Chicago, IL. EPA 905/R-00/008.

Di Toro, D.M. and J.A. McGrath. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. Environ. Toxicol. Chem. 19:1971-1982.

Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, A.R. Carlson, and G.T. Ankley. 1992. Acid-volatile sulfide predicts the acute toxicity of cadmium and nickel in sediments. Environ. Sci. Technol. 26:96-101.

Di Toro, D.M., J.D. Mahony, D.J. Hansen, K.J. Scott, M.B. Hicks, S.M. Mayr, and M.S. Redmond. 1990. Toxicity of cadmium in sediments: The role of acid-volatile sulfide. Environ. Toxicol. Chem. 9:1487-1502.

Eljarrat, E., J. Caoxach, J. Rivera, M. De Torres, and A. Ginebreda. 2001. Toxic potency assessment of non- and mono-ortho PCBs, PCDDs, PCDFs, and PAHs in northwest Mediterranean sediments (Catalonia, Spain). Environ. Sci. Technol. 35:3589-3594.

En Chem, Inc. 1999a. Congener specific determination of polychlorinated biphenyls (PCBs) in soils and sediments by capillary column gas chromatography. En Chem SOP SVO-64, Revision No. 1. En Chem, Inc., Madison, WI.

En Chem, Inc. 1999b. Acid volatile sulfides and simultaneously extractable metals in sediment. En Chem SOP WCM-63, Revision No. 0. En Chem, Inc., Madison, WI.

ENSR. 1996. St. Louis River July 1995 field investigation. ENSR Consulting and Engineering, St. Louis Park, MN. Document Number 5480-005-400.

Feyerherm, J. and C. Wardlaw. 2001. Healthy harbors, restored rivers. A community guide to cleaning up our waterways. Sierra Club, Great Lakes Ecoregion Program, Madison, WI.

Ghosh, U., J.W. Talley, and R.G. Luthy. 2001. Particle-scale investigation of PAH desorption kinetics and thermodynamics from sediment. Environ. Sci. Technol. 35:3468-3475.

Glass, G.E., J.A. Sorensen, G.R. Rapp, Jr., M. Balcer, and L. Schwarzkopf. 1998. Mercury subsurface maxima in sediments: A diagnostic for anthropogenic origins. Pages 467-486 in Ebinghaus, Turner, Lacerda, Vasiliev, and Solomons, (eds.). Mercury contaminated sites: Characterization, risk, and remediation. Springer-Verlag, Heidelberg.

GLNPO (Great Lakes National Program Office). 1997. Health and safety and environmental compliance manual.   U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL.

Hawthorne, S.B. and C.B. Grabanski. 2000. Vaporization of polycyclic aromatic hydrocarbons (PAHs) from sediments at ambient conditions. Environ. Sci. Technol. 34:4348-4353.

IJC (International Joint Commission). 1989. Great Lakes water quality agreement of 1978 (as amended by Protocol signed November 18, 1987). International Joint Commission, Windsor, ON.

Ingersoll, C.G. and D.D. MacDonald. 1999. An assessment of sediment injury in the West Branch of the Grand Calumet River. Volume I. Prepared for Environmental Enforcement Section, Environment and Natural Resources Division, United States Department of Justice, Washington, DC. 161 pp.

Ingersoll, C.G., D.D. MacDonald, N. Wang, J.L. Crane, L.J. Field, P.S. Haverland, N.E. Kemble, R.A. Lindskoog, C. Severn, and D.E. Smorong. 2001. Predictions of sediment toxicity using consensus-based freshwater sediment quality guidelines. Arch. Environ. Contam. Toxicol. 41:8-21.

IT Corporation. (International Technology Corporation). 1997. Remedial investigation data report, sediment operable unit, St. Louis River/Interlake Duluth Tar site. Volume 1 of 5. IT Corp., St. Paul, MN.

Jepsen, R., J. McNeil, and W. Lick. 2000. Effects of gas generation on the density and erosion of sediments from the Grand River. J. Great Lakes Res. 26:209-219.

Kellner, D.K., T. Kroska, and K. Plass. 1999. Historic reconstruction of property ownership and land use along the Lower St. Louis River. St. Louis River Citizens Action Committee. Duluth, MN.

King, P. 2001. Analysis of sediment cores to assess chlorinated bornanes and chlorinated bornenes in the St. Louis River. Environmental Outcomes Division, Minnesota Pollution Control Agency, St. Paul, MN.

Latchat Instruments. 1994. Ammonia (phenate) in 2 M KCl soil extracts. QuikChem Method 12-107-06-1-A. Lachat Instruments, Milwaukee, WI.

Liu, C., J.A. Jay, R. Ika, J.P. Shine, and T.E. Ford. 2001. Capping efficiency for metal-contaminated marine sediment under conditions of submarine groundwater discharge. Environ. Sci. Technol. 35:2334-2340.

Lodge, K.B. 1996. A method for the particle-size analysis of freshwater sediments using the Horiba LA-900 analyzer. Department of Chemical Engineering, University of Minnesota, Duluth, MN.

Loganathan, B.G., K.N. Irvine, K. Kannan, V. Pragatheeswaran, and K.S. Sajwan. 1997. Distribution of selected PCB congeners in the Babcock Street Sewer District: A multimedia approach to identify PCB sources in combined sewer overflows (CSOs) discharging to the Buffalo River, New York. Arch. Environ. Contam. Toxicol. 33:130-140.

Lubin, A.N., M.H. Williams, and J.C. Lin. 1995. Statistical techniques applied to sediment sampling. U.S. Environmental Protection Agency, Region 5, Chicago, IL.

MacDonald, D.D., C.G. Ingersoll, and T.A. Berger. 2000a. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch. Environ. Contam. Toxicol. 39:20-31.

MacDonald, D.D., L.M. DiPinto, J. Field, C.G. Ingersoll, E.R. Long, and R.C. Swartz. 2000b. Development and evaluation of consensus-based sediment effect concentrations for polychlorinated biphenyls (PCB). Environ. Toxicol. Chem. 19:1403-1413.

MDH (Minnesota Department of Health). 1993. General method for metals determination by stabilized temperature graphite furnace atomic absorption spectroscopy. MDH Method GEN-STGFAA (September 1, 1993). Minnesota Department of Health, Minneapolis, MN.

MDH. 1995. Percent moisture sed/soil. MDH Method 261. Minnesota Department of Health, Minneapolis, MN.

MDH. 1997. Procedure for the determination of polyaromatic hydrocarbons in solid matrices by gas chromatography/selected ion monitoring-mass spectrometry. MDH Method 513 (June 3, 1997). Minnesota Department of Health, Minneapolis, MN.

MDH. 2000. Minnesota fish consumption advisory. Health Risk Assessment Unit, Minnesota Department of Health, St. Paul, MN.

MPCA and WDNR (Minnesota Pollution Control Agency and Wisconsin Department of Natural Resources). 1992. The St. Louis River system remedial action plan. Stage One. Minnesota Pollution Control Agency, St. Paul, MN and Wisconsin Department of Natural Resources, Madison, WI.

MPCA and WDNR. 1995. The St. Louis River system remedial action plan. Progress report. Minnesota Pollution Control Agency, St. Paul, MN and Wisconsin Department of Natural Resources, Madison, WI.

Perminova, I.V., N.Y. Grechishcheva, D.V. Kovalevskii, A.V. Kudryavtsev, V.S. Petrosyan, and D.N. Matorin. 2001. Quantification and prediction of the detoxifying properties of humic substances related to their chemical binding to polycyclic aromatic hydrocarbons. Environ. Sci. Tech. 35:3841-3848.

Persaud, D., R. Jaagumagi, and A. Hayton. 1993. Guidelines for the protection and management of aquatic sediment quality in Ontario. Ontario Ministry of Environment and Energy, Ottawa, ON. Report No. ISBN 0-7729-9248-7.

Redman, S. and T. Janisch. 1995. Newton Creek system sediment contamination site characterization report. Sediment Management and Remediation Techniques Program, Wisconsin Department of Natural Resources, Madison, WI.

Rosemount Analytical. 1990a. Analysis of sludges and solids for carbon. Application Note TOC-011. Rosemount Analytical, Dohrmann Division, Cincinnati, OH.

Rosemount Analytical. 1990b. Extending the carbon concentration range of the boat sampler. Application Note TOC-012. Rosemount Analytical, Dohrmann Division, Cincinnati, OH.

Rosemount Analytical. 1991. DC-80 total organic carbon analyzer systems manual. Revision N. Rosemount Analytical, Dohrmann Division, Cincinnati, OH.

Schneider, A.R., H.M. Stapleton, J. Cornwell, and J.E. Baker. 2001. Recent declines in PAH, PCB, and toxaphene levels in the northern Great Lakes as determined from high resolution sediment cores. Environ. Sci. Technol. 35:3809-3815.

Schubauer-Berigan, M. and J.L. Crane. 1996. Preliminary contaminant assessment of the Thomson, Forbay, and Fond du Lac Reservoirs. Water Quality Division, Minnesota Pollution Control Agency, St. Paul, MN.

Schubauer-Berigan, M. and J.L. Crane. 1997. Survey of sediment quality in the Duluth/Superior Harbor: 1993 sampling results. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA 905-R97-005.

Service Environmental and Engineering. 2001. Phase IIIB work plan and sampling and analysis plan for the re-opened RI/FS sediment operable unit, SLRIDT Site, Duluth, MN. Service Environmental and Engineering, St. Paul, MN.

Smith, V.E. and S.G. Rood. 1994. Sediment sampling surveys. In: ARCS Assessment Guidance Document, pp. 33-56. U.S. Environmental Protection Agency, Great Lakes National Program Office, Chicago, IL. EPA 905-B94-002.

Swartz, R.C. 1999. Consensus sediment quality guidelines for PAH mixtures. Environ. Toxicol. Chem. 18:780-787.

Thibodeaux, L.J., K.T. Valsaraj, and D.D. Reible. 2001. Bioturbation-driven transport of hydrophobic organic contaminants from bed sediment. Environ. Eng. Sci. 18:215-223.

TMA (Thermo Analytical). 1996. Sampling and analysis of sediments from the Duluth-Superior Harbor: September 1995 – April 1996. Thermo Analytical, Ypsilanti, MI.

Ullrich, S.M., T.W. Tanton, and S.A. Abdrashitova. 2001. Mercury in the aquatic environment: A review of factors affecting methylation. Critical Rev. Environ. Sci. Technol. 31:241-293.

U.S. Army Corps of Engineers. 2001. Nature's effect on Great Lakes' water levels. U.S. Army Corps of Engineers—Detroit District. Great Lakes Update Vol. No. 143.

USEPA (United States Environmental Protection Agency). 1983. Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency, Office of Research and Development, Cincinnati, OH. EPA-600/4-79-020.

USEPA. 1991. EPA methods for the determination of metals in environmental samples. U.S. Environmental Protection Agency, Office of Research and Development, Washington, DC. EPA/600/4-91/010.

USEPA. 1993. Methods for measuring the acute toxicity of effluents and receiving waters to freshwater and marine organisms, 4th edition. U.S. Environmental Protection Agency, Office of Research and Development. EPA/600/4-90/027F.

USEPA. 1994. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. U.S. Environmental Protection Agency, Office of Research and Development, Duluth, MN. EPA 600/R-94/024.

USEPA. 1995. QA/QC guidance for sampling and analysis of sediments, water, and tissues for dredged material evaluations: Chemical evaluations. U.S. Environmental Protection Agency, Office of Water, Washington, DC. EPA 823-B-95-001.

USEPA. 1997. The incidence and severity of sediment contamination in surface waters of the United States. Volume 1: National sediment quality survey. U.S. Environmental Protection Agency, Office of Science and Technology, Washington, DC. EPA 823-R-97-006.

USEPA. 2000a. Methods for measuring the toxicity and bioaccumulation of sediment-associated contaminants with freshwater invertebrates. U.S. Environmental Protection Agency, Office of Research and Development, Office of Water, Washington, DC. EPA/600/R-99/064.

USEPA. 2000b. Prediction of sediment toxicity using consensus-based freshwater sediment quality guidelines. Great Lakes National Program Office, Chicago, IL. EPA 905/R-00/007.

Van Metre, P.C, B.J. Mahler, and E.T. Furlong. 2001. Response to comment on "Urban sprawl leaves its PAH signature." Environ. Sci. Technol. 35:1890-1891.

Walker, D.A. and S.P. Hall. 1976. Duluth-Superior Harbor cultural resources study. Archeology Department, Minnesota Historical Society, St. Paul, MN.

Washington Department of Ecology. 2001. Whatcom Waterway site, Bellingham Georgia-Pacific log pond. Washington Department of Ecology, Northwest Regional Office, Bellevue, WA. Publication #01-09-061.

WDNR (Wisconsin Department of Natural Resources). 1995. Guidance for sediment assessment in the state of Wisconsin. Bureau of Water Resources, Wisconsin Department of Natural Resources, Madison, WI.

WDNR. 2001. Glass furnace technology (GFT) project fact sheet Phase III: Pilot-scale melter. Wisconsin Department of Natural Resources, Madison, WI. (web site reference: http://www.dnr.state.wi.us/org/water/wm/lowerfox/minergy/index.html)

Wenck Associates. 1995. Harbor sediment sampling documentation report. Wenck Associates, Inc., Maple Plain, MN.

West, Inc. and D.D. Gulley. 1994. Toxstat version 3.4. Western EcoSystems Technology, Inc. Cheyenne, WY.