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Survey of Sediment Quality In The Duluth/Superior Harbor:

1993 SAMPLE RESULTS

Minnesota Pollution Control Agency
Protecting Minnesota's Environment and Quality of Life

Minnesota Pollution Control Agency

DATE: July 9, 1997

TO: Recipients of the separate Executive Summary (EPA 905-R97-005a) and/or full final report of "Survey of Sediment Quality in the Duluth/Superior Harbor: 1993 Sampling Results" (EPA 905-R97-005)

FROM: Judy L. Crane, Water Quality Division

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SUBJECT: Errata/clarification to the above reports

Executive Summary Corrections

Due to a software glitch, some of the data points in Figures 2, 3, 4, 8, 9, 10, and 14 appeared as the wrong color. This problem occurred when the files for final report production were brought into a new version of the software package. Enclosed are the corrected figures. Please staple the new figures into your report.

Additional Clarifications/Corrections to Full Report

The toxaphene results given in Tables 3-14 and 3-15 differ for sites DSH 34 and DSH 40. This is because the mean of the analytical duplicates were reported in Table 3-14, whereas the analytical laboratory had provided Dr. Swackhamer with just the results from the first run for her comparison in Table 3-15. Whether the mean or original value are used does not affect the interpretation of the results by GC/SIM in Table 3-15.

In Table 3-22, replace dibenzo(a,1)pyrene with dibenzo(a,l)pyrene (i.e., replace the number 1 with the letter l).

SURVEY OF SEDIMENT QUALITY IN THE DULUTH/SUPERIOR HARBOR: 1993 SAMPLING RESULTS

Submitted to

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ACKNOWLEDGMENTS

This report was initially written by Mary Schubauer-Berigan, formerly of the Minnesota Pollution Control Agency (MPCA) Water Quality Division. Judy Crane (MPCA) edited, revised, and finalized this document. Mary Schubauer-Berigan, Dan Helwig, and Harold Wiegner formed the primary MPCA project team responsible for designing this investigation. Jerry Flom, Patti King, John Thomas, Karen Kroll, Jill Jacoby, Mary Ann Koth, Carolyn Voelkers, Sandy Bissonnette, Judy Mader, Gary Simonsen, and Mark Stuart, all of the MPCA Water Quality Division, assisted with sediment sampling. Steve Simmer, Heidi Bauman, Katie Peukart, and Bob Beresford, all of the MPCA Duluth Regional Office, also helped collect samples. Sampling assistance was also received from the following Wisconsin Department of Natural Resources (WDNR) staff: Karen Plass, Nancy Larson, Kim Walz, Scott Redman, Tom Janisch, and Frank Koshere. Personnel from the Great Lakes National Program Office (GLNPO) operated GLNPO's Research Vessel (R/V): the Mudpuppy. The use of the R/V Mudpuppy and GLNPO's vibracorer device was essential for collecting sediment samples.

Carol Hubbard, MPCA Water Quality Division, performed the sediment toxicity tests with assistance from Harold Wiegner, Patti King, Jerry Flom, and Mary Schubauer-Berigan. The analytical support of the University of Minnesota's Trace Organics Lab (Irene Moser and Keith Lodge) and Natural Resources Research Institute (Rich Axler, Joe Schubauer-Berigan, Chris Owen, Geri Tesser, John Ameel, Anastasia Bamford, Gloria Bly, and Kent Johnson), AScI Corporation (Elliott Smith, Joe Rathbun, and Laura Huellmantel), St John's University (Dan Steck), Texas A&M University (Terry Wade), and Twin City Testing (Deneen Walker) contributed greatly to the study. Scot Beebe, of the MPCA Water Quality Division, assisted with the analysis of data. James Beaumaster and Patti King, MPCA Water Quality Division, provided graphical and spreadsheet support.

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LIST OF ACRONYMS AND ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
AC	Alternating Current
ACOE	Army Corp of Engineers
AOC	Area of Concern
ARCS	Assessment and Remediation of Contaminated Sediments
As	Arsenic
ASTM	American Society of Testing and Materials
1-BT	Monobutyltin
2-BT	Dibutyltin
4-BT	Tetrabutyltin
Cd	Cadmium
cm	Centimeter
Co	Company
Cr	Chromium
^{137}Cs	Cesium 137 Radioisotope
Cu	Copper
CV	Coefficient of Variation
DC	Direct Current
DDD	Metabolite of DDT
DDE	Metabolite of DDT
DDT	Dichloro-diphenyl-trichloroethane
DSD	Duluth Steam District
DSH	Duluth/Superior Harbor
EC50	The median effective concentration causing an effect to 50% of test organisms
EPA	Environmental Protection Agency
ft	Feet
GC/ECD	Gas Chromatography/Electron Capture Detection
GC/FPD	Gas Chromatography/Flame Photometric Detector
GC/MS	Gas Chromatography/Mass Spectrometry
GC/SIM	Gas Chromatography/Selective Ion Methodology
GIS	Geographic Information System
GLNPO	Great Lakes National Program Office
GPS	Global Positioning System
HCB	Hexachlorobenzene
Hg	Mercury

LIST OF ACRONYMS AND ABBREVIATIONS

IDL	Instrument Detection Limit
IJC	International Joint Commission
KCl	Potassium Chloride
kg	Kilogram
LaMP	Lakewide Management Plan
LEL	Lowest Effect Level
m	Meter
MDL	Method Detection Limit
mg	Milligram
mm	Millimeter
MN	Minnesota
MPCA	Minnesota Pollution Control Agency
MQL	Method Quantitation Limits
N/A	Not Applicable
NC	Not Collected
ND	Not Detected
NEL	No Effect Level
NH_3^+	Ammonia
Ni	Nickel
NRRI	Natural Resources Research Institute
NO	Not Obtained
NOAA	National Oceanographic and Atmospheric Administration
NT	Not Toxic
OCS	Octachlorostyrene
OMOEE	Ontario Ministry of Environment and Energy
PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
pH	Equal to the negative logarithm of the hydrogen ion concentration
POTW	Publicly Owned Treatment Works
ppb	Part Per Billion
ppt	Part Per Trillion
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
QC	Quality Control

LIST OF ACRONYMS AND ABBREVIATIONS

RAP	Remedial Action Plan
RCF	Relative Contamination Factor
R-EMAP	Regional Environmental Monitoring and Assessment Project
RI/FS	Remedial Investigation/Feasibility Study
RPD	Relative Percent Difference
R/V	Research Vessel
S	South
SD	Standard Deviation
SE	Southeast
SOP	Standard Operating Procedure
SQC	Sediment Quality Criteria
SQOC	Sediment Quality Objective Concentration
SRM	Standard Reference Material
SW	Southwest
T	Toxic
TBT	Tributyltin
TCDD	Tetrachlorodibenzo-p-dioxin (as in 2,3,7,8-TCDD)
TCDF	Tetrachlorodibenzofuran (as in 2,3,7,8-TCDF)
TOC	Total Organic Carbon
μg	Microgram
UMD	University of Minnesota-Duluth
W	West
WDNR	Wisconsin Department of Natural Resources
WI	Wisconsin
WLSSD	Western Lake Superior Sanitary District
wt.	Weight
XRF	X-ray Fluorimetry
Zn	Zinc

EXECUTIVE SUMMARY

The Duluth/Superior Harbor has been designated as part of the St. Louis River Area of Concern (AOC) by the International Joint Commission (IJC). Contaminated sediments contribute to impaired uses in this AOC. The degree of sediment contamination in depositional areas outside the shipping channels is not well documented in the harbor, which has a long history of industrialization. In order to obtain a cohesive dataset, a sediment quality assessment was conducted in the St. Louis River estuary during September 1993. This study was designed to support the assessment goals of the Phase I sediment strategy for the St. Louis River Remedial Action Plan (RAP).

This survey included the collection of sediment cores from 40 sites suspected to exhibit contamination (Table 1, Figure 1). The U.S. EPA Research Vessel, the Mudpuppy, was used to collect sediment samples between the Fond du Lac Dam and Duluth/Superior entries during September 1993. A vibracore sampler (10 cm diameter) was used for collecting up to 3-m deep cores. The surficial (0-30 cm) layer was analyzed for the following contaminants: 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) and 2,3,7,8-tetrachlorodibenzofuran (TCDF), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), thirteen pesticides, mercury (Hg), lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), nickel (Ni), zinc (Zn), total organic carbon (TOC), and ammonia. Up to five sections per core (at 30 cm increments) were analyzed for mercury, PCBs (congeners and Aroclors), PCB immunoassay, PAH fluorescence screen, and TOC. Six of the 40 vibracore samples were sectioned in 2 to 5 cm increments and dated using the radioisotopic tracer ^{137}Cesium. In addition, surface gravity cores were collected from six sites, selected by their proximity to commercial, private or public shipyards, boat docks, and loading facilities; these samples were analyzed for tributyltin and three other butylated forms of tin (i.e., mono-, di-, tetra-). Surficial sediments, collected with a Ponar, were evaluated for acute toxicity to two benthic invertebrates: the amphipod, *Hyalella azteca* (*H. azteca*), and midge, Chironomus tentans (*C. tentans*). The Ponar samples were also evaluated for acute toxicity to the bacterium *Photobacterium phosphoreum* (Microtox^{R} test) and genotoxicity to the bacterium *Vibrio fischeri* (Mutatox^{R}). All analytical and toxicity test methods followed the data quality objectives of the Quality Assurance Project Plan.

The distribution of surficial (i.e., 0-30 cm) contaminants varied widely throughout the harbor. Color charts showing the distribution of mercury, PCBs, PAHs, 2,3,7,8-TCDD/TCDF, toxaphene, p,p'-DDD + o,p'-DDT, and heavy metals are given in Figures

2 - 15. The concentrations of mercury and PCBs varied with depth in the sediment cores. Although the mercury concentrations at some sites (e.g., DSH 24 and DSH 34) rapidly decreased below the surficial layer, other sites (e.g., DSH 12, DSH 36, DSH 25, and DSH 40) showed both declines and increases in mercury concentrations at depth. For PCBs, the sediment profiles for DSH 03, DSH 20, DSH 31, and DSH 40 showed PCB peaks below the surface. Sites DSH 12 and DSH 34 had the greatest PCB concentrations in the surficial sediments.

Acute toxicity to *C. tentans* was evident at three of the 40 sites. The *H. azteca* test only passed quality assurance requirements for 12 sites; no acute toxicity was observed at these sites. One-quarter of all sites were toxic to the microbe *Photobacterium phosphoreum*, whereas about half the sites were genotoxic to the bacterium *Vibrio fischeri*. For the sediment toxicity test results, there was little comparability between the *C. tentans* results and the Microtox^{R} and Mutatox^{R} results.

The surficial sediment chemistry data for 17 contaminants and TOC were compared to sediment quality guidelines developed by the Ontario Ministry of Environment and Energy (OMOEE). The State of Minnesota has not developed sediment quality guidelines, and the U.S. EPA has only developed draft sediment quality criteria for five organic contaminants. The OMOEE guidelines provide a biologically-based benchmark that can be used to compare to the results of this study. The OMOEE Low Effect Level (LEL) guidelines correspond to the level of sediment contamination that can be tolerated by the majority of benthic organisms, and at which actual ecotoxic effects become apparent. The OMOEE Severe Effect Level (SEL) corresponds to the level at which pronounced disturbance of the sediment dwelling community can be expected. Relative contamination factors (RCFs) were calculated for 17 contaminants by normalizing the contaminant concentration by the respective LEL value (i.e., RCF = Contaminant Concentration/LEL). The individual RCFs were summed to yield a total RCF value for each site. Total RCF values that exceeded 17 indicated that some ecotoxic effects may be present at the sampling sites.

Table 2 contains a summary table of the total RCF values, as well as the sediment chemistry and toxicity test results. The table is organized with the total RCF values in descending order. Thus, an indication of the most contaminated to least contaminated sites can be derived from this table. It is important to note that correlations cannot be made between the toxicity test results and sediment chemistry data; this is because the sediment chemistry measurements were based on the upper 30 cm of the vibracore samples, whereas the toxicity tests were run on approximately the upper 20 cm of sediments obtained using a Ponar dredge.

A number of sites exceeded the OMOEE LEL values for heavy metals, PCBs, and PAHs (Table 2). PAH contamination was widespread in the harbor, and may have resulted partly from the historical storage, shipment, and use of coal in the Duluth/Superior Harbor. Sites in the Superior Harbor generally had relatively fewer exceedances of heavy metal, PCB, and PAH LELs than sites in the Duluth Harbor. Some of this difference may be due to different watershed inputs as the Nemadji River drains into the Superior Harbor, and the St. Louis River drains into the Duluth Harbor. In addition, the Duluth Harbor watershed has a greater industrial/commercial/residential base than the Superior Harbor watershed. Thus, there is a greater probability of anthropogenic point and nonpoint sources of contamination in the Duluth portion of the harbor. The Duluth portion of the harbor is also impacted by two Superfund sites: USX and Interlake/Duluth Tar.

Table 2 also provides a qualitative priority for further study at each site. The USX Superfund site was the most contaminated site evaluated in this study. This site, along with the Interlake/Duluth Tar Superfund site, have been undergoing additional investigations as part of the potentially responsible parties legal obligations. Other sites that were rated highly for further study included the bay surrounding the Western Lake Superior Sanitary District (WLSSD) and Coffee/Miller Creek outfalls, Fraser Shipyards, Minnesota Slip, area between the M.L. Hibbard Plant/DSD No. 2 and Grassy Point, and in the old 21st Ave. West Channel. Other areas, such as Slip C and off the Superior POTW outfall, were listed as medium priority. It is important to note that this study was limited in scope and was not meant to characterize large areas as to the extent of contamination. In addition, a sediment hotspot investigation was carried out by the Minnesota Pollution Control Agency (MPCA) during 1994 to further characterize several of the aforementioned priority sites. The results of this hotspot investigation should be used to decide whether or not further site characterization and/or remediation is needed at these sites.

Table 1. Summary of site codes and descriptions of sites included in the 1993 Duluth/Superior Harbor sediment assessment. Sites in Wisconsin are bold and italicized, whereas sites in Minnesota are in normal typeface.

Site Number	Site Description
DSH 01	***Burlington Northern Taconite facility (Superior)***
DSH 02	***Barkers Island Channel, East End (Superior)***
DSH 03	***Off Superior POTW***
DSH 04	Public launch area, Minnesota Point
DSH 05	***Off Superior Fiber Products former discharge***
DSH 06	***Base of East Gate Basin, Superior***
DSH 07	Hearding Island deep hole
DSH 08	Corps of Engineers vessel yard
DSH 09	***Near Globe Elevators (Superior)***
DSH 10	***Interstate Island deep hole***
DSH 11	WLSSD, just west of outfall
DSH 12	Old 21st Ave. W. Channel
DSH 13	DM&IR taconite storage facility
DSH 14	East of Erie Pier (Scrap yard at International Welders & Machinists)
DSH 15	***West of Incan Superior dock***
DSH 16	North of M.L. Hibbard plant/Duluth Steam District (DSD) No. 2
DSH 17	South of M.L. Hibbard plant/DSD No. 2
DSH 18	***Loon's Foot Landing Inlet (Superior)***
DSH 19	C. Reiss coal dock
DSH 20	Channel between Hearding Island and Park Point
DSH 21	Mouth of Stryker Embayment
DSH 22	Near Stryker Embayment, just west of current channel
DSH 23	***Across channel from Tallas Island, east of buoy #28***
DSH 24	Off Un-named Creek (USX Superfund site)
DSH 25	Near Wire Mill Settling Pond (USX Superfund site)

Table 1. Continued.

Site Number	Site Description
DSH 26	Mud Lake (near ME International)
DSH 27	***Kimballs Bay (no known contaminant source)***
DSH 28	***Allouez Bay, Superior***
DSH 29	Slip C (near end)
DSH 30	New Duluth (site of old paint factory)
DSH 31	***Fraser Shipyards, first slip west of drydocks # 1 and 2***
DSH 32	***Across Howard's Bay Channel from Fraser Shipyards Slip***
DSH 33	305 m S-SW of WLSSD outfall
DSH 34	91 m SE of WLSSD outfall
DSH 35	24 m W of Rice's Point, E of 21st Ave. W. Channel
DSH 36	61 m S of Coffee Creek outfall and near Miller Creek Outfall
DSH 37	Slip C, in front of Superwood plant
DSH 38	Slip C, near Great Lakes Towing Co.
DSH 39	Slip C, just up from Cutler Magner Co.
DSH 40	Minnesota Slip, near William Irvin ore boat

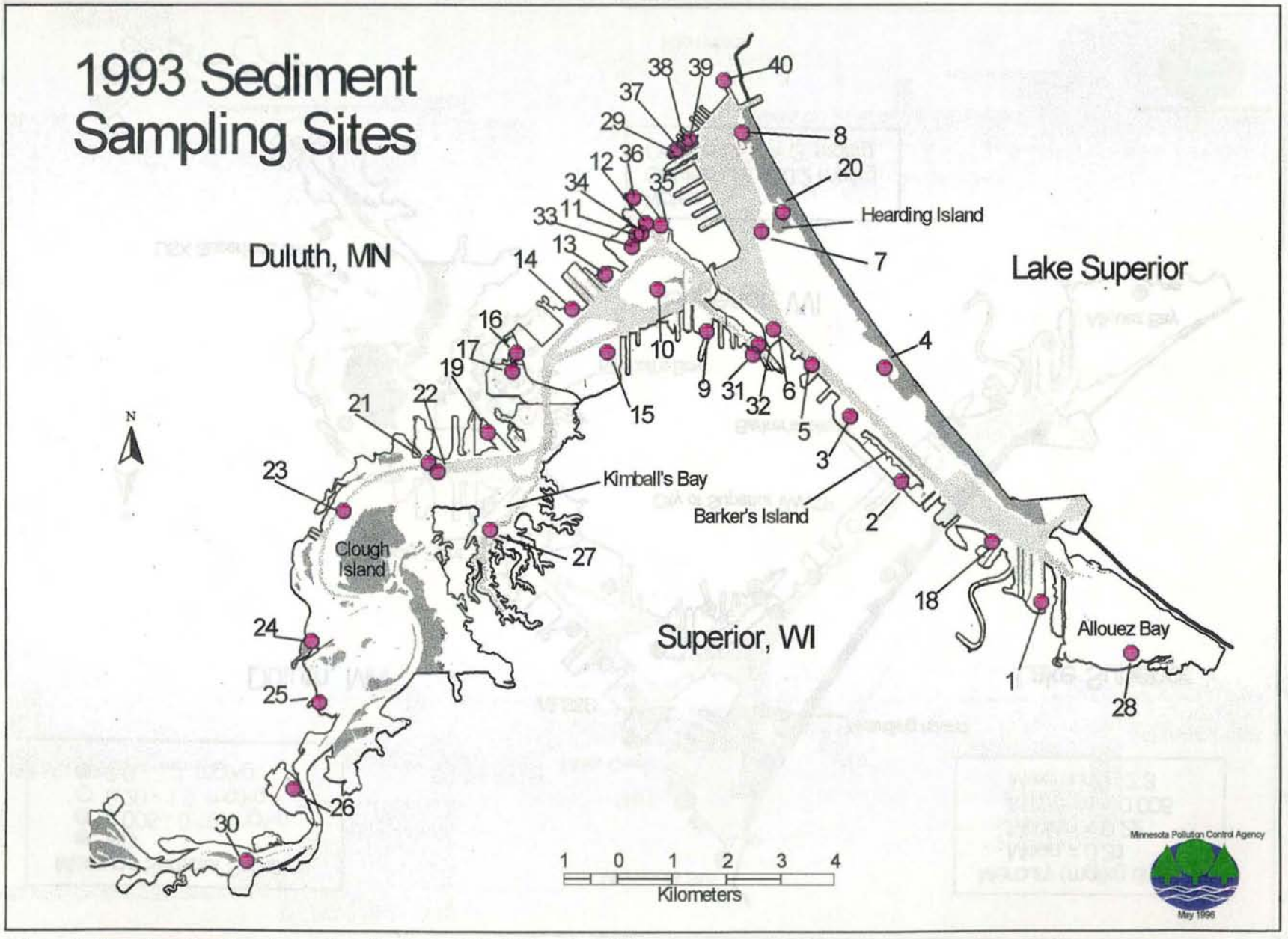

Figure 1. Location of sediment sampling sites in the Duluth/Superior Harbor.

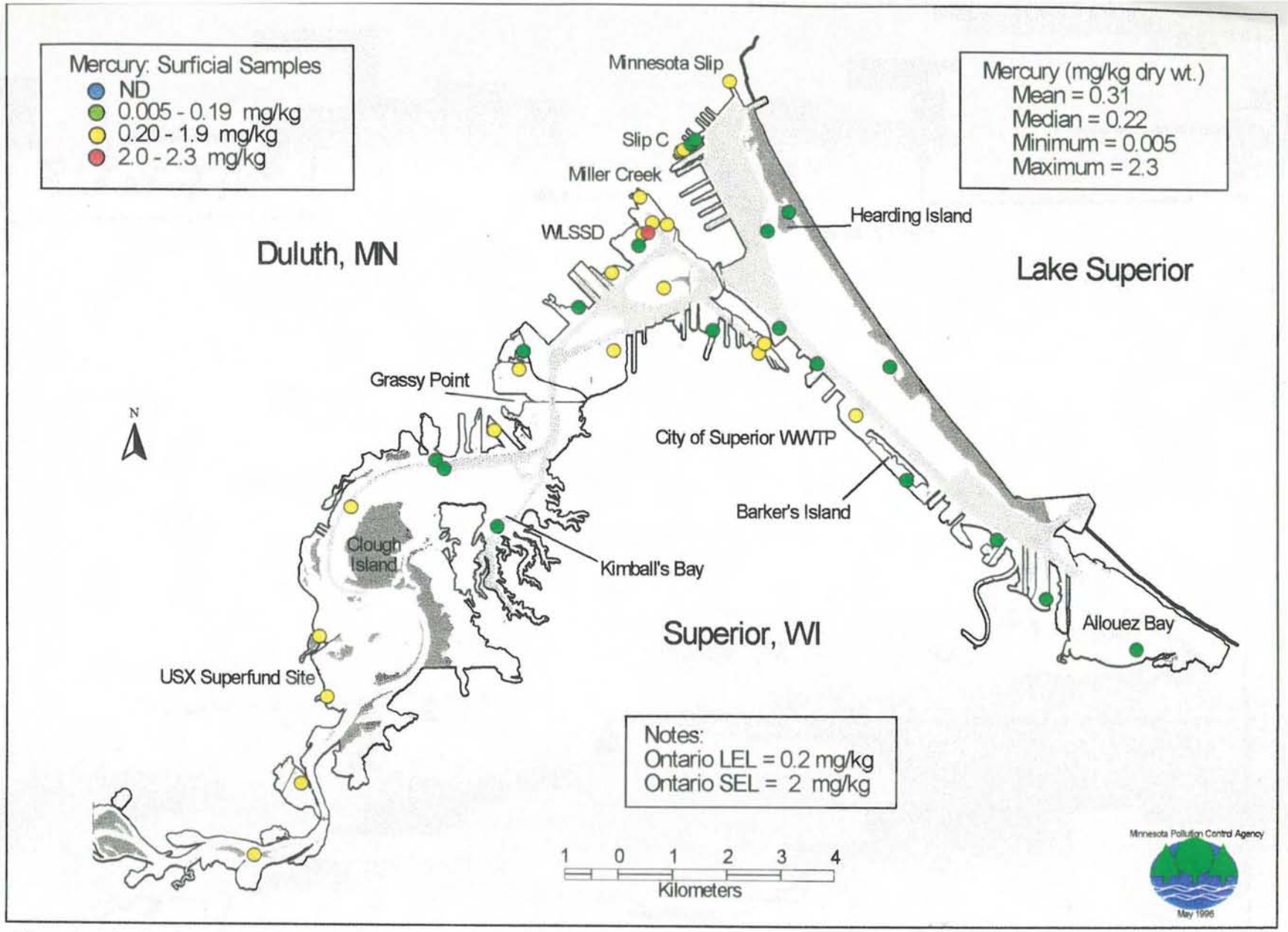

Figure 2. Distribution of surficial mercury concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

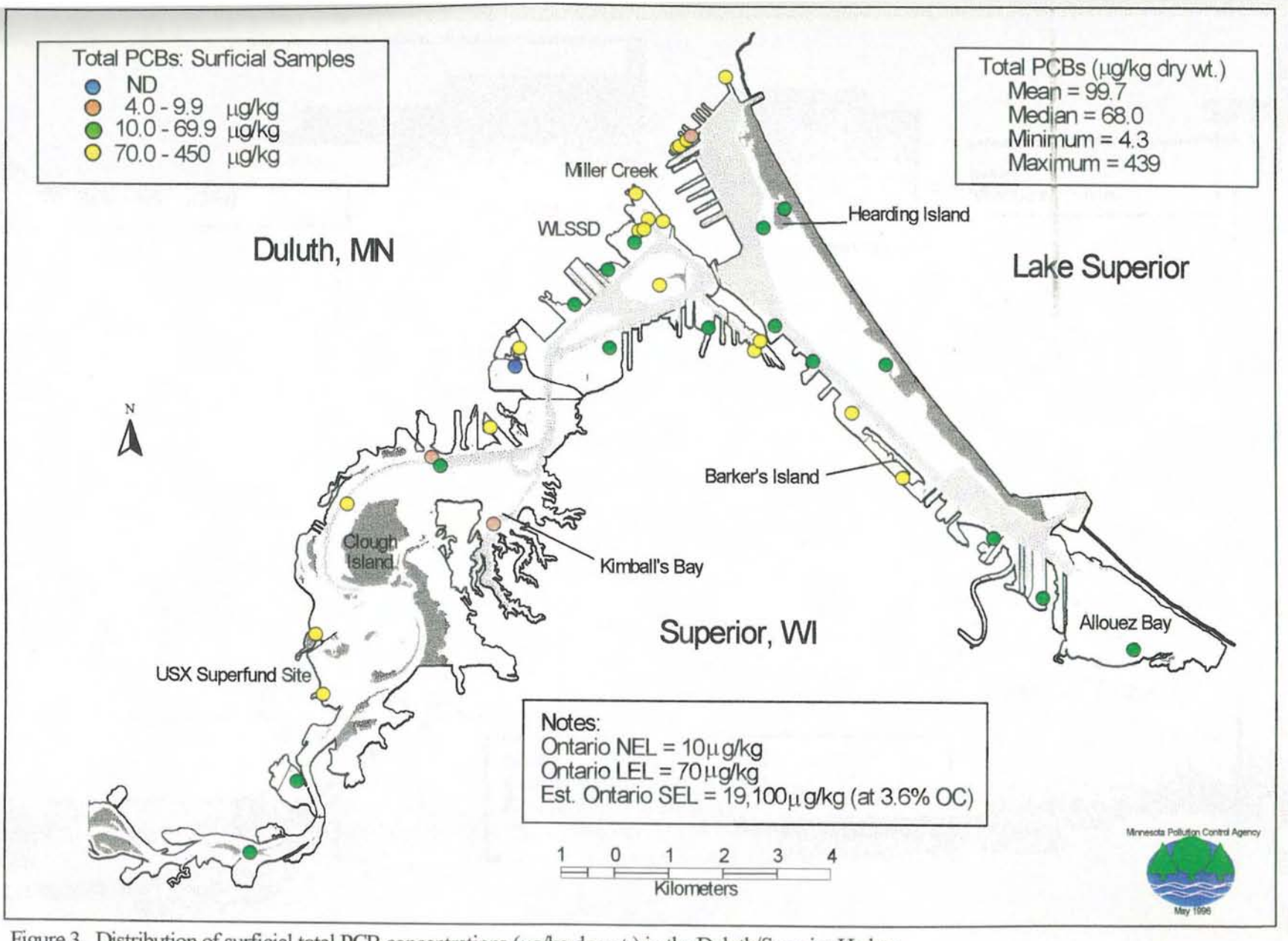

Figure 3. Distribution of surficial total PCB concentrations (µg/kg dry wt.) in the Duluth/Superior Harbor.

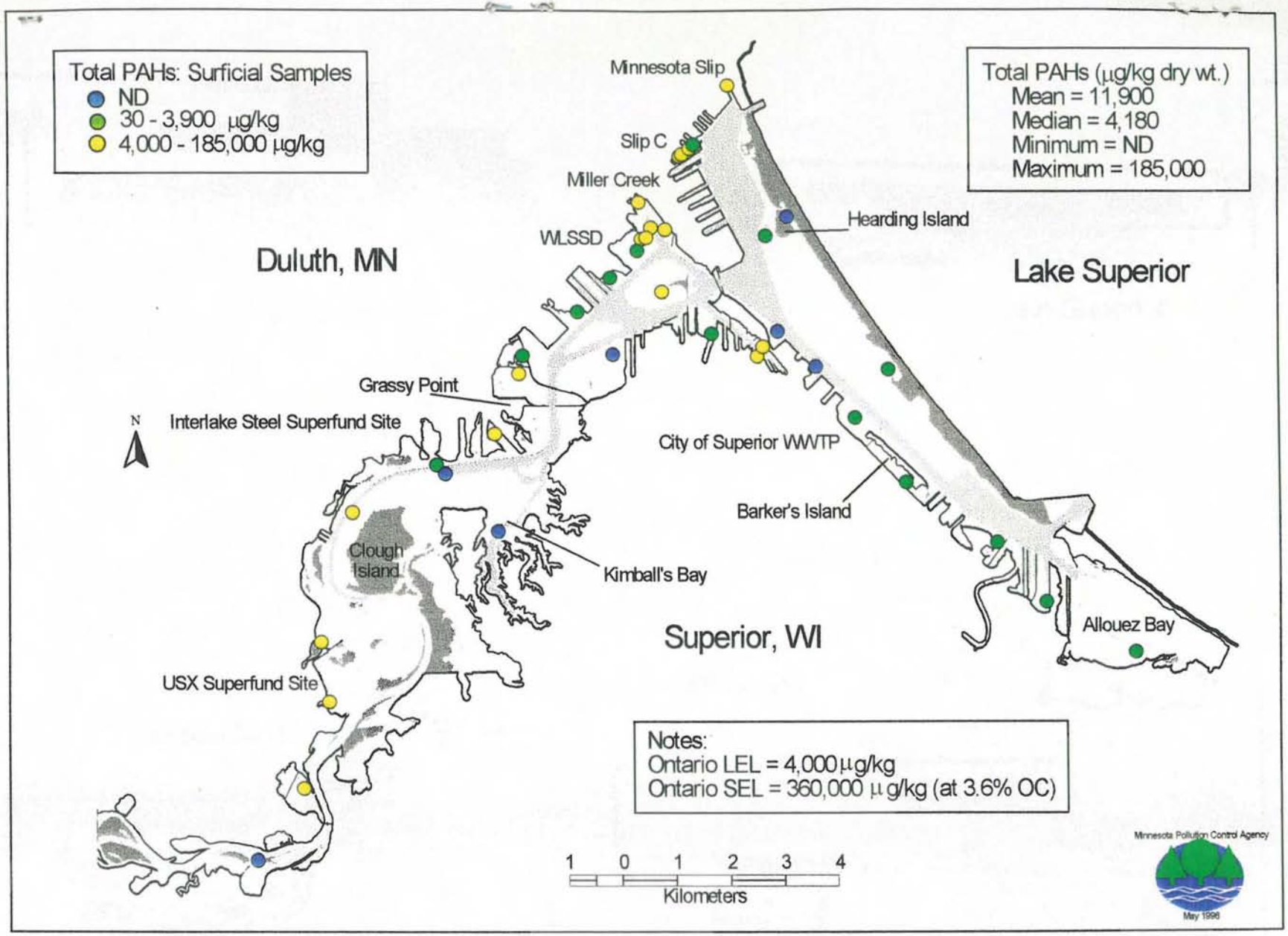

Figure 4. Distribution of surficial total PAH concentrations (µg/kg dry wt.) in the Duluth/Superior Harbor.

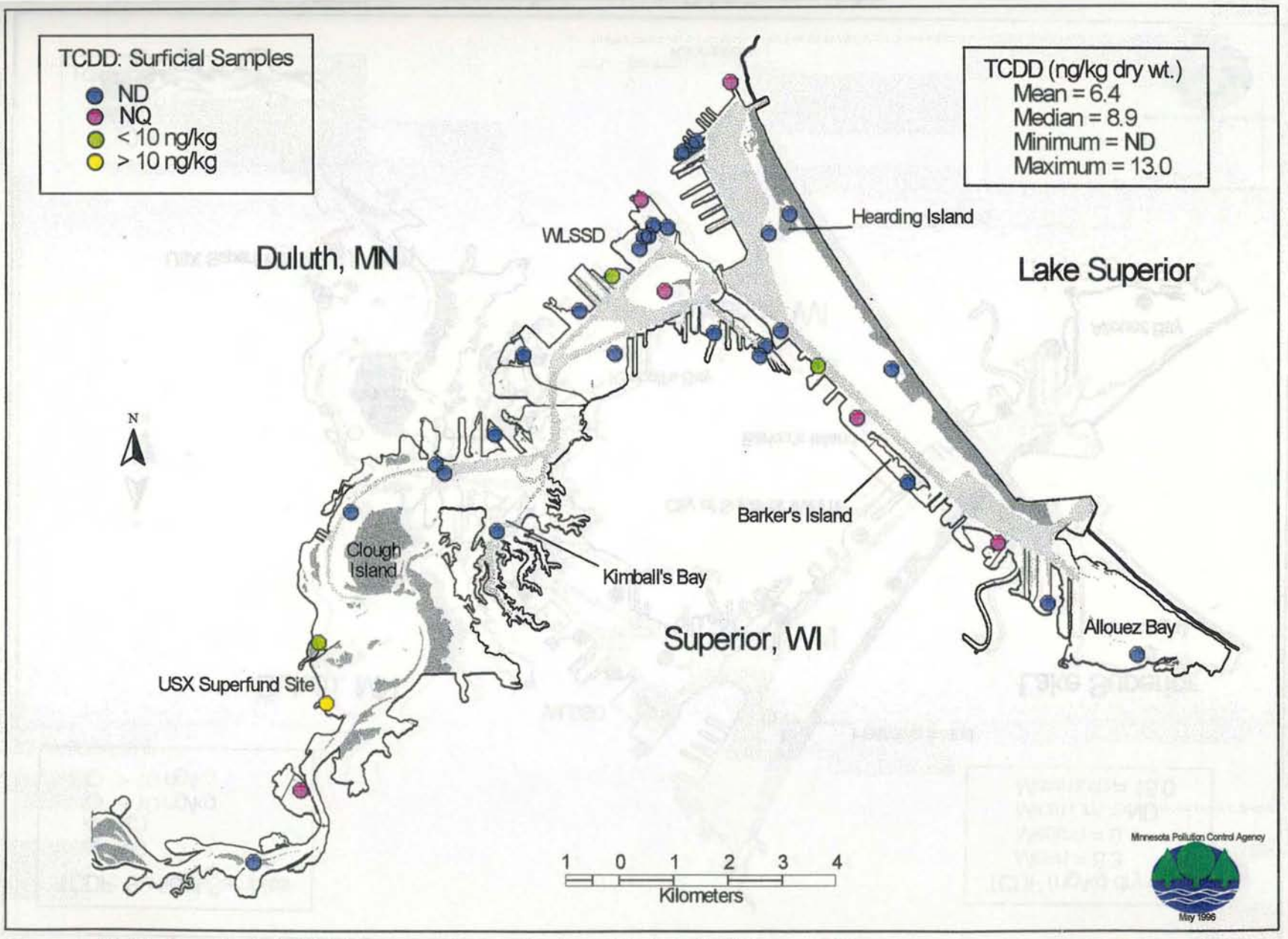

Figure 5. Distribution of surficial TCDD concentrations (ng/kg dry wt.) in the Duluth/Superior Harbor.

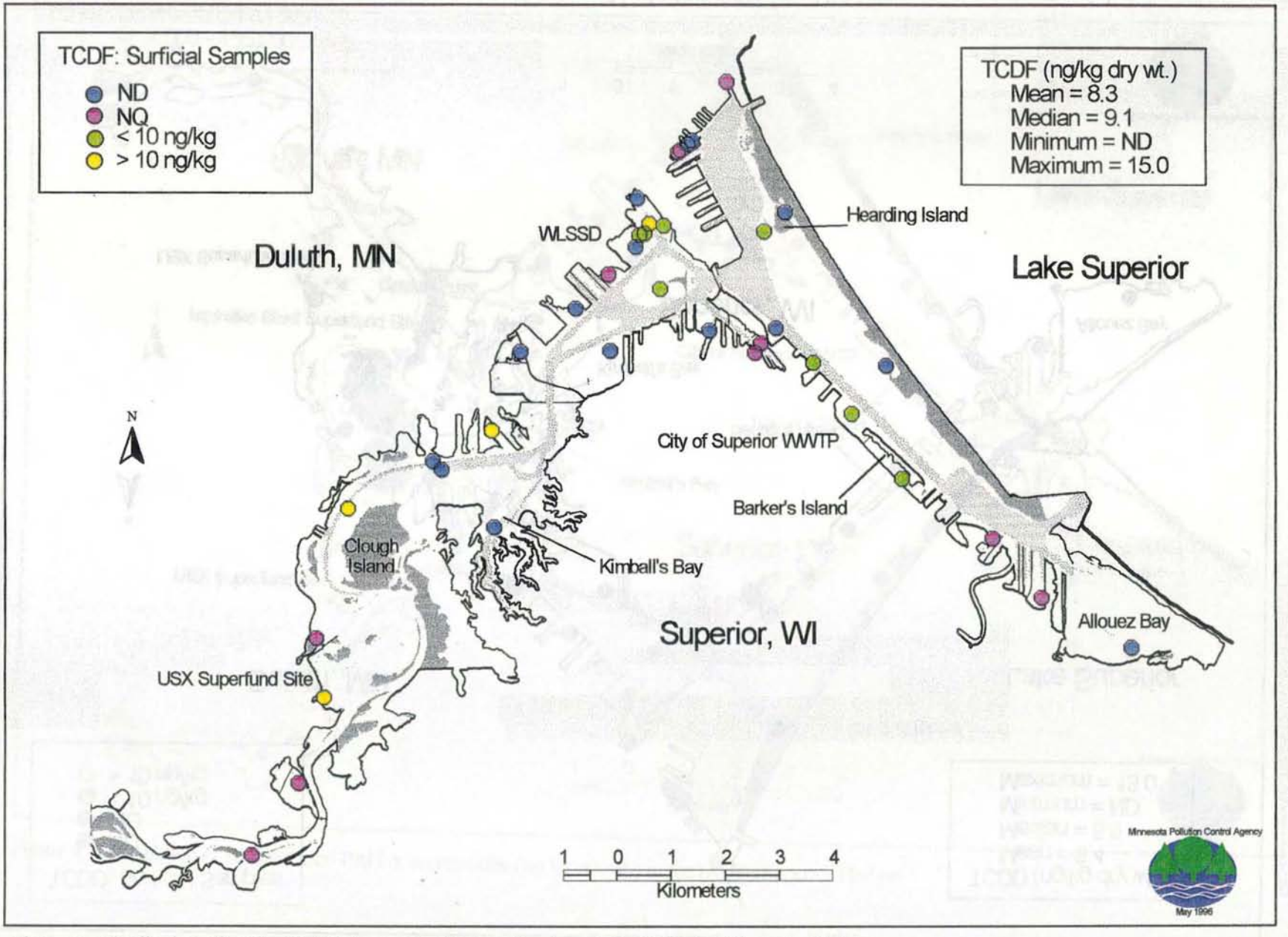

Figure 6. Distribution of surficial TCDF concentrations (ng/kg dry wt.) in the Duluth/Superior Harbor.

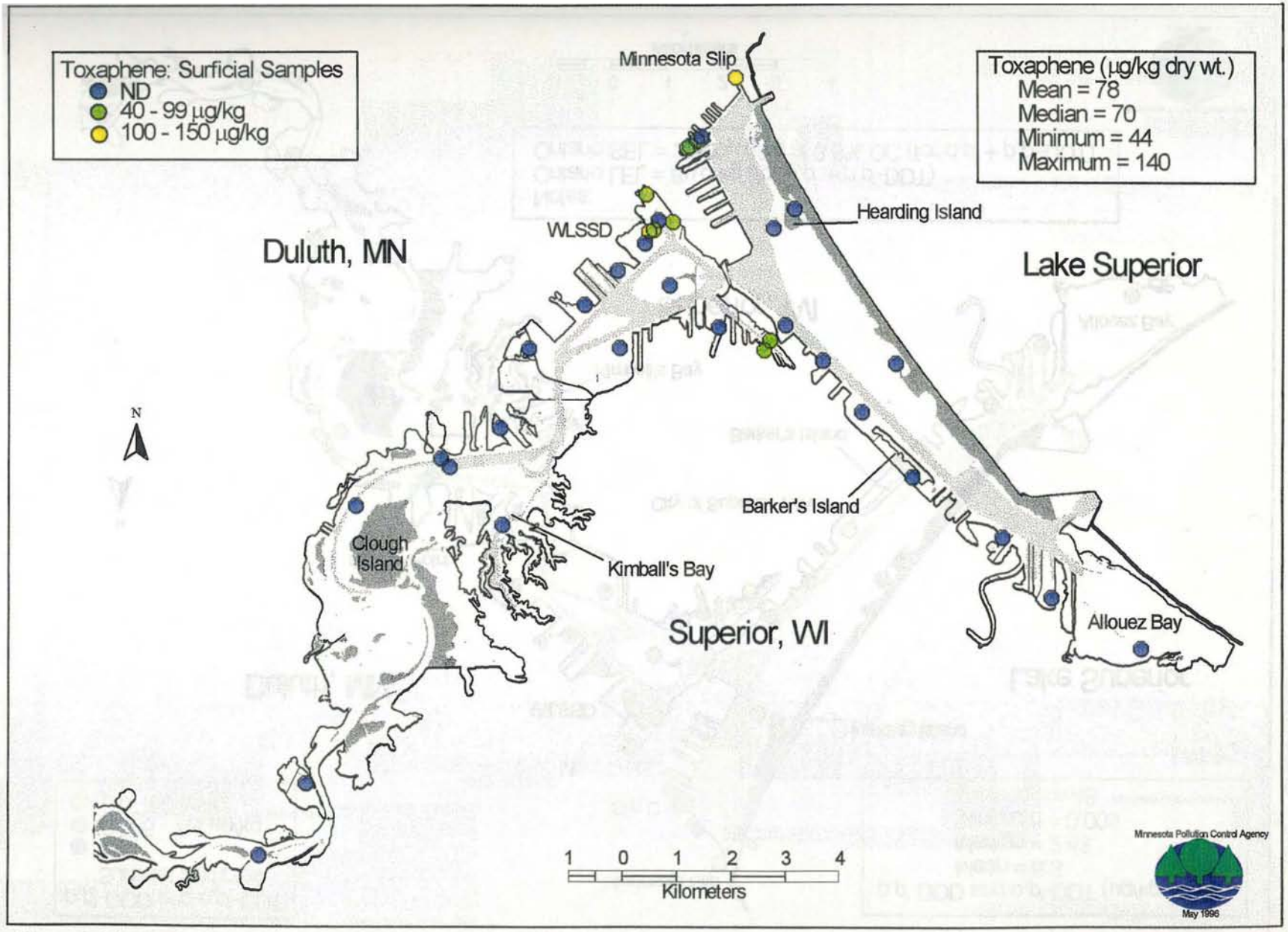

Figure 7. Distribution of surficial toxaphene concentrations (µg/kg dry wt.) in the Duluth/Superior Harbor.

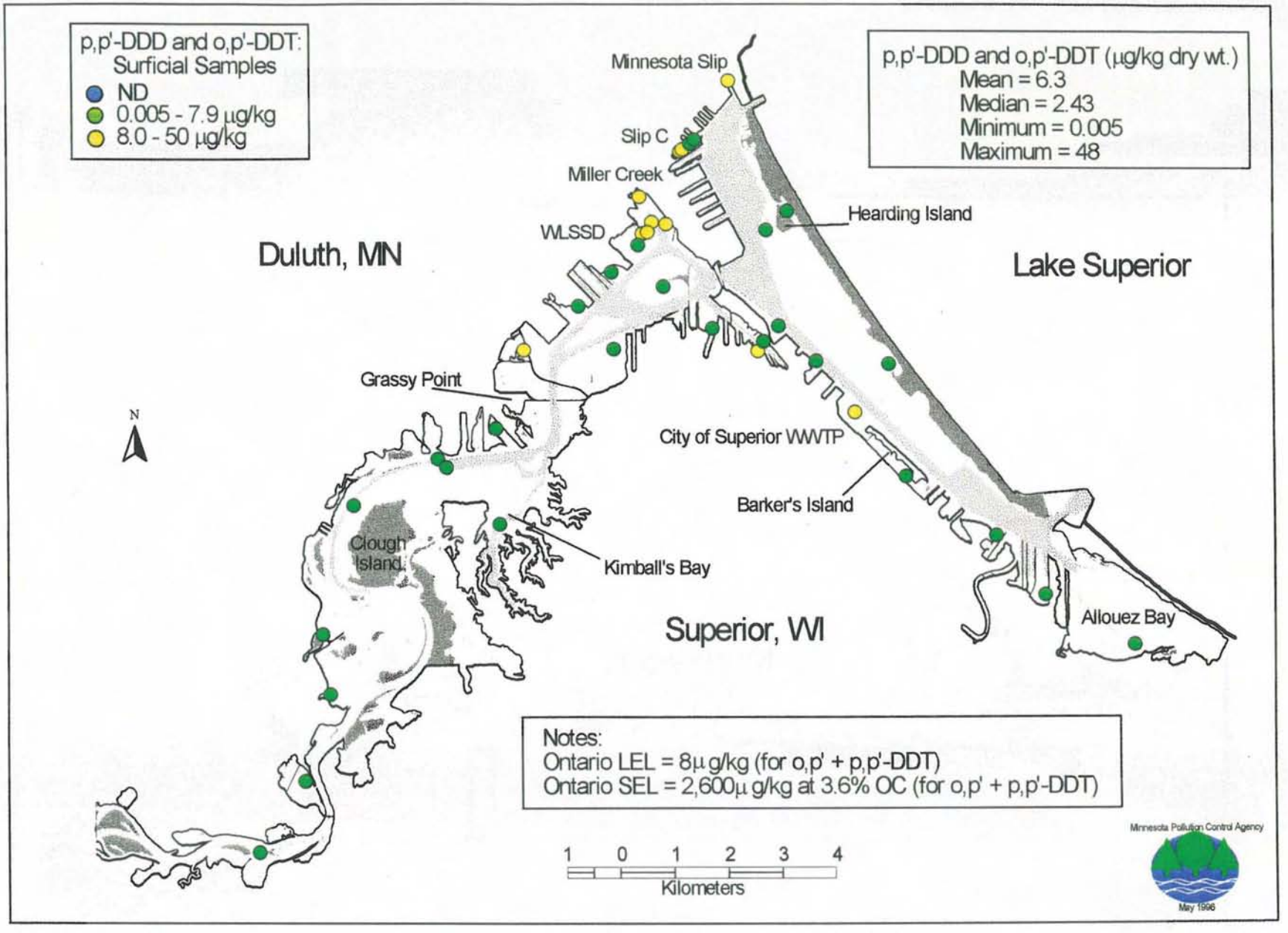

Figure 8. Distribution of surficial p,p'-DDD and o,p'-DDT concentrations (µg/kg dry wt.) in the Duluth/Superior Harbor.

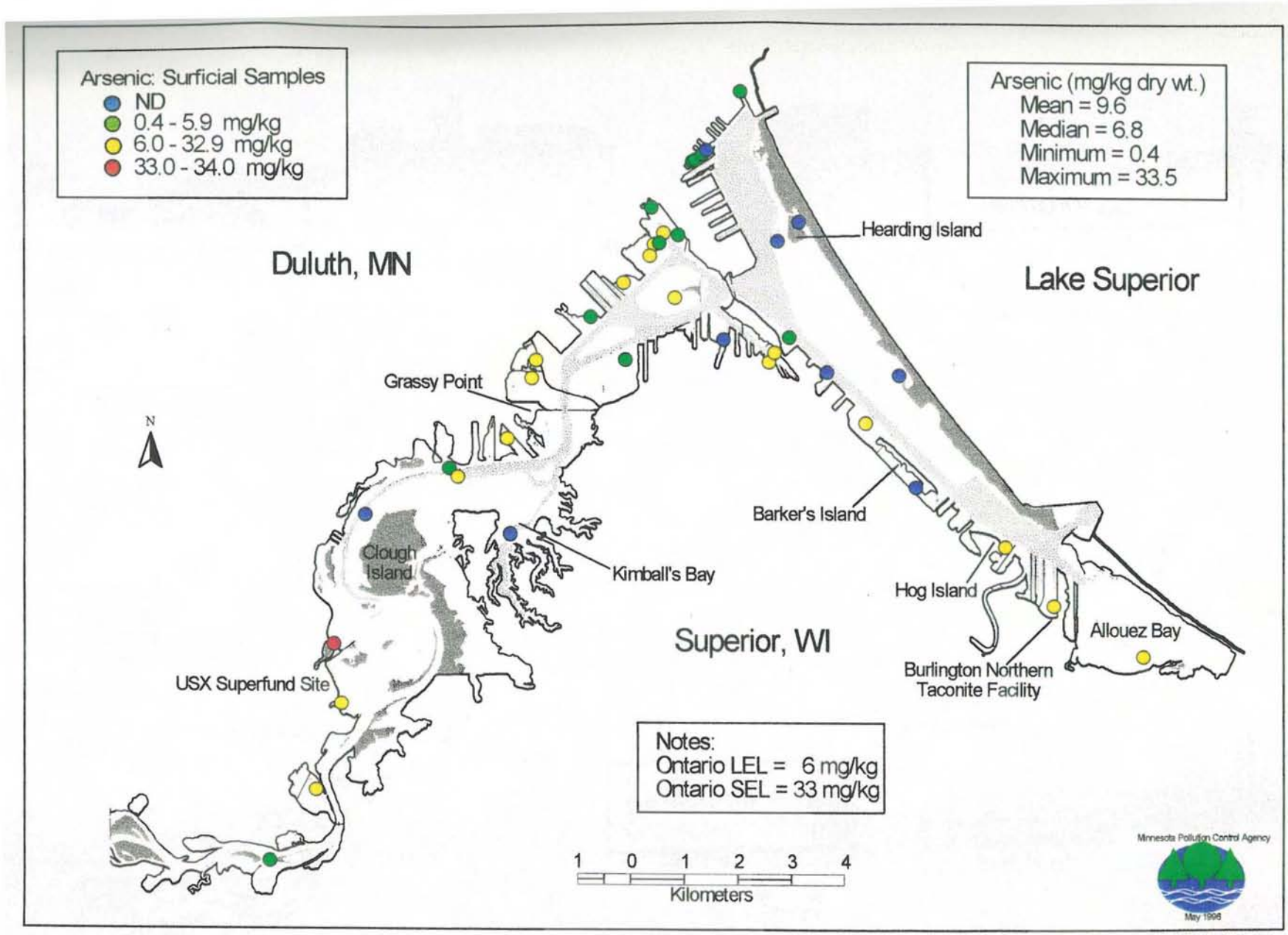

Figure 9. Distribution of surficial arsenic concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

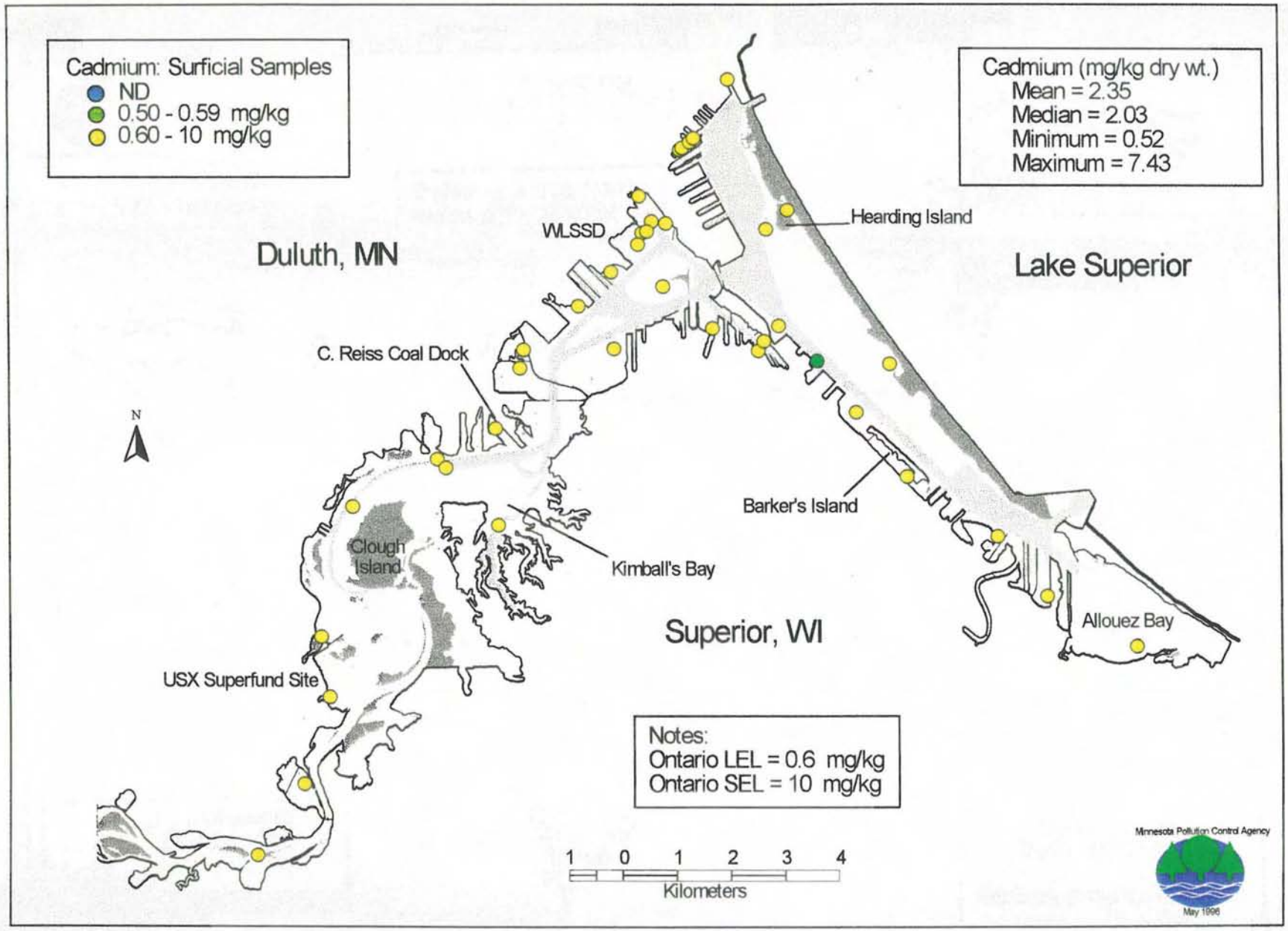

Figure 10. Distribution of surficial cadmium concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

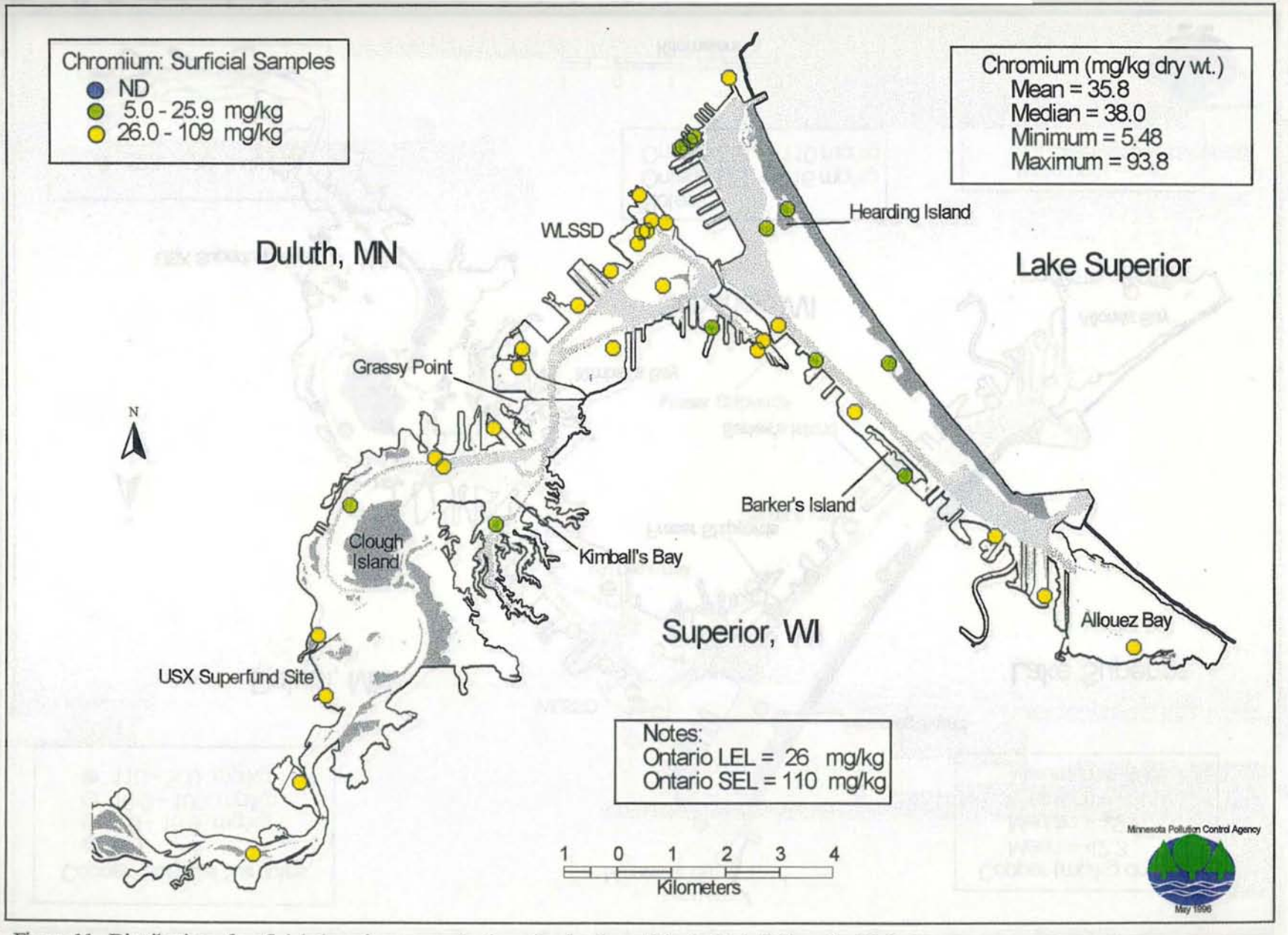

Figure 11. Distribution of surficial chromium concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

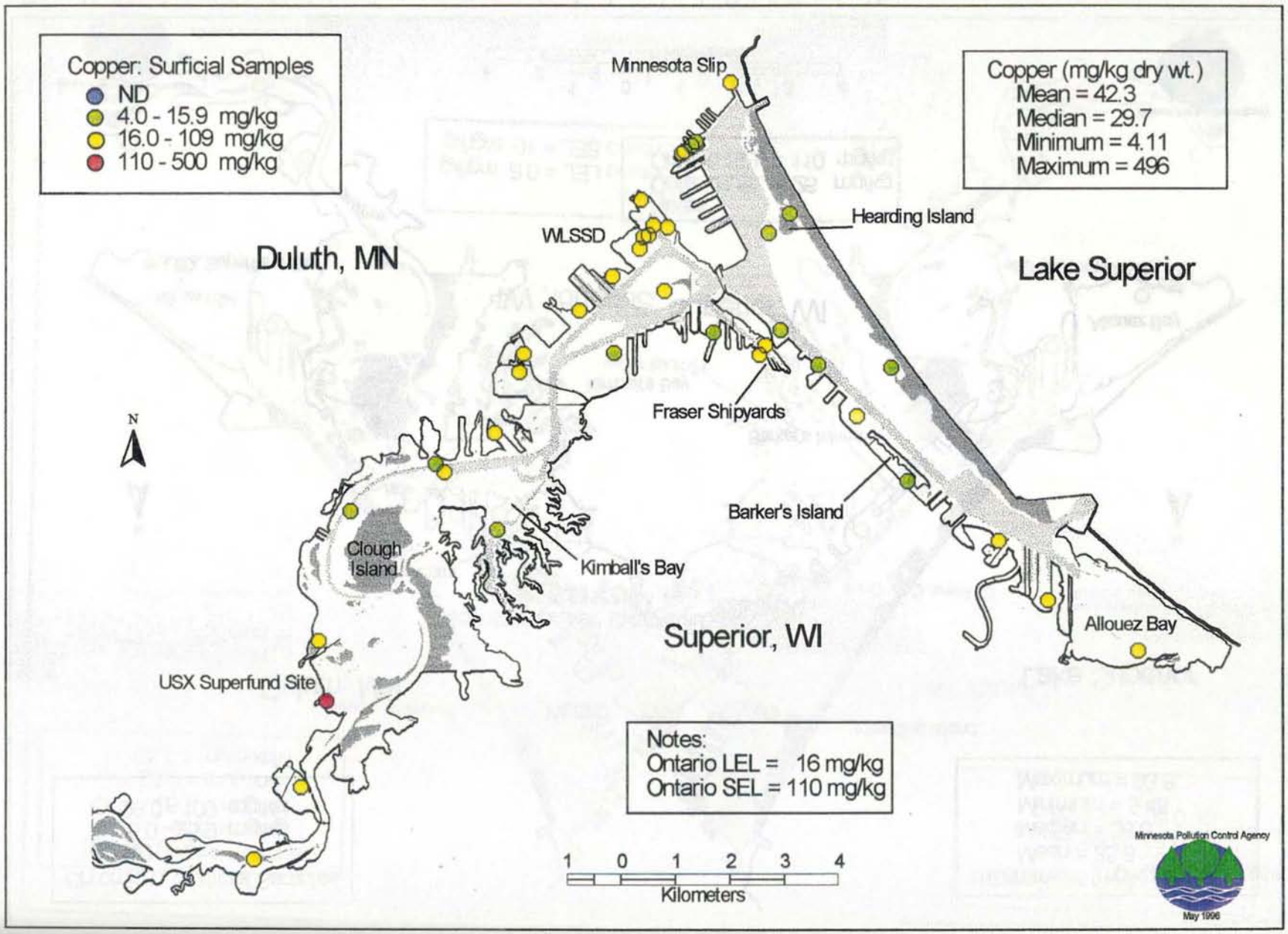

Figure 12. Distribution of surficial copper concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

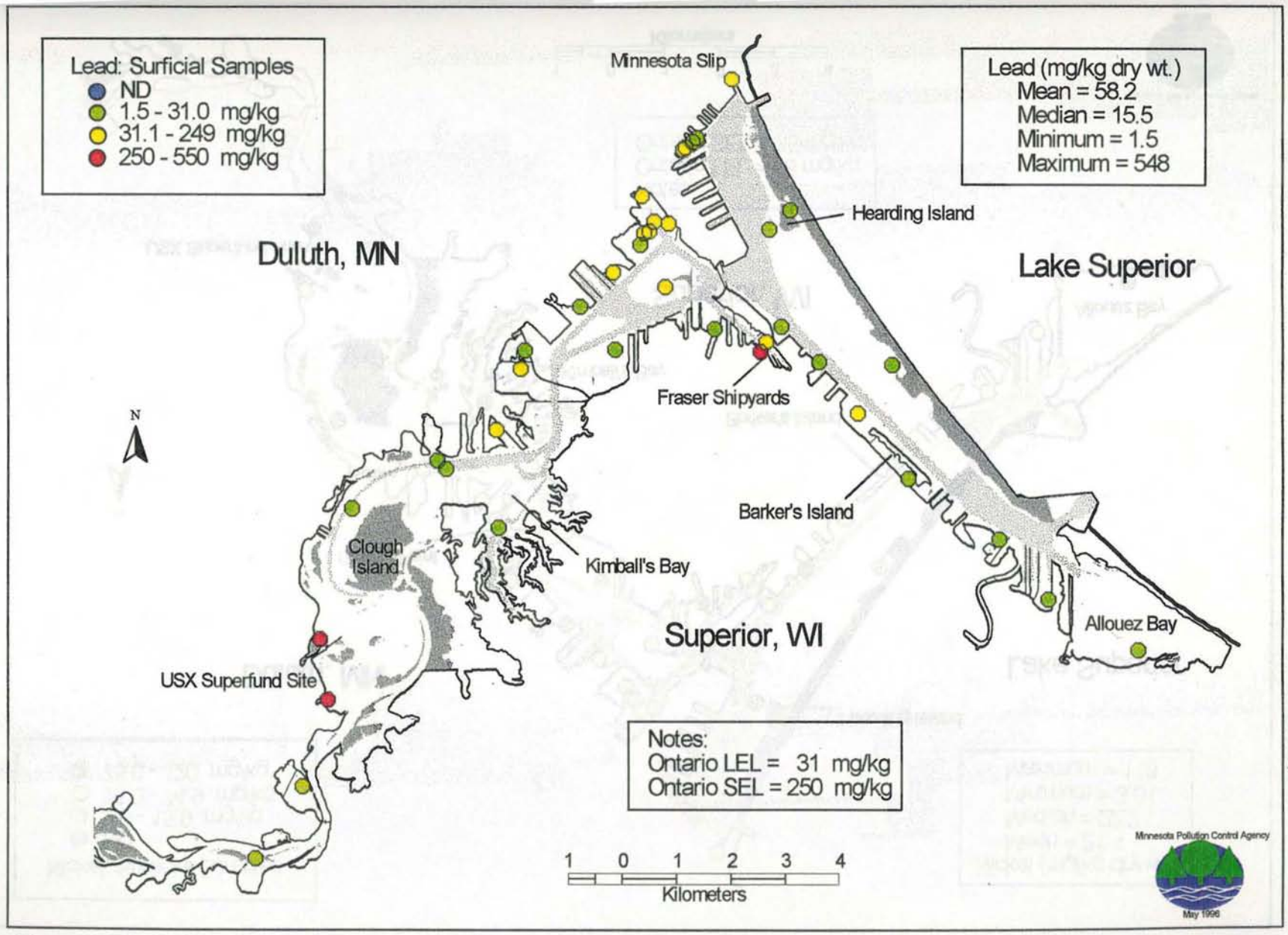

Figure 13. Distribution of surficial lead concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

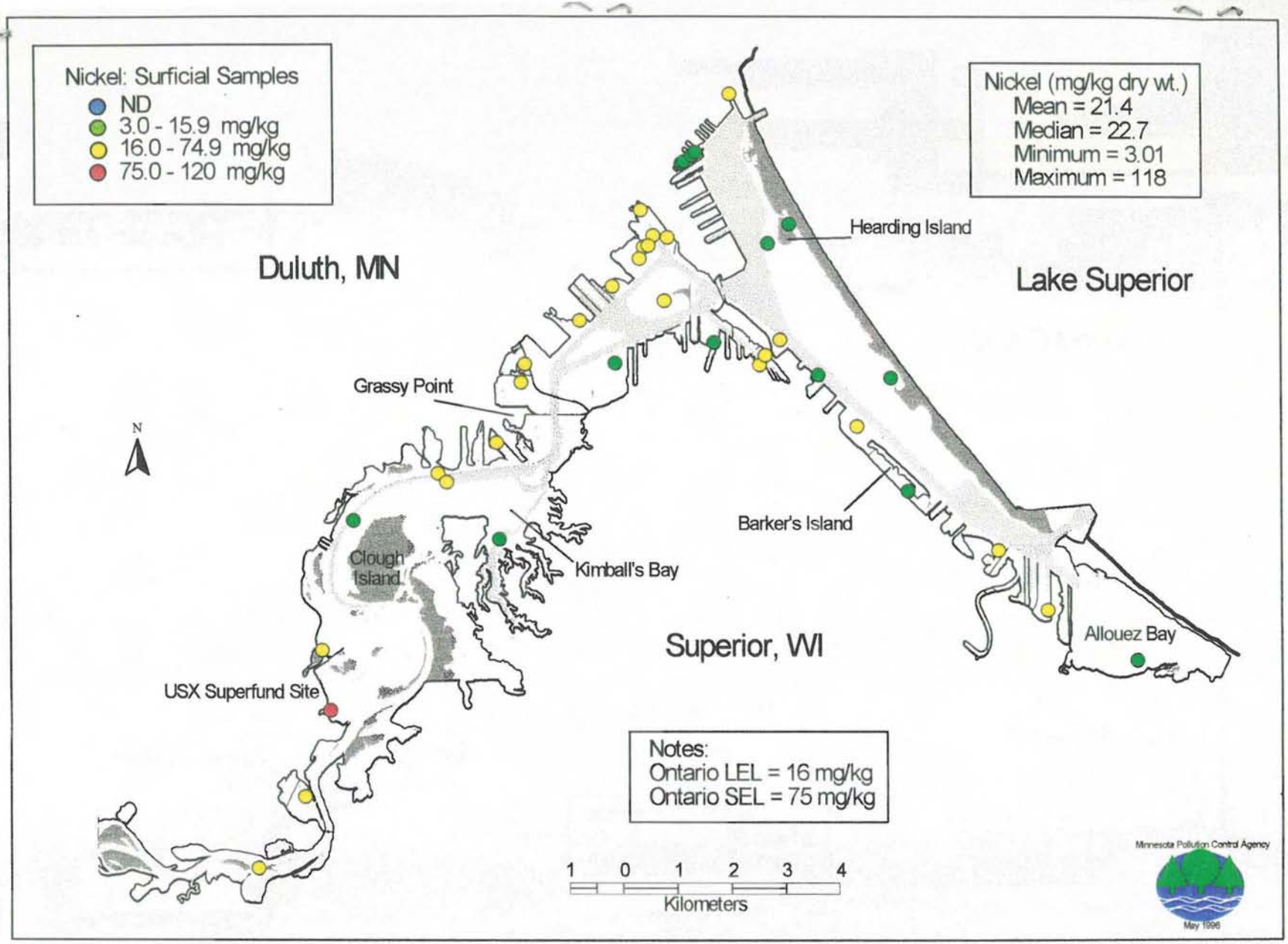

Figure 14. Distribution of surficial nickel concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

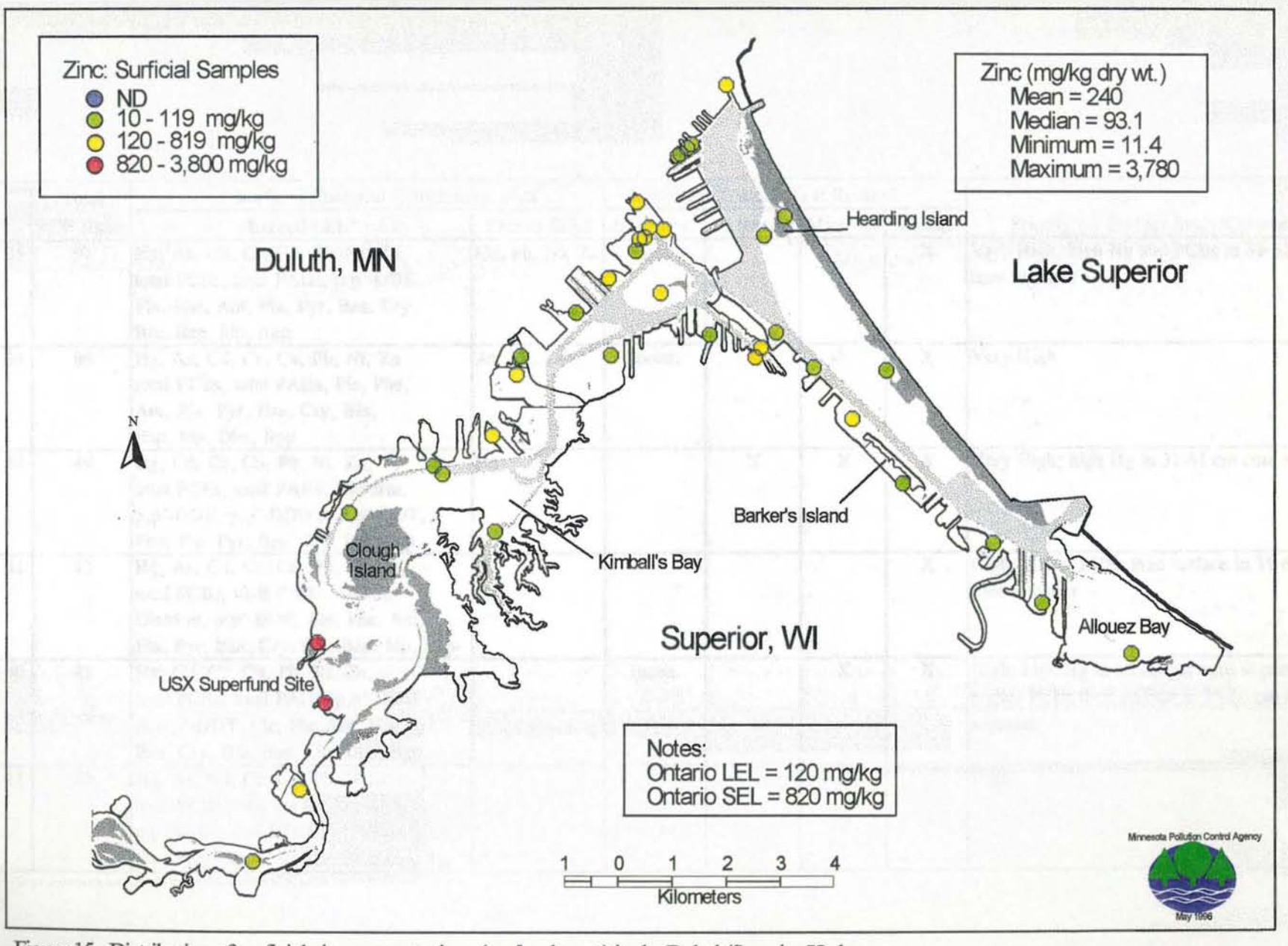

Figure 15. Distribution of surficial zinc concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

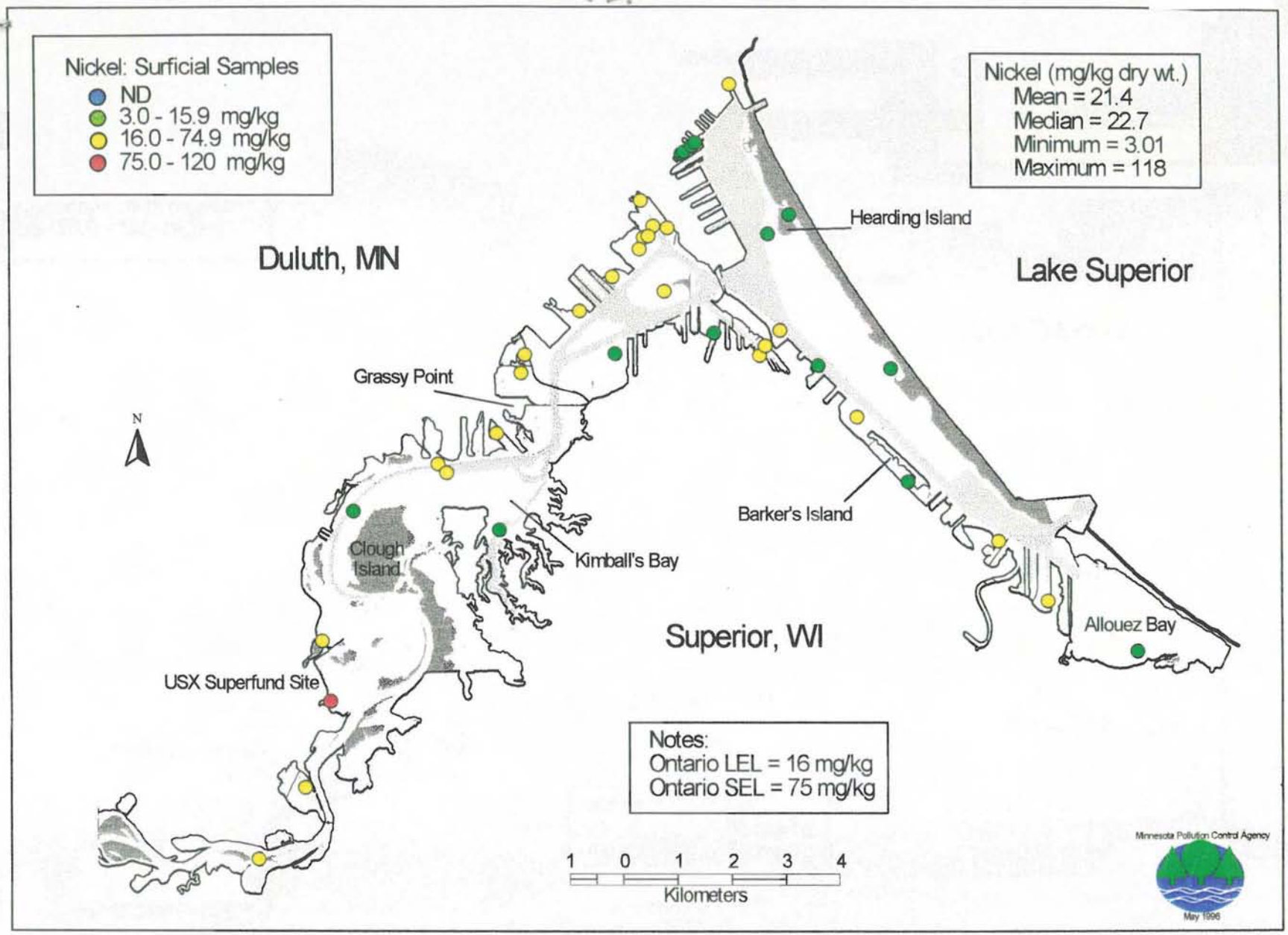

Figure 14. Distribution of surficial nickel concentrations (mg/kg dry wt.) in the Duluth/Superior Harbor.

Table 2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 36	35	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDE, p,p'-DDD & o,p'-DDT, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	High; high Hg in 122-216 cm core segment, high PCBs in most deeper core segments
DSH 17	30	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.				High; surficial PCB sample lost for this site and could not be included in total RCF calculation
DSH 12	30	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDE, p,p'-DDD & o,p'-DDT, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp		Incon.		X	X	High; high Hg in 163-180 cm core segment, PCBs elevated in other core segments but less than surface
DSH 35	25	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp				X		Medium; high Hg in 31-61 cm core segment
DSH 19	23	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fle, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	Medium; high Hg in 31-61 cm core segment
DSH 29	22	Hg, Cd, Cu, Pb, Zn, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	Medium; high Hg and PCBs in all deeper core segments
DSH 10	22	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fla, Pyr, Baa, Cry, Bfa, Bap				X		Medium

Table 2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 03	21	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs		Incon.			X	Medium; higher PCBs than surface in 61-91 cm core segment
DSH 32	20	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp						Medium; higher Hg than surface in 31-61 cm core segment
DSH 37	19	Hg, Cd, Cu, Pb, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp		Incon.		X	X	Medium; higher Hg than surface in 31-61 cm and 61-91 cm core segments
DSH 13	18	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, Cry, Bfa		Incon.		X		Medium
DSH 18	18	As, Cd, Cr, Cu, Ni		Incon.			X	Medium
DSH 16	18	As, Cd, Cr, Cu, Ni, total PCBs, p,p'-DDD & o,p'-DDT		Incon.				Medium; higher Hg than surface in 81-122 cm core segment, higher PCBs than surface in 51-81 cm core segment
DSH 26	17	Hg, As, Cd, Cr, Cu, Ni, Zn, total PAHs, Phe, Pyr, Bfa, Bap, Bgp		Incon.			X	Low
DSH 01	16	As, Cd, Cr, Cu, Ni		Incon.			X	Low; higher PCBs than surface in 61-91 cm core segment
DSH 28	14	As, Cd, Cr, Cu, Ni, Pyr, Bfa					X	Low

Table 2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 33	13	Hg, As, Cd, Cr, Cu, Ni		Incon.		X		Low
DSH 23	12	Hg, Cd, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.			X	Low
DSH 30	11	Hg, Cd, Cr, Cu, Ni		Incon.				Low
DSH 38	10	Cd, Pb, total PCBs, total PAHs, Phe, Pyr, Baa, Cry, Bfa		Incon.			X	Medium; higher Hg and PCBs than surface in 31-61 cm core segment
DSH 22	9.4	As, Cd, Cr, Cu, Ni		Incon.				Very Low
DSH 21	8.6	Cd, Cr, Ni, Bpg		Incon.				High; high PAHs (RCF = 22) observed at this site when it was resampled in 1994
DSH 15	8.3	Hg, Cd, Cr					X	Very Low
DSH 14	8.2	Cd, Cr, Cu, Ni, Bfa		Incon.	X			Very Low
DSH 06	7.3	Cd, Cr, Ni		Incon.				Very Low
DSH 20	6.3	Cd		Incon.		X	X	Very Low
DSH 04	5.9	Cd		Incon.				Very Low
DSH 09	5.6	Cd, Bfa, Bgp						Very Low
DSH 02	5.2	Cd, total PCBs		Incon.		X	X	Low; high surficial PCBs, other core segments not analyzed for PCBs
DSH 27	5.1	Cd					X	Very Low
DSH 07	4.6	Cd		Incon.			X	Very Low
DSH 39	3.5	Cd		Incon.				Very Low
DSH 05	3.4			Incon.				Very Low
DSH 08	-	No vibracore sediment sample collected		Incon.		X		Insufficient information to evaluate

[1]Codes: Fle=Fluorene; Phe=Phenanthrene; Ant=Anthracene; Fla=Fluoranthene; Pyr=Pyrene; Baa=Benz(a)anthracene; Cry=Chrysene; Bfa=Benzofluoranthene; Bap=Benzo(a)pyrene; Idp=Indeno(123-cd)pyrene; Dba=Dibenz(a,h)anthracene; Bgp=Benzo(g,h,i)perylene

[2]Incon. = Inconclusive test results due to control failure

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The Duluth/Superior Harbor has been designated as part of the St. Louis River Area of Concern (AOC) by the International Joint Commission (IJC) (Figure 1-1). This designation resulted from the 1978 Great Lakes Water Quality Agreement between the United States and Canada. The Stage I Remedial Action Plan (RAP), prepared jointly by Minnesota and Wisconsin state agencies, identified sediment contamination within the estuary as a primary factor impairing many beneficial uses, including: fish consumption, dredging activities, aesthetics, and fish, wildlife, and benthic populations and habitat [Minnesota Pollution Control Agency/Wisconsin Department of Natural Resources (MPCA/WDNR), 1992]. Contaminants of concern in the sediments include: mercury (Hg), polychlorinated biphenyls (PCBs), 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), polycyclic aromatic hydrocarbons (PAHs), and a variety of other metals and organic compounds. The following areas of the AOC have been identified as having elevated levels of sediment contaminants (MPCA/WDNR, 1992):

- Embayment that receives discharge from the Western Lake Superior Sanitary District (WLSSD) in Duluth, MN, and historically received discharge from a previous sewage treatment plant
- Interlake/Duluth Tar Superfund site in Duluth, MN
- U.S. Steel (USX) Superfund site in Duluth, MN
- Newton Creek and Hog Island Inlet of Superior Bay in Superior, WI
- Crawford Creek Wetland/Koppers Co. in Superior, WI.

During the past four years, the MPCA has been actively involved in delineating the extent of sediment contamination in the St. Louis River AOC. These studies include:

- Preliminary assessment of contaminated sediments and fish in the Thomson, Forbay, and Fond du Lac Reservoirs (Schubauer-Berigan and Crane, 1996)
- Survey of sediment quality in the Duluth/Superior Harbor: 1993 sampling results of contaminants in depositional areas outside the shipping channels

- Survey of sediment quality in the Duluth/Superior Harbor: 1994 sampling results of contaminants in hotspot areas
- Regional Environmental Monitoring and Assessment Program (R-EMAP) surveying, sampling, and testing: 1995 and 1996 sampling results.

The above investigations have been conducted with the cooperation and financial support of either the U.S. Environmental Protection Agency (EPA) or the Great Lakes National Program Office (GLNPO). These studies will support the assessment goals of the Phase I sediment strategy for the RAP. In this report, the results of the 1993 survey of sediment quality in the Duluth/Superior Harbor will be presented. Reports for the 1994 sediment survey and R-EMAP project are in the process of being prepared. The status and distribution of these reports can be determined by contacting Judy Crane at the MPCA office in St. Paul, MN. The raw data from most of these investigations are being entered into two similar, but separate, GIS-based databases for the Duluth/Superior Harbor. The databases are funded by U.S. Army Corps of Engineers and GLNPO. The GLNPO database contains more quality assurance/quality control (QA/QC) information, and an electronic copy of this database is included in Appendix A. ,

1.2 PROJECT DESCRIPTION

Sediment contamination in the Duluth/Superior Harbor is of concern, not only for the impairment of beneficial uses identified in the RAP (MPCA/WDNR, 1992), but also because of the close proximity to Lake Superior. Sediments in this AOC are likely to be a source of contaminants to Lake Superior through mechanisms such as resuspension, partitioning to the water column, advective transport, volatilization, and biotic uptake. Thus, it is important to reduce the loading of contaminants to Lake Superior to protect this natural resource.

Previous to this investigation, sediments in the Duluth/Superior Harbor had not been well characterized for either contaminants or toxic effects. In addition, historical sources of contaminants have not been characterized for the entire St. Louis River AOC. Over time, sections of the harbor have been filled in with material that may have been obtained from unknown, contaminated sites. Therefore, it may be difficult to determine potentially responsible parties at some sites.

The Stage I RAP report (MPCA/WDNR, 1992) identified a critical need for an estuary-wide sediment survey measuring horizontal and vertical chemical concentrations, as well as toxicity to benthic organisms. This project, by simultaneously analyzing areas known to be contaminated, as well as unknown sites, was intended to provide a consistent framework for

prioritizing remedial sediment activities at contaminated sites, as well as suggesting contaminants and endpoints of concern for each site for any future investigations.

The MPCA surveyed 40 sites in depositional areas of the Duluth/Superior Harbor during the fall of 1993 and summer of 1994. Most of the sites were selected for sediment analysis based on known proximity to current or former source discharges. Two sites were selected as indicators of ambient sediment conditions in areas not known to be affected by point sources, although effects from nonpoint sources could not be determined. Six sites were selected for the assessment of site variability within a spatially large depositional area (the WLSSD/Miller Creek Bay), and four sites for a spatially small depositional area (Slip C).

1.3 PROJECT OBJECTIVES

The primary objectives of this investigation were to:

- Quantify the level of sediment contamination in selected sections of cores from the Duluth/Superior Harbor. Contaminants of concern included: mercury, tributyltin and other priority metals [i.e., arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), nickel (Ni), and zinc (Zn)], thirteen pesticides, PCBs, 2,3,7,8-TCDD and 2,3,7,8-tetrachlorodibenzofuran (TCDF), PAHs, ammonia (NH_3^+), and total organic carbon (TOC).

- Compare the utility of two screening-level analytical techniques (i.e., PCB immunoassay and PAH fluorometry) with detailed methods for the semi-quantitation of PCBs and PAHs.

- Measure vertical distributions of PCBs, mercury, TOC, and PAHs (using a PAH fluorescence screening method) at up to five strata at all sites.

- Assess the toxic potential of surficial sediments to two benthic macroinvertebrates (i.e., *Hyalella azteca* and *Chironomus tentans*).

- Assess the acute toxicity and genotoxicity of surficial sediments to two different microbes.

- Date the presence of identified chemicals by ^{137}Cs on a subset of sediment cores.

- Prioritize areas for more intensive site surveys in the future.

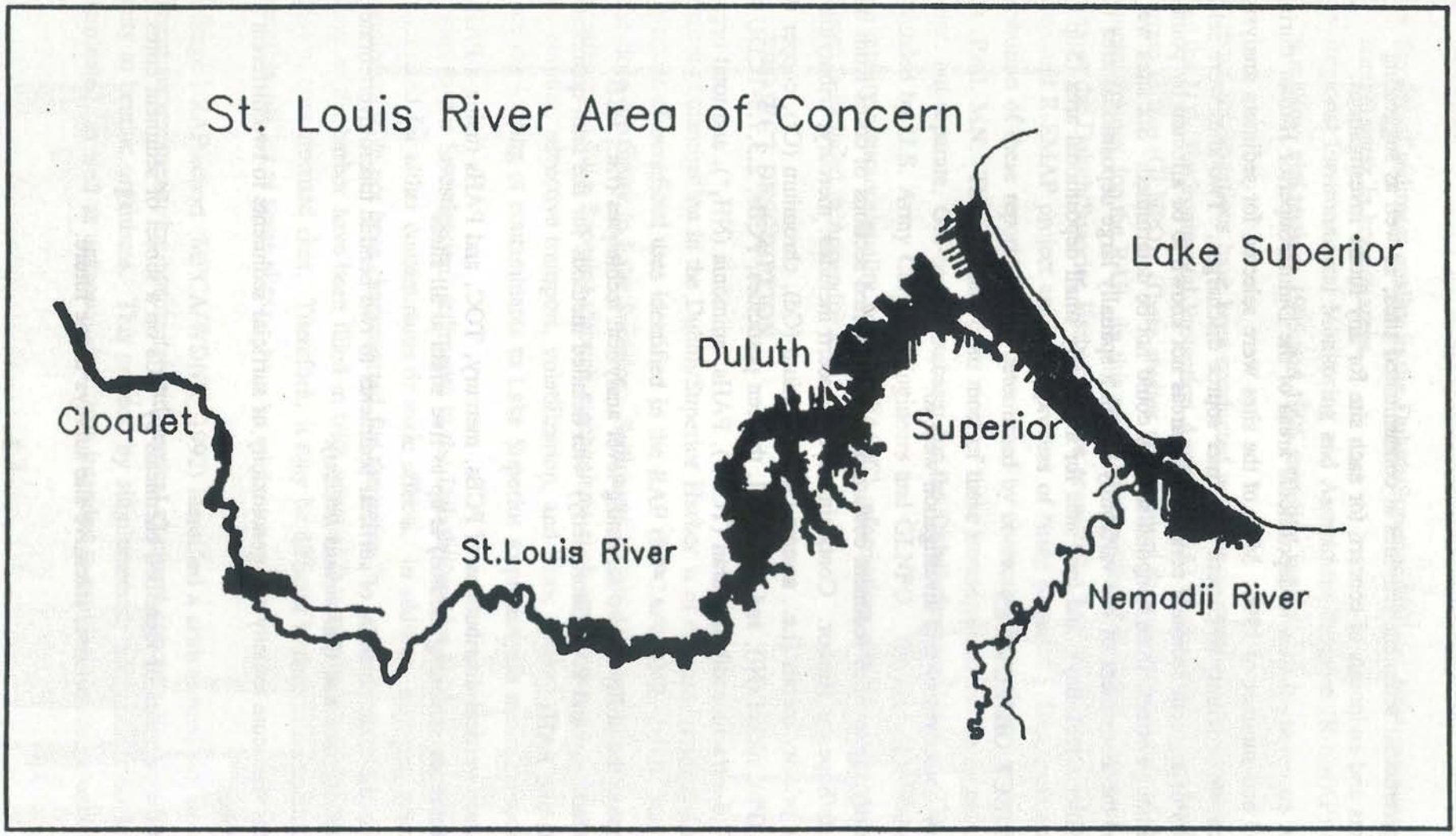

Figure 1-1. Site map of the St. Louis River AOC.

CHAPTER 2

METHODS

2.1 FIELD METHODS

2.1.1 Preliminary Site Selection

A "worst-case" sampling design (U.S. EPA, 1992a) was used to select preliminary sites for this investigation. Final site selection occurred while in the field as described in Section 2.1.2. The "worst-case" sampling design incorporated available historical information on contamination, sources, bathymetry, currents, and other factors (U.S. EPA, 1992a). This sampling design was appropriate since one of the goals of this study was to identify the most heavily contaminated areas downstream of the Fond du Lac dam, rather than to provide data on the overall quality of the sediments in the Duluth/Superior Harbor. Thus, this study could be used to determine the potential for a contamination problem, which could be followed up with more complete sampling at a later date.

Suspected contaminant hotspots were identified either from sediments determined to be contaminated in previous studies (MPCA/WDNR, 1992; Glass et al., 1993) or by evaluation of likely sources of contamination due to past or continuing point sources. The USX and Interlake Steel/Duluth Tar Superfund sites were selected for evaluation of sediment contamination within the St. Louis River outside of the boundaries initially established during the remedial investigations (Barr Engineering, 1985; Malcolm Pirnie, 1991). Navigational maps of the St. Louis River and Duluth/Superior Harbor were evaluated to identify areas of high deposition for sampling at other sites in the study area.

2.1.2 Sediment Collection

Sediments for chemical analyses and toxicity testing were collected on board the U.S. EPA's R/V Mudpuppy, a monohull aluminum barge with an overall length of 9.2 m, a 2.4 m beam, and a draft of 0.5 m (Smith and Rood, 1994). This vessel was designed for collecting deep cores in depositional areas, and can be operated in shallow, confined areas. The Mudpuppy was equipped with Loran positioning capabilities, an electric generator, two electric winches (110-volt AC and 12-volt DC), a vibracoring system, and a horizontal, bow-mounted boom with 746 kg lifting capacity for lifting cores (Smith and Rood, 1994). In addition, a GPS unit was employed with post-survey correction to locate coring positions.

Actual coring locations were selected by first determining the extent of soft, depositional sediments within each sampling area. This was achieved using one of two methods. One method involved informally surveying the area with a shallow draft, 7.3 m boat prior to sampling. The bottom substrate was examined with a small modified Hongve gravity corer, to determine suitability for sampling with the vibracorer, and the selected location was then flagged using a small buoy. A second method of locating sampling positions was to sample with the small gravity corer, while on the Mudpuppy, at randomly selected locations until a suitable substrate was obtained. The number of attempts required to locate depositional sediments was noted in the field notebook. Table 2-1 and Figures 2-1 and 2-2 indicate the sites examined in this study.

Sediment chemistry analyses, with the exception of tributyltin, were performed on 30-cm sections of sediment obtained from a 3-m vibracore sample. As decided prior to the survey, the cores were sectioned in 30 cm intervals, beginning with the surface sediment layer. Samples for tributyltin analyses were collected using only the top 10 cm of the small gravity corer in order to collect a more intact surface layer. The vibracoring system may not always collect intact surface layers. However, vibracoring is a versatile and efficient method for collecting long sediment cores (Smith and Rood, 1994).

Vibracore samples were collected as described in Smith and Rood (1994). The vibracorer head was attached to a stainless steel 3-m core tube containing a 2-mm (wall thickness), clear polyethylene core tube liner. In brief, cores were collected by lowering the vibracorer into the water column, using an electric winch, until the nose cone contacted the sediment surface. The vibracoring head was then powered up while slowly releasing the tension on the cable supporting the vibracorer. The sampler was maintained upright by releasing tension on the cable while the vibracorer penetrated the sediment surface. Sediment refusal depth was defined as the point at which cable tension could not be further released (i.e., the point at which the vibracorer could penetrate no further into the sediment).

A Ponar grab sampler was used to collect sediment samples within 2 m of the vibracore sample. These sediments were used for the Microtox^{R}, Mutatox^{R}, and sediment toxicity tests.

2.2 LABORATORY METHODS

Standard operating procedures (SOPs) for the chemical analyses and toxicity assays are appended to the Quality Assurance Project Plan (QAPP) for this project (Schubauer-Berigan, 1993). The methods and relevant QA/QC parameters are cited here for reference purposes.

2.2.1 Chemical Analyses

2.2.1.1 Established Methods

Established methods were used to measure the following analytes: 2,3,7,8-TCDD and 2,3,7,8-TCDF; Aroclor and congener PCBs; PAHs; thirteen pesticides; arsenic (As) copper (Cu), chromium (Cr), cadmium (Cd), lead (Pb), mercury (Hg), nickel (Ni), tributyltin, and zinc (Zn); ammonia; total organic carbon (TOC); and ^{137}Cs. These analytical methods are summarized in Tables 2-2 and 2-3. In summary, sediment measurements of 2,3,7,8-TCDD and TCDF were performed by high resolution gas chromatography/low resolution mass spectroscopy (GC/MS) using acid/base, silver nitrate/silica gel, copper, alumina, and carbon columns for cleanup. EPA SW 846 method 8081 (capillary column GC) was used for the PCB Aroclors/congeners in sediments, using Florisil for cleanup. Individual PAHs were analyzed using Method 8270 (with Soxhlet extraction); pesticides were measured using the same method and GC/electron capture detection (ECD). Mercury was measured via method EPA 245.5 by cold-vapor atomic absorption spectroscopy (AAS), using high-temperature acid digestion cleanup. Most of the remaining metals (As, Cd, Cr, Cu, Ni, Pb, and Zn) were measured using U.S. EPA/ACOE method 81-1. Metals were also measured using X-ray metals analysis. Tributyltin was measured using GC/flame photometric detection (FID). TOC was measured by the sample ignition method using U.S. EPA/Army Corp of Engineers (ACOE) method 81-1. Ammonia was measured using Agronomy Soils Method 33-3 (KCl extraction). Selected sediment cores were analyzed for ^{137}Cs as detailed in the QAPP (Schubauer-Berigan, 1993). ^{137}Cs concentrations corresponding to the dates 1954 and 1964, based on the initiation and peak, respectively, in analyte concentrations were determined.

2.2.1.2 Screening Methods

Two screening methods, the PAH fluorometric screen and PCB immunoassay, were used in this investigation (Tables 2-2 and 2-3). Method modifications were made where necessary. For example, in the PCB immunoassay, sediments were dried prior to analysis in order to improve the method quantitation limit and facilitate comparison with the GC/ECD PCB analysis (in which sediments were also dried). Several methodological alterations were made in the PAH fluorescence screen. These changes necessitated the preparation of a new SOP from that initially included in the QAPP.

2.2.2 Toxicity Tests

2.2.2.1 Benthic Invertebrate Tests

The parameters for the toxicity tests are described in Tables 2-4 and 2-5. The use of *Hyalella azteca* and *Chironomus tentans* as sensitive species for determining toxicity of freshwater sediments followed modified procedures described in ASTM (1993). However, the specific test system to be used for these assays is not indicated in the methods. The toxicity tests were conducted by the MPCA in accordance with ASTM methods, and used a portable mini-diluter system described in Benoit et al. (1993). Three replicates of each sample were tested. Sediment from West Bearskin Lake (Gunflint Trail, MN) was used as the control sediment. The acute (mortality) and chronic (growth) tests were conducted for 10 days, with an assigned overlying water renewal schedule of 2 volume additions per day. Overlying water for the tests was nonchlorinated well water. The overlying water was monitored daily for pH, dissolved oxygen, and temperature. Methods for preparing glassware, food, reconstituted water, and for performing reference toxicant tests and acute/chronic toxicity tests are described in the QAPP for this survey.

The *Hyalella azteca* and *Chironomus tentans* tests were required to meet QA requirements such as acceptable control sediment survival (mean survival of 80% for *H. azteca* and 70% for *C. tentans*), and acceptable performance on reference toxicant tests (i.e., test results within 2 standard deviations of the running mean for all monthly tests). Reference toxicant tests were not performed with *C. tentans*, because they do not survive well in water-only tests.

2.2.2.2 Microtox^{R} and Mutatox^{R} Tests

The procedures for the Microtox^{R} and Mutatox^{R} tests with *Photobacterium phosphoreum* and *Vibrio fischeri*, respectively, are described in the product manual (Microbics Inc., 1993). Sediment interstitial porewater was used as the test phase, because it is less expensive than the whole sediment assay and also allows dilution of the test medium so that relative toxicity can be ascertained. The porewater was prepared by centrifugation and was tested unfiltered within 48 hours of preparation. In the Microtox^{R} test, all sediments were initially screened for toxicity using the 90% whole porewater assay. Those sediments that were toxic were subjected to the porewater EC50 dilution test (i.e., the effective concentration at which luminescence was reduced to 50% of the control luminescence), beginning with 100% porewater concentrations and diluting up to four-fold. The EC50 was calculated graphically using system software.

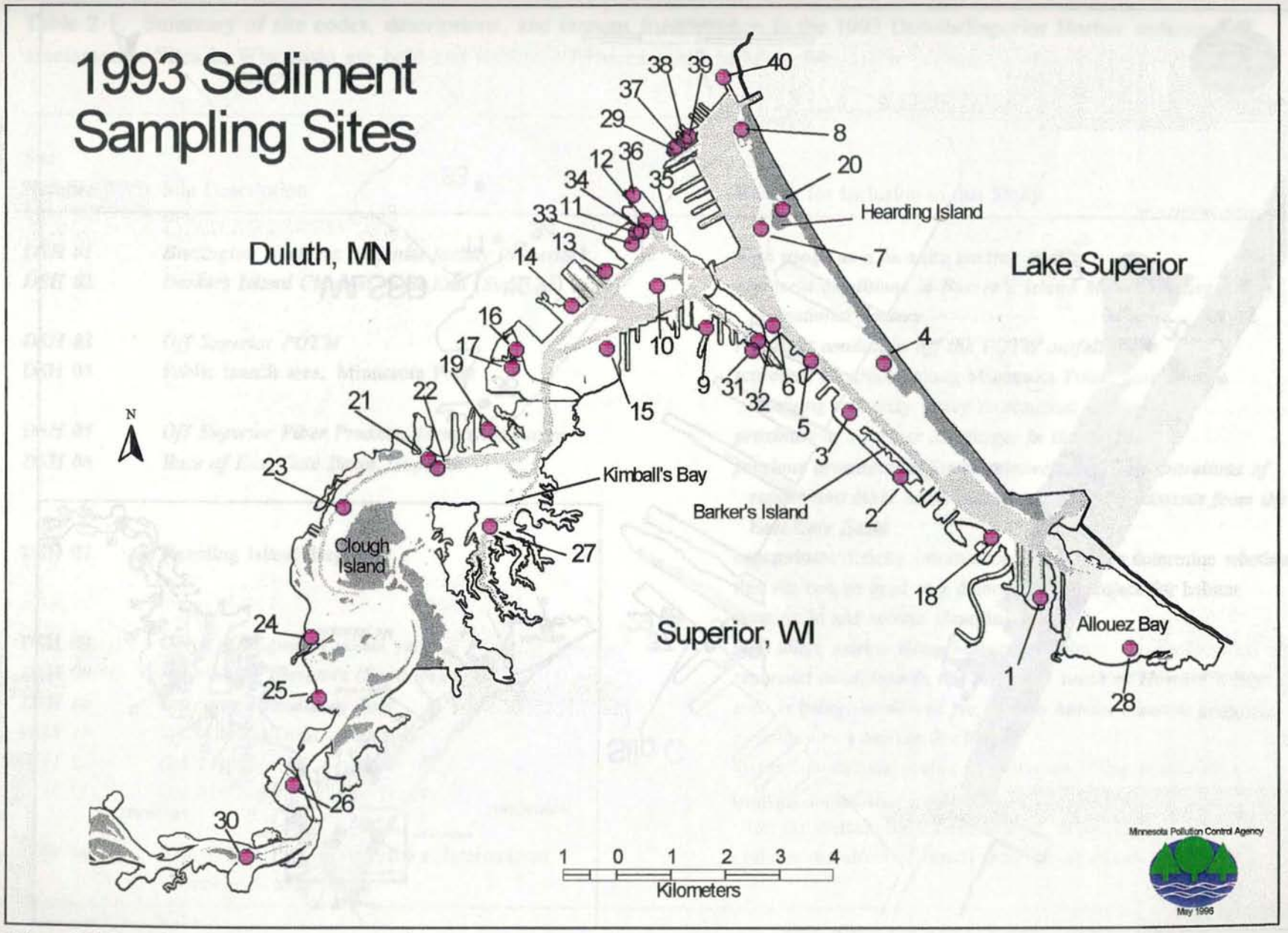

Figure 2-1. Location of sediment sampling sites in the Duluth/Superior Harbor.

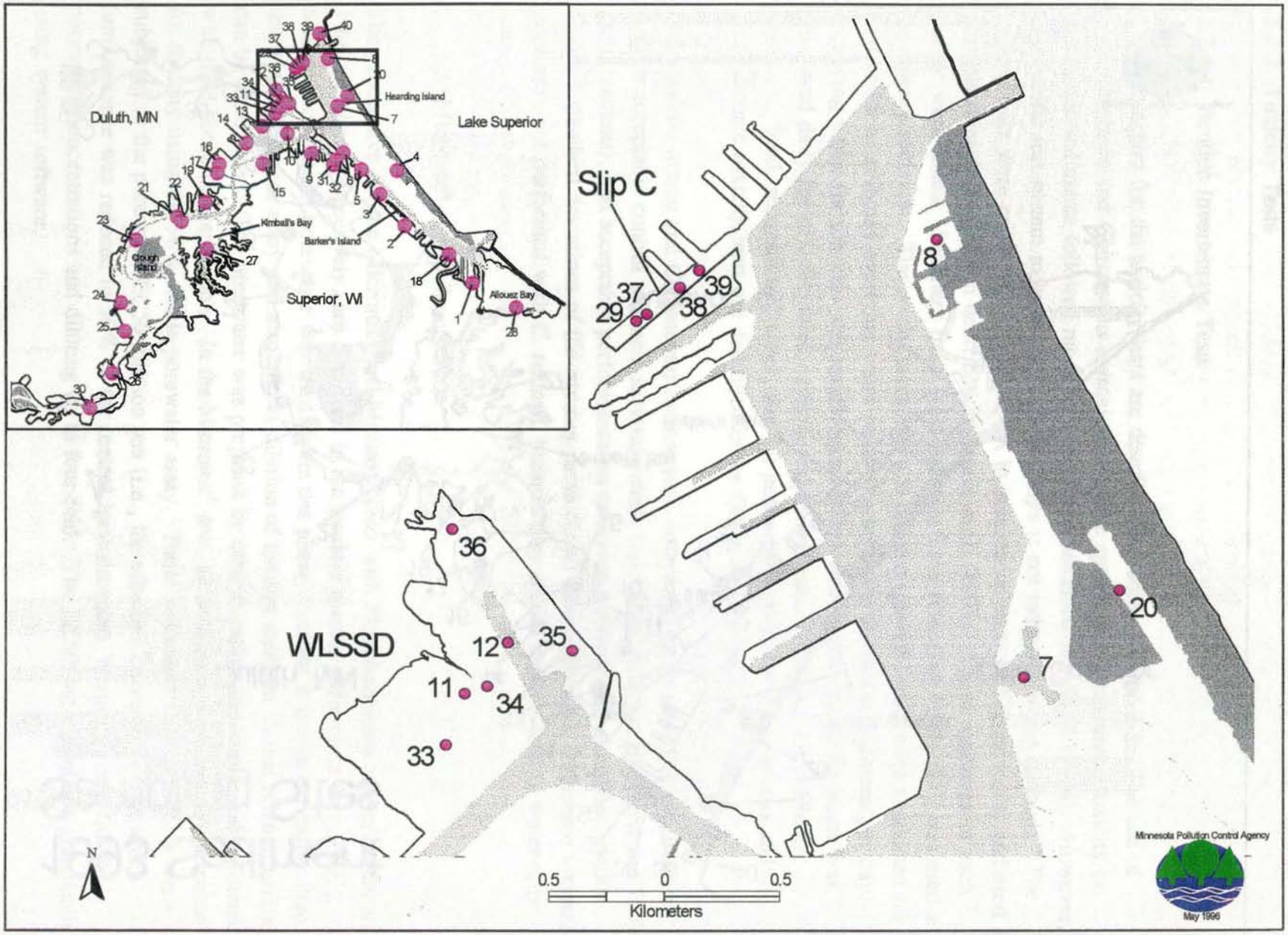

Figure 2-2. Detailed map of site locations in the vicinity of WLSSD and Slip C.

Table 2-1. Summary of site codes, descriptions, and reasons for inclusion in the 1993 Duluth/Superior Harbor sediment assessment. Sites in Wisconsin are bold and italicized, whereas sites in Minnesota are in normal typeface.

Site Number	Site Description	Reason for Inclusion in this Study
DSH 01	***Burlington Northern Taconite facility (Superior)***	***high usage as a taconite loading facility***
DSH 02	***Barkers Island Channel, East End (Superior)***	***represent conditions in Barker's Island Marina; heavy use by recreational boaters***
DSH 03	***Off Superior POTW***	***represent conditions off the POTW outfall***
DSH 04	Public launch area, Minnesota Point	represent conditions along Minnesota Point, near an area receiving relatively heavy recreational boating use
DSH 05	***Off Superior Fiber Products former discharge***	***proximity to a former discharger in the harbor***
DSH 06	***Base of East Gate Basin, Superior***	***previous investigation found relatively high concentrations of copper and other heavy metals in dredged sediments from the East Gate Basin***
DSH 07	Hearding Island deep hole	contaminant/toxicity information is needed to determine whether this site can be used as a demonstration project for habitat creation in and around Hearding Island
DSH 08	Corps of Engineers vessel yard	high usage marina along Minnesota Point
DSH 09	***Near Globe Elevators (Superior)***	***represent conditions in the large bay south of Howard's Bay***
DSH 10	***Interstate Island deep hole***	***area is being considered for various habitat creation projects***
DSH 11	WLSSD, just west of outfall	proximity to a current discharger
DSH 12	Old 21st Ave. W. Channel	assess contaminant profile of sediments filling in this channel
DSH 13	DM&IR taconite storage facility	evaluate potential contamination associated with ore loading at a site just outside the limestone dock of this facility
DSH 14	East of Erie Pier (Scrap yard at International Welders & Machinists)	evaluate the effect of runoff from the scrapyard and Erie Pier

Table 2-1. Continued.

Site Number	Site Description	Reason for Inclusion in this Study
DSH 15	***West of Incan Superior dock***	***represent sediment conditions in St. Louis Bay, along the Wisconsin shoreline***
DSH 16	North of M.L. Hibbard plant/Duluth Steam District (DSD) No. 2	Glass et al. (1993) found high mercury concentrations in this area
DSH 17	South of M.L. Hibbard plant/DSD No. 2	same reason as for DSH 16
DSH 18	***Loon's Foot Landing Inlet (Superior)***	determine if contamination from Hog Island Inlet could be affecting this area
DSH 19	C. Reiss coal dock	determine contamination resulting from this coal loading facility
DSH 20	Channel between Hearding Island and Park Point	address citizen and RAP Committee concerns about elevated mercury concentrations in sediments behind Hearding Island
DSH 21	Mouth of Stryker Embayment	address the extent of contamination outside the bay to resolve a data gap in the Remedial Investigation/Feasibility Study (RI/FS) for the Interlake Steel/Duluth Tar Superfund site
DSH 22	Near Stryker Embayment, just west of current channel	concern over the potential transport of contaminated sediment from Stryker Bay to the ship channel; this area has been considered in the past for possible channel extension
DSH 23	***Across channel from Tallas Island, east of buoy #28***	***evaluate sediment quality downstream of the USX Superfund site***
DSH 24	Off Un-named Creek (USX Superfund site)	RI/FS suggests the site is contaminated with heavy metals and PAHs
DSH 25	Near Wire Mill Settling Pond (USX Superfund site)	same reason as for DSH 24
DSH 26	Mud Lake (near ME International)	proximity to two industrial dischargers, ME International and USX
DSH 27	***Kimballs Bay (no known contaminant source)***	***reference site to evaluate "background" concentrations of contaminants***

Table 2-1. Continued.

Site Number	Site Description	Reason for Inclusion in this Study
DSH 28	***Allouez Bay, Superior***	***assess potential contamination from the former City of Superior landfill on Wisconsin Point***
DSH 29	Slip C (near end)	assess intra-site variability of potential contamination at this site
DSH 30	New Duluth (site of old paint factory)	assess sediment contamination downstream of an old paint factory
DSH 31	***Fraser Shipyards, first slip west of drydocks # 1 and 2***	***WDNR suggested sediment contamination existed in this area, primarily from heavy metals***
DSH 32	***Across Howard's Bay Channel from Fraser Shipyards Slip***	***same reason as for DSH 31***
DSH 33	305 m S-SW of WLSSD outfall	proximity to a current discharger; assess intra-site variability
DSH 34	91 m SE of WLSSD outfall	same reason as for DSH 33
DSH 35	24 m W of Rice's Point, E of 21st Ave. W. Channel	same reason as for DSH 33
DSH 36	61 m S of Coffee Creek outfall and near Miller Creek Outfall	assess contamination from the Miller and Coffee Creek storm sewers
DSH 37	Slip C, in front of Superwood plant	same reason as for DSH 29
DSH 38	Slip C, near Great Lakes Towing Co.	same reason as for DSH 29
DSH 39	Slip C, just up from Cutler Magner Co.	same reason as for DSH 29
DSH 40	Minnesota Slip, near William Irvin ore boat	historical industrial and shipping operations in the vicinity of this slip

Table 2-2. Summary of sediment analytical methods.

Analyte	Method (description)	Sample cleanup	Precision	Accuracy
2,3,7,8-TCDD & 2,3,7,8-TCDF	SW846 (GC/MS)	acid/base, $AgNO_3$/silica gel, Cu, alumina, carbon	50% RPD	$\pm$50%
PCBs	EPA SW846--8081 (capillary column GC)	Florisil	50% RPD	50-120%
PAHs	Method 8270 (capillary column GC)	GPC	50% RPD	18-137%
Pesticides	Method 8270 (capillary column GC)	Soxhlet extraction	50% RPD	50-120%
Hg	EPA 245.5 (cold vapor AAS)	N/A	50% RPD	80-120%
As	EPA 206.5 (hydride generation)	N/A	50% RPD	80-120%
Cd, Cu, Pb Zn, Ni, Cr	Nitric acid/hydrogen peroxide digestion. Flame/furnace AAS	N/A	50% RPD	80-120%

Table 2-2. Continued.

Analyte	Method (description)	Sample cleanup	Precision	Accuracy
Tributyltin	N/A	None	30% RPD	75-125%
Ammonia	KCl extraction (Soils method 33.3: exchangeable ammonia)	N/A	50% RPD	80-120%
TOC	Total organic carbon Sample ignition method 1	N/A	50% RPD	80-120%
^{137}Cs	Radioisotope counting	N/A	N/A	85-115%
PCB Immunoassay	N/A	Drying	50% RPD	60-140%
X-ray metal analysis	N/A	None	50% RPD	60-140%
PAH fluorometric analysis	N/A	None	50% RPD	60-140%

Table 2-3. Summary of quality assurance parameters for sediment analytical methods.

Analyte	Calibration initial	Calibration ongoing	Blanks	IDL[1]	MDL[2]
2,3,7,8-TCDD & 2,3,7,8-TCDF	5 pt. curve	Every 7 samples	Every 7 samples	1 pg/g	1.1 pg/g
PCBs	3 pt. curve	Every 12 samples	Every 7 samples	10 ng/g	10 ng/g
PAHs	5 pt. curve	Every 12 samples	Every 20 samples	33 ng/g	330 ng/g
Pesticides	3 pt. curve	Every 12 samples	Every 7 samples	4 ng/g	20 ng/g
Hg	4 pt. curve	Every 20 samples	Every 20 samples	2.6 ng/g	13 ng/g
As	4 pt. curve	Every 20 samples	Every 20 samples	10 ng/g	100 ng/g
Cd, Cu, Pb Zn, Ni, Cr	4 pt. curve	Every 20 samples	Every 20 samples	100 ng/g 100 ng/g	Cd: 0.5 mg/kg All rest: 1 mg/kg

[1] IDL, Instrument Detection Limit: the concentration equivalent of the analyte signal which is equal to three times the standard deviation of a series of ten replicate measurements of a reagent blank signal at the same wavelength.

[2] MDL, Method Detection Limit: the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.

Table 2-3. Continued.

Analyte	Calibration initial	Calibration ongoing	Blanks	IDL	MDL
Tributyltin	3 pt. curve	Every 12 samples	Every 12 samples	2.5 ng/g (as Sn)	5 ng/g (as Sn)
Ammonia	3 pt. curve	Every 20 samples	Every 20 samples	500 ng/g	1000 ng/g
TOC	% of SRM	Every 20 samples	Every 20 samples	0.1%	
^{137}Cs	4 pt. curve	Every run	Every 10 samples	N/A	N/A
PCB Immunoassay	4 pt. curve	Every 20 samples	Every 20 samples	8.3 ng/g	60 ng/g
X-ray metal analysis	4 pt. curve	Every 20 samples	Every 20 samples	see SOP	
PAH fluorometric analysis	4 pt. curve	Every 20 samples	Every 16 samples	N/A	N/A

Table 2-4. Summary of toxicology methods.

Analyte	Method # (description)	Sample cleanup	Precision	Accuracy
Photobacterium phosphoreum Microtox[R]	Microbics Inc., 1993 (Porewater 90% screen/ 100% dilution EC50 assay)	None	30% RPD	Acceptable control performance
Vibrio fischeri Mutatox[R]	Microbics Inc., 1993 (100% genotoxicity assay)	None	N/A	" "
Hyalella azteca toxicity tests	ASTM E 1383 (10-day test)	None	50% RSD	NaCl Reference toxicity test
Chironomus tentans toxicity tests	ASTM E 1383 (10-day test)	None	50% RSD	N/A

Table 2-5. Summary of quality assurance parameters for sediment toxicology methods.

Analyte	Calibration initial	Calibration ongoing	Blanks	IDL ng/g	MDL ng/g
Photobacterium phosphoreum Microtox[R]	N/A	N/A	Diluent water		N/A
Vibrio fischeri Mutatox[R]	N/A	N/A	Diluent water		N/A
Hyalella azteca toxicity tests	N/A	N/A	West Bearskin L. control sediment		N/A
Chironomus tentans toxicity tests	N/A	N/A	West Bearskin L. control sediment		N/A

CHAPTER 3

RESULTS AND DISCUSSION

3.1 SITE LOCATIONS AND FIELD OBSERVATIONS

3.1.1 Site Locations, Water Depth, and Core Sections Analyzed

Sediment sampling was conducted during September 13-28, 1993. As discussed in Section 3.2.8.1, it was also necessary to collect five additional sediment samples on May 11, 1994 for PAH analyses. The rest of this section will pertain to the 1993 field sampling effort.

Site coordinates for this survey were to be identified using a Loran and Global Positioning System (GPS). However, the 1993 GPS coordinates were not usable due to operator error. The Loran coordinates were recorded in the field notebook; subsequent mapping of the Loran coordinates using GIS showed most of the positions to be far off the actual locations sampled. Therefore, because most of the locations were sampled in fairly well-defined slips, bays or channels, it was decided to use field information to locate the sites as precisely as possible on the National Oceanographic and Atmospheric Administration (NOAA) chart for the Duluth/Superior Harbor; this was done while in the field as a backup to the Loran and GPS methods. The geographic positions of the coordinates were determined to within 1/2 second by interpolation of the sites on the NOAA chart. The resulting positions are indicated in Table 3-1.

The Corps of Engineers vessel yard (DSH 08) was highly unsuitable for contaminant assessment due to a stone and sand substrate. No vibracore sample could be collected here; a Ponar grab sample was collected for toxicity testing and butyltin analysis. Similarly, the substrate was too sandy to take a vibracore sample at the east end of Barkers Island Channel (DSH 02); two Ponar samples were taken from this site for sediment chemistry and toxicity testing. A problem was also encountered with collecting the vibracore sample off the Superior Fiber Products former discharge (DSH 05). A full core could not be collected at DSH 05 due to water washing through the core; approximately 30 cm of the core length was retrieved. A Ponar grab sample was collected at DSH 05 for additional sediment chemistry and toxicity testing.

One site was initially intended to assess contamination within Hog Island Inlet, in the context of comparison to contamination in the rest of the Duluth/Superior Harbor. Hog Island Inlet and its tributary, Newton Creek, have been under intensive monitoring by the WDNR due to elevated levels of ammonia, certain PAHs, and heavy metals. Sampling the inlet proved impossible, as the R/V Mudpuppy could not pass through its extremely shallow mouth from the harbor. Therefore, in consultation with researchers at the WDNR (who were present on the boat), it was decided to analyze contaminants present at a site in Loon's Foot Landing Inlet (DSH 18). This area was not analyzed intensively during the WDNR survey, and it was unknown to what extent contamination from Hog Island Inlet could be affecting this area (Scott Redman, WDNR, personal communication, 1993).

The water depth at the point of core collection is shown in Table 3-2. The shallowest site sampled with the R/V Mudpuppy was DSH 05 (off the Superior Fiber Products former discharge) at less than 30 cm. The deepest site at which sediment was collected was DSH 07 (Hearding Island deep hole) at 8.4 m. The majority of sites at which sediment cores were collected were less than 3 m deep. The median water depth at the sites sampled was 2.3 m.

The median core length collected from the Duluth/Superior Harbor was 122 cm. If the core was longer than 120 cm, the fifth core section comprised the bottom 30 cm of the core length. Table 3-1 shows the depth of the core sections collected at each site. Twenty-one core sites were less than or equal to 120 cm in length, probably due to refusal by stiff clay, sand, wood chips, or bedrock. The longest cores were approximately 230 cm in length and were obtained at the following sites: DSH 13 (DM&IR taconite storage facility), DSH 19 (C. Reiss coal dock), and DSH 27 (Kimballs Bay).

3.1.2 Sediment Core Depths

Sediment depth measurements given in this study should be considered as approximate, especially those cores in deep water sites. These qualifications should be considered for any future sediment assessments to be conducted, especially if different sampling equipment is used.

During vibracore sampling, the depth of penetration (i.e., displacement) through the sediment was measured using 30-cm markings on the head cable. The core length was measured after extrusion of the core liner on the deck of the R/V Mudpuppy. The retrieved length of core was calculated as:

$$\text{Retrieved Length (\%)} = \frac{\text{Core Length (cm)} \times 100}{\text{Core Displacement (cm)}}$$

$$\text{Core Compaction (\%)} = 100 - \text{Retrieved Length (\%)}$$

Sites with compaction of the core exceeding 50% are noted in Table 3-2. It should be noted, however, that there are a number of independent events which can reduce (compress) the length of the recovered core. Reduction can occur in a core from compression of the sediments. It can also be caused by the partially filled core tube acting as a solid and displacing deeper soft sediment layers, from the core catching head assembly displacing soft surficial sediments, or by vibrations causing liquefaction of unconsolidated surface sediments inside the core tube. Cores with missing sediments are referred to as discontinuous cores. In addition, depth of penetration can be overestimated if not taken vertically. The greater the coring angle from vertical, the longer the length of the recovered core is relative to the actual sediment depth sampled. In water depths approaching or greater than 3 m, visual verification of vertical penetration was difficult or impossible due to the highly colored waters. With an unknown combination of these events taking place, it is relatively rare to recover a continuous core equal to the penetration depth.

3.1.3 Sediment Physical Description

The field descriptions of the Ponar grab samples and vibracore sediment core sections are given in Tables 3-3 and 3-4, respectively. A wide variety of sediment types were observed in the Duluth/Superior Harbor. The sediments varied from mostly sand (e.g., DSH 04, DSH 05, DSH 07, DSH 14, DSH 20) to mostly clay (e.g., DSH 03, DSH 06). In general, sediments from sites near Minnesota Point were predominantly sand, whereas sediments near the Wisconsin shoreline of Superior Bay were mostly clay. Many cores displayed noticeable contamination from visual inspections. Sediments from the slips in Superior Bay, the WLSSD/Miller and Coffee Creek embayment, and near the USX Superfund site contained visible oil. Sediment from sites near the M.L. Hibbard/Duluth Steam District (DSD) No. 2 plant contained material which appeared to be gritty fly ash and coal residue. The native substrate for most of the sediments appeared to be an extremely stiff gray or red clay, which was reached in most cores by 1 m. Many of the sediment cores contained a band of woody debris, at variable depth and thickness (Table 3-4), which corresponded to the historical activities of sawmills adjacent to the harbor near the turn of the century.

3.2 CHEMICAL ANALYSES

Chemical results are presented in graphical format in the following sections. In addition, maps of the surficial contaminant distributions are given in the Executive Summary for selected contaminants. The analytical data is provided in electronic format in Appendix A. All chemical concentrations given in this section are reported on a dry weight basis.

In order to interpret the chemical data, it is useful to compare the data to some kind of benchmark such as a criteria or guideline value. The U.S. EPA has developed draft sediment quality criteria for five nonionic organic compounds: acenaphthene, dieldrin, endrin, fluoranthene, and phenanthrene (U.S. EPA, 1994). Additional sediment quality criteria will be developed by the EPA for nonionic organic compounds and for metals once the methodology has been approved. The Great Lakes States and EPA Regions will use the EPA's sediment criteria to assist in the ranking of contaminated sediment sites needing further assessment, to target hot spots within an area for remediation, and to serve as a partial basis for the development of State sediment quality standards. These criteria will also be used to assist in selecting methods for contaminated sediment remediation and for determining whether a contaminated site should be added or removed from its list of designated Areas of Concern (U.S. EPA, 1994).

The State of Minnesota has not developed sediment quality criteria, or guidelines, for contaminants. However, other jurisdictions from Canada, the Netherlands, and the United States (e.g., New York) have developed sediment quality values (Crane et al., 1993) which may be useful to compare to the results of this investigation. The Ontario Ministry of Environment and Energy (OMOEE) guidelines may be the most useful to compare to the results of this survey, because their guidelines are based on freshwater toxicity data. Many other jurisdictions incorporate marine data into their derivation of guidelines or criteria. The OMOEE currently uses a three-tiered approach in applying sediment quality guidelines (Persaud et al., 1993):

- **No Effect Level (NEL)**: the level at which contaminants in sediments do not present a threat to water quality, biota, wildlife, and human health. This is the level at which no biomagnification through the food chain is expected.

- **Lowest Effect Level (LEL)**: the level of sediment contamination that can be tolerated by the majority of benthic organisms, and at which actual ecotoxic effects become apparent.

- **Severe Effect Level (SEL)**: the level at which pronounced disturbance of the sediment dwelling community can be expected. This is the concentration of a compound that would be detrimental to the majority of the benthic species in the sediment.

The NEL, LEL, and/or SEL values (given as dry weight) have been included on the graphs for many of the contaminants listed in the following sections. In some cases, background levels of contaminants may exceed the LEL value. In this case, the background level should be used in place of the LEL value. For northeastern Minnesota, there is insufficient data for most contaminants to determine background concentrations. The OMOEE guidelines are only used in this report as general benchmark values since they have no regulatory impact in Minnesota.

3.2.1 Ammonia

Ammonia was measured in two ways in the samples. In the first method, whole sediment ammonia concentrations were measured using potassium chloride (KCl) extraction. In the second method, interstitial water was extracted using high-speed centrifugation in glass tubes, and porewater concentrations were measured directly using an ammonium-ion analyzer. Both measurements were performed in order to properly evaluate the concentrations affecting biota. While the U.S. Army Corps of Engineers and EPA Region 5 have historically used whole sediment ammonia concentrations for evaluating potential hazards, the research community has tended to evaluate ammonia toxicity to benthic organisms based on porewater concentrations (Schubauer-Berigan et al., 1995).

Table 3-5 shows the whole sediment and porewater ammonia concentrations for the surficial Duluth/Superior Harbor sediments. The median whole sediment ammonia concentration was 37.8 mg/kg, and the median porewater concentration was 2.8 mg/L. The distribution of whole sediment ammonia in the Duluth/Superior Harbor sites is shown in Figure 3-1. The sites with the highest whole sediment ammonia concentrations tended to be associated with slips in the northern section of the Duluth Harbor basin (DSH 29, DSH 40), the sites near the two area wastewater treatment plants (DSH 11, DSH 12, DSH 34), and the area near Loon's Foot Landing Inlet (DSH 18). All of these sites exceeded 100 mg/kg which is the cutoff for Ontario Open Water Disposal Guidelines (Persaud et al., 1993).

Although KCl-extractable concentrations were high for some sediments, the porewater concentrations were not always correspondingly high in these sediments. Three of the sites with high whole sediment concentrations had the highest levels of porewater ammonia (DSH 40, DSH 34, DSH 29). However, other sites with very low levels of whole sediment

ammonia (e.g., DSH 07, the Hearding Island deep hole, 14.6 mg/kg) had relatively high levels of porewater ammonia (8.5 mg/L at this site). The reason for this is not known. None of the porewater concentrations appear to be sufficient to cause toxicity to the benthic species tested. *Chironomus tentans*, *Hyalella azteca*, and *Photobacterium phosphoreum* are all likely to tolerate ammonia concentrations as high as 16 mg/L at the pH ranges present in the Duluth/Superior Harbor (Ankley et al. 1990; Schubauer-Berigan et al., 1995).

3.2.2 Total Organic Carbon

TOC was measured in most depth segments of the sediment cores (Figure 3-2, Table 3-6). Hydrophobic organic contaminants, such as PCBs, preferentially associate with TOC. Thus, it is useful to normalize PCB concentrations for TOC when comparing the distribution of PCBs in an area. TOC levels varied widely throughout the survey area. The median, surficial TOC concentration was 3.4% (n=39) with a range of 0.10 - 39.8% TOC. The lowest surficial levels (0.1 - 0.5%) were found at very sandy sites, such as the mouth of Slip C (DSH 39) and the deep hole at Hearding Island (DSH 07). Approximately 82% of the surficial TOC values were less than 5.6%. In comparison, the OMOEE LEL value is 1% TOC, and the SEL value is 10% TOC (Persaud et al., 1993). The OMOEE values are probably too restrictive to compare to TOC concentrations in the Duluth/Superior Harbor as the median TOC measurement in the deepest core sections was 2.1% (n=19) with a range of 0.14 - 7.3% TOC. Thus, the background concentration of surficial TOC in the harbor is probably around 2% TOC.

High surficial TOC levels (10-40%) were observed at the area north of the Hibbard/DSH No. 2 coal storage facility (DSH 16), at Allouez Bay (DSH 28), at the C. Reiss coal dock (DSH 19), and near Stryker Embayment (DSH 22). The elevated levels in Allouez Bay were most likely due to the predominance of semi-decomposed plant material (Table 3-4). The core from DSH 16 was composed of a gritty substance which appeared to be coal. Any coal in this material would most likely be responsible for the high TOC levels in the upper three sections of this core. The lower two sections of the DSH 16 core had TOC levels less than 10%. The core from DSH 19 was a dark brown sandy silt which may have contained coal. For DSH 22, this core was composed of soft brown silt underlain by sand and wood chips. The elevated levels of TOC in this core may be due to wood chips and other organic material.

3.2.3 Mercury

Mercury was measured in most depth segments of the sediment cores. Surficial mercury concentrations ranged from 0.005 - 2.3 mg/kg throughout the estuary (Figure 3-3, Table 3-7). The modal (i.e., most frequent) concentration in the surficial sediments was in the range of 0.16 - 0.32 mg/kg. The median surficial concentration was 0.22 mg/kg, just above the OMOEE LEL value of 0.2 mg/kg (Persaud et al., 1993). Surficial concentrations were highest at the site nearest the discharge from WLSSD (DSH 34; 2.3 mg/kg). Levels at this site were more than 2.5 times greater than at the next most contaminated site, which was also near the WLSSD discharge (DSH 11; 0.84 mg/kg).

The mercury core profiles for some of the more contaminated sites are shown in Figures 3-4 to 3-6. The core profiles include three sites in the vicinity of WLSSD (DSH 12, DSH 34, and DSH 36), two sites at USX (DSH 24 and DSH 25), and Minnesota Slip (DSH 40). Although the mercury concentrations at some of these sites (e.g., DSH 24 and DSH 34) rapidly decreased below the surficial layer, the other sites showed both declines and increases in mercury concentrations at depth (Figures 3-4 to 3-6). For these sites, mercury concentrations dropped to less than 0.10 mg/kg at depths deeper than 30 cm.

The highest mercury concentrations in the sediment cores were associated with areas with known industrial discharges and waste production. For example, the 1990 mercury discharge from WLSSD, the largest wastewater treatment plant in the Lake Superior basin, was estimated as 22 kg/yr (Tetra Tech, 1996). Some sediment mercury is also probably due to the atmospheric deposition of mercury resulting from natural degassing of the earths crust (WHO, 1996) and from combustion of incinerators and coal (Glass et al., 1990), as well as mining and industrial uses (Tetra Tech, 1996). The Duluth/Superior Harbor used to be a major port for the storage and transport of coal from the late 1800s to early 1900s; at that time, coal-powered ships were used to transport the coal. For example, the amount of coal received by ship at the docks of Superior in 1883 was 13,430 tons, and it steadily increased to 6,577,356 tons by 1918 [Ron Peterson, Fraser Shipyards, personal communication (supported by unpublished shipping information), 1996]. At one time, Superior held the record of being the greatest coal port in the world. A coal gasification plant and storage facility used to be located in Canal Park, adjacent to Minnesota Slip, and this facility could have contributed to the historical input of mercury at site DSH 40.

Mercury has also been used as a slimicide in the pulp and paper industry, and as an antifouling and mildew-proofing agent in paints (Friberg and Vostal, 1972 as cited in U.S. EPA, 1993). Mercury can volatilize from surfaces painted with mercury-containing paints,

and it can also be retained as a component of paint chips that have been scraped or sandblasted from ships. The deposition of paint chips in the sediments of some boat slips and ship repair areas (e.g., Fraser Shipyards) may have contributed to the mercury load in the sediments. In addition, upstream sources of mercury in the St. Louis River have contributed to the sediment load of mercury in the Duluth portion of the harbor.

Mercury is a contaminant of concern in the Thomson, Forbay, and Fond du Lac Reservoirs, of which Thomson Reservoir appears to serve as the primary catchment basin for sediment-associated contaminants (Schubauer-Berigan and Crane, 1996). These reservoirs represent impoundments of the St. Louis River which drain into the Duluth portion of the harbor. The greatest concentrations of mercury (up to 2 mg/kg in Thomson Reservoir) correspond to the period from 1950-1960 (Schubauer-Berigan and Crane, 1996). The surficial levels of mercury in the reservoirs are now approaching background levels. Thus, historical loadings of mercury from these reservoirs may have contributed to the historical profile of mercury in the lower St. Louis River and Duluth Harbor sediments.

Generally, lower mercury concentrations (i.e., <0.16 mg/kg) were present in cores taken from the Superior Harbor basin, except for the Superior POTW. The Nemadji River flows into this basin. For most of the Superior sites, the concentrations of mercury in the cores appears to correspond to background levels for sediments affected only by watershed or atmospheric inputs of mercury. This statement is supported by data from eighty remote lakes in Minnesota which exhibited sediment mercury concentrations of 0.034 to 0.33 mg/kg, with an average of 0.16 mg/kg (Sorensen et al., 1990).

3.2.4 Other Heavy Metals

3.2.4.1 Atomic Absorption Spectroscopy

Arsenic, chromium, copper, cadmium, lead, nickel, and zinc were measured by atomic absorption spectroscopy in the surficial core sections of all the study sites except DSH 08 (Table 3-8). All heavy metal concentrations referred to in the following subsections are expressed as mg/kg (ppm) dry weight. Site DSH 05 has two samples shown; one is a surficial core sample, and the other (DSH 05--P) is a Ponar sample collected from the same site.

Arsenic

Arsenic concentrations ranged from not detectable to 33.5 mg/kg in the Duluth/Superior Harbor (Figure 3-7, Table 3-8). The median arsenic concentration among the sites was 6.8 mg/kg with a mean value of 9.6 mg/kg. Arsenic was not detected at eight sites, including Kimball's Bay (DSH 27). The area of greatest arsenic contamination (33.5 mg/kg) was near the USX Superfund site off the Un-named Creek discharge (DSH 24). In comparison, the OMOEE LEL value is 6 mg/kg, whereas the SEL value is 33 mg/kg. Seventeen sites bracketed this range, with the DSH 24 site slightly exceeding the SEL. Since arsenic was not detected at several sites, it appears that the other sites were contaminated with arsenic from anthropogenic sources.

Arsenic is a by-product of nonferrous metal (lead, zinc, and copper) mining and smelting operations (NAS, 1977 as cited in U.S. EPA, 1993). Thus, arsenic appears to have been produced as a by-product of operations at USX. The USX Superfund site was utilized by U.S. Steel from 1915-1979 for the purposes of coke production, steel production, and materials storage (MPCA/WDNR, 1992). All effluents from operations in the vicinity of the Coke Plant were discharged into the St. Louis River via the Un-named Creek. Discharges from the mill's hot rolling process, pickling, cold rolling, and galvanizing operations were channeled into the Wire Mill Settling Basin (MPCA/WDNR, 1992).

High arsenic concentrations were also observed at the Burlington Northern Taconite facility (DSH 01), in the vicinity of the M.L. Hibbard Plant/DSD No. 2 (DSH 16-17), at the Loon's Foot Landing Inlet (DSH 18), at the Interstate Island deep hole (DSH 10), and in the vicinity of WLSSD (DSH 11-12). The sources of arsenic at these sites can not be determined. The other major anthropogenic sources of arsenic to waterways include the importation of arsenic compounds for use in rodenticide and other pesticide formulations. Although rodenticides are frequently applied in harbor areas to control rat populations, it is unknown how much of this material may have been used in the vicinity of the harbor.

Cadmium

Cadmium concentrations ranged from 0.52 - 7.4 mg/kg at the sample sites (Figure 3-8, Table 3-8). The median concentration was 2.0 mg/kg, whereas the mean was 2.4 mg/kg. In comparison, the mean background concentration of surficial cadmium in three northern Minnesota lakes was not detectable at a detection limit of 0.5 mg/kg (Heiskary, 1996). The OMOEE LEL value for cadmium is 0.6 mg/kg, whereas the OMOEE SEL value is 10 mg/kg (Persaud et al., 1993). The SEL value was not exceeded at any of the study sites.

The highest cadmium concentrations were observed at the USX Superfund sites (DSH 24-25). Cadmium is commonly found in zinc, lead, and copper deposits (May and McKinney, 1981 as cited in U.S. EPA, 1993), and is released to the environment during the smelting and refining of ores. Thus, cadmium would be expected to be found at this site. As described in the following section, the DSH 25 sample site at USX was extremely contaminated with copper.

Other anthropogenic sources of cadmium include the following: electroplating, application of phosphate fertilizers, surface mine drainage, waste disposal operations, as well as the manufacture of paints, alloys, batteries, and plastics (U.S. EPA, 1993). The contribution of these sources to the loading of cadmium to the sediments is unknown.

Chromium

Chromium concentrations ranged from 5.5 - 93.8 mg/kg at the study sites (Figure 3-9, Table 3-8). The median concentration was 38 mg/kg, whereas the mean was 35.8 mg/kg. The mean and median exceeded the mean surficial background concentration of 22 mg/kg chromium observed at three northern Minnesota reference lakes (Heiskary, 1996). The OMOEE LEL value for chromium is 26 mg/kg, whereas the SEL value is 110 mg/kg. As with cadmium, the mean level of chromium at the study sites exceeded the LEL value. The OMOEE has published background levels of some metals for Great Lakes pre-colonial sediment Horizons, of which chromium was 31 mg/kg (Persaud et al., 1993). Thus, the OMOEE background value for chromium also exceeded the LEL value.

The relative pattern of chromium contamination at the study sites was similar to that of nickel, and to a lesser extent, to zinc. The Wire Mill Pond at USX (DSH 25) had the highest chromium contamination of 93.8 mg/kg. Twenty-seven sites had chromium concentrations ranging between 30 - 63 mg/kg.

Some of the industrial uses of chromium which may have contributed to contamination in the Duluth/Superior Harbor include the following: electroplating, steelmaking, and photographic industries; other industries that use chromium salts; and industries that add chromate compounds to cooling water for corrosion control (APHA/AWWA/WEF, 1995). The contribution of any of these sources to contamination in the Duluth/Superior Harbor is unknown.

Copper

Copper concentrations ranged from 4.1 - 496 mg/kg at the sample sites (Figure 3-10, Table 3-8). The median concentration was 29.7 mg/kg, whereas the mean was 42.3 mg/kg copper. In comparison, the mean copper concentration at three northern Minnesota reference lakes was 16 mg/kg (Heiskary, 1996), and the background copper level in Great Lakes pre-colonial sediments was 25 mg/kg (Persaud et al., 1993). The OMOEE LEL value for copper is 16 mg/kg (Persaud et al., 1993) which was less than the median copper concentration measured at the study sites. The OMOEE SEL value of 110 mg/kg copper was grossly exceeded at the USX Wire Mill Pond (DSH 25). This exceedance reflects the usage of copper for the production of wire at USX. Twenty-five sites had copper concentrations ranging between 16 - 83 mg/kg, of which Minnesota Slip (DSH 40), Fraser Shipyards (DSH 31), and the area around WLSSD (DSH 12, DSH 34, and DSH 36) had the highest copper concentrations in this range.

Other anthropogenic sources for copper may be derived from electrical industries, as well as from water supply systems and lake managers that use copper salts to control algal growth. The contribution of the sources to the Duluth/Superior Harbor has not been determined.

Lead

Lead concentrations ranged from 1.5 - 548 mg/kg at the sample sites (Figure 3-11, Table 3-8). The median concentration was 15.5 mg/kg, whereas the mean was 58.2 mg/kg. The mean was skewed by four high lead concentrations at the USX Superfund sites (DSH 24-25), Fraser Shipyards (DSH 31), and Minnesota Slip (DSH 40). The lead concentrations at the other sites were all less than 107 mg/kg lead.

In comparison, the mean lead concentration at three northern Minnesota reference lakes was 32 mg/kg (Heiskary, 1996), and the background lead level in Great Lakes pre-colonial sediments was 23 mg/kg (Persaud et al., 1993). Anthropogenic sources of lead were thought to have contributed to the lead levels in some of Heiskary's study lakes (Heiskary, 1996). The OMOEE LEL value for lead is 31 mg/kg, whereas the SEL value is 250 mg/kg (Persaud et al., 1993). The lead concentration was less than the LEL at 22 sites, whereas three sites exceeded the SEL in the Duluth/Superior Harbor.

Lead is derived primarily from the mining and processing of limestone and dolomite deposits, which are often sources of copper and zinc, too (May and McKinney, 1981 as cited in U.S. EPA, 1993). Lead is also a minor component of coal and is found in fly ash

resulting from coal combustion. Historically, lead was used in paints, in solder used in plumbing and food cans, and as a gasoline additive (U.S. EPA, 1993). At present, lead is used primarily in batteries, electric cable coverings, some exterior paints, ammunition, and sound barriers (U.S. EPA, 1993).

The processing of mineral ore at USX (DSH 24-25) was probably the major contributor of lead at this site. Lead was also very high at Fraser Shipyards (DSH 31) which was the site for much transport of coal, as well as for building, repairing, and repainting ships. Lead was also high at Minnesota Slip; a historical coal gasification plant and coal storage area near this slip may have contributed to a portion of the lead load in the sediments. The relative importance of other anthropogenic sources of lead to the harbor was not determined.

Nickel

Nickel concentrations ranged from 3.0 - 118 mg/kg at the study sites (Figure 3-12, Table 3-8). The median concentration was 22.7 mg/kg, whereas the mean was 21.4 mg/kg nickel. The OMOEE LEL value for nickel is 16 mg/kg, whereas the SEL value is 75 mg/kg (Persaud et al., 1993). Although the LEL value was exceeded at 25 sites in the harbor, most site values were below the background level of nickel observed in Great Lakes pre-colonial sediment horizons (i.e., 31 mg/kg). The USX Wire Mill Pond site (DSH 25) was the only site that exceeded the OMOEE SEL value.

The most important anthropogenic sources of nickel include fossil fuel combustion, nickel ore mining, smelting and refining activities, and the electroplating industries [Canadian Council of Resource and Environment Ministers (CCREM), 1987]. The high sediment nickel concentration observed at DSH 25 is consistent with past industrial activities at the USX Wire Mill site.

Zinc

Zinc concentrations ranged from 11.4 - 3780 mg/kg at the study sites (Figure 3-13, Table 3-8). The median concentration was 93.1 mg/kg, whereas the mean was 240 mg/kg. The mean value was skewed by two exceedingly high zinc values at USX (DSH 24-25). Values at all other sites were less than 300 mg/kg zinc. Twenty-three sites had surficial zinc concentrations less than the OMOEE LEL value of 120 mg/kg zinc. Other sites showing high levels of zinc included the area around WLSSD (several sites), south of the M.L. Hibbard/DSD No. 2 plant (DSH 17), Fraser Shipyards (DSH 31-32), and Minnesota Slip (DSH 40).

Zinc is used in coatings to protect iron and steel, in alloys for die casting, in brass, in dry batteries, in roofing and exterior fittings for buildings, and in some printing processes. The principal sources of zinc to aquatic systems include municipal wastewater effluents, zinc mining, smelting, and refining activities, wood combustion, waste incineration, iron and steel production, and other atmospheric emissions (CCREM, 1987). The high sediment zinc values observed at DSH 24 and DSH 25 are consistent with past industrial uses of zinc at the USX site.

3.2.4.2 X-ray Fluorimetry

X-ray fluorimetry (XRF) was performed on a subset of samples to ascertain its utility as a low-cost, rapid analytical alternative to the traditional method of atomic absorption spectroscopy (AAS) (Table 3-9). Table 3-10 shows the comparison of metal determinations by the two methods. The accuracy of the XRF method was determined by calculating the relative percent difference (RPD) between the two methods, using the AAS determinations as the "true" value. A negative RPD indicates a fluorimetry method measurement less than the "true" AAS determination, whereas a positive RPD indicates the opposite.

Examining the RPDs indicates the methods showed mediocre comparability; of the 28 measurements for which both methods obtained quantifiable levels, only 20 (71%) were within allowable QC limits for metal determinations (50% RPD). The vast majority of the RPDs were positive, indicating that the XRF method tended to overestimate the metal concentrations, as measured by atomic absorption spectroscopy. When non-detectable measurements (for either method) were added to the comparison, the comparability was unchanged: of 48 measurements, 33 (69%) were either within 50% RPD of the AAS determination, or were consistent with the AAS determination.

The x-ray metal determination was most accurate for nickel, copper, lead, and zinc, and was least accurate for arsenic, cadmium, and mercury. In the case of mercury, the metal was never detected by the XRF method, making its utility in the Duluth/Superior Harbor sediment assessment very low. Because of the tendency of the method to overestimate metal concentrations in these sediments, XRF may be useful as a screening tool when accompanied by more traditional metal measurement methods. However, because of the high proportion of non-detectable arsenic and mercury determinations, XRF is not useful for measuring these two metals in sediments.

3.2.5 PCBs

PCBs were measured in most sediment sections obtained from the Duluth/Superior Harbor cores. PCBs were determined by both GC/ECD (Aroclor and congener-specific analyses) and using the PCB immunoassay method. The following section is a discussion of the results of both analytical methods.

3.2.5.1 GC/ECD Method

PCBs were quantitated on a congener-specific basis, as well as by Aroclor mixtures. A software program, COMSTAR, was used to estimate PCBs as Aroclors 1242, 1248, 1254, 1260, and total PCBs. However, this program does not fully take into account the weathering or enrichment of PCB congeners in the environment that make-up an Aroclor mixture. Thus, there may be some error associated with dividing up the total PCB concentration into Aroclor components. Only total PCB concentrations will be discussed in this section. It was beyond the scope of this project to provide a detailed assessment of the congener data. A database of congener-specific sediment data is being accumulated for the Duluth/Superior Harbor from three different MPCA investigations. The MPCA would like to evaluate the congener data at a future date. These data can be assessed to evaluate trends in the distribution and fate of PCB congeners in the Duluth/Superior Harbor. For example, information on the enrichment and depletion of PCB congeners, determination of congeners which have the highest potential for toxicity and bioaccumulation, and evaluation of congener trends which may be associated with particular watershed sources of congeners can be determined from this data set.

The total PCB concentrations for the core sections are given in Table 3-11. The distribution of surficial PCB concentrations is shown in Figure 3-14. Surficial PCB concentrations ranged from 4.3 - 439 μg/kg with a mean of 99.7 μg/kg and a median value of 68 μg/kg PCBs. In comparison, the OMOEE No Effect Level (NEL) is 10 μg/kg, and the LEL is 70 μg/kg (Persaud et al., 1993). Nineteen sites exceeded the LEL for the suficial sediments. The most contaminated surficial sites were located in the vicinity of WLSSD and Miller/Coffee Creeks. Bahnick and Markee (1985) reported an average concentration of 175 ng/L PCBs in effluent from WLSSD; they estimated that WLSSD effluent was a major source of PCBs to the Duluth/Superior Harbor. Another possible source of PCBs in the WLSSD/Miller and Coffee Creek embayment may have been a series of PCB-contaminated electrical transformers that were buried on the WLSSD property many years ago. Some of these transformers were discovered in 1994 during the construction of a recycling facility near Miller and Coffee Creeks (J. Stollenwerk, MPCA Division of Water Quality, personal

communication). While adequate steps were taken to contain and properly remove these transformers once found, it is unknown what impact they may have had on sediments or groundwater during the period of their burial.

PCBs have also been detected upstream in the Thomson, Forbay, and Fond du Lac Reservoirs. From a limited sampling effort in 1992, total PCBs were highest in Thomson Reservoir sediments; PCBs were detected at 108 μg/kg in the 0-4 cm core section up to a peak of 299 μg/kg in the 136-144 cm section (Schubauer-Berigan and Crane, 1996). Thomson Reservoir appears to serve as the primary catchment basin for sediment-associated contaminants. Forbay and Fond du Lac Reservoirs appear to receive PCB inputs principally from Thomson Reservoir (Schubauer-Berigan and Crane, 1996). A MPCA sediment survey conducted in 1980 along the Cloquet portion of the St. Louis River found the highest PCB concentrations in Scanlon and Thomson Reservoirs (240 and 120 μg/kg, respectively). The potential sources of PCBs to the reservoirs could not be determined, in part, due to a lack of PCB effluent data for the two largest industries upstream of the Thomson Reservoir. If PCBs were discharged in industrial effluent in the St. Louis River AOC, this effluent would have been diverted to WLSSD in the late 1970s for treatment. A portion of the existing PCB-contaminated sediments in the reservoirs could have been resuspended and transported downstream to the Duluth/Superior Harbor. The suspended solids load of the St. Louis River consists of eroded soil, resuspended material, and biological material; most of this load settles within the harbor (Bahnick and Markee, 1985). Stortz and Sydor (1980) determined that resuspension of bottom sediments by ship traffic is an important secondary source of turbidity in the harbor. However, most of the material resuspended by ship traffic is rapidly redistributed to the low turbulence areas within the shipping channels (Stortz and Sydor, 1980). Thus, PCB-contaminated sediments can be resuspended and re-worked in the Duluth/Superior Harbor.

Other sources of PCBs to the St. Louis River AOC could have arisen from landfills, atmospheric deposition, leaking PCB-contaminated equipment, and shipping activities. Minnesota Power has taken steps to reduce the use of PCB capacitors and PCB-contaminated substation equipment at its electrical power operations in the upstream portion of the St. Louis River AOC (Lake Superior Binational Program, 1996). PCBs were never manufactured in the Lake Superior basin, and their presence in Lake Superior is attributed mostly to atmospheric deposition (Jeremiason et al., 1994). Thus, some of the PCB load in the St. Louis River AOC watershed has arisen from atmospheric deposition in addition to other sources.

Sediment core profiles of normalized, total PCB concentrations for six selected sites are given in Figures 3-15 to 3-17. None of these sites exceeded the OMOEE SEL of 530,000 μg/kg organic carbon (oc) of PCBs. The sediment profiles for sites DSH 03 (off Superior POTW), DSH 20 (channel between Hearding Island and Park Point), DSH 31 (Fraser Shipyards), and DSH 40 (Minnesota Slip) indicate PCB peaks below the surface. Sites DSH 12 (old 21st Ave. West Channel) and DSH 34 (91 m southeast of WLSSD outfall) had the greatest PCB concentrations in the surficial sediments.

As discussed in Section 3.4, cesium dating was conducted on a core from DSH 20; the cesium profile for this core indicated there was a great deal of sediment mixing. Since DSH 20 was located in the channel between Hearding Island and Park Point, both dredging and ship traffic operations could have contributed to sediment mixing at this site. The highest level of PCBs observed in any core segment occurred in the 36-66 cm section of the DSH 40 core. Historical sources of PCBs appeared to have contributed to this contaminant profile.

The total PCB concentrations measured in this study are low in comparison to some other Great Lakes AOCs. For example, PCB levels in whole sediment samples from the Indiana Harbor and Saginaw River AOCs ranged up to two orders of magnitude higher than the worst level of contamination observed in this survey (Ingersoll et al., 1993). However, since PCBs are bioaccumulative compounds, they have the potential to cause adverse effects to biota and humans at sufficiently high exposure concentrations. For the St. Louis River, PCB contamination has resulted in a do not eat advisory for carp (15-20 inches) near Cloquet and Scanlon; an advisory for 20-25 inch carp exists from Fond du Lac Reservoir to Lake Superior (Minnesota Department of Health, 1996). Fish have been found to spend a disproportionately large amount of time in the WLSSD/Miller and Coffee Creek Embayment during the winter months due to increased water temperatures resulting from WLSSD effluent (Kutka and Richards, 1993). Thus, these fish will have a longer exposure period to sediment and effluent-derived contaminants such as PCBs and mercury. Whether these fish would be exposed to contaminant levels sufficient to cause harm to them or other fish eaters has not been determined.

3.2.5.2 Immunoassay

The PCB immunoassay was assessed in this survey for use as a screening tool, compared to the more traditional GC/ECD method for analyzing total PCB levels. The results of the PCB immunoassay are given in Table 3-12. Method modifications were necessary in order to improve quantitation limits (e.g., sediments were dried prior to analysis). The method detection limit (MDL) for this assay (40-67 μg/kg) was still much higher than that obtained

by the GC/ECD method (1.7 μg/kg). The method quantitation limit (MQL) (i.e., two to ten times the MDL) for the immunoassay method was 120 μg/kg. Only 17 of the 195 samples analyzed by immunoassay were found at levels above the MQLs (Table 3-12).

Figure 3-18 shows the relationship between the two analytical methods. While the two methods had fairly good comparability (e.g., a chi-square test of matched-site data compatibility found the two methods in agreement in a significant percentage of cases), the low ratio of "hits" using the immunoassay data, even in a hotspot assessment, suggests this method is not suited to routine monitoring of sediment contamination for PCBs in the Duluth/Superior Harbor. That is, the majority of sites will probably be below the immunoassay's method detection and quantitation limits.

3.2.6 2,3,7,8-TCDD/TCDF

Surficial sediment concentrations of 2,3,7,8-TCDD (hereafter referred to as dioxin) and 2,3,7,8-TCDF (hereafter referred to as furan) are given in Table 3-13 and Figures 3-19 and 3-20, respectively. Due to difficulties associated with extracting the samples, dioxin was detected at very few sites. Dioxin concentrations ranged from 0.9 - 13 ng/kg at four sites. The highest concentrations were observed at the two USX sites (DSH 24-25) followed by the DM&IR taconite storage facility (DSH 13), and the Superior Fiber Products former discharge (DSH 05-ponar sample). Because of matrix interference, 11 samples could not be analyzed at a satisfactory detection limit of 5.0 ng/kg. The interferents were likely to be PAH compounds; most of the samples with unsatisfactory quantitation limits tended to have high levels of PAHs or other contaminants (e.g., DSH 11: WLSSD outfall; DSH 23: across channel from Tallas Island; DSH 29, DSH 37, DSH 39: Superwood Slip; DSH 31, DSH 32: Fraser Shipyards; and especially DSH 36: near Miller/Coffee Creek outfall). In these samples, no amount of sample preparation or cleanup could remove these interferences (Irene Moser, UMD-NRRI Trace Organics Lab analyst, personal communication, 1994).

Furan was detected and quantified more frequently in the Duluth/Superior Harbor sediments (Figure 3-20, Table 3-13). 2,3,7,8-TCDF could only be quantified at twelve sites. Samples that could not be quantified tended to show the presence of other contaminants like PAHs (e.g., DSH 29, DSH 31, DSH 33, DSH 37, DSH 40), which may have caused matrix interferences during sample analysis. The highest furan concentrations were found at DSH 23 (across channel from Tallas Island) and DSH 25 (USX Wire Mill Settling Pond outfall) followed by DSH 19 (C. Reiss coal dock), DSH 12 (old 21st Ave. West Channel), DSH 11 (west of WLSSD outfall), DSH 35 (near Rice's Point), and DSH 03 (off Superior POTW).

The sources of dioxin to the Duluth/Superior Harbor may be partly attributable to upstream sources. The MPCA collected sediment cores from the Thomson, Forbay, and Fond du Lac Reservoirs for dioxin analysis in 1992. Dioxin was not detected in the surface and bottom sections of the cores from all three reservoirs (Schubauer-Berigan and Crane, 1996). Dioxin concentrations, up to a maximum of 14.9 pg/g (in Fond du Lac Reservoir), were detected in the middle sections of the cores; based on cesium-137 dating, maximum concentrations were reached in either the mid-1940s (Thomson Reservoir) or the mid-1950s (Forbay and Fond du Lac Reservoirs) (Schubauer-Berigan and Crane, 1996).

Other sources of dioxin to the Lake Superior basin have been discussed in the Lake Superior Lakewide Management Plan (Lake Superior Binational Program, 1996). Anthropogenic sources of dioxins may be released into the environment during: industrial processes, fuel combustion, incineration, and the production or use of contaminated chemicals such as pesticides. Three pulp and paper mills that discharge effluent to WLSSD have been identified to have the potential to emit dioxins based on chlorine use by the mill itself, or in the pulp or recycled material used by the mill (Lake Superior Binational Program, 1996). In 1990, dioxins were detected in the effluent from the primary clarifiers at one of the paper mills discharging to WLSSD; furan has been detected in WLSSD sludge, but it could not be attributed to any particular source (Lake Superior Binational Program, 1996). Dioxin has also been detected in effluent from Murphy Oil in Superior, WI (Lake Superior Binational Program, 1996). Sediment samples from the vicinity of Murphy Oil were not collected for this investigation due to ongoing sediment work by the WDNR.

Dioxin can also be released to the atmosphere through the smelting and refining of nonferrous metals such as aluminum, copper, nickel, and magnesium (Lake Superior Binational Program, 1996). Many fuels, including wood, coal, natural gas, oil, gasoline, and diesel can also potentially release dioxins when burned (Lake Superior Binational Program, 1996). Dioxins observed at DSH 25 may be due, in part, to the coke operations and metallic slags produced in the Wire Mill operations at USX. Cutting oils, including petroleum, were used in the vicinity of Un-named Creek (DSH 24) and may have contributed to dioxins at this site. Dioxin can also be emitted from incineration activities. The only municipal solid waste incinerator in the U.S. Lake Superior basin occurs at WLSSD; WLSSD also incinerates wastewater treatment plant sludge (Lake Superior Binational Program, 1996). Other sources of dioxin include its inclusion in other compounds as an impurity, such as PCBs and pentachlorphenol (PCP). PCP was used to treat railroad ties from 1955 to 1979 at Kopper, Inc. in Superior, WI; WDNR is monitoring dioxins in groundwater, waste disposal ponds, and a drainage ditch leaving this site ((Lake Superior

Binational Program, 1996). The Koppers site was not included in this investigation due to existing work being carried out by WDNR.

No detectable concentrations of dioxin were found in fish tissue collected from the Thomson and Fond du Lac Reservoirs (Schubauer-Berigan and Crane, 1993). According to the U.S. EPA's Ecological Risk Assessment for Dioxin document (Cook et al. 1993), areas with sediment concentrations as low as 2.0 ng/kg dioxin, with a TOC of 5%, can cause harmful effects in fish-eating biota. Since the dioxin measurements in this study were based on the upper 30 cm of sediment, it can not be assumed that this reflects the concentration of dioxin in the biologically active zone (i.e., upper 10-15 cm). In addition, better analytical capabilities would be needed to lower the detection limit to 2.0 ng/kg and to resolve analytical problems with interferences. Thus, future monitoring efforts would be useful to determine if dioxins are accumulating in fish tissue to an extent that may present an ecological or human health risk in the St. Louis River AOC.

The source of 2,3,7,8-TCDF to the Duluth/Superior Harbor is unknown. Two possibilities are the discharges of historical and current WLSSD effluent into the harbor, and the transport of resuspended dioxin-like compounds from the upper St. Louis River reservoirs. Other sources, as previously mentioned for dioxins, may be sources of furans as well.

3.2.7 Pesticides

A total of 13 pesticides were analyzed in surficial sediments at the study sites (Table 3-14). Included in this list were some of the critical pollutants targeted by the Zero Discharge Demonstration Program and identified in the Stage 1 LaMP for Lake Superior in 1990 (Lake Superior Binational Program, 1996). These critical pollutants included the pesticides chlordane, DDT (and its metabolites of DDD and DDE), dieldrin, hexachlorobenzene (HCB), toxaphene, and the organochlorine octachlorostyrene. The other pesticides analyzed for this project included lindane, aldrin, endrin, and other metabolites of DDT. All uses of DDT, dieldrin, endrin, HCB, and toxaphene were banned in the 1980s; chlordane and lindane have only been allowed for restrictive uses since the mid-to-late 1980s (U.S. EPA, 1993). Many of these organochlorine pesticides were historically used in large amounts, and they are not easily degraded or metabolized. Thus, these pesticides persist in the environment, and they can bioaccumulate through aquatic and piscivorous food chains (U.S. EPA, 1993).

Of the pesticides analyzed in this study, chlordane was not detected at any sites, and most of the other pesticides were detected at low levels (Table 3-14). The pesticide analyses were

confounded, in some cases, by the presence of interferences, primarily in samples with high-to-moderate levels of PAHs (e.g., DSH 24, DSH 40, DSH 25, DSH 29, and DSH 17). For DSH 17, this sample could not be analyzed for any pesticides due to interferences in the sample. The detection limits of all samples varied, depending on the amount of analytical interferences present in the samples. Dieldrin and endrin could not be quantitated in 12 samples because they were destroyed in the cleanup process.

The pesticide values in Table 3-14 were compared to available background sediment concentrations and the OMOEE LEL values (Persaud et al., 1993). The background values were based on the highest of the Lake Huron or Lake Superior mean surficial sediment concentrations (Persaud et al., 1993). The greatest exceedances were for p,p'-DDD + o,p'-DDT and p,p'-DDE. The sites with the greatest exceedances for pesticides included the vicinity of WLSSD/Miller and Coffee Creeks (DSH 11, DSH 12, DSH 34, DSH 36), Fraser Shipyards (DSH 31), Minnesota Slip (DSH 40), and Slip C (DSH 29 and DSH 37). Octachlorostyrene was present at low levels, but no information was found concerning its biological effects or distribution elsewhere.

Toxaphene was detected at 10 sites, with the highest concentrations occurring at DSH 40 (Minnesota Slip) and DSH 11 (just west of the WLSSD outfall). The extracts of these samples were re-run on a more sensitive instrument [i.e., gas chromatography selective ion methodology (GC/SIM)] at Dr. Deborah Swackhamer's laboratory at the University of Minnesota-Minneapolis (Table 3-15). In general, the toxaphene values were on the same order of magnitude as those analyzed by a GC using electron capture detector. Toxaphene was higher in the Duluth/Superior Harbor sediments than in Great Lakes sediments which run around 15 ng/g (Deborah Swackhamer, University of Minnesota, personal communication, 1996). Additional surficial sediment samples were collected in the vicinity of WLSSD during June 1996 for toxaphene analysis; the analytical results are not yet available to include in this report. The sources of toxaphene to the Duluth/Superior Harbor are not known. Toxaphene was the most heavily used pesticide in the United States between 1966 and the mid-1970s; it was used primarily on cotton fields in the southern United States. Toxaphene was banned in the United States during 1982.

Detectable pesticide concentrations were normalized to the sediment organic carbon levels observed in this study (Table 3-16). The U.S. EPA has proposed draft sediment quality criteria for dieldrin and endrin, and these criteria were not exceeded in this study. The OMOEE SEL values for eight pesticides were also not exceeded at the study sites.

The particular sources of pesticides to the Duluth/Superior Harbor have not been determined, but potential sources will be discussed here. Anthropogenic sources of HCB to the Lake Superior basin are discussed in the Lake Superior LaMP (Lake Superior Binational Program, 1996). However, source identification for HCB is difficult due to potential contamination in other organochlorine chemicals that may be used in the basin. The pesticide contamination observed in the vicinity of WLSSD/Miller and Coffee Creeks may be mostly due to discharges of effluent and stormwater. Pesticide contamination was also observed in several boat slips. Some pesticide sources may have been due to accidental spills or releases from ship traffic; in addition, the ship propellers may stir up sediments at these sites, thus delaying the deposition of cleaner sediments over more contaminated sediments. Other potential sources of pesticide contamination in the harbor include: atmospheric transport and deposition resulting from aerial drift of pesticides, volatilization from applications in terrestrial environments, and wind erosion of treated soil (U.S. EPA, 1993).

3.2.8 PAHs

3.2.8.1 Gas Chromatography/Mass Spectrometry (GC/MS)

GC/MS PAH analyses were conducted on September 9, 1993 and October 13, 1993 for samples collected during September 1993. However, the detection levels were higher than the original data quality objectives and there was blank contamination at very low levels. This was caused, in part, by the presence of analytical interferents and high water content in several of the sediment matrices (letter from Deneen Walker, Project Manager at Twin City Testing to Luke Charpentier, MPCA analytical coordinator), as well as the fact that the dilution series for the standard curves were set too high (thus leading to elevated quantitation limits). Because of these analytical difficulties, it was decided by MPCA Water Quality staff (in conjunction with the GLNPO Project Manager) to send archived sediment samples from half of the sites to the contract laboratory for the extraction and analysis of PAH compounds. In addition, five of the sites were re-sampled during June 1994, as close to the original site as possible. These samples were extracted and analyzed at the same time as the archived sediment samples in order to give another measure of sediment contamination.

<u>September 1993 Samples (analyzed September and October 1993)</u>

The original PAH results of surficial sediments (i.e., approximately 0-30 cm) are given in Figure 3-21 and Table 3-17. In some samples, PAHs were detected at low levels and were estimated below the detection limit established for each compound. A total of 17 PAH compounds were quantitated. Due to the high detection limits, PAH compounds that were

not detected were excluded from the tabulation of total PAHs. Eighteen sites had total PAH concentrations above the OMOEE LEL value of 4000 μg/kg (Persaud et al., 1993).

The most PAH contaminated site was at DSH 24 (off Un-named Creek at USX) which was 3.5 times more contaminated than the next highest site at DSH 40 (Minnesota Slip). Sites DSH 25 (near USX Wire Mill Settling Pond), DSH 29 (near end of Slip C), and DSH 17 (south of M.L. Hibbard Plant/DSD No. 2) had less than one-half the amount of PAH contamination at DSH 40. The level of contamination observed at these sites was most likely due to industrial activities and the shipment of coal. Industrial activities that produce PAHs include coal coking (which took place at USX), production of coal tar (which took place at Duluth Tar), and historic coal gasification plants (one such plant was located in Canal Park, close to Minnesota Slip). Coal was used historically at the M.L. Hibbard Plant/DSD No. 2 and many coal storage piles and loading/unloading facilities were historically present in many areas of the Duluth/Superior Harbor (e.g., Howard's Pocket).

Individual PAHs that contributed most significantly to the total PAH levels varied according to the site (Table 3-17). However, certain compounds emerged as most prevalent: phenanthrene, anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes, benzo(a)pyrene, and naphthalene. OMOEE LEL values are available for 12 PAH compounds. Detected PAH compound concentrations that exceeded the LEL are shown in bold typeface in Table 3-17.

PAH compounds are best evaluated individually by normalizing the concentrations to TOC. Table 3-18 shows TOC-normalized PAH concentrations for those sites and compounds with detectable surficial concentrations. Normalized PAH concentrations were highest, in descending order, at: DSH 24 (off Un-named Creek at USX), DSH 40 (Minnesota Slip), DSH 25 (near the Wire Mill Settling Pond), DSH 36 (near Miller Creek outfall), and at DSH 29 and DSH 37 (Slip C sites). The normalized PAH concentrations were compared to the OMOEE SEL values for 12 PAH compounds; no exceedances were found. In addition, the U.S. EPA has proposed sediment quality criteria (SQC) for three PAH compounds: fluoranthene, acenaphthene, and phenanthrene as 620, 130, and 180 mg/kg oc, respectively. The SQC value for phenanthrene was exceeded at DSH 24 (off Un-named Creek at USX) (Table 3-18). No other exceedances of the EPA SQC were observed in this study.

The presence of PAHs in some samples was easily detected by field observations. A comparison of the presence/absence of an oil sheen or petroleum odor (Table 3-4) and analytical determination of these compound shows that for sampling locations near the USX Superfund site (DSH 24-25), Minnesota Slip (DSH 40), WLSSD/Miller and Coffee Creek

Embayment (DSH 34-36), and Slip C (DSH 37), high levels of PAHs were associated with field observations. However, other locations with PAH concentrations exceeding the OMOEE LEL did not give visible evidence of their presence, including Fraser Shipyards (DSH 31) and the region south of the M.L. Hibbard plant/DSD No. 2 (DSH 17). In the latter case, however, other visual cues (i.e., fly ash and coal residues) suggested the presence of complex organic compounds.

September 1993 Samples (analyzed July 1994)

In order to achieve lower detection limits, archived split samples from the September 1993 field collection were extracted and quantitated during July 1994. The results are presented in Table 3-19. The results of the initial analyses (in which extrapolation beyond the standard curve was used to estimate low levels of PAHs) were compared to those of the later analyses (which had lower detection limits) for total PAHs (Table 3-20). The relative percent difference (RPD) and coefficient of variation (CV) was determined for samples from the same site. Samples that had nondetectable total PAH concentrations were counted as 0 μg/kg to yield a conservative comparison. The data quality objectives for this study specified a RPD of $\leq 50\%$ for total PAHs. Six of 14 sample sites had RPDs $\leq 50\%$. The RPD measures the precision of duplicate chemical analyses. Since these measurements were of split samples with a nine month lag in the analysis time, there may have been some loss of PAHs through volatilization during sample storage or else difference in the analytical extraction efficiency. In addition, the lower detections limits of the samples quantitated during July 1994 resulted in the detection of several previously undetected samples (DSH 05, DSH 06, DSH 30). Thus, the aforementioned reasons probably contributed to the higher RPD values at eight sites. The CV is the sample standard deviation expressed as a percentage of the sample mean. The CV values ranged from 0 to 141%. As with the RPD calculation, the difference in detection limits probably contributed the greatest amount of variation between samples from the same site. A few samples (DSH 21, DSH 26, DSH 40) appeared to lose PAHs following sample storage.

June 1994 Samples (analyzed July 1994)

Sediments from five sites sampled during the 1993 survey (DSH 21, DSH 22, DSH 23, DSH 26, DSH 27) were collected again on June 11, 1994 and analyzed during July 1994 in conjunction with the re-analyses described above. The coordinates of these sampling locations are shown in Table 3-21.

The samples were not collected in the same manner as the 1993 samples. Short gravity corers were used to collect the top 15 cm of sediments. In addition, corresponding samples for TOC were not collected. Cores were collected from DSH sites thought to be relatively uncontaminated, in order to obtain "background" concentrations of PAHs adjacent to the Interlake/Duluth Tar and USX Superfund sites. While in the field, attempts were made to obtain sediments from sites as close as possible to those sampled in 1993. In the case of site DSH 21 (a shallow area just outside Stryker Embayment at the Interlake/Duluth Tar Superfund site), it was obvious during collection that this sample was contaminated with PAHs (there was a strong petroleum odor as well as a black oil sheen during sampling). The sample collected in September 1993 did not show this level of visual contamination.

The PAH analyses of the 1994 samples are given in Table 3-22. The results are not directly comparable to the 1993 samples due to differences in the core depths (i.e., 15 cm versus 30 cm) and slight differences in sample locations contributing to sediment heterogeneity. Total PAH concentrations ranged from 208 - 90,300 μg/kg for the five sites sampled in 1994 (Table 3-22). There was an insufficient number of samples collected to determine background levels of PAHs in the harbor. The R-EMAP investigation the MPCA and Natural Resources Research Institute are currently conducting in the St. Louis River AOC will more adequately identify background levels of contaminants in this AOC.

Total PAH concentrations exceeded the OMOEE LEL of 4,000 μg/kg at DSH 21 (mouth of Stryker Embayment) and DSH 23 (across channel from Tallas Island). An estimate of the organic carbon normalized total PAH concentration was made by using the 1993 TOC values for DSH 22 (10% TOC) and DSH 23 (5.3% TOC) for sites DSH 21 and DSH 23, respectively. The 1993 TOC value at DSH 21 appeared to be too low based on the amount of PAH contamination measured in the 1994 sample. Thus, the TOC measurement from a nearby, more contaminated site (DSH 22) was used. The estimated TOC-normalized values for DSH 21 and DSH 23 were 903 and 158 mg/kg oc, respectively. Both of these values were less than the OMOEE SEL value of 10,000 mg/kg oc (Persaud et al., 1993).

3.2.8.2 Fluorescence Screen

In addition to the GC/MS PAH analyses, the 1993 core sections were analyzed using a PAH fluorescence screening method. This method has been under development for several years, and it has been adapted for use in Great Lakes harbors (Smith and Filkins, 1992; Smith and Rood, 1994). The fluorescence screen is rapid and relatively inexpensive compared to the GC/MS method. However, this method has not been used previously in the Duluth/Superior

Harbor, and it was not known how well it would compare to the GC/MS results from this study.

The results of the fluorescence screen method are shown in Table 3-23. A statistical comparison between the PAH fluorescence screen and GC/MS results could not be made due to the following reasons:

- The initial GC/MS analyses were not sufficiently sensitive (i.e., the quantitation limits were too high); this could lead to underprediction of the true sample concentration by GC/MS analysis.
- The samples were not analyzed during the same time period (the GC/MS method was performed approximately 6 months to 1 year prior to the fluorescence method on the split samples).
- The GC/MS method identified a discrete number of PAH compounds, whereas the fluorescence method is functionally defined, and measures the sum total of all compounds that fluoresce under the given conditions. Thus, this could lead to overprediction of the total PAH concentrations.

The surficial PAH fluorescence screening results tended to overpredict the GC/MS results by zero to three orders of magnitude. On a qualitative basis, the ranking of the most contaminated sites differed from using the GC/MS results. The surficial screening results indicated that the most contaminated sites, in descending order, were: DSH 09 (near Globe Elevators), DSH 37 (Slip C in front of Superwood plant), DSH 36 (near Miller Creek outfall), DSH 38 (Slip C, near Great Lakes Towing Co.), DSH 24 (off Un-named Creek at USX), and DSH 32 (across channel from Fraser Shipyards). In comparison, the most contaminated surficial sediments, as determined by GC/MS, were DSH 24, DSH 40, DSH 25, DSH 29, DSH 17, and DSH 23. Although DSH 24 was by far the most PAH contaminated site when using the GC/MS data, it was ranked fifth in contamination using the PAH screening results. DSH 09 had the most contaminated surficial sediments, as determined by the PAH screening method, whereas it was one of the lesser contaminated sediments, as determined by GC/MS. Thus, the relative ranking of contaminated sites was not consistent between the two methods, and the screening method appeared to have limited utility for this study. As discussed in Owen et al. (1995), the accuracy of this screening technique will be improved by calibrating the screening method against a wide range of directly measured PAHs (by GC/MS) that have low detection limits and good precision.

The PAH screen showed some trends in concentrations with sediment depth throughout the harbor (Table 3-23). While some sites showed a tendency for total PAH levels to decrease

to low levels with depth (e.g., DSH 04, DSH 07, DSH 09, DSH 10, DSH 11, DSH 13, DSH 20, DSH 35), at many other sites, PAHs either remained high or increased downcore (e.g., DSH 01, DSH 03, DSH 14, DSH 16, DSH 18, DSH 19, DSH 22, DSH 24, DSH 25, DSH 26, DSH 28, DSH 29, DSH 30, DSH 36, DSH 38, DSH 40). Several of these results were supported by the field book physical descriptions which gave visual or olfactory evidence of PAH-like compounds below the sediment surface. Sites DSH 01, DSH 12, DSH 16, DSH 18, DSH 24, DSH 25, DSH 34, DSH 36, DSH 37, DSH 38, and DSH 40 all gave physical indications of the presence of PAH-like compounds below the surficial sediment layer (Table 3-4). Therefore, field observations may be sufficient for determining the worst sites in the Duluth/Superior Harbor to have quantitated by GC/MS for PAHs.

3.2.9 Tributyltin

Tributyltin is an antifouling agent in marine paint that is used to paint ship hulls, boat docks, and buoys. Tributyltin and three other butylated forms of tin (i.e., mono, di, and tetra-) were measured in six samples, selected by their proximity to commercial, private or public shipyards, boat docks, or loading facilities. The sites selected for butyltin analyses were DSH 01 (near the Burlington Northern Taconite Loading Facility), DSH 02 (Barkers Island boatyard), DSH 08 (U.S. Army Corps of Engineers Shipyard), DSH 20 (behind Hearding Island), DSH 31 (Fraser Shipyards), DSH 40 (Minnesota Slip). Results of the butyltin analysis [reported as tin (Sn)] are given in Table 3-24; the results for tributyltin are also converted from tin to tributyltin (TBT) by multiplying the results by 2.5. Concentrations of tributyltin were greatest in sediment from Fraser Shipyards (DSH 31), at 178 μg/kg TBT, and were lowest at DSH 01, at 3.3 μg/kg TBT. The remainder of the samples had intermediate tributyltin concentrations. Overall, the mean concentration of tributyltin at the six sites was 74 $\pm$ 63 (SD) μg/kg TBT. Monobutyltin and dibutyltin were present at the six sites in concentrations ranging from 1.7 μg/kg Sn to 54.1 μg/kg Sn. Tetrabutyltin was not detected in any of the samples.

Tributyltin is designed to slowly leach from marine paints after it is applied. Tributyltin can be released to the water column through leaching from paint on boats or from paint chips or dust from maintenance facilities (e.g., dry docks, sandblasting residues). Nontarget water column and benthic organisms are subject to exposure and potential toxicity from butyltins; this is primarily a concern in marine environments. Tributyltin is highly toxic to aquatic organisms with the toxicity of butyltin compounds decreasing with decreasing number of butyl groups. Mono- and dibutyltin compounds are at least one to two orders of magnitude less toxic than tributyltin. In addition, the organotin compounds are bioaccumulated through

the food chain, causing potential harm to fish, as well as (potentially) human fish consumers (Krone et al., 1989).

Due to the demonstrated toxicity of tributyltin to aquatic organisms, especially marine oyster and mussel beds, restrictions were placed on the use of tributyltin in marine paints by the State of Wisconsin, U.S. EPA, and several European countries during the late 1980s (Tom Janisch, WDNR, personal communication, 1996). Some recent data on tributyltin in sediments from the Superior Harbor, and past water column monitoring by WDNR statewide, indicates that tributyltin is present in sediments and water of Wisconsin marinas (Tom Janisch, WDNR, personal communication, 1996). In addition, tributyltin appears to be very persistent in the sediments and can desorp back to the water column, dependent on its partitioning coefficient.

The WDNR has used two different partitioning models to derive sediment quality objective concentrations (SQOCs) for tributyltin found in Wisconsin sediments. The first model uses an equilibrium partitioning water quality criteria approach to estimate environmentally safe concentrations of tributyltin in sediments. This approach assumes that: 1) the partitioning of tributyltin between the sediment solids and porewater is controlled in a predictable manner by a continuous equilibrium between the two phases, 2) sediment organic carbon determines the bioavailability of tributyltin in the sediment porewater, 3) the toxicity of tributyltin to benthic organisms is governed by their exposure to tributyltin dissolved in sediment porewater and does not include other exposure pathways such as ingestion of contaminated sediment or food, and 4) benthic organisms are as sensitive to tributyltin levels as water quality organisms upon which water quality criteria are generally based. Recent literature indicates that organic carbon is not a good predictor for tributyltin sorption and release in the sediments (Tom Janisch, WDNR, personal communication, 1996). For this study, there appeared to be no positive correlation between tributyltin and TOC for the limited data set available. Depending on the water chemistry, tributyltin may be a neutral or nonpolar compound at higher pHs and may otherwise exist in the cationic form. Thus, sole use of the equilibrium partitioning model may not be appropriate to predict its chemical behavior, and the tributyltin results from this study were not compared to the Wisconsin SQOCs. This model also does not take into account the higher partition coefficient that is probably associated with tributyltin in paint chips; thus, tributyltin in sediment deposited paint chips may be less bioavailable.

The second partitioning model used by the WDNR is based on the ratio of tributyltin in the overlying water column to the concentration in the sediment. Based on partitioning coefficient values, the water column tributyltin concentration can be predicted based on the

measured sediment concentrations. These water column concentrations can then be compared to U.S. EPA acute and chronic water quality criteria for tributyltin. The WDNR used literature-derived partitioning coefficients to estimate water column concentrations of tributyltin at some ship building sites in Wisconsin (Tom Janisch, WDNR, personal communication, 1996). WDNR extrapolated partition coefficients from some marine sediments, and they made the assumption that the partitioning of tributyltin between the sediment and overlying water had reached an equilibrium. This partitioning model was not used for the data set from this study because: 1) site-specific field derived partitioning values would be more appropriate to use and 2) inadequate information is available about the chemical behavior of tributyltin.

3.3 TOXICITY TESTS

Four organisms were included in the suite of toxicity tests conducted in this sediment survey: the amphipod *Hyalella azteca* (10-d lethality), the midge *Chironomus tentans* (10-d lethality and growth), the bacterium *Photobacterium phosphoreum* (Microtox^{R}), and the bacterium *Vibrio fischeri* (Mutatox^{R}). Whole-sediment tests were conducted with *H. azteca* and *C. tentans*, whereas porewater was used in the Microtox^{R} and Mutatox^{R} tests. The toxicity test results are shown in Table 3-25, and are described in the following sections for each organism and endpoint.

In attempting to explain toxicity for any of the species, it is important to note that the chemical analyses are <u>not</u> synoptic with the toxicity test results. The surficial analytical chemistry was performed on the 0-30 cm section of the vibracore for each site, whereas the toxicity tests were conducted using the Ponar grab sample (0-20 cm) from each site. Therefore, caution should be used in interpreting toxicity based on particular contaminant profiles.

3.3.1 10-day Sediment Toxicity Tests

The 10-day toxicity tests were conducted on seven batches of samples, all of which were run within two months of sample collection. Detailed information on the sample collection and handling, methods, water quality and survival results, data analysis, and *H. azteca* reference toxicant test results are provided in MPCA laboratory reports given in Appendix B. In general, the pH ranges of all the toxicity tests were acceptable. However, dissolved oxygen occasionally fell below 40% saturation in the *C. tentans* tests. Temperature was slightly less than the recommended range of 23 $\pm$ 1°C (U.S. EPA, 1994) for most tests (i.e., down to 20°C). Sediments for DSH 18 and DSH 19 were accidently frozen prior to testing. The

samples were thawed out and used in the sediment toxicity tests. Changes in the sediment matrix may have resulted from freezing, and it is not known whether similar survival data would have resulted from using unfrozen sediments.

In order for the test to pass, the mean control survival for *H. azteca* had to be greater or equal to 80%. For *C. tentans*, a mean control survival of 70% or greater was required for the test to pass. Survival data from acceptable tests were analyzed statistically using TOXSTAT (Gulley and WEST, Inc., 1994), a statistical software package obtained from the University of Wyoming. All survival data were expressed as a proportion and were transformed using an arc sine-square root transformation prior to analysis. Zero variance survival data from the *C. tentans* tests were excluded from the statistical analysis because nonparametric statistics could not be run on the three replicates. A minimum of four replicates is needed to run nonparametric statistics. In most cases, the survival data of excluded tests was greater or equal to the mean control survival. For site DSH 24, there was 0% mean survival (and thus zero variance) in the *C. tentans* tests; this result was obviously statistically less than the control and was excluded from the statistical analysis. The Shapiro-Wilk's test for normality and Bartlett's test for homogeneity of variance were run on the transformed data. Next, an Analysis of Variance (ANOVA) was conducted, and the data were analyzed statistically using a one-tailed Dunnett's test ($\alpha = 0.05$). A sample was considered toxic when mean percent survival was significantly lower than mean control survival.

3.3.1.1 Acute Toxicity to *Hyalella azteca*

Table 3-25 shows the mean percent survival of *H. azteca* resulting from the 40 toxicity tests. A problem was encountered with 28 of the sediments in that the survival of the control organisms did not meet quality control requirements (i.e., 80% mean survival after 10 days). Of the 12 tests that passed, none of the samples were statistically less than the control. The health of the organisms was suspect, as they also performed poorly in the sodium chloride reference toxicant test over that period (refer to the laboratory reports in Appendix B). Unfortunately, sufficient sediment volume was not available to retest these sediments. Therefore, the potential toxicity of 28 sites to the amphipod is not known.

3.3.1.2 Acute Toxicity to *Chironomus tentans*

The survival of *C. tentans* in the 10-day sediment toxicity tests is given in Table 3-25. Control survival was acceptable for all of the *C. tentans* tests. Of the 40 sites tested, three sites were acutely toxic to the midge: DSH 14 (the bay east of Erie Pier), DSH 24 (the USX

Un-named Creek outfall), and DSH 34 (the WLSSD discharge). DSH 24 was extremely toxic; no survival was observed in any of the replicates. This site was one of the most contaminated in the survey with respect to heavy metals (Pb, Cr, Ni, Cd, and Zn), mercury, and PAHs.

3.3.1.3 Chronic Toxicity to *Chironomus tentans*

Growth (weight) was measured at the end of the *C. tentans* test to assess chronic effects. Although the dried *C. tentans* were weighed, the balance on which they were weighed was not calibrated with standard weights. Therefore, the data are suspect since the internal calibration of the balance may have drifted with time. Due to this quality assurance problem, the growth data could not be analyzed statistically.

3.3.4 Acute Toxicity to *Photobacterium phosphoreum* (Microtox^R)

The Microtox^R and Mutatox^R tests were conducted using sediment porewater instead of whole sediment. Porewater was used for Microtox^R and Mutatox^R because this procedure is technically more-developed than the bulk sediment tests. In addition, the use of porewater minimized test expenses and enhanced comparability with other studies. The porewater was isolated by centrifuging whole sediment at 10,000 *g* in glass tubes. Of the 40 sites tested in an initial screen for acute toxicity to *P. phosphoreum* (Microtox^R), 16 sites were toxic. These toxic sediment porewaters were then subjected to a dilution series test in order to establish an EC50 (i.e., effective porewater concentration at which luminescence is reduced by 50%). This was done to evaluate relative toxicity of the various sediments. Decreasing EC50s signify increasing toxicity. Of the 16 toxic samples evaluated for EC50s, 9 were not toxic in the EC50 screen. Therefore, these samples were considered marginally toxic. The sites showing the lowest EC50s (therefore the highest toxicity) were DSH 24 (USX Un-named Creek outfall), DSH 02 (east end of Barkers Island), DSH 10 (Interstate Island deep hole), DSH 11 (west of WLSSD outfall), DSH 08 (U.S. Army Corps of Engineers vessel yard), DSH 13 (DM&IR taconite storage facility), and DSH 33 (south/southwest of WLSSD outfall).

3.3.5 Genotoxicity to *Vibrio fischeri* (Mutatox^R)

Like the Microtox^R test, the Mutatox^R test was conducted using porewater rather than whole sediment. It was developed to provide a rapid alternative to the Ames assay for mutagenicity (Microbics, Inc., 1993). The Mutatox^R test system is designed to detect potential genotoxins. Genotoxins are chemical or physical agents which, in addition to being mutagens (i.e., affect

a cell's DNA by altering its base sequence), change chromosome structure, number, shape, or position (Azur Environmental, 1996). The test uses a strain of *Vibrio fischeri* that has been genetically altered to suppress natural luminescence. Certain genotoxins present in some sediments may cause back-mutation of these altered organisms to the "wild type" (i.e., back to the light-producing strain). Therefore, this assay tests for the opposite endpoint of the Microtox^R test. Increased light emission over that of the controls suggests the presence of genotoxic agents in the sediment porewater. One problem in interpreting the results of this test is that mutagenic sediments that are also acutely toxic in the Microtox^R test may suppress the light output of bacteria they have mutated back to the wild strain. Thus, the potential exists to obtain false negative results for the Mutatox^R assay. Because the Microtox^R assay was conducted synoptically, the potential for this result was evaluated. Some compounds become mutagenic only following activation by enzymes in the mammalian liver. In addition to direct mutagenicity, the Mutatox^R test also determines the mutagenicity of sites following activation with the S9 enzyme, which emulates hepatic (i.e., liver) function during exposure. In this way, sites that are not directly mutagenic can be evaluated for their potential to be activated to mutagenicity in the mammalian liver.

Of the 40 sites tested for potential genotoxins, 21 sites detected genotoxic agents. These included DSH sites 01-03, 7, 12, 18-20, 23-29, 31, 34, 36-38, and 40. One site (DSH 15) was mutagenic following enzyme activation. Many of the genotoxic sediments were contaminated by heavy metals, mercury, PAHs, and pesticides (e.g., DSH sites 12, 19, 23-25, 29, 31, 34, 36-38, and 40), any of which could account for genotoxic agents. However, other sites showed much lower levels of these contaminants; thus, the source of their genotoxic agents is unknown (e.g., DSH sites 01, 02, 07, 18, 20, 27, and 28). Therefore, caution should be used in interpreting the results of the Mutatox^R test. Use of this test for evaluating contaminated sediments is in the early stages, and the effects of naturally-occurring sediment compounds on this test is not known.

3.4 CESIUM DATING OF SEDIMENT CORES

Five sediment cores were dated by measuring the presence of the radioactive element ^{137}Cs. The measurements were performed by Dr. Daniel Steck of St. John's University's Schaefer Environmental Radiation Laboratory. The cores selected for cesium dating were collected in the inner and outer Duluth/Superior Harbor areas: DSH 36 (near Miller/Coffee Creek outfalls), DSH 38 (Superwood Slip near Great Lakes Towing Co.), DSH 11 (just west of WLSSD outfall), DSH 20 (channel between Hearding Island and Park Point), and DSH 28 (Allouez Bay). Cores were sectioned in 2.5 cm increments, beginning with the surficial sediments. Twenty of these sections were analyzed for the presence of ^{137}Cs. Dating was

achieved by noting the initiation of cesium in the sediment profile (i.e., the lowest depth at which it was detected). This depth corresponds to the year 1954, when surface testing of atomic weapons in the western U.S. led to widespread deposition of airborne ^{137}Cs on surface waters of the eastern U.S. Testing peaked in the year 1964; therefore, this year corresponded to the highest concentrations of ^{137}Cs in the sediment profile. Yearly sedimentation rates may be calculated for the period between 1954 and 1964 by subtracting the core depth of the ^{137}Cs peak (1964) from the core depth of ^{137}Cs initiation (1954) and dividing by 10 (the number of years elapsed). Similarly, yearly deposition rates can be calculated for 1964 to present by dividing the depth of the 1964 peak by the number of years elapsed.

The sedimentation rates for the five cores evaluated are shown in Table 3-26. Dr. Steck's laboratory noted that two of the cores, DSH 36 and DSH 38, showed "classic" ^{137}Cs profiles, with easily distinguishable peaks and edges. The cores also appeared to have similar sedimentation rates over the entire period of 1954-1993 (1.14 and 0.94 cm/yr, respectively). Two of the cores (DSH 11 and DSH 20) showed unusual results. DSH 11 appeared to have the entire period 1954-1964 crowded into the top 7.5 cm (i.e., the ^{137}Cs initiation and peak were within 7.5 cm of the core surface), and core DSH 20 showed a uniformly decreasing cesium profile toward the bottom of the core. According to Dr. Steck, this suggests that there was a great deal of sediment mixing at DSH 20. He did not know what could account for the profile observed in core DSH 11. The fifth core, DSH 28 showed no ^{137}Cs content in any of the four sections analyzed. This suggests that insufficient sediment depth was sampled.

The findings of the cesium dating suggest either a very slow sediment deposition rate at sites DSH 11 and DSH 20 during the past 37 years, or else indicate that a great deal of mixing has occurred. Both of these areas are subject to high circulation patterns from water movement due both to flow from the St. Louis River and the Lake Superior seiche. It is possible that the apparent shallow depth of the cesium peak in the DSH 11 core is caused by scouring of more recent surficial sediments due to storms, effluent discharges, or other random events.

In contrast to DSH 11 and DSH 20, relatively higher deposition rates were calculated for sites DSH 36 and DSH 38. Both of these locations are near flow sources with the potential for heavy sedimentation. DSH 36, which showed the highest sedimentation rates of all the cores, is near the outfalls of Miller and Coffee Creeks. These creeks drain the majority of the area of the west end of Duluth, as well as the Miller Hill watershed. Runoff of both contaminants and sediment is likely to be high from these watershed sources (John Thomas,

MPCA, personal communication). In 1993, staff from the U.S. Soil and Water Conservation Service conducted a sediment sounding of the bay near the old 21st Ave. W. ship channel, and they found that a great deal of sedimentation had filled in the channel since the late 1970s. A likely source of the additional sediment is probably from Miller and Coffee Creeks, according to the Natural Resources Conservation Service (formerly the U.S. Soil and Water Conservation Service) (Paul Sandstrom, personal communication). Similarly, site DSH 38 very likely has had much sedimentation occurring in recent years; it is near a stormwater overflow outlet for the City of Duluth which is in the nearby Cutler-Magner Slip. During high rainstorm events and spring run-off events, high loads of sediment may have been deposited to this area. The fact that identifiable peaks and edges were obtained in these cores suggests that not much mixing has occurred in these sediments in recent years.

The observation that no cesium was found in the core sections from DSH 28 in Allouez Bay suggests that inadequate depth was sampled from this site. Field observations indicated that most of the shallow core collected from this site was composed of peaty organic material deposited from the surrounding wetlands. Unfortunately, the vibracorer was not able to penetrate this peaty layer to obtain underlying sediments.

In summary, it is likely that cesium dating will not be very useful for identifying recent sedimentation rates in the exposed areas of the Duluth/Superior Harbor. This is due primarily to the high mixing rates caused by the fluctuating seiche of Lake Superior, the flow of the St. Louis River, ship traffic, and storm events. However, in more isolated bays and slips, cesium dating could provide a useful date marker for recent contamination events.

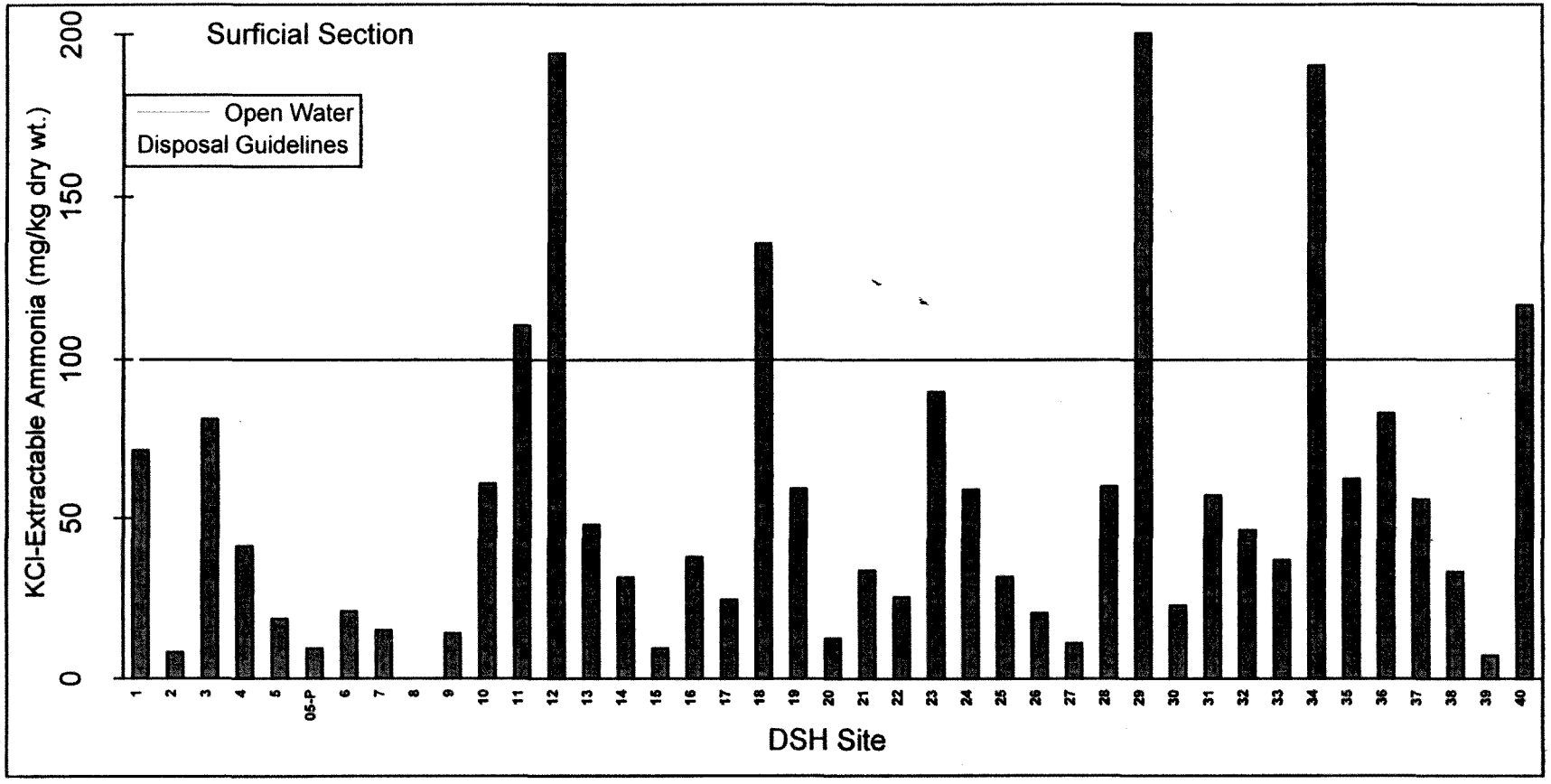

Figure 3-1. Distribution of surficial KCL-extractable ammonia at the sample sites.

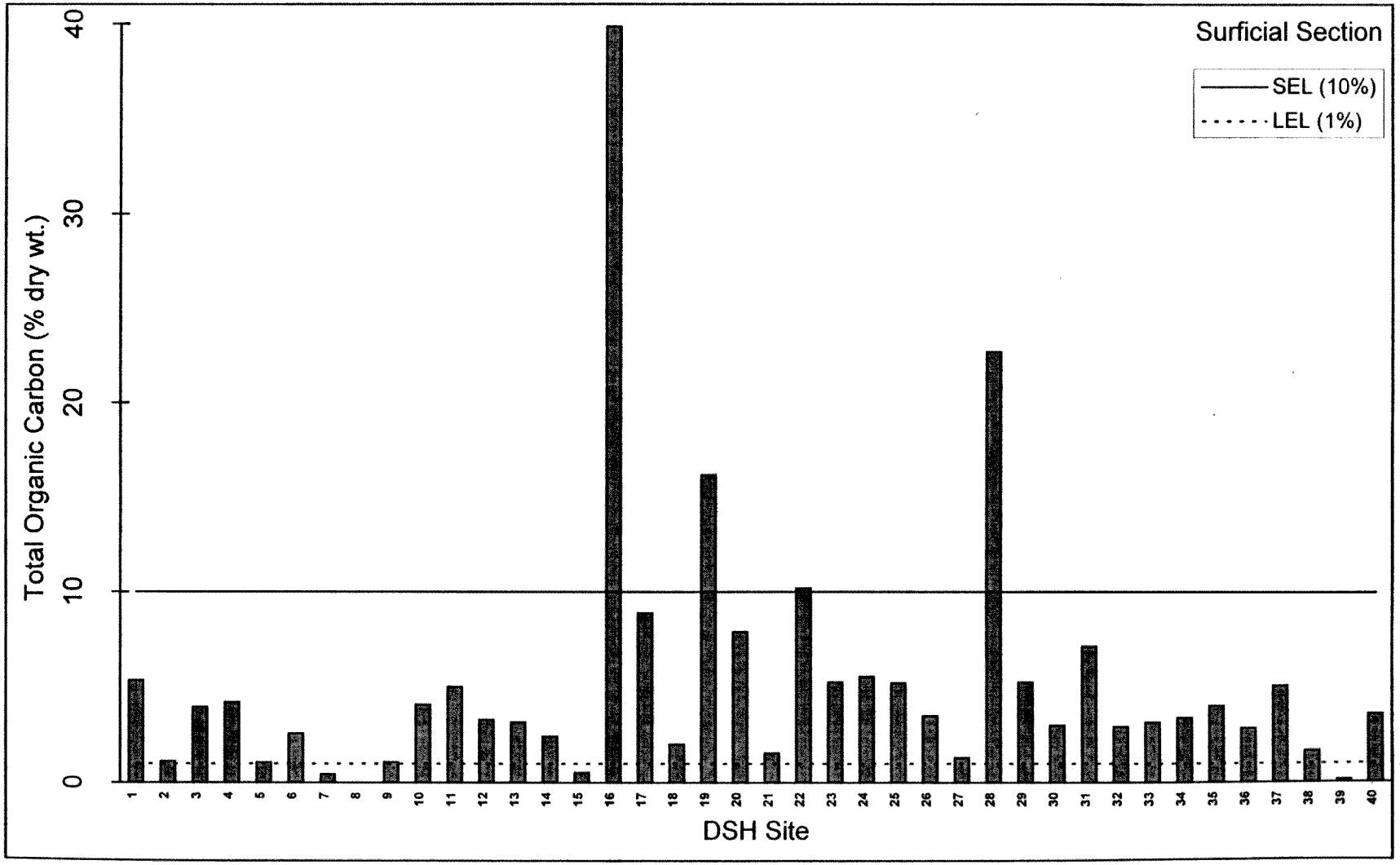

Figure 3-2. Distribution of surficial TOC at the sample sites.

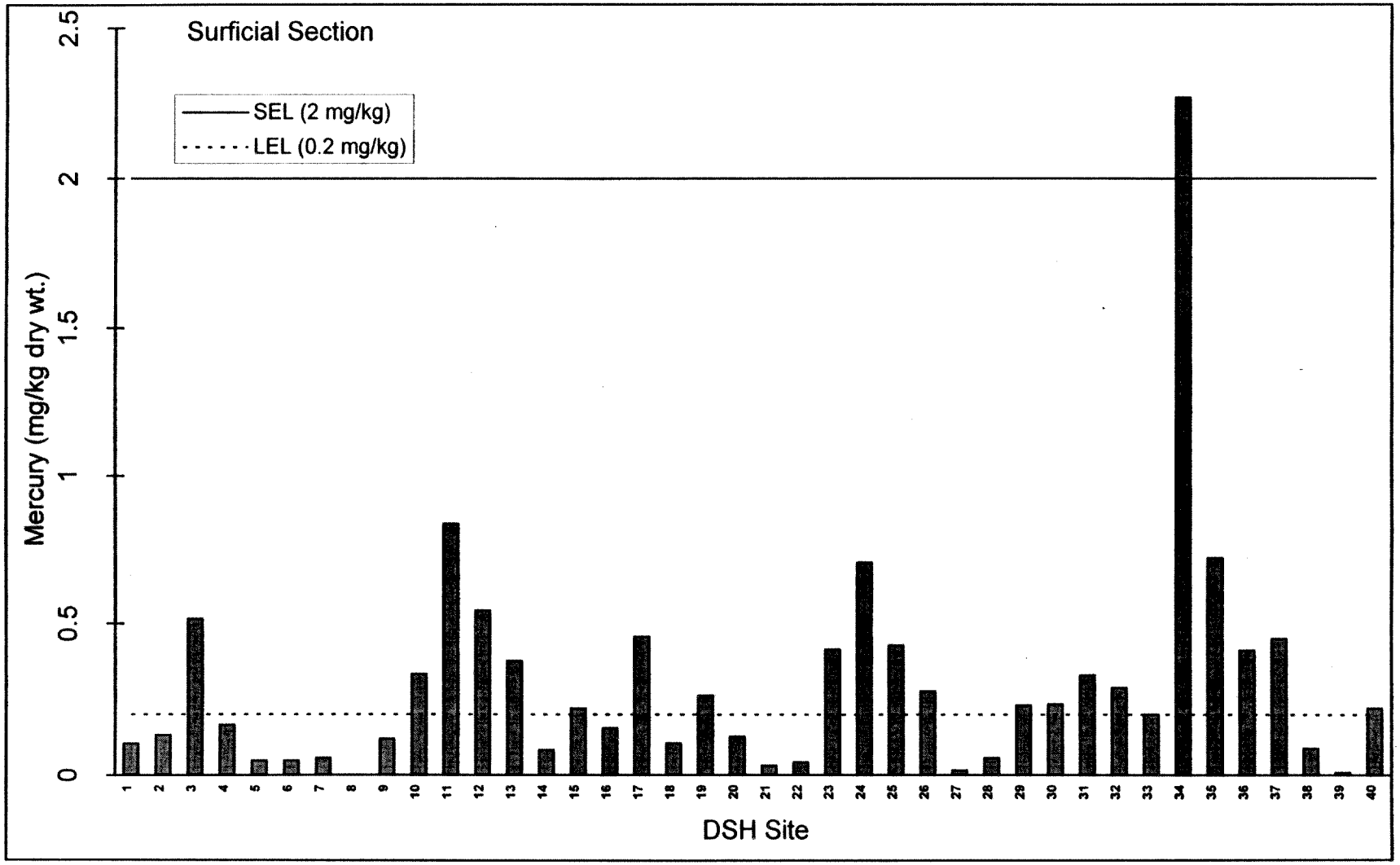

Figure 3-3. Distribution of surficial mercury at the sample sites.

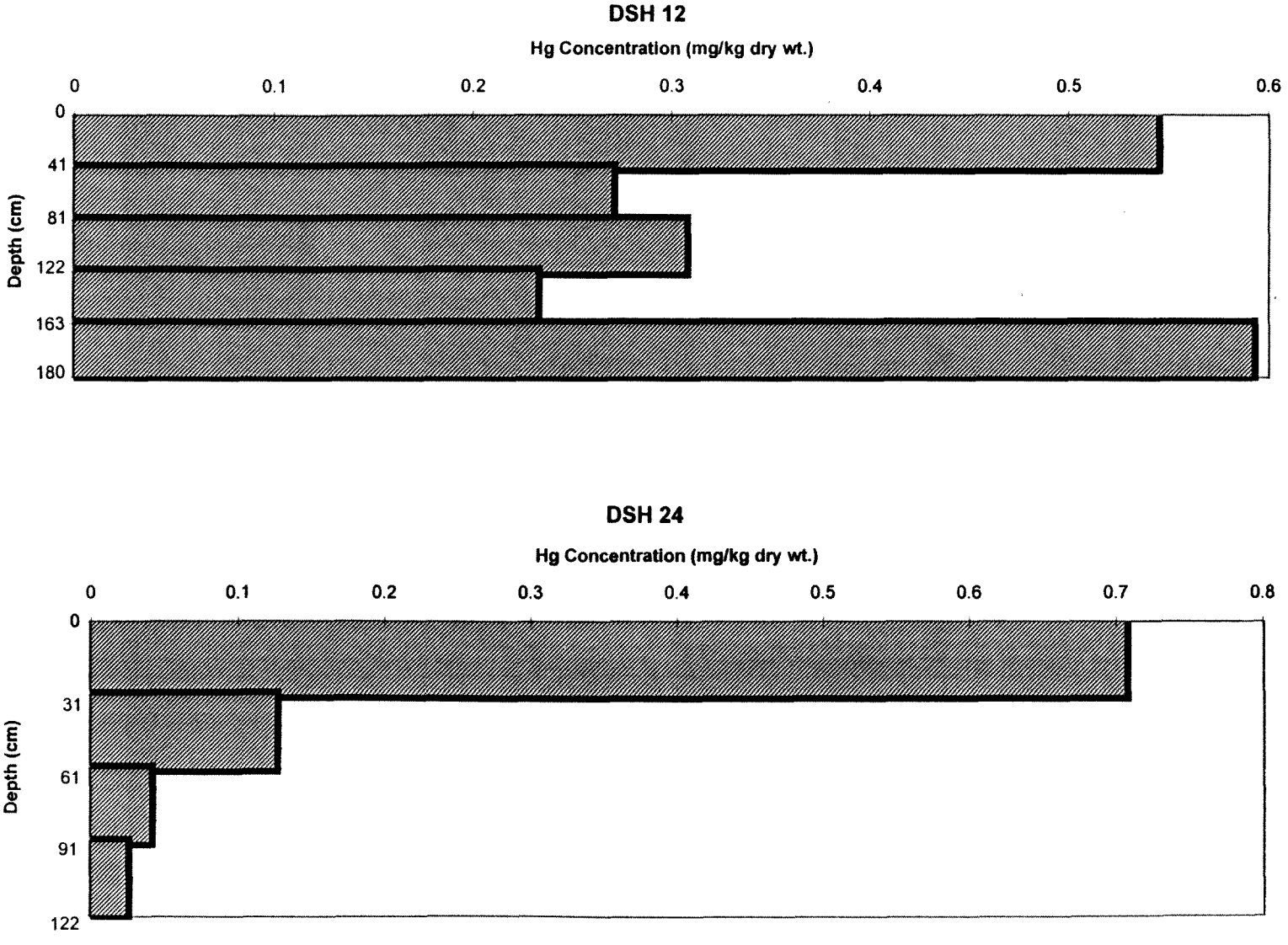

Figure 3-4. Depth profile of mercury at sites DSH 12 and DSH 24.

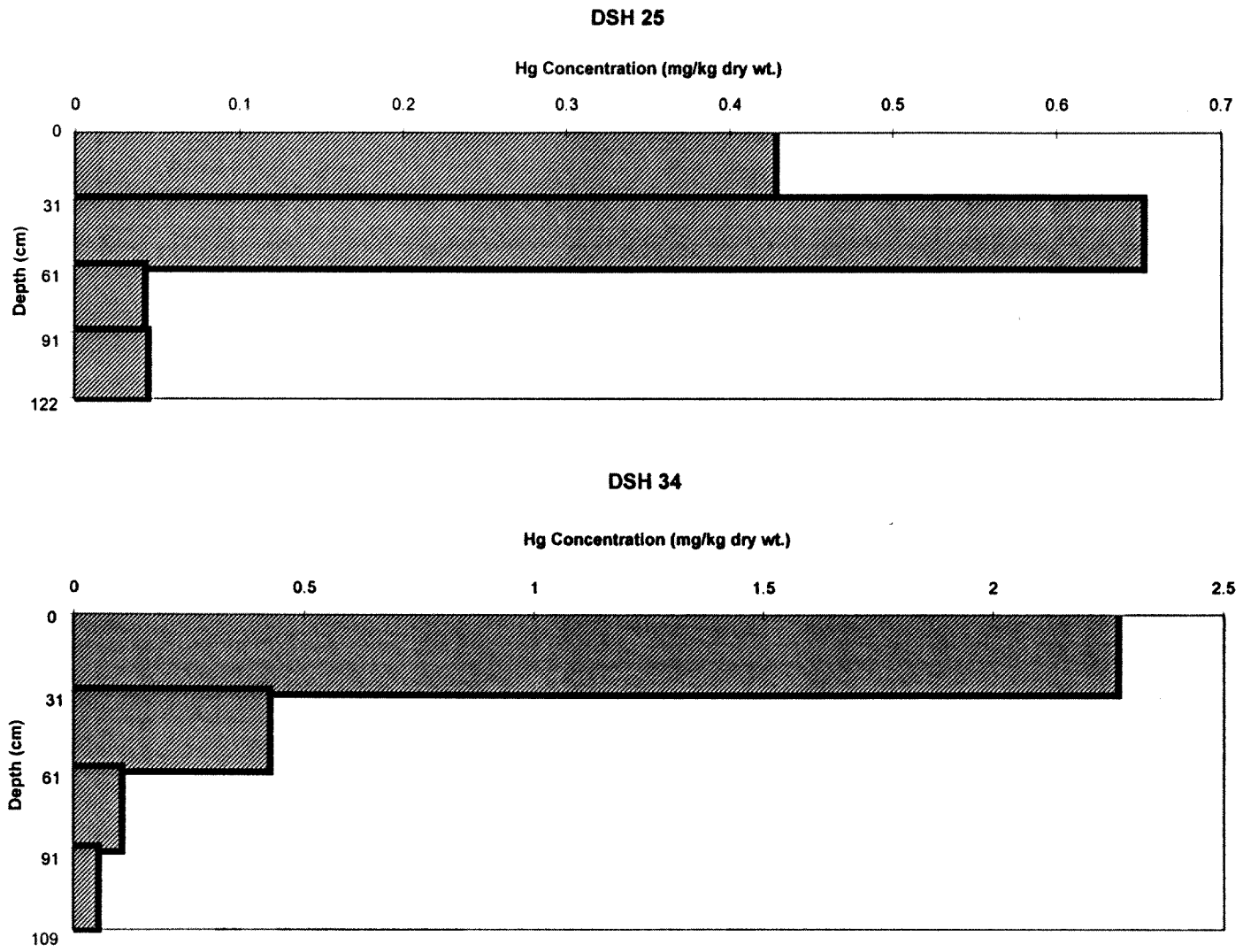

Figure 3-5. Depth profile of mercury at sites DSH 25 and DSH 34.

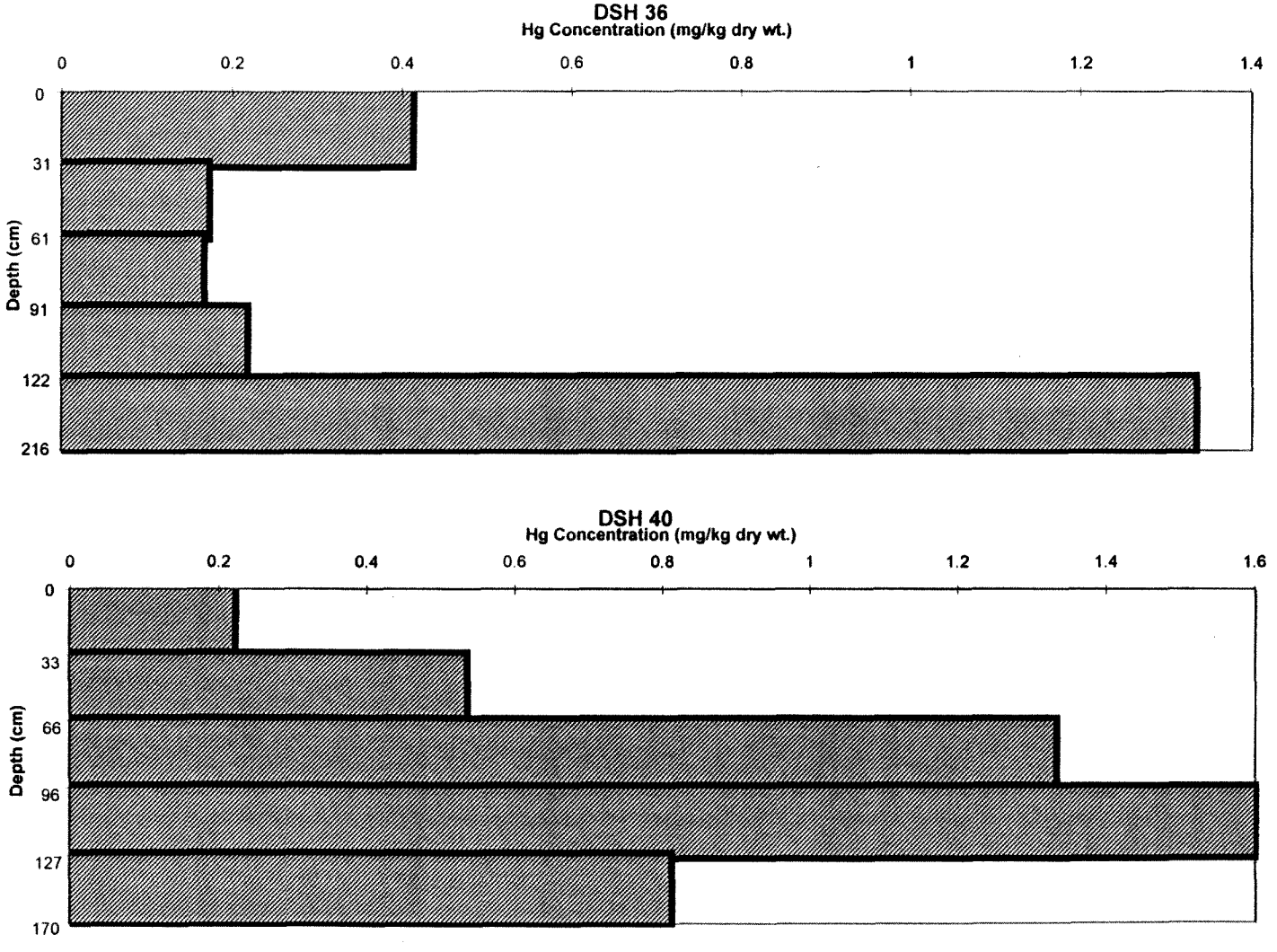

Figure 3-6. Depth profile of mercury at sites DSH 36 and DSH 40.

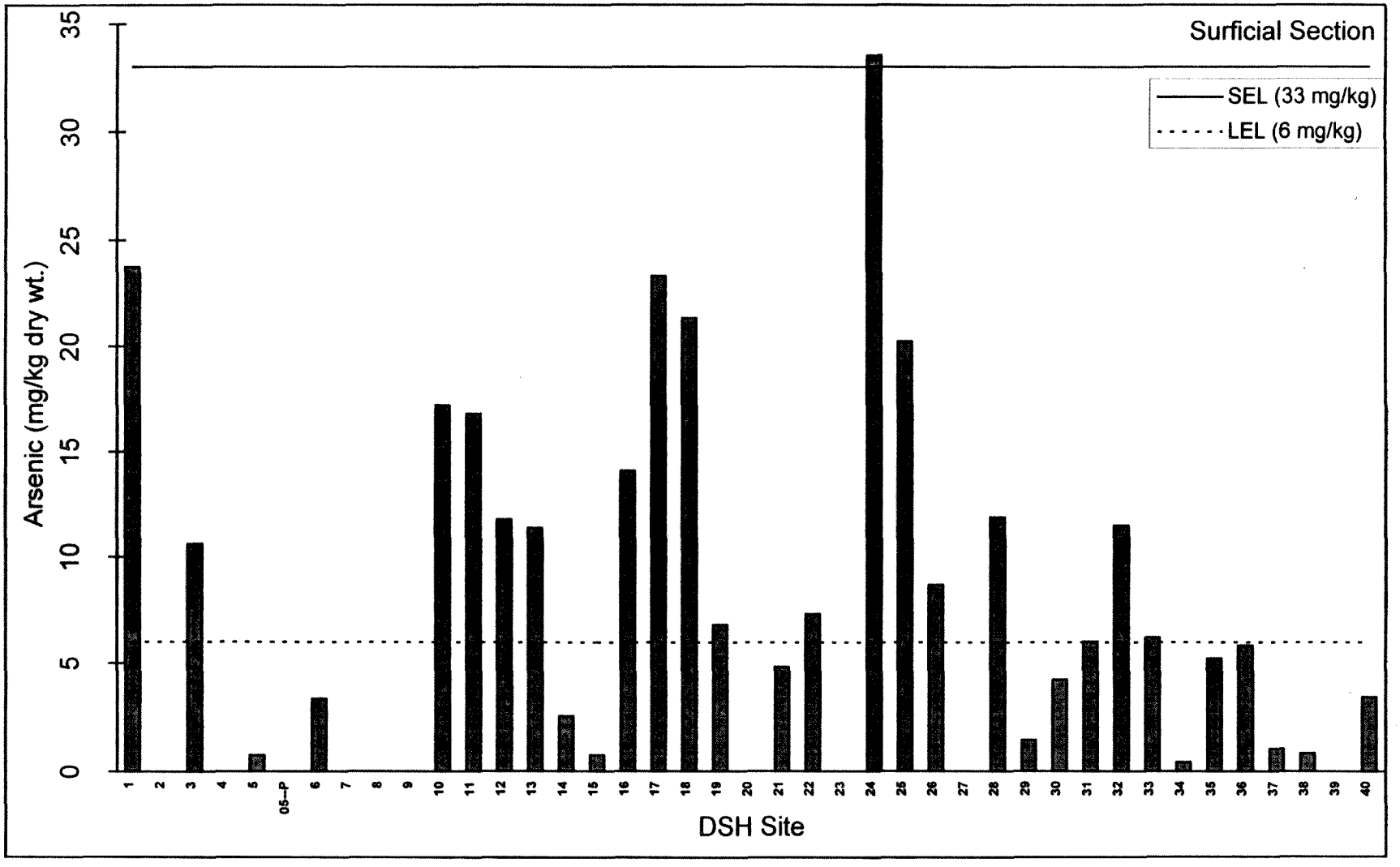

Figure 3-7. Distribution of surficial arsenic at the sample sites.

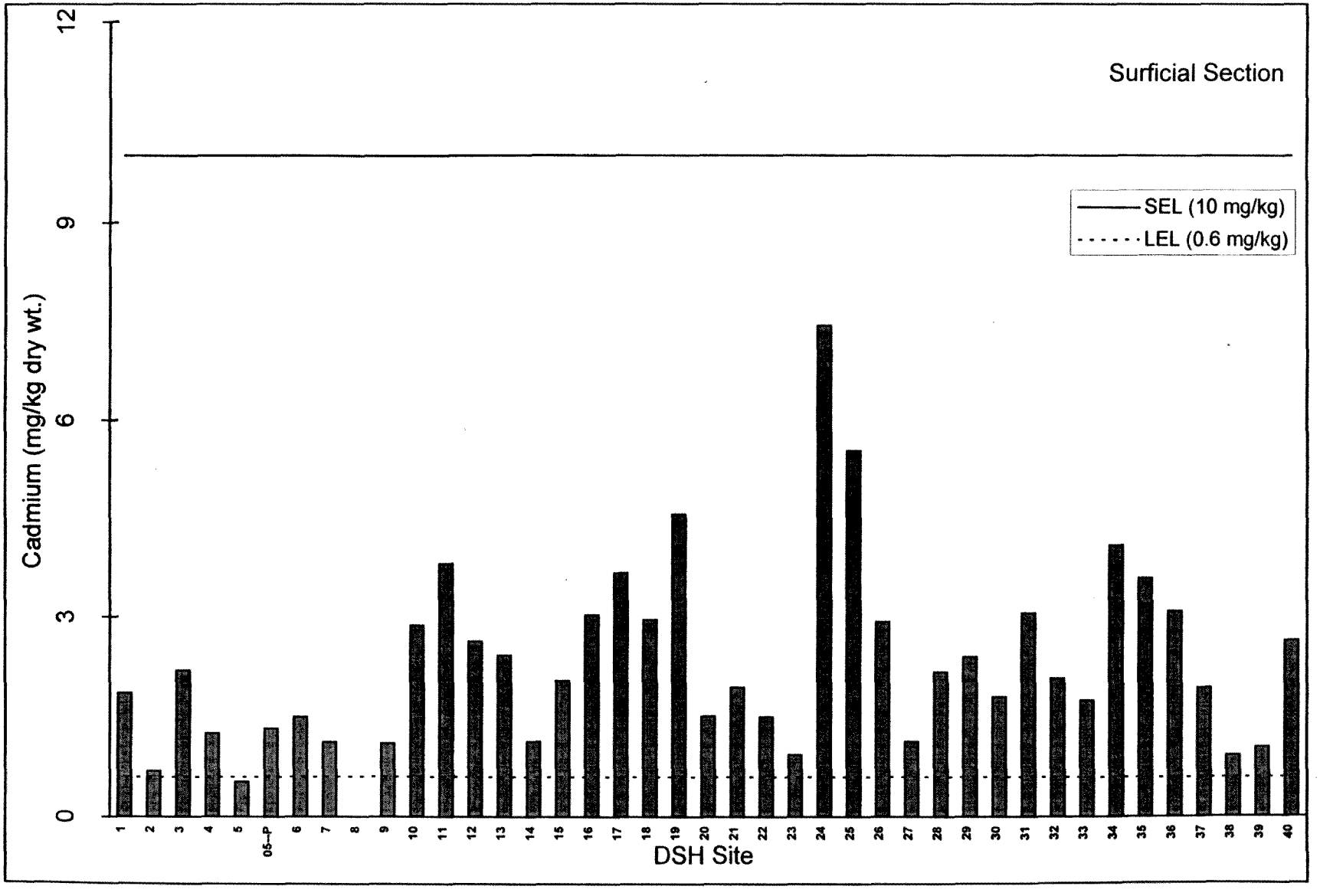

Figure 3-8. Distribution of surficial cadmium at the sample sites.

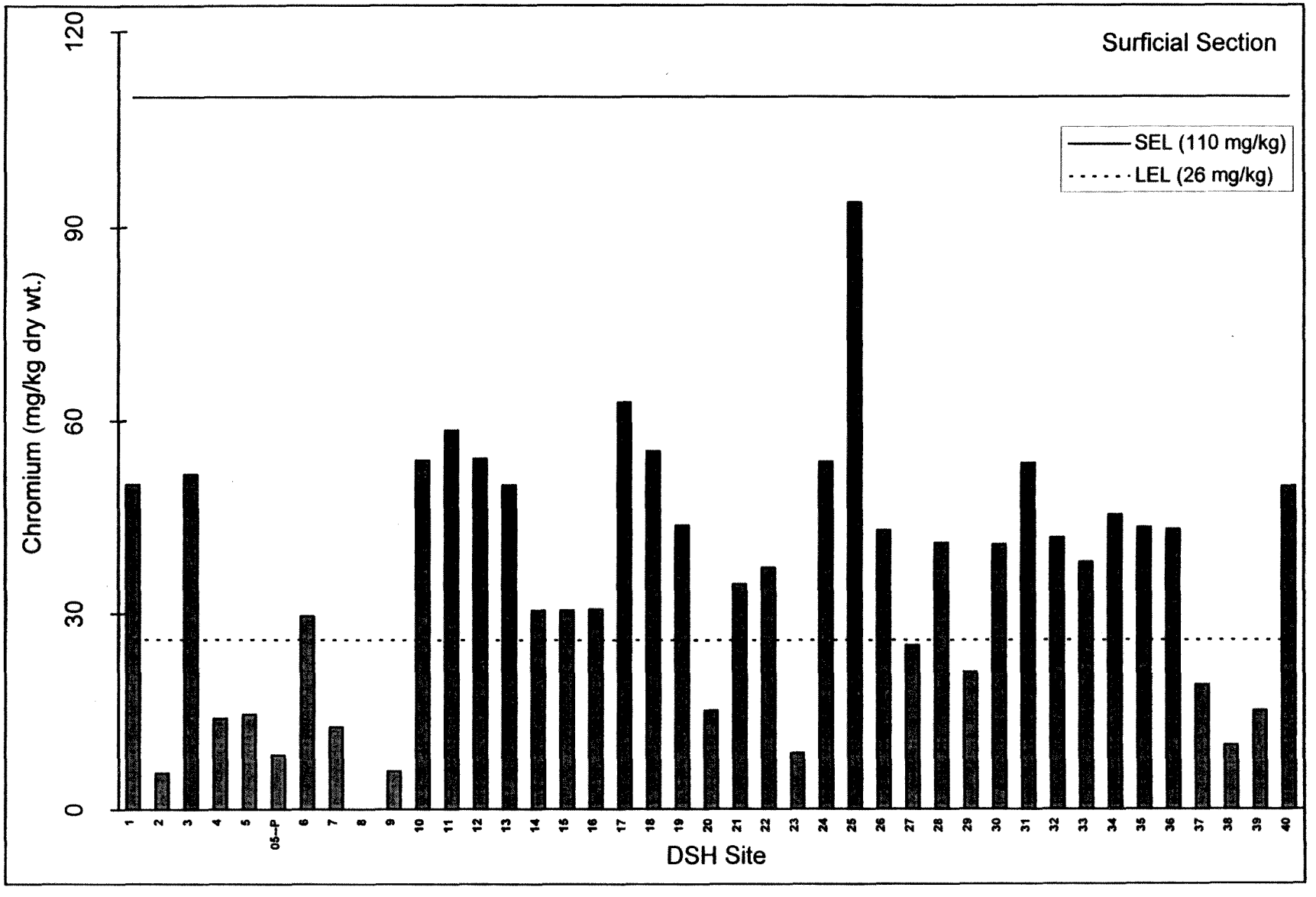

Figure 3-9. Distribution of surficial chromium at the sample sites.

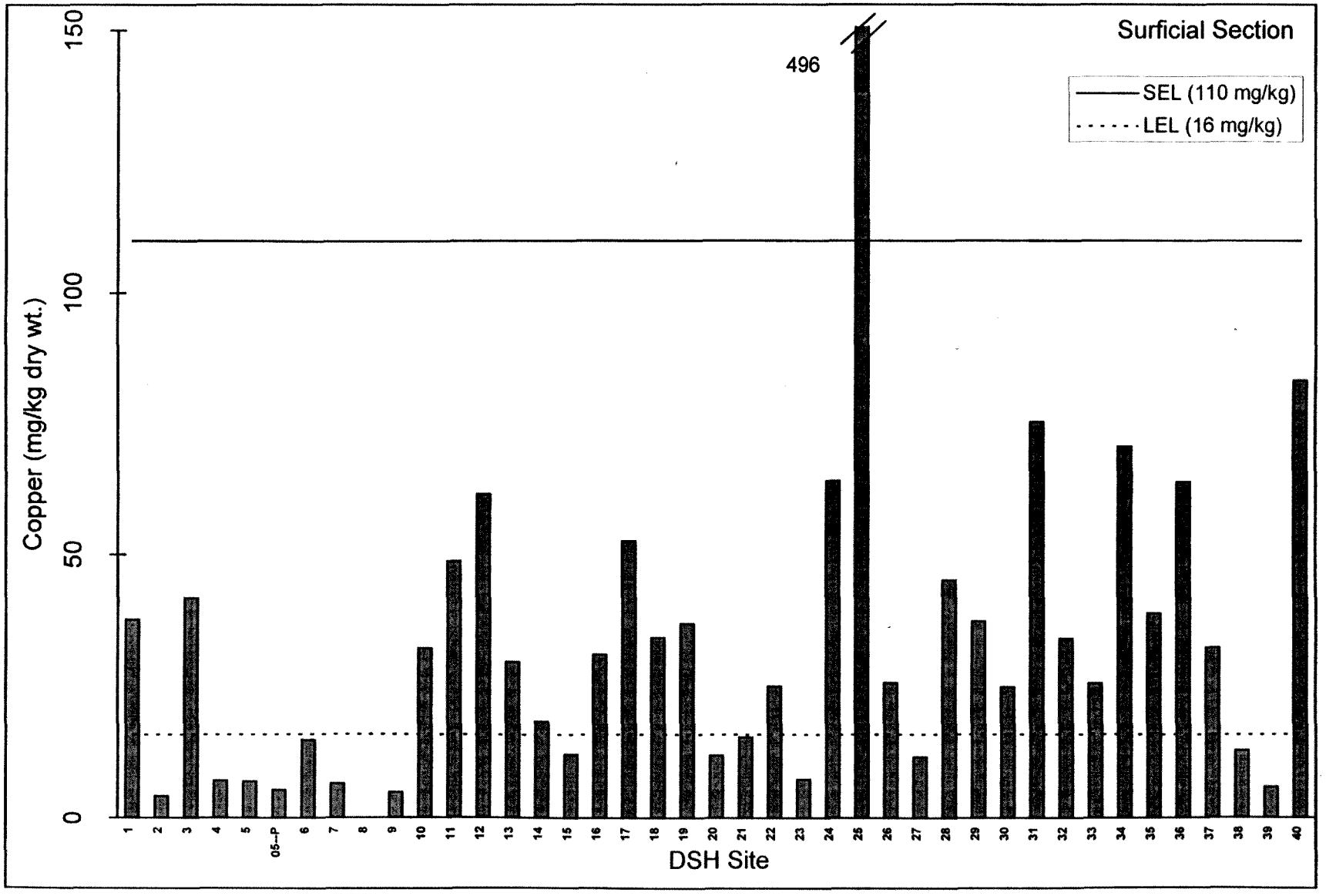

Figure 3-10. Distribution of surficial copper at the sample sites.

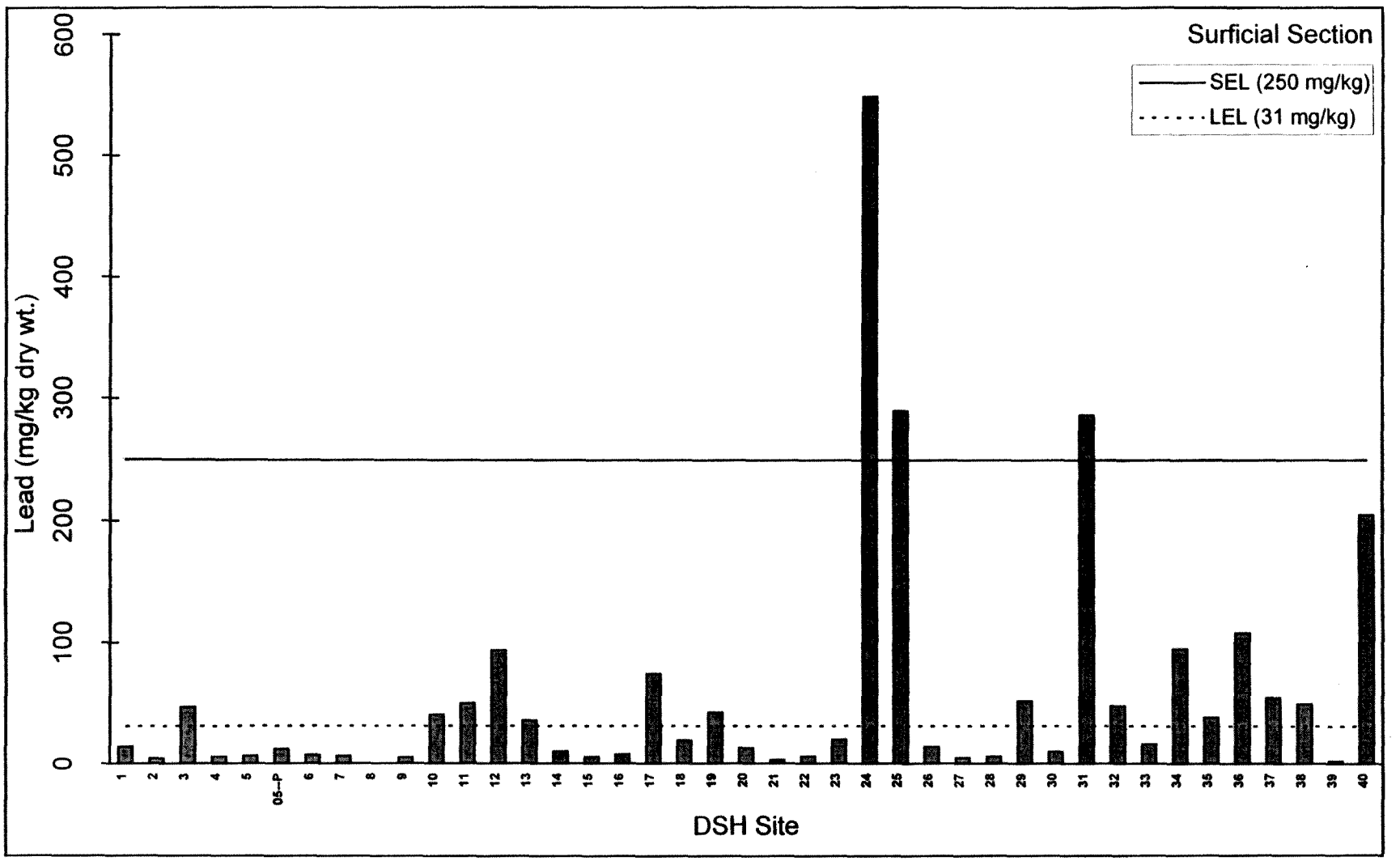

Figure 3-11. Distribution of surficial lead at the sample sites.

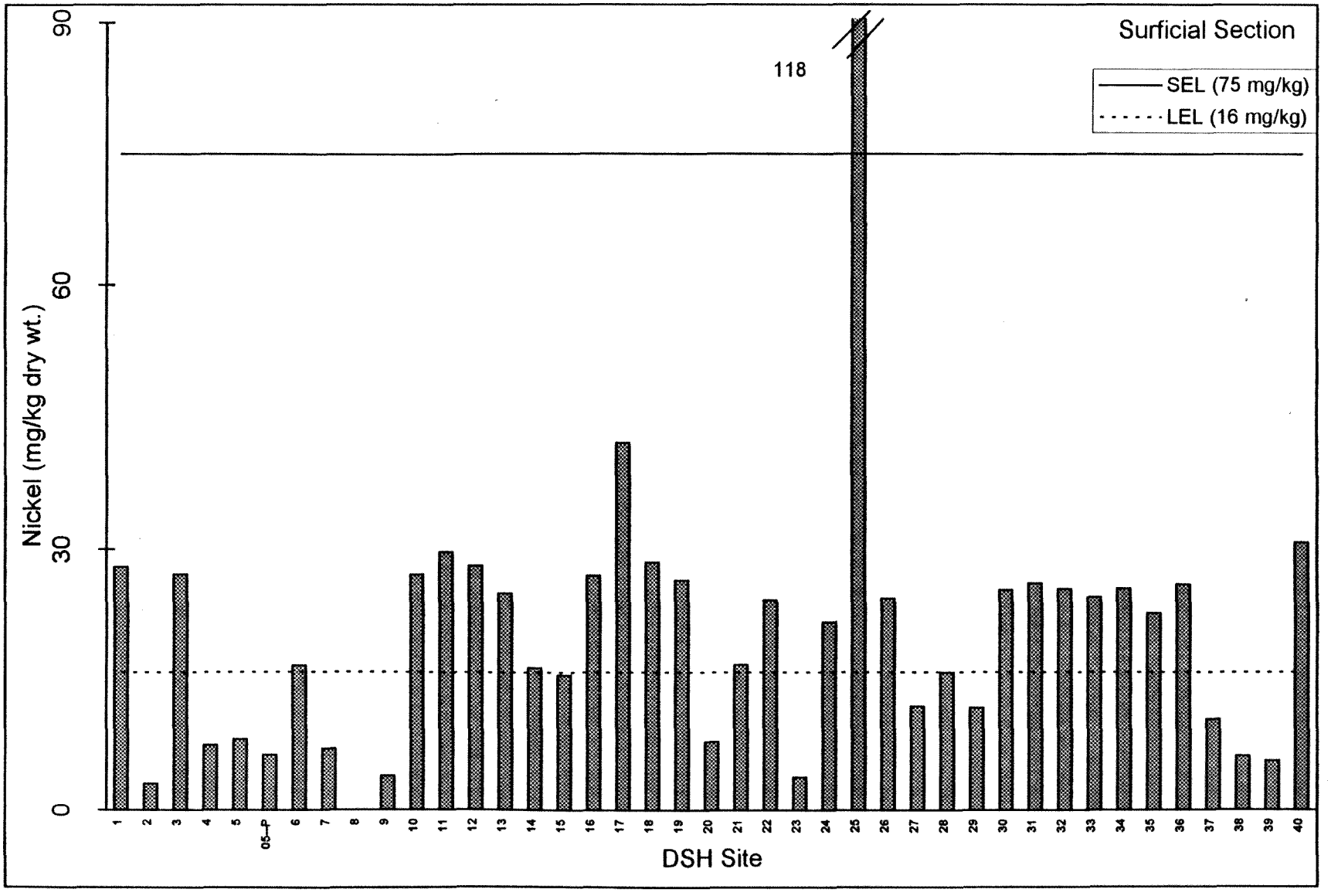

Figure 3-12. Distribution of surficial nickel at the sample sites.

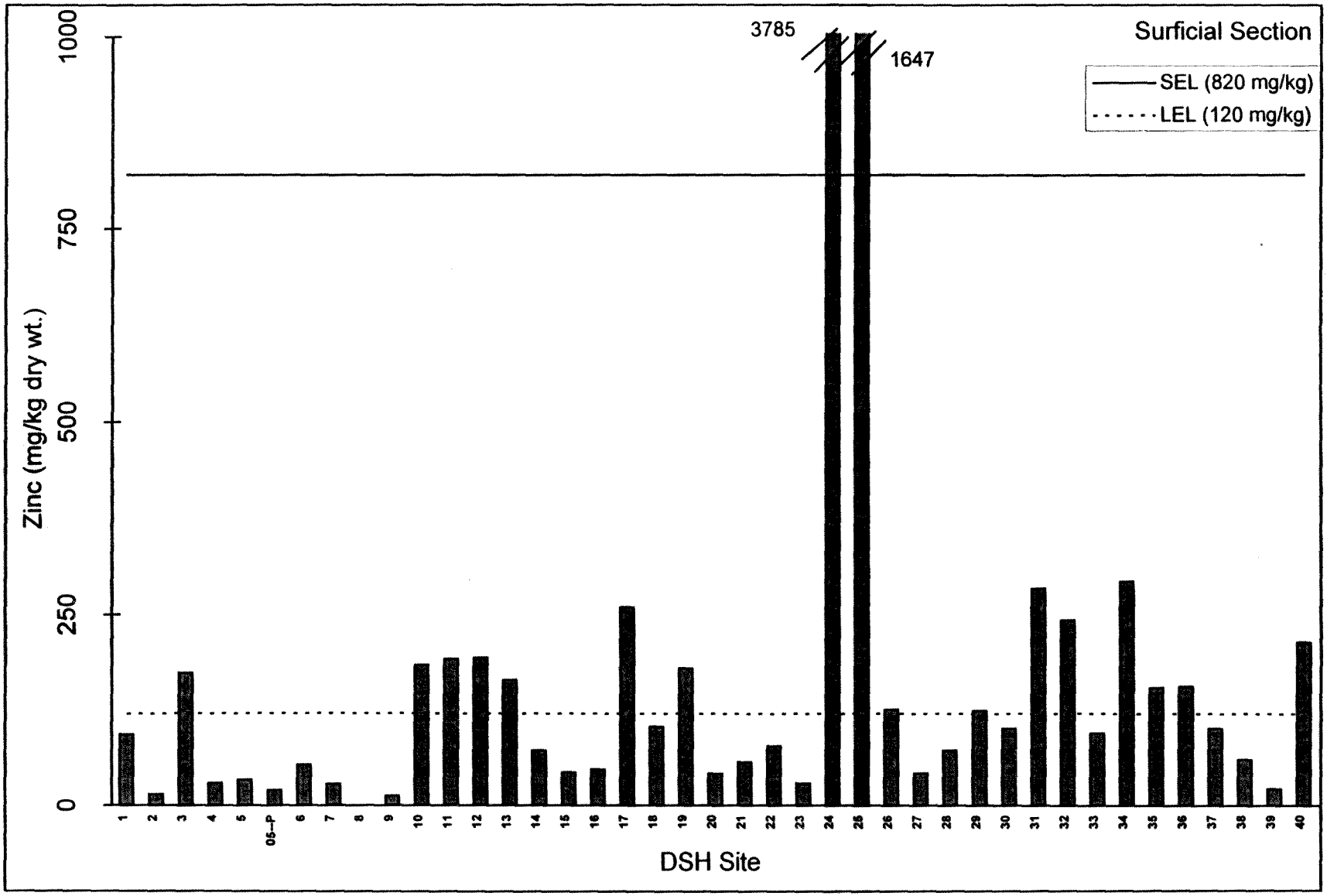

Figure 3-13. Distribution of surficial zinc at the sample sites.

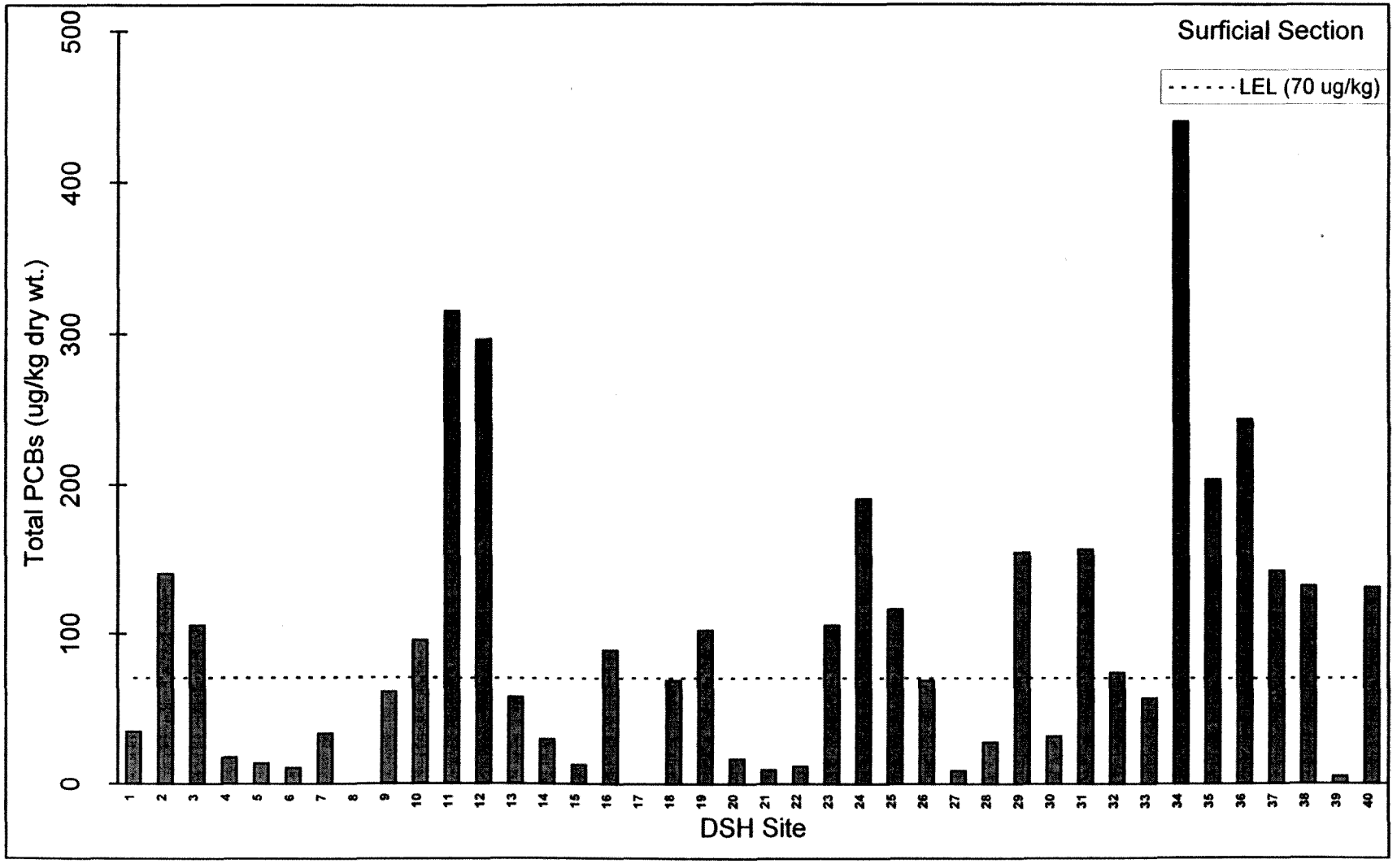

Figure 3-14. Distribution of surficial, total PCBs at the sample sites.

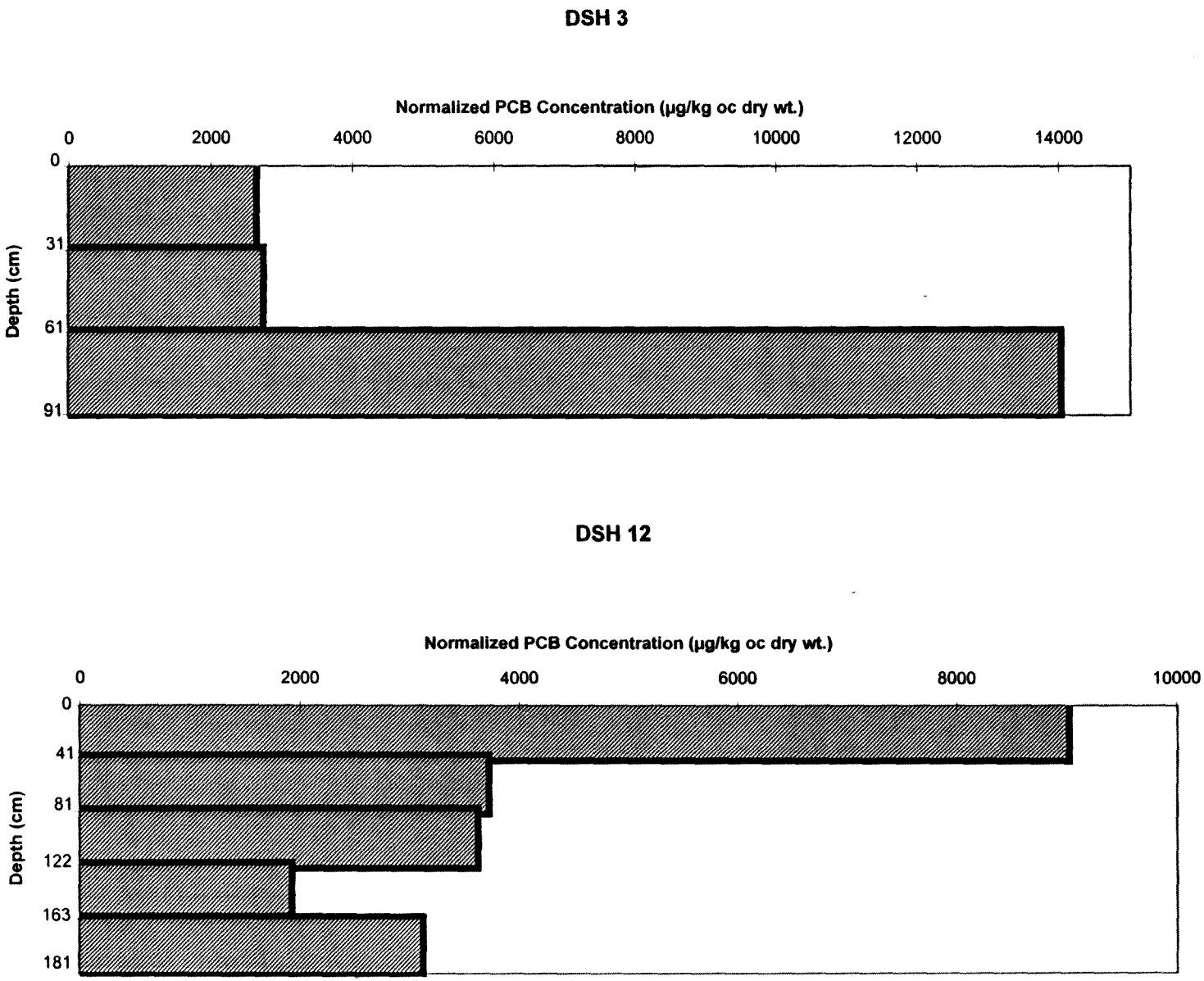

Figure 3-15. Depth profile of normalized, total PCBs at sites DSH 03 and DSH 12.

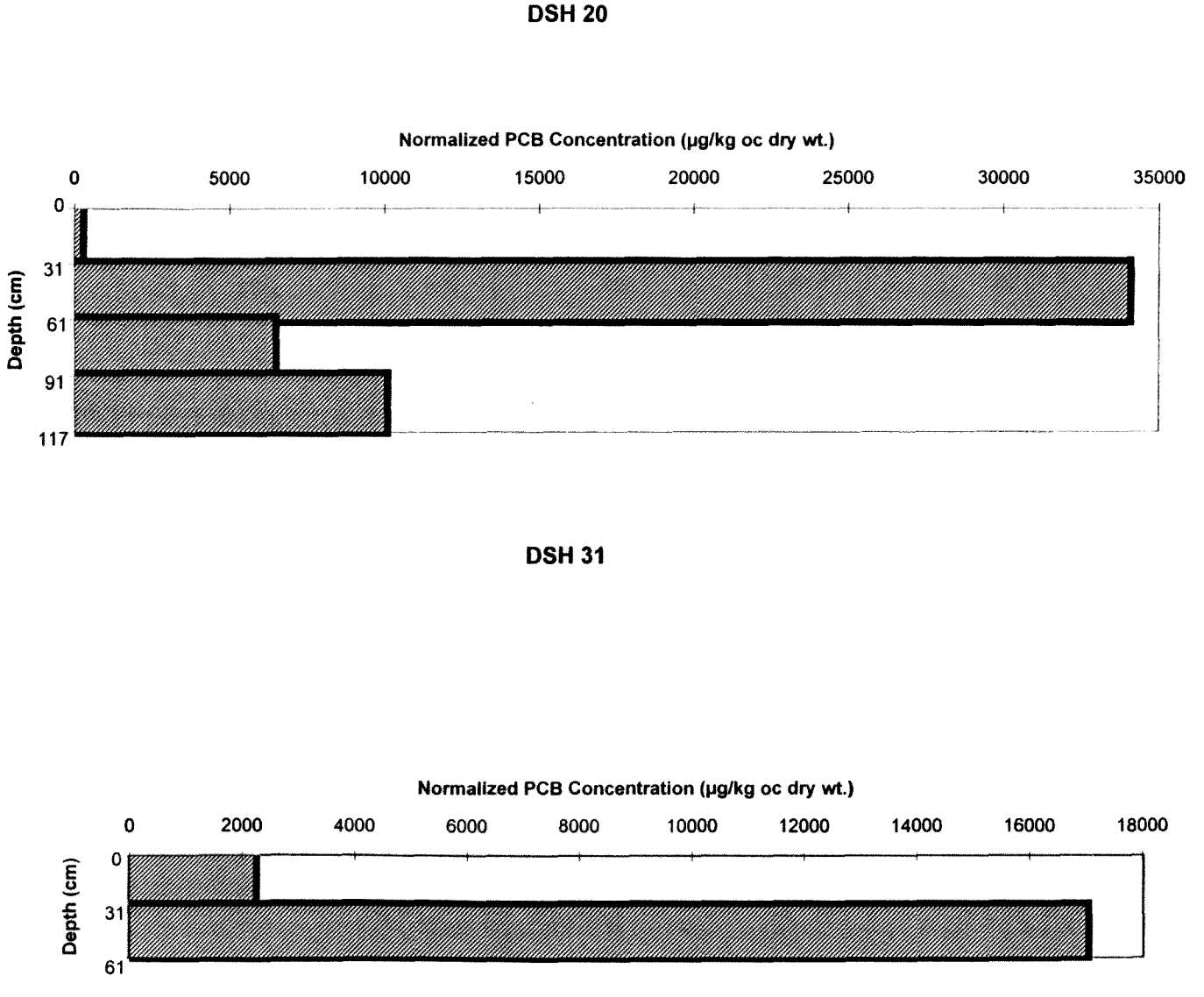

Figure 3-16. Depth profile of normalized, total PCBs at sites DSH 20 and DSH 31.

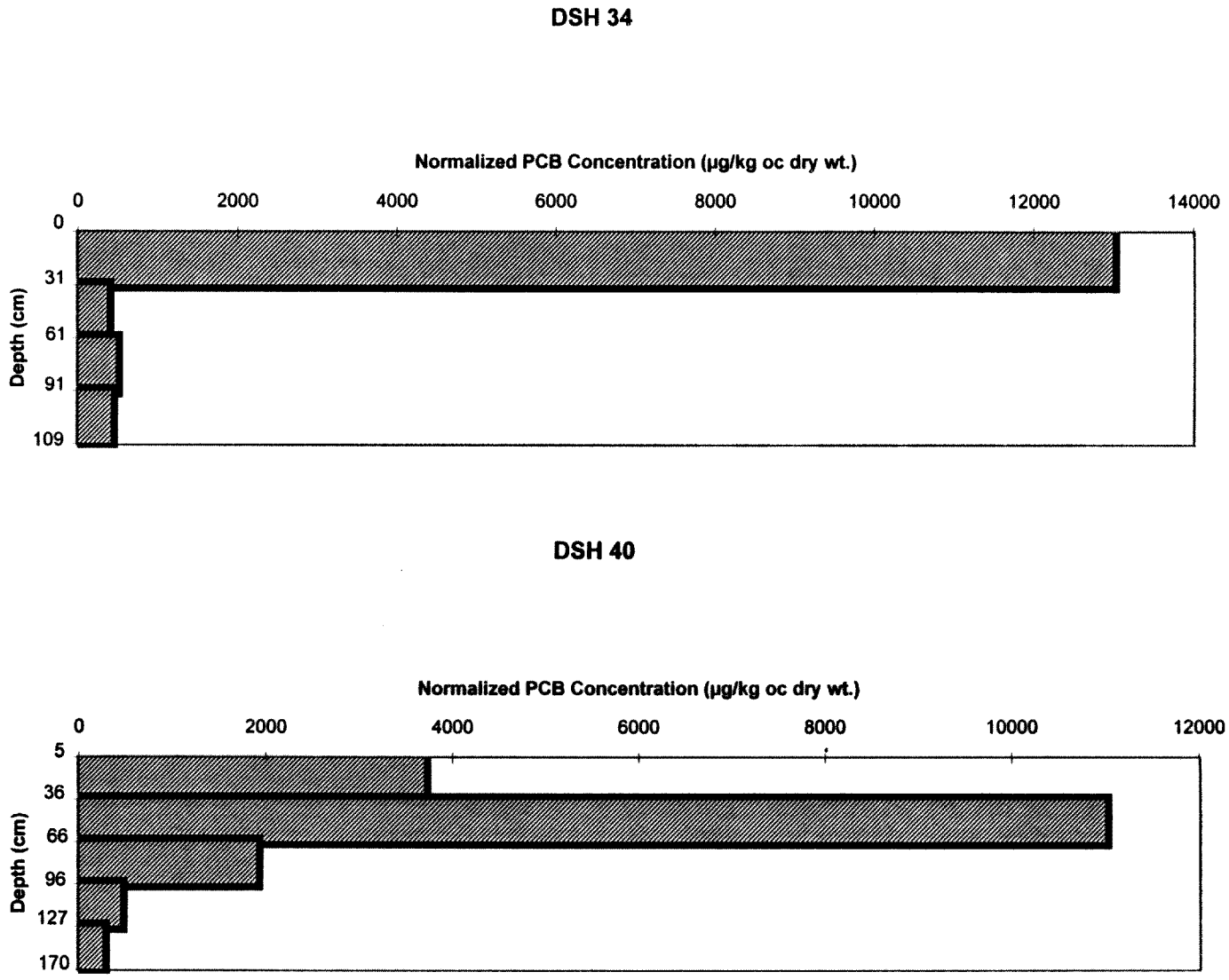

Figure 3-17. Depth profile of normalized, total PCBs at sites DSH 34 and DSH 40.

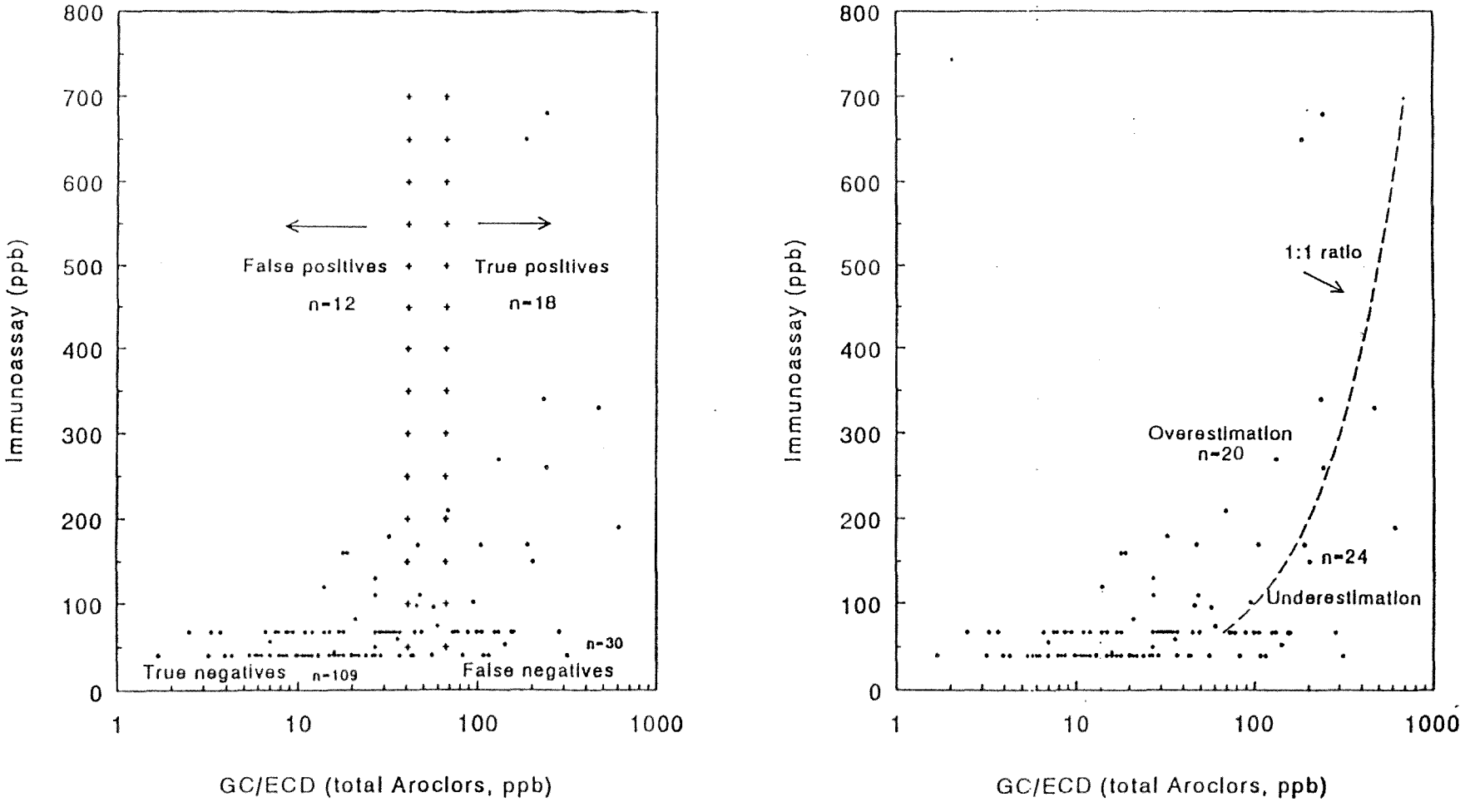

Figure 3-18. Relationship between PCB immunoassay and GC/ECD method. Chart on left shows screening veracity of the immunoassay method, showing number of false positive, true positive, false negative and true negative results; vertical "+" bars indicate the two detection limits of the immunoassay method. Chart on right shows the quantitation accuracy of the immunoassay method; the dashed line indicates perfect concordance between the methods.

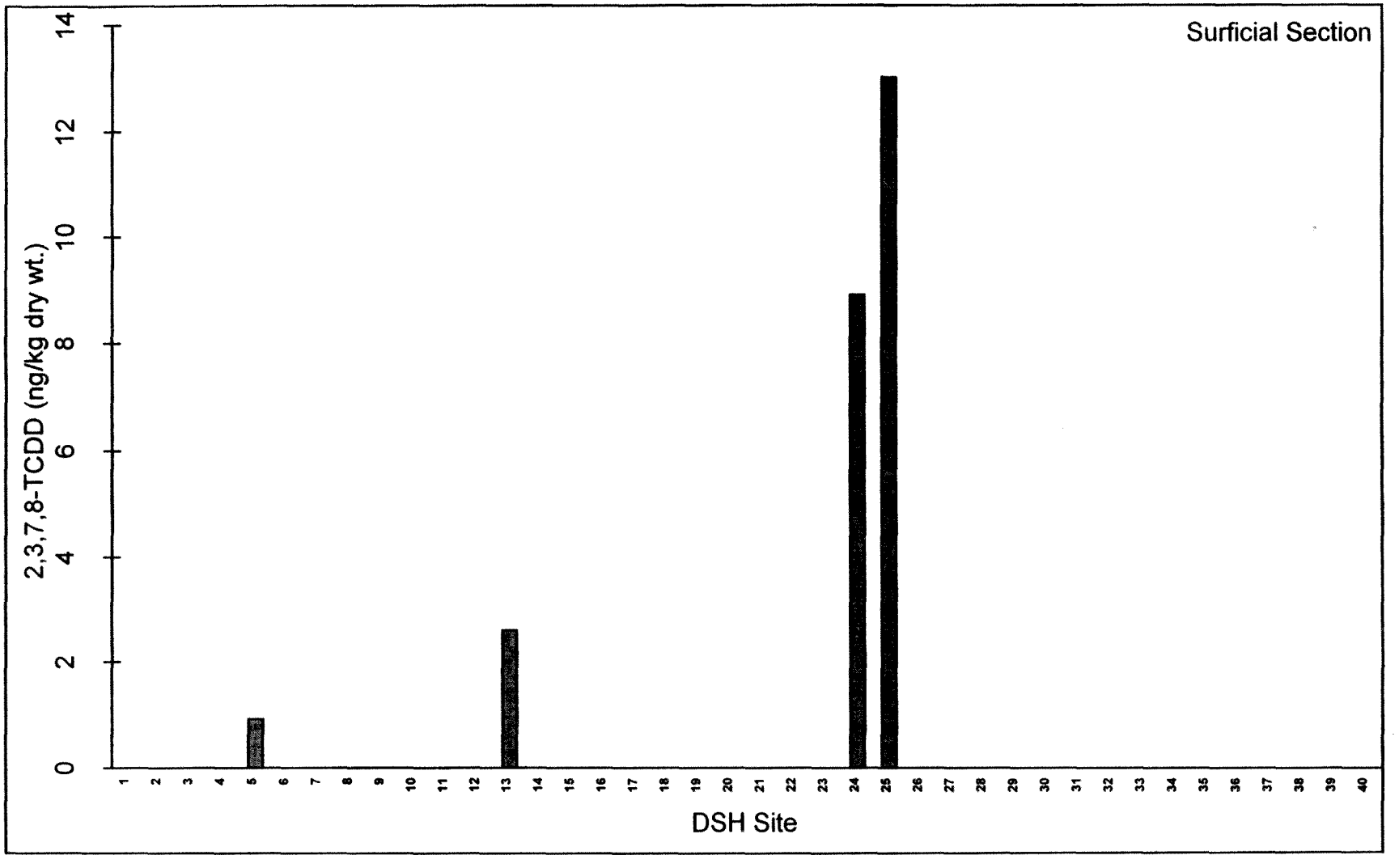

Figure 3-19. Distribution of surficial 2,3,7,8-TCDD at the sample sites.

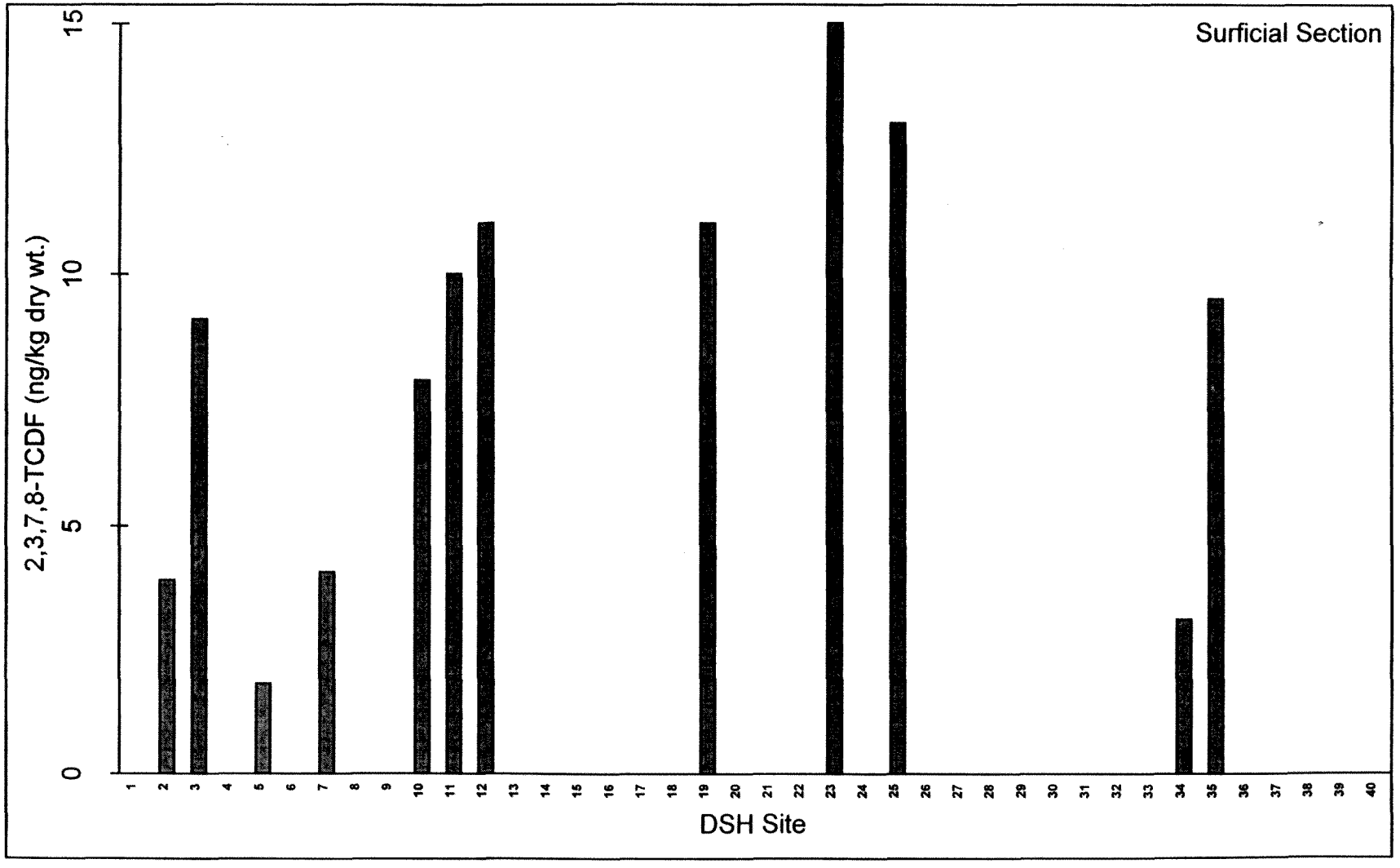

Figure 3-20. Distribution of surficial 2,3,7,8-TCDF at the sample sites.

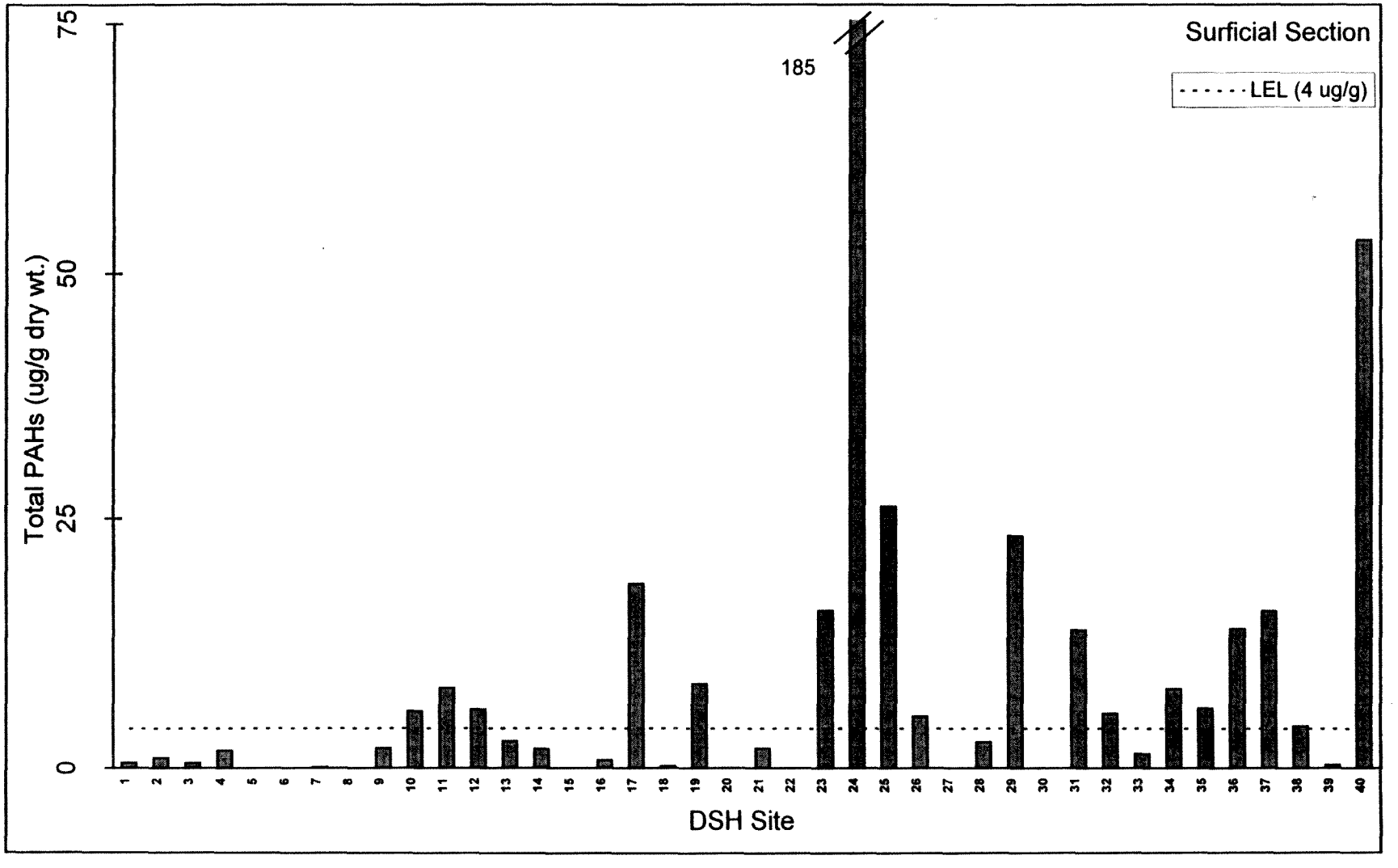

Figure 3-21. Distribution of surficial, total PAHs at the sample sites.

Table 3-1. Approximate location of sites and depth of vibracore sections analyzed.

Site	Date	Latitude	Longitude	Core Depth (cm)	Sections Analyzed (in cm)				
					1	2	3	4	5
DSH 01	9/21/93	46°41.618'N	92°01.130'W	170	0-31	31-61	61-91	91-122	122-152
DSH 02	9/21/93	46°42.870'N	92°03.225'W	0	NC[1]	NC	NC	NC	NC
DSH 03	9/22/93	46°43.545'N	92°03.982'W	155	0-31	31-61	61-91	NC	NC
DSH 04	9/22/93	46°44.041'N	92°03.456'W	244	0-31	31-61	61-91	91-122	169-198
DSH 05	9/22/93	46°44.081'N	92°04.562'W	31	0-31	NC	NC	NC	NC
DSH 06	9/22/93	46°44.447'N	92°05.130'W	102	0-31	31-61	61-90	NC	NC
DSH 07	9/21/93	46°45.451'N	92°05.296'W	91	0-31	31-61	NC	NC	NC
DSH 08	9/13/93	46°46.467'N	92°05.574'W	0	NC	NC	NC	NC	NC
DSH 09	9/24/93	46°44.431'N	92°06.142'W	71	0-31	31-61	NC	NC	NC
DSH 10	9/24/93	46°44.870'N	92°06.882'W	183	0-31	31-61	61-91	91-122	122-152
DSH 11	9/24/93	46°45.427'N	92°07.189'W	112	0-31	31-61	61-91	91-112	NC
DSH 12	9/13/93	46°45.545'N	92°07.041'W	206	0-41	41-81	81-122	122-163	163-180
DSH 13	9/23/93	46°45.028'N	92°07.669'W	234	0-31	31-61	61-91	91-122	203-234
DSH 14	9/14/93	46°44.675'N	92°08.178'W	152	0-30	30-61	61-91	91-122	122-152
DSH 15	9/24/93	46°44.228'N	92°07.651'W	211	0-31	31-61	61-91	91-122	167-183
DSH 16	9/14/93	46°44.228'N	92°09.024'W	163	0-20	20-51	51-81	81-122	122-152
DSH 17	9/23/93	46°44.041'N	92°09.089'W	102	0-31	31-61	61-91	NC	NC
DSH 18	9/21/93	46°42.240'N	92°01.864'W	173	0-31	31-61	61-91	91-122	122-152
DSH 19	9/23/93	46°43.415'N	92°09.473'W	231	0-31	31-61	61-91	91-122	198-229
DSH 20	9/27/93	46°45.650'N	92°04.970'W	137	0-31	31-61	61-91	91-117	NC

[1]NC: not able to be collected due to unsuitable substrate

Table 3-1. Continued.

Site	Date	Latitude	Longitude	Core Depth (cm)	Sections Analyzed (in cm)				
					1	2	3	4	5
DSH 21	9/17/93	46°43.106'N	92°10.367'W	76	0-31	31-61	61-76	NC	NC
DSH 22	9/17/93	46°43.016'N	92°10.237'W	191	0-31	31-61	61-76	91-122	145-175
DSH 23	9/17/93	46°42.626'N	92°11.663'W	163	0-31	31-61	61-91	91-122	122-152
DSH 24	9/23/93	46°41.285'N	92°12.166'W	147	0-31	31-61	61-91	91-122	NC
DSH 25	9/23/93	46°40.659'N	92°12.059'W	145	0-31	31-61	61-91	91-122	NC
DSH 26	9/20/93	46°39.764'N	92°12.459'W	122	0-31	31-61	61-91	NC	NC
DSH 27	9/23/93	46°42.415'N	92°09.450'W	244	0-31	31-61	61-91	91-122	198-229
DSH 28	9/27/93	46°41.081'N	91°59.781'W	74	0-31	31-64	NC	NC	NC
DSH 29	9/14/93	46°46.285'N	92°06.592'W	168	5-36	36-66	66-96	96-127	127-157
DSH 30	9/20/93	46°39.024'N	92°13.176'W	170	0-31	31-61	61-91	91-122	122-152
DSH 31	9/24/93	46°44.191'N	92°05.450'W	56	0-31	31-51	NC	NC	NC
DSH 32	9/24/93	46°44.289'N	92°05.361'W	137	0-31	31-61	61-91	91-122	NC
DSH 33	9/27/93	46°45.309'N	92°07.254'W	178	0-31	31-61	61-91	91-122	122-152
DSH 34	9/27/93	46°45.443'N	92°07.112'W	125	0-31	31-61	61-91	91-109	NC
DSH 35	9/27/93	46°45.524'N	92°06.822'W	152	0-31	31-61	61-91	91-122	122-137
DSH 36	9/27/93	46°45.809'N	92°07.225'W	231	0-31	31-61	61-91	91-122	185-216
DSH 37	9/28/93	46°46.301'N	92°06.556'W	94	0-31	31-61	61-74	NC	NC
DSH 38	9/28/93	46°46.362'N	92°06.444'W	117	0-31	31-61	61-91	NC	NC
DSH 39	9/28/93	46°46.402'N	92°06.379'W	137	0-31	31-61	61-91	91-122	NC
DSH 40	9/14/93	46°47.008'N	92°05.840'W	198	5-36	36-66	66-96	96-127	140-170

[1]NC: not able to be collected due to unsuitable substrate

Table 3-2. Water depth sampled and sediment core length.

Site	Water depth (m)	Core displacement (cm)	Core length (cm)	Retrieved Length (% of penetration depth)
DSH 01	5.49	244	170	70
DSH 02	3.33	18	0	0
DSH 03	3.81	244	155	64
DSH 04	2.93	305	244	80
DSH 05	0	61	30	49
DSH 06	0.22	152	102	67
DSH 07	8.53	189	91	48*
DSH 08	N/A	0	0	-
DSH 09	1.07	198	71	36*
DSH 10	2.13	244	183	75
DSH 11	2.44	152	112	74
DSH 12	7.92	335	206	61
DSH 13	2.29	351	234	67
DSH 14	1.52	333	152	46*
DSH 15	1.22	305	211	69
DSH 16	1.83	305	175	57
DSH 17	2.59	213	102	48*
DSH 18	7.01	274	173	63
DSH 19	2.13	231	0	0
DSH 20	2.03	229	137	60
DSH 21	2.74	292	76	26*
DSH 22	1.83	257	191	74
DSH 23	2.90	351	163	46*
DSH 24	1.37	244	147	60
DSH 25	1.68	168	145	86
DSH 26	2.74	244	122	50
DSH 27	1.98	274	244	89
DSH 28	1.98	152	74	49*
DSH 29	6.10	213	168	79
DSH 30	1.68	213	170	80
DSH 31	3.51	107	56	52
DSH 32	1.98	259	137	53
DSH 33	2.29	305	178	58
DSH 34	3.96	274	124	45*
DSH 35	2.29	213	152	71
DSH 36	1.52	305	231	76
DSH 37	5.49	305	94	31*
DSH 38	5.79	259	117	45*
DSH 39	7.62	244	137	56
DSH 40	4.88	305	198	65

* Sites with core compaction of $\geq 50\%$ of penetration depth.

Table 3-3. Physical description of Ponar grab samples.

Site	Description of Ponar grab samples
DSH 01	Silty clay with detritus, oil sheen
DSH 02	Light brown silt/sand mixture, oil sheen
DSH 03	Brown silty clay
DSH 04	Fine brown silty clay
DSH 05	Loose, silty, fibrous sand; slight sheen
DSH 06	Brown, fine sand
DSH 07	Loose, unconsolidated silt
DSH 08	Reddish sand
DSH 09	Light brown sand; some algae growth
DSH 10	Uniform, soft clayey silt
DSH 11	Odorous, mucky silt
DSH 12	Grayish-brown silt/clay; oil sheen
DSH 13	Dark brown silty clay; taconite pellets
DSH 14	Medium brown sand
DSH 15	Reddish sand with fine silt
DSH 16	Sand mixed with gritty ash particles
DSH 17	Dark brown fibrous silty sand
DSH 18	Soft, loose dark brown clay mixture
DSH 19	Dark brown sandy silt
DSH 20	Soft brown silt, slight oil sheen
DSH 21	Mostly sand
DSH 22	Soft brown silt
DSH 23	Soft brown silt/sand
DSH 24	Dark brown silt, oil sheen
DSH 25	Silt and oil mixture
DSH 26	Reddish sand, silt clay mixture
DSH 27	Medium brown soft, silty clay
DSH 28	Plant detritus with silt
DSH 29	Soft brown silt, slight oil sheen
DSH 30	Oxidized iron, very soft silt; Sulfide odor
DSH 31	Medium brown fibrous sand and gravel
DSH 32	Light brown floccy silt (2 cm) atop coarse sand
DSH 33	Clean silt overlaying thick black oil
DSH 34	Clean silt (1 cm) over thick black oil
DSH 35	Clean silt over moderate black oil
DSH 36	Silt with slight oil sheen
DSH 37	Brown silty sand with oil sheen
DSH 38	Brown sandy silt with oil
DSH 39	Reddish brown sand with oil
DSH 40	Dark brown, oily silt

Table 3-4. Physical description of sediment cores collected using the vibracorer.

Site	Depth of Visible Oil	Depth of Wood Chips	Other Comments
DSH 01	0-45 cm	None	Clay/sand
DSH 02	N/A	N/A	No vibracore collected
DSH 03	None	45-50 cm	Mostly clay
DSH 04	None	45-91 cm	Mostly sand
DSH 05	None	None	1-ft core; all sand
DSH 06	None	61-74 cm	Mostly clay
DSH 07	None	None	Mostly sand
DSH 08	N/A	N/A	No vibracore collected
DSH 09	None	51-61 cm	Sand to clay
DSH 10	None	None	Silt to clay
DSH 11	8-15 cm	93-111 cm	Silt to clay
DSH 12	0-45 cm	163-180 cm	Silt to clay
DSH 13	None	76-78 cm	Silt/sand to clay
DSH 14	None	81-91 cm	Mostly sand
DSH 15	None	122-127 cm	Sand to clay
DSH 16	None	122-127 cm	Fly ash and pulverized coal to 91 cm
DSH 17	None	41-43 cm	Black, gritty ash to 41 cm
DSH 18	91-122 cm	None	Soft, blackish clay/silt
DSH 19	None	95-105 cm	All dark brown sandy silt
DSH 20	0-5 cm	None	0-15 cm silt--remainder is sand
DSH 21	None	15-76 cm	Mostly wood chips
DSH 22	None	10-86 cm	Sand and wood chips
DSH 23	None	61-91 cm	Silt/sand and wood chips
DSH 24	0-41 cm	None	Heavy black oil on surface to clay

Table 3-4. Continued.

Site	Depth of Visible Oil	Depth of Wood Chips	Other Comments
DSH 25	0-51, 91-104 cm	51-91 cm	Heavy black oil through core
DSH 26	None	None	Silt to red clay
DSH 27	None	None	Mostly stiff gray clay
DSH 28	None	None	2-ft core; all plant detritus
DSH 29	None	61-96 cm	Silt to clay to sand; Gas bubbles.
DSH 30	None	41-91 cm	Silt to sandy clay
DSH 31	None	None	1.5-ft core; gravel to hard clay
DSH 32	None	8-31 cm	Sand to clay
DSH 33	8-15 cm	None	Silt to clay
DSH 34	0-38 cm	76-91 cm	Oily sand to clean clay
DSH 35	8-15 cm	41-71 cm	Oily silt/sand to brown clay
DSH 36	0-21, 27-43 cm	185-215 cm	Oily silt/clay to sawdust to fibers
DSH 37	0-41 cm	51-61 cm	Oily silt to red sand
DSH 38	0-68 cm	31-45 cm	Heavy oil; sandy; coal chunks
DSH 39	0-2 cm	None	Oil to reddish sand
DSH 40	5-36, 96-127 cm	None	Oil to clean silt to oil

Table 3-5. KCl-extractable and porewater ammonia concentrations in surficial (approximately 0-30 cm) sediments from the Duluth/Superior Harbor.

Site	KCl-Extractable Ammonia Concentration mg/kg dry wt.	Porewater Ammonia Concentration mg/L
DSH 01	71.3	3.38
DSH 02	7.71	2.82
DSH 03	81.2	2.92
DSH 04	41.0	2.51
DSH 05	18.2	0.91
DSH 05-P	8.90	--
DSH 06	20.5[1]	7.87
DSH 07	14.6	8.47
DSH 08	--	--
DSH 09	13.7	1.89
DSH 10	60.9	2.74
DSH 11	110	--
DSH 12	194	2.63
DSH 13	48.0	--
DSH 14	31.4[1]	5.63
DSH 15	9.07	3.28
DSH 16	37.8	2.20
DSH 17	24.4	0.50
DSH 18	135	1.74
DSH 19	59.4	2.08
DSH 20	12.3	1.34
DSH 21	33.6	0.81
DSH 22	25.2	1.64
DSH 23	89.8	2.12
DSH 24	59.0	1.15
DSH 25	31.4[1]	2.72
DSH 26	20.1	9.54
DSH 27	10.7	3.32
DSH 28	60.1	--
DSH 29	200	9.24

[1]Mean of two replicates

Table 3-5. Continued.

Site	KCl-Extractable Ammonia Concentration mg/kg dry wt.	Porewater Ammonia Concentration mg/L
DSH 30	22.6	3.59
DSH 31	57.2	6.87
DSH 32	46.2	5.99
DSH 33	36.7	5.94
DSH 34	190	11.4
DSH 35	62.4[1]	4.72
DSH 36	83.1	5.54
DSH 37	56.0	7.52
DSH 38	32.9	2.55
DSH 39	6.83	0.79
DSH 40	116	15.6

[1]Mean of two replicates

Table 3-6. TOC concentrations in sediment cores from the Duluth/Superior Harbor. Core sections are listed in order from the surface to bottom. Table 3-1 gives the sampling depths associated with each numbered core section.

Site	TOC (percent dry wt.) in each Core Section				
	1	2	3	4	5
DSH 01	5.36	4.15	8.37	8.56	5.86
DSH 02	1.09				
DSH 03	3.96[1]	0.63	0.19	NO[2]	NO
DSH 04	4.21	9.37[1]	5.23	0.08	0.14
DSH 05	1.04	Ponar--1.27[1]	NO	NO	NO
DSH 06	2.55	1.23	1.55	NO	NO
DSH 07	0.40[1]	0.07	NO	NO	NO
DSH 08	NO	NO	NO	NO	NO
DSH 09	1.05	1.42	NO	NO	NO
DSH 10	4.08	1.19	1.07	0.95	1.37
DSH 11	5.02	4.78[1]	5.00	11.16	NO
DSH 12	3.29	2.67	3.49[1]	4.00[1]	5.06
DSH 13	3.16	3.09	1.64	1.86	1.35
DSH 14	2.40	1.00	0.33	0.90	0.58
DSH 15	0.49	1.27	1.04	1.68	1.39
DSH 16	39.80	25.77	19.16	9.42[1]	2.09
DSH 17	8.86	1.11	2.17	NO	NO
DSH 18	1.98	1.92	1.72	2.17	2.03[1]
DSH 19	16.10	26.30	13.76	8.54	0.89
DSH 20	7.89	0.08	0.09	0.08	NO
DSH 21	1.53[1]	1.60	NO	NO	NO
DSH 22	10.15	20.20[1]	1.89	0.28	0.64
DSH 23	5.27	6.57	3.70	4.13	5.90
DSH 24	5.56	3.25	2.42	1.09[1]	NO
DSH 25	5.23	7.88	10.37[1]	8.61	NO
DSH 26	3.49[1]	3.33[1]	2.34[1]	NO	NO
DSH 27	1.29	3.01	2.84	3.78	2.16
DSH 28	22.68	33.73	NO	NO	NO
DSH 29	5.26	8.96	7.66	3.79	4.87
DSH 30	2.98	2.49	1.65	1.57	1.29
DSH 31	7.13	0.46	NO	NO	NO
DSH 32	2.91	3.93	1.66	1.73[1]	NO
DSH 33	3.15[1]	3.02	3.48	2.59	2.26[1]
DSH 34	3.38	5.47[1]	4.97	4.94	NO
DSH 35	4.03	3.43	2.28	4.73	3.83
DSH 36	2.84	4.16	5.42	4.02	7.31
DSH 37	5.08	2.73	2.06	NO	NO
DSH 38	1.65	3.20	1.01	NO	NO
DSH 39	0.10	0.12	0.18[1]	0.09	NO
DSH 40	3.58[1]	5.72[1]	8.29[1]	6.84[1]	2.96[1]

[1]Mean of at least 2 replicate analyses; [2]NO = section not obtained

Table 3-7. Mercury concentrations in sediment cores from the Duluth/Superior Harbor. Core sections are listed in order from the surface to bottom. Table 3-1 gives the sampling depths associated with each numbered core section.

Site	Mercury Concentration (mg/kg dry wt.) in each Core Section				
	1	2	3	4	5
DSH 01	0.102	0.091	0.164	0.131	0.110
DSH 02	0.129	NO[1]	NO	NO	NO
DSH 03	0.513	0.176	<0.001	NO	NO
DSH 04	0.162	LOST	0.017	0.005	0.002
DSH 05	0.045	0.040	NO	NO	NO
DSH 06	0.045	0.022	0.019	NO	NO
DSH 07	0.054	0.004	NO	NO	NO
DSH 08	NO	NO	NO	NO	NO
DSH 09	0.117	0.009	NO	NO	NO
DSH 10	0.331	0.031	0.019	NO	NO
DSH 11	0.838	0.068	0.060	0.060	NO
DSH 12	0.544	0.270	0.307	0.232	0.592
DSH 13	0.375	0.092	0.026	0.032	0.014
DSH 14	0.080	0.016	0.083	0.012	0.017
DSH 15	0.217	0.020	0.020	0.020	0.018
DSH 16	0.152	0.237	0.159	0.316	0.034
DSH 17	0.457	0.043	0.014	NO	NO
DSH 18	0.102	0.214	0.160	0.131	0.168
DSH 19	0.260	0.373	0.164	0.091	0.006
DSH 20	0.124	0.020	0.001	0.005	NO
DSH 21	0.028	0.020	NO	NO	NO
DSH 22	0.039	0.045	0.007	0.016	0.010
DSH 23	0.414	0.190	0.121	0.071	0.062
DSH 24	0.706	0.125	0.040	0.024	NO
DSH 25	0.427	0.652	0.041	0.043	NO
DSH 26	0.274	0.192	0.049	NO	NO
DSH 27	0.012	0.152	0.041	0.051	0.045
DSH 28	0.054	0.063	NO	NO	NO

[1]NO: Section not obtained during coring

Table 3-7. Continued

Site	Mercury Concentration (mg/kg dry wt.) in each Core Section				
	1	2	3	4	5
DSH 29	0.227	0.393	0.298	0.219	0.354
DSH 30	0.231	0.036	0.017	0.015	0.014
DSH 31	0.327	0.047	NO	NO	NO
DSH 32	0.286	0.516	0.049	0.013	NO
DSH 33	0.198	0.053	0.065	0.033	0.028
DSH 34	2.267	0.419	0.098	0.048	NO
DSH 35	0.720	0.115	0.038	0.054	0.038
DSH 36	0.410	0.170	0.164	0.215	1.333
DSH 37	0.449	0.444	0.456	NO	NO
DSH 38	0.086	0.436	0.112	NO	NO
DSH 39	0.005	0.003	0.007	0.003	NO
DSH 40	0.219	0.532	1.330	1.600	0.809

[1]NO: Section not obtained during coring

Table 3-8. Heavy metal concentrations in surficial sections (0-30 cm) of sediment cores from the Duluth/Superior Harbor, measured by cold vapor atomic absorption spectroscopy. All concentrations are expressed as dry weight, in mg/kg (ppm).

Site	As	Pb	Cu	Cr	Cd	Ni	Zn
DSH 01	23.7	13.7	37.6	49.9	1.84	27.9	91.9
DSH 02	ND[1]	3.65	4.11	5.48	0.68	3.01	13.7
DSH 03	10.6	46.1	41.6	51.5	2.18	27.1	172
DSH 04	ND	4.89	7.11	13.8	1.24	7.51	28.4
DSH 05	0.7	5.88	6.92	14.4	0.52	8.19	32.3
DSH 05--P	ND	11.4	5.31	8.17	1.31	6.37	18.8
DSH 06	3.3	6.41	14.8	29.6	1.48	16.7	51.8
DSH 07	ND	5.53	6.45	12.4	1.11	7.05	26.7
DSH 08	NO	NO	NO	NO	NO	NO	NO
DSH 09	ND	4.28	4.76	5.71	1.09	3.90	11.4
DSH 10	17.2[2]	39.6[2]	32.2[2]	53.7[2]	2.86[2]	27.1[2]	183[2]
DSH 11	16.8	49.2	48.7	58.4	3.80	29.6	192
DSH 12	11.8	93.3	61.4	54.0	2.62	28.1	193
DSH 13	11.4	34.9	29.7	49.9	2.41	25.0	164
DSH 14	2.5	9.23	18.3	30.4	1.12	16.5	70.3
DSH 15	0.7	4.84	12.1	30.5	2.03	15.6	41.6
DSH 16	14.1	6.81	31.1	30.6	3.02	27.0	45.5
DSH 17	23.3	73.8	52.5	62.8	3.66	42.0	260
DSH 18	21.3	18.6	34.2	55.2	2.95	28.4	102
DSH 19	6.8	41.7	36.9	43.7	4.56	26.4	180
DSH 20	ND[2]	12.3	11.9	15.0	1.50	7.90	40.1
DSH 21	4.8	2.47	15.3	34.6	1.93	16.8	55.3
DSH 22	7.3	5.11	25.1	37.2	1.49	24.2	76.2
DSH 23	ND	19.2	7.31	8.46	0.92	3.77	27.7
DSH 24	33.5	548	63.9	53.5	7.43	21.6	3780
DSH 25	20.2	289	495	93.8	5.53	118	1650
DSH 26	8.7	13.3	25.7	42.9	2.92	24.3	124
DSH 27	ND	4.11	11.6	25.0	1.12	12.0	40.7
DSH 28	11.9	5.26	45.0	40.9	2.16	15.9	70.8
DSH 29	1.4	51.1	37.3	20.9	2.39	11.8	123
DSH 30	4.2	9.37[2]	24.9[2]	40.7[2]	1.79[2]	25.3[2]	99.4[2]

[1]ND; Not detected

[2]Mean of at least 2 replicate analyses

Table 3-8. Continued.

Site	As	Pb	Cu	Cr	Cd	Ni	Zn
DSH 31	6.0	286	75.2	53.3	3.05	26.1	285
DSH 32	11.5	47.1	34.1	41.8	2.07	25.4	243
DSH 33	6.2	15.5	25.6	38.0	1.74	24.5	93.1
DSH 34	0.4	94.2	70.4	45.3	4.09	25.5	294
DSH 35	5.2	37.6	38.8	43.4	3.59	22.7	153
DSH 36	5.8	107	63.7	43.0	3.09	25.9	155
DSH 37	1.0	54.1	32.4	19.0	1.94	10.5	99.4
DSH 38	0.8	48.9	12.9	9.68	0.92	6.23	58.8
DSH 39	ND	1.50	5.78	15.0	1.04	5.66	20.8
DSH 40	3.4[2]	205	83.2[2]	49.8[2]	2.65[2]	30.7[2]	214[2]
Mean	**9.6**	**58.2**	**42.3**	**35.8**	**2.4**	**21.4**	**240**
SD	**8.3**	**105**	**76.6**	**19.4**	**1.4**	**18.3**	**629**
Median	**6.8**	**15.5**	**29.7**	**38.0**	**2.0**	**22.7**	**93.1**
Minimum	**0.4**	**1.5**	**4.1**	**5.5**	**0.52**	**3.0**	**11.4**
Maximum	**33.5**	**548**	**496**	**93.8**	**7.4**	**118**	**3780**

[1]ND; Not detected
[2]Mean of at least 2 replicate analyses

Table 3-9. X-Ray fluorescence determination of metals concentrations (mg/kg dry wt.) from selected sites and core depths.

SAMPLE #	Cd	Ni	Cu	Pb	Hg	Zn	As
DSH 05-01	ND	<15	15.9	17.0	ND	39.9	<3.43
DSH 05-P	<2	16.9	19.1	12.0	<4	52.9	4.53
DSH 11-01	2.91	37.4	53.9	59.0	<4	242	<5.47
DSH 11-02	<2	32.4	30.2	<5	ND	90.5	9.54
DSH 11-03	ND	36.3	33.7	12.5	ND	94.3	<3.62
DSH 11-04	ND	32.6	24.9	<5	ND	107	5.39
DSH 17-01	ND	41.7	66.5	82.7	ND	326	12.6
DSH 17-02	ND	<15	16.3	12.1	ND	34.5	ND
DSH 17-03	4.07	22.3	19.3	13.3	ND	24.1	ND
DSH 22-02	<2	31.9	34.2	17.4	ND	67.2	<3.54
DSH 22-03	ND	<15	20.0	15.1	<4	30.0	ND
DSH 22-04	ND	17.5	20.9	9.17	ND	26.8	ND
DSH 22-05	<2	19.0	18.8	9.92	ND	28.2	3.66
DSH 24-01	<2	ND	74.8	446	ND	1630	109
DSH 24-02	2.06	ND	25.0	59.3	ND	220	<5.44
DSH 24-03	<2	15.0	35.6	9.38	<4	71.6	4.52
DSH 24-04	<2	17.9	18.0	6.63	ND	47.3	5.62
DSH 27-01	<2	<15	16.5	<5	ND	38.6	6.12
DSH 27-02	ND	<15	31.1	27.1	ND	130	<4.05
DSH 27-03	ND	36.5	25.6	8.04	<4	75.9	<3.28
DSH 27-04	<2	33.1	25.3	15.3	ND	93.4	<4.67
DSH 27-05	ND	30.2	19.3	9.76	ND	89.0	5.02
DSH 32-02	<2	34.8	55.7	94.1	<4	192	ND
DSH 32-03	ND	21.2	22.3	17.7	<4	41.1	3.80
DSH 36-01	4.02	41.2	81.8	119	<4	190	ND
DSH 36-02	4.59	32.0	52.2	54.9	ND	125	<5.07
DSH 36-03	ND	18.6	42.9	22.6	ND	115	4.39
DSH 36-04	<2	<15	42.0	24.9	ND	101	5.73

Table 3-10. Comparison of metal determinations made by atomic absorption spectroscopy (AAS) vs. x-ray fluorimetry (XRF), in surficial (<30 cm) sediments of the Duluth/Superior Harbor. The relative percent difference (RPD) of the measurements is given for each sample and metal. All concentrations are in mg/kg dry wt.

Site	As	Cd	Ni	Cu	Pb	Hg	Zn
DSH 05-1							
(AAS)	0.7	0.52	8.19	6.92	5.88	0.045	32.3
(XRF)	<3.43	ND (2.0)	<15	15.9	17.0	N.D. (4)	39.9
RPD	**Con.[1]**	**Con.**	**Con.**	**130%**	**189%**	**Con.**	**23.5%**
DSH 05-Ponar							
(AAS)	ND	1.31	6.37	5.31	11.4	--	18.8
(XRF)	4.53	<2.0	16.9	19.1	12.0	<4	52.9
RPD	**Incon.[2]**	**Con.**	**165%**	**260%**	**5.0%**	**--**	**181%**
DSH 11-01							
(AAS)	16.8	3.80	29.6	48.7	49.2	0.838	192
(XRF)	<5.47	2.91	37.4	53.9	59.0	<4	242
RPD	**Incon.**	**-23.4%**	**26.2%**	**10.7%**	**20.0%**	**Con.**	**26.3%**
DSH 17-1							
(AAS)	23.3	3.66	42.0	52.5	73.8	0.457	260
(XRF)	12.6	ND (2.0)	41.7	66.5	82.7	N.D.	326
RPD	**-45.2%**	**Incon.**	**-0.69%**	**26.7%**	**12.0%**	**Con.**	**25.1%**
DSH 24-1							
(AAS)	33.5	7.43	21.6	63.9	548	0.706	3780
(XRF)	109	<2	ND (15)	74.8	446	N.D.	1630
RPD	**225%**	**Incon.**	**Incon.**	**17.0%**	**-18.6%**	**Con.**	**-56.9%**
DSH 27-1							
(AAS)	ND	1.12	12.0	11.6	4.11	0.012	40.7
(XRF)	6.12	<2	<15	16.5	<5	ND	38.6
RPD	**Incon.**	**Con.**	**Con.**	**42.4%**	**Con.**	**Con.**	**-5.25%**
DSH 36-1							
(AAS)	5.8	3.09	25.9	63.7	107.18	0.410	155
(XRF)	ND (5.47)	4.02	41.2	81.8	119	<4	190
RPD	**Con.**	**30.1%**	**59.0%**	**28.5%**	**11.0%**	**Con.**	**22.5%**

[1]Con.; XRF measurement was consistent with AAS measurement
[2]Incon.; XRF measurement was inconsistent with AAS measurement

Table 3-11. Total PCB concentrations in sediment cores from the Duluth/Superior Harbor. Core sections are listed in order from the surface to bottom. Table 3-1 gives the sampling depths associated with each numbered core section.

	Total PCBs (μg/kg dry wt.) in each Core Section				
Site	**1**	**2**	**3**	**4**	**5**
DSH 01	34.0	45.0	78.0	49.0	17.0
DSH 02	140	NO[1]	NO	NO	NO
DSH 03	105	17.0	27.0	NO	NO
DSH 04	17.0	7.8	12.0	2.5	3.7
DSH 05	13.0	--Ponar: 16.0	NO	NO	NO
DSH 06	10.0	7.9	11.0	NO	NO
DSH 07	32.5[2]	6.6	NO	NO	NO
DSH 08	NO	NO	NO	NO	NO
DSH 09	60.0	10.6	NO	NO	NO
DSH 10	95.0	10.0	12.0	11.0	11.0
DSH 11	315	5.4	6.3	44.0	NO
DSH 12	296	100	125	75.0	158
DSH 13	57.0	17.0	12.0	22.0	3.2
DSH 14	29.0	18.0	17.0	7.5	8.6
DSH 15	12.0	2.6	8.2	17.0	14.0
DSH 16	88.5[2]	54.0	105	29.0	14.0
DSH 17	lost	15.0	8.7	NO	NO
DSH 18	68.0	73.0	32.0	33.0	19.0
DSH 19	102	83.0	43.0	9.8	6.0
DSH 20	16.0	27.0	5.8	8.3	NO
DSH 21	8.8	30.0	NO	NO	NO
DSH 22	11.0	35.0	9.4	3.3	7.5
DSH 23	105	11.0	8.8	15.0	27.0
DSH 24	190	7.0	5.9	5.4	NO
DSH 25	116	109	19.0	18.0	NO
DSH 26	68.0	49.0	37.0	NO	NO
DSH 27	8.3	37.0	20.0	11.0	4.0
DSH 28	27.0	47.0	NO	NO	NO
DSH 29	154	470	284	106	99.0
DSH 30	31.0	17.0	11.0	14.0	15.0

[1]NO: Section not obtained during coring
[2]Mean of duplicate values

Table 3-11. Continued.

Site	Total PCBs (μg/kg dry wt.) in each Core Section				
	1	2	3	4	5
DSH 31	156	79.0	NO	NO	NO
DSH 32	73.0	26.0	13.0	16.0	NO
DSH 33	56.0	20.0	18.0	21.0	13.0
DSH 34	439	20.0	24.0	21.0	NO
DSH 35	203	14.0	12.0	10.0	10.0
DSH 36	243	242	46.0	69.0	234
DSH 37	142	36.0	48.0	NO	NO
DSH 38	132	185	20.0	NO	NO
DSH 39	4.3	11.0	6.0	7.0	NO
DSH 40	131	612	157	31.0	7.8

[1]NO: Section not obtained during coring
[2]Mean of duplicate values

Table 3-12. PCB immunoassay determinations in sediment cores from the Duluth/Superior Harbor. Core sections are listed in order from the surface to bottom. Table 3-1 gives the sampling depths associated with each numbered core section.

	Total PCBs (μg/kg dry wt.) in each Core Section				
Site	**1**	**2**	**3**	**4**	**5**
DSH 01	<67	<67	<67	<67	<67
DSH 02	<67	NO[1]	NO	NO	NO
DSH 03	170	110[2]	<40	NO	NO
DSH 04	<67	<67	<67	<67	<67
DSH 05	41[2]	--Ponar: 44[2]	NO	NO	NO
DSH 06	<40	<40	<40	NO	NO
DSH 07	180[2]	<67	NO	NO	NO
DSH 08	NO	NO	NO	NO	NO
DSH 09	74[2]	<40	NO	NO	NO
DSH 10	102[2]	<40	<40	<40	<40
DSH 11	<40	<40	<40	<40	NO
DSH 12	<67	<67	<67	<67	<67
DSH 13	96[2]	<40	<40	<40	<40
DSH 14	<67	<67	<67	<67	<67
DSH 15	<40	<40	<40	<40	<40
DSH 16	<67	<67	<67	<67	<67
DSH 17	<40	<40	<40	NO	NO
DSH 18	<67	<67	<67	<67	<67
DSH 19		<40	<40	<40	<40
DSH 20	78[2]	<40	<40	<40	NO
DSH 21	<67	<67	NO	NO	NO
DSH 22	<67	<67	<67	<67	<67
DSH 23	<67	<67	<67	<67	
DSH 24	170	56[2]	<40	<40	NO
DSH 25	<40	<40	160	160	NO
DSH 26	<67	<67	<67	NO	NO
DSH 27	<40	<40	<40	<40	<40
DSH 28	130	170	NO	NO	NO
DSH 29	<67	330	<67	<67	<67
DSH 30	<67	<67	<67	<67	<67
DSH 31			NO	NO	NO

[1]NO: Section not obtained during coring

[2]Less than method quantitation limit (estimated)

Table 3-12. Continued.

Site	Total PCBs (μg/kg dry wt.) in each Core Section				
	1	2	3	4	5
DSH 32		<40	<40	<40	NO
DSH 33	<40	<40	<40	<40	<40
DSH 34	970	50[2]	<40	82[2]	NO
DSH 35	150	120	<40	<40	<40
DSH 36	680	260	98[2]	210	340
DSH 37	53[2]	59[2]	110[2]	NO	NO
DSH 38	270	650	41[2]	NO	NO
DSH 39	<40	<40	<40	<40	NO
DSH 40	<67	190	<67	<67	<67

[1]NO: Section not obtained during coring

[2]Less than method quantitation limit (estimated)

Table 3-13. 2,3,7,8-TCDD/TCDF concentrations in surficial sediment core samples from the Duluth/Superior Harbor.

Site	TCDD (ng/kg dry wt.)	Detection Limit	TCDF (ng/kg dry wt.)	Detection Limit
DSH 01	ND[1]	1.6	NQ	1.6
DSH 02	ND	0.9	3.9	--
DSH 03	NQ	2.3	9.1	--
DSH 04	ND	1.5	ND	1.5
DSH 05	NQ	2.6	NQ	2.1
DSH 05-P	0.9	--	1.8	--
DSH 06	ND	0.9	ND	1.4
DSH 07	ND[2]	1.8	4.0[2]	--
DSH 08	NO	NO	NO	NO
DSH 09	ND	1.6	ND	1.4
DSH 10	NQ	2.5	7.9	--
DSH 11	ND	11	10	--
DSH 12	ND	1.7	11	--
DSH 13	2.6	--	NQ	17
DSH 14	ND	0.8	ND	1.9
DSH 15	ND[2]	0.6	ND[2]	0.35
DSH 16	ND	1.6	ND	3.0
DSH 17	--	--	--	--
DSH 18	NQ	17	NQ	5.6
DSH 19	ND	3.8	11	--
DSH 20	ND	2.3	ND	4.7
DSH 21	ND[2]	2.0	ND[2]	0.45
DSH 22	ND	2.2	ND	1.1
DSH 23	ND	11	15	--
DSH 24	8.9	--	NQ	2.1
DSH 25	13	--	13	--
DSH 26	NQ	4.0	NQ	7.8
DSH 27	ND	1.3	ND	1.6
DSH 28	ND	1.8	ND	4.8
DSH 29	ND	14	NQ	29
DSH 30	ND	6.2	NQ	9.0

[1]Codes: NO = Section not obtained during coring; ND = Not Detected; NQ = Not Quantified

[2]Mean of duplicate values

Table 3-13. Continued.

Site	TCDD (ng/kg dry wt.)	Detection Limit	TCDF (ng/kg dry wt.)	Detection Limit
DSH 31	ND	6.8	NQ	20
DSH 32	ND[2]	5.3	NQ[2]	2.6
DSH 33	ND	2.6	ND	7.6
DSH 34	ND	3.5	3.1	--
DSH 35	ND	6.1	9.5	--
DSH 36	NQ	62	ND	8.8
DSH 37	ND	7.4	NQ	31
DSH 38	ND	2.4	ND	2.0
DSH 39	ND	5.5	ND	1.2
DSH 40	NQ[2]	4.4	NQ[2]	7.3

[1]Codes: NO = Section not obtained during coring; ND = Not Detected; NQ = Not Quantified

[2]Mean of duplicate values

Table 3-14. Pesticide concentrations (μg/kg dry wt.) in surficial sediment core samples from the Duluth/Superior Harbor. Detection limits are given in parentheses. Any associated blank concentrations have been deducted from reported concentrations. **Boldface** concentrations exceed Lake Huron/Lake Superior background (Persaud et al., 1993). *Italicized* concentrations exceed OMOEE LEL guidelines (Persaud et al., 1993).

Core section 1

Site	HCB[1]	Lindane	Aldrin	OCS[1]	o,p'-DDE	Dieldrin	p,p'-DDE	o,p'-DDD	Endrin	p,p'-DDD & o,p'-DDT	p,p'-DDT	Chlordane	Toxaphene
DSH 01	0.04	0.07	0.13	0.07	0.11	NQ	0.84	0.32	NQ	1.90	0.17	ND (20)	ND (20)
DSH 02	0	0.01	0.05	0.02	0.06	NQ	0.63	0.34	NQ	1.42	0.20	ND (20)	ND (20)
DSH 03	0.13	0.21	ND (2.2)	ND (0.40)	0.56	NQ	**4.46**	ND (1.1)	NQ	***10.0***	0.51	ND (20)	ND (20)
DSH 04	0	0.09	0.16	0.02	0.02	NQ	0.51	0.53	NQ	2.43	0.21	ND (20)	ND (20)
DSH 05	0.03	0.01	ND (1.3)	0.05	0.08	NQ	0.21	0.16	NQ	0.45	0.04	ND (20)	ND (20)
DSH 05-P	0	0.06	0.06	0.04	0.07	NQ	0.27	0.13	NQ	0.46	0.07	ND (20)	ND (20)
DSH 06	0	0.09	ND (0.24)	0.06	0.06	NQ	0.04	0.03	NQ	0.21	0.22	ND (20)	ND (20)
DSH 07[2]	0.01	0.03	0.17	0.04	0.11	NQ	0.63	0.27	NQ	0.75	0.16	ND (20)	ND (20)
DSH 08	Core sample could not be collected												
DSH 09	0.15	ND (1.5)	0.10	0.20	0.41	0.06	1.06	0.78	ND (0.30)	4.9	ND (0.13)	ND (1.3)	ND (9.3)
DSH 10	0.35	ND (1.5)	ND (0.55)	ND (0.06)	0.29	ND (1.2)	1.7	0.97	0.28	**5.6**	ND (0.19)	ND (2.7)	ND (19)
DSH 11	0.16	ND (2.2)	ND (0.20)	ND (0.01)	1.1	***3.5***	***8.5***	3.0	ND (0.46)	***12***	0.78	ND (9.4)	113
DSH 12	0.17	ND (3.4)	ND (10.1)	ND (0.57)	0.73	0.42	***6.26***	3.6	ND (0.06)	***10.2***	0.91	ND (7.7)	ND (62.3)
DSH 13	0.32	ND (2.1)	ND (0.01)	ND (0.02)	0.31	ND (0.53)	1.8	1.0	0.33	**5.7**	ND (0.03)	ND (3.2)	ND (16)
DSH 14	0.12	ND (1.4)	0.15	ND (0.02)	0.50	0.14	0.19	0.21	0.10	1.3	ND (0.01)	ND (3.5)	ND (19)
DSH 15	0.12	ND (1.6)	0	ND (0.01)	0.08	0.06	0.09	ND (0.01)	0.07	0.25	ND (0.01)	ND (2.0)	ND (4.8)
DSH 16[2]	0.71	ND (1.8)	**1.1**	ND (0.01)	0.16	***1.0***	1.4	1.5	0.33	***8.1***	0.57	ND (10)	ND (9.7)
DSH 17	Sample could not be analyzed due to interferences												

[1]HCB = Hexachlorobenzene; OCS = Octachlorostyrene

[2]Mean of duplicate values

ND = Not Detected; NQ = Not Quantified, dieldrin and endrin were destroyed during clean-up; N/A = Not Available

Table 3-14. Continued. See previous page for a description of footnotes and codes.

Site	HCB[1]	Lindane	Aldrin	OCS[1]	o,p'-DDE	Dieldrin	p,p'-DDE	o,p'-DDD	Endrin	p,p'-DDD & o,p'-DDT	p,p'-DDT	Chlordane	Toxaphene
						Core section 1							
DSH 18	0	ND (0.09)	ND (0.44)	0.173	0.10	ND (0.09)	1.08	0.62	ND (0.15)	2.49	0.00	ND (3.3)	ND (11)
DSH 19	0.23	ND (0.80)	ND (2.6)	ND (0.59)	0.15	ND (2.0)	1.96	1.5	ND (2.6)	2.75	0.95	ND (3.0)	ND (27)
DSH 20	0.53	ND (0.91)	ND (0.78)	ND (0.49)	0.14	ND (0.34)	0.74	0.52	ND (0.70)	2.25	ND (2.9)	ND (3.4)	ND (19)
DSH 21	0	ND (2.1)	ND (0.78)	0.073	0.05	ND (0.17)	ND (0.58)	ND (0.31)	ND (0.38)	0.00	ND (0.34)	ND (3.8)	ND (15)
DSH 22	0	ND (5.6)	ND (1.2)	0.153	ND (0.60)	ND (0.95)	0.06	0.07	ND (0.57)	0.19	ND (1.8)	ND (7.3)	ND (11)
DSH 23	0.21	ND (0.16)	ND (1.7)	0.60	0.07	ND (1.08)	2.6	1.0	ND (0.11)	3.09	ND (3.0)	ND (9.6)	ND (18)
DSH 24	0.11	ND (5.0)	ND (0.06)	8.5	0.88	NQ	**3.3**	0.76	NQ	1.7	3.0	--	--
DSH 25	0.99	ND (4.8)	ND (0.21)	ND (0.10)	ND (0.5)	NQ	***12***	3.0	NQ	1.4	0.56	--	--
DSH 26	0.07	ND (0.98)	ND (5.1)	ND (3.6)	0.06	ND (0.33)	1.1	0.35	ND (0.20)	2.09	ND (1.5)	ND (12)	ND (9)
DSH 27[2]	0	ND (0.54)	0.228	0.093	0.025	ND (0.03)	0.09	ND (0.79)	ND (0.03)	0.105	ND (1.0)	ND (3.6)	ND (6.8)
DSH 28	0.23	ND (5.1)	ND (0.03)	ND (0.14)	ND (0.04)	**1.4**	0.49	0.23	ND (0.51)	0.22	0.18	ND (2.1)	ND (14)
DSH 29	0.21	ND (4.3)	ND (0.83)	2.7	0.63	**1.3**	**3.2**	2.0	ND (0.91)	**9.3**	1.2	ND (3.6)	64
DSH 30	0.10	ND (2.4)	ND (0.12)	ND (0.21)	0.02	ND (0.24)	0.75	0.12	0.20	0.95	ND (0.03)	ND (3.2)	ND (18)
DSH 31	0.40	ND (2.3)	***3.4***	0.21	0.80	***3.9***	***6.7***	5.4	ND (0.35)	*36*	20	ND (7.6)	70
DSH 32	0.21	ND (2.1)	0.89	0.22	0.38	ND (0.74)	1.8	1.3	ND (0.06)	**6.5**	ND (0.37)	ND (3.5)	76
DSH 33	0.17	ND (1.9)	ND (0.75)	ND (0.02)	0.28	0.44	0.80	**0.23**	0.26	2.0	ND (0.25)	ND (4.8)	ND (18)
DSH 34[2]	0.19	ND (5.2)	ND (0.14)	ND (0.10)	2.6	***2.5***	***24***	7.2	ND (0.52)	***31***	2.3	ND (15)	81
DSH 35	0.24	ND (2.0)	ND (0.05)	ND (0.05)	0.69	0.07	**4.8**	2.0	0.01	**8.2**	0.26	ND (3.5)	74
DSH 36	0.28	ND (2.5)	ND (0.08)	ND (0.10)	1.2	NQ	***7.6***	7.3	NQ	***48***	5.7	ND (7.9)	62
DSH 37	0.38	ND (3.3)	ND(0.03)	0.19	0.49	0.02	**3.2**	1.8	0.08	***8.4***	0.86	ND (2.3)	60
DSH 38	0.56	ND (2.9)	ND(0.02)	0.11	0.58	0	1.8	0.80	0.19	3.6	0.01	ND (2.0)	44
DSH 39	0.03	ND (2.0)	0.09	ND (0.01)	0.01	0.01	ND (0.004)	0.02	0.02	0.15	0.10	ND (2.5)	ND (2.9)
DSH 40[2]	**2.0**	ND (3.4)	ND (0.02)	3.1	0.69	NQ	**4.5**	2.0	NQ	***10***	1.9	ND (5.2)	140
Bkgd	1	1	1			1	3		1	5		1	
LEL	20	3	2			2	5		3	8		7	

Table 3-15. Comparison of toxaphene extracts analyzed by GC/ECD and GC/SIM.

Site	Toxaphene Concentration (ng/g) GC/ECD	GC/SIM
DSH 11	113	85
DSH 32	76	100
DSH 34	69	109
DSH 36	62	60
DSH 37	60	133
DSH 40	147	204

Table 3-16. TOC-normalized pesticide analyses of Duluth/Superior Harbor sediments. All concentrations are in μg/kg oc dry weight. Dashes indicate samples lacking a detected pesticide value. Chlordane was excluded from table due to nondetectable values.

Station	HCB	Lindane	Aldrin	OCS	Dieldrin	Endrin	o,p'-DDE	p,p'-DDE	Total DDE	o,p'-DDD	p,p'-DDD & o,p'-DDT	p,p'-DDT	Toxaphene
DSH 01	0.75	1.3	2.4	1.3	--	--	2.1	15.7	17.7	6.0	35.5	3.2	--
DSH 02	0	0.92	4.6	1.8	--	--	5.5	57.8	63.3	31.2	130	18.4	--
DSH 03	3.3	5.3	--	--	--	--	14.1	112	126.8	--	254	12.9	--
DSH 04	0	2.1	3.8	0.48	--	--	0.48	12.1	12.6	12.6	57.7	5.0	--
DSH 05	2.9	1.0	--	4.8	--	--	7.7	20.2	27.9	15.4	43.3	3.9	--
DSH 06	0	3.5	--	2.4	--	--	2.4	1.6	3.9	1.2	8.2	8.6	--
DSH 07	2.5	7.5	42.5	10.0	--	--	27.5	158	185	67.5	188	38.8	--
DSH 08	Not	Collected											
DSH 09	14.3	--	9.5	19.1	5.7	--	39.1	101	140	74.3	467	--	--
DSH 10	8.6	--	--	--	--	6.9	7.1	41.7	48.8	23.8	137	--	--
DSH 11	3.2	--	--	--	69.7	--	21.9	169	191	59.8	239	15.5	2250
DSH 12	5.2	--	--	--	12.8	--	22.2	190	212	109	312	27.7	--
DSH 13	10.1	--	--	--	--	10.4	9.8	57.0	66.8	31.7	180	--	--
DSH 14	5.0	--	6.3	--	5.8	4.2	20.8	7.9	28.8	8.8	54.2	--	--
DSH 15	24.5	--	0	--	12.2	14.3	16.3	18.4	34.7	--	51.0	--	--
DSH 16	1.8	--	2.8	--	2.5	0.83	0.40	3.5	3.9	3.8	20.4	1.4	--
DSH 17		Sample	could	not	be	anal.							
DSH 18	0	--	--	8.7	--	--	5.1	54.6	59.6	31.3	126	0	--
DSH 19	1.4	--	--	--	--	--	0.93	12.2	13.1	9.3	17.1	5.9	--
DSH 20	6.7	--	--	--	--	--	1.8	9.4	11.2	6.6	28.5	--	--
DSH 21	0	--	--	4.8	--	--	3.3	--	3.3	--	0	--	--
DSH 22	0	--	--	1.5	--	--	--	0.59	0.59	0.69	1.9	--	--

Table 3-16. Continued.

Station	HCB	Lindane	Aldrin	OCS	Dieldrin	Endrin	o,p'-DDE	p,p'-DDE	Total DDE	o,p'-DDD	p,p'-DDD & o,p'-DDT	p,p'-DDT	Toxaphene
DSH 23	4.0	--	--	11.4	--	--	1.3	49.3	50.7	19.0	58.6	--	--
DSH 24	2.0	--	--	1540	--	--	15.8	59.4	75.2	13.7	30.6	54.0	--
DSH 25	18.9	--	--	--	--	--	--	229	229	57.4	26.8	10.7	--
DSH 26	2.0	--	--	--	--	--	1.7	31.5	33.2	10.0	59.9	--	--
DSH 27	0	--	17.7	7.2	--	--	1.9	7.0	8.9	--	8.1	--	--
DSH 28	1.0	--	--	--	6.2	--	--	2.2	2.2	1.0	0.97	0.79	--
DSH 29	4.0	--	--	51.3	24.7	--	12.0	60.8	72.8	38.0	177	22.8	1220
DSH 3O	3.4	--	--	--	--	6.7	0.67	25.2	25.8	4.0	31.9	--	--
DSH 31	5.6	--	47.7	3.0	54.7	--	11.2	94.0	105	75.7	505	281	982
DSH 32	7.2	--	30.6	7.6	--	--	13.1	61.9	74.9	44.7	223	--	2610
DSH 33	5.4	--	--	--	14.0	8.3	8.9	25.4	34.3	7.3	63.5	--	--
DSH 34	5.6	--	--	--	74.0	--	76.9	710	787	213	917	68.1	2400
DSH 35	6.0	--	--	--	1.7	0.25	17.1	119	136	49.6	203	6.5	1840
DSH 36	9.9	--	--	--	--	--	42.3	268	310	257	1690	201	2180
DSH 37	7.5	--	--	3.7	0.39	1.6	9.7	63.0	72	35.4	165	17.0	1180
DSH 38	33.9	--	--	6.7	--	11.5	35.2	109	144	48.5	218	0.61	2670
DSH 39	30.0	--	90.0	--	10.0	20.0	10.0	--	10.0	20.0	150	100	--
DSH 40	55.9	--	--	86.6	--	--	19.3	126	145	55.9	279	53.1	3910
OMOEE SEL	24,000	1,000	8,000		91,000	130,000		19,000			7,100		
EPA SQC					9,000	4,100							

Table 3-17. PAH analyses, conducted October 1993, for samples collected during September 1993. All measurements are reported as μg/kg dry weight and are corrected for associated blank concentration. Samples exceeding the OMOEE LEL are given in bold print.

Station	Acy	Ace	Fle	Phe	Ant	Car	Fla	Pyr	Baa	Cry	Bfa	Bap	Idp	Dba	Bgp	Nap	2Mn	TPAH
DSH 01	<1900	<1900	<1900	60	<1900	<1900	150	40	<1900	137	81	<1900	<1900	<1900	<1900	<1900	<1900	468
DSH 02	<1600	<1600	<1600	<1600	<1600	<1600	80	210	<1600	107	101	150	<1600	<1600	**300**	<1600	<1600	948
DSH 03	<1900	<1900	<1900	<1900	<1900	<1900	120	70	<1900	137	121	<1900	<1900	<1900	<1900	<1900	<1900	448
DSH 04	<1900	<1900	<1900	430	<1900	<1900	330	460	112	<1900	151	90	<1900	<1900	130	<1900	<1900	1700
DSH 05	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	ND
DSH 06	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	ND
DSH 07	<1400	<1400	<1400	<1400	<1400	<1400	0	0	<1400	<1400	31	<1400	<1400	<1400	<1400	<1400	<1400	31
DSH 09	<1400	<1400	<1400	150	<1400	<1400	260	480	170	240	**250**	180	<1400	<1400	**190**	<1400	<1400	1920
DSH 10	<2200	<2200	<2200	280	<2200	<2200	**940**	**1100**	**620**	**680**	**1200**	**540**	<2200	<2200	<2200	260	<2200	5620
DSH 11	<2300	<2300	<2300	**600**	<2300	<2300	**1100**	**1800**	**740**	**800**	**1280**	**650**	**460**	<2300	**500**	<2300	<2300	7930
DSH 12	<1900	<1900	<1900	540	<1900	<1900	**1110**	**950**	**532**	**697**	**1131**	**420**	**327**	<1900	100	<1900	<1900	5810
DSH 13	<1700	<1700	<1700	150	<1700	<1700	450	330	272	**367**	**551**	130	107	<1700	<1700	250	<1700	2610
DSH 14	<1400	<1400	<1400	180	<1400	<1400	330	260	242	277	**321**	100	147	<1400	<1400	<1400	<1400	1860
DSH 15	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	ND
DSH 16	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	<3000	720	<3000	720
DSH 17	<2100	680	**690**	**2070**	**609**	240	**2010**	**1750**	**1112**	**1107**	**1701**	**760**	**407**	<2100	**550**	3300	1000	18500
DSH 18	<1800	<1800	<1800	<1800	<1800	<1800	50	0	<1800	<1800	81	<1800	<1800	<1800	<1800	<1800	<1800	131
DSH 19	<2100	<2100	**220**	**670**	209	<2100	**1110**	**850**	**792**	**867**	**1311**	**610**	**447**	<2100	110	470	670	8340
DSH 20	Sample	Lost																
DSH 21	<1500	<1500	<1500	160	<1500	<1500	310	380	182	207	141	200	<1500	<1500	**320**	<1500	<1500	1900
DSH 22	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	<2800	ND

Table 3-17. Continued.

Station	Acy	Ace	Fle	Phe	Ant	Car	Fla	Pyr	Baa	Cry	Bfa	Bap	Idp	Dba	Bgp	Nap	2Mn	TPAH
DSH 23	<2200	610	570	1470	350	<2200	2010	1850	1212	1207	1881	930	467	<2200	550	2000	630	15700
DSH 24	1800	560	5300	25000	6600	870	30000	30000	13000	13000	20100	9600	8000	2000	5600	10000	1300	185000
DSH 25	260	850	830	3270	809	<1800	2910	3950	2212	2807	2241	1630	1437	<1800	1150	1000	520	26300
DSH 26	<2000	300	<2000	970	169	<2000	660	950	302	257	281	390	197	<2000	620	40	<2000	5140
DSH 27	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	<1400	ND
DSH 28	<2000	<2000	<2000	240	<2000	<2000	430	550	280	320	430	280	<2000	<2000	<2000	<2000	<2000	2530
DSH 29	<1600	510	570	3770	689	300	4310	3750	1912	2007	2971	1330	937	<1600	<1600	220	<1600	23300
DSH 30	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	<1900	ND
DSH 31	<1800	<1800	230	1700	380	<1800	1500	2700	1100	1400	1930	960	900	<1800	770	<1800	180	13800
DSH 32	<1600	<1600	<1600	560	<1600	<1600	800	1400	520	550	860	420	300	<1600	<1600	<1600	<1600	5410
DSH 33	<1600	<1600	<1600	<1600	<1600	<1600	300	380	<1600	180	280	210	<1600	<1600	<1600	<1600	<1600	1350
DSH 34	<1800	<1800	<1800	710	<1800	<1800	1100	1600	690	910	1590	740	<1800	<1800	<1800	300	230	7870
DSH 35	<1900	<1900	<1900	420	<1900	<1900	1100	1200	530	600	1170	520	<1900	<1900	400	<1900	<1900	5940
DSH 36	<1900	<1900	<1900	1200	190	<1900	1900	2600	1100	1400	2460	1200	870	<1900	960	<1900	<1900	13900
DSH 37	<1900	250	290	2100	380	<1900	1800	3900	1400	1400	1940	960	740	<1900	<1900	280	240	15700
DSH 38	<1500	<1500	150	720	<1500	<1500	610	900	350	360	390	250	<1500	<1500	<1500	250	200	4180
DSH 39	<1200	<1200	<1200	130	<1200	<1200	<1200	140	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	<1200	270
DSH 40	<1600	930	720	5870	1519	740	8110	8050	4012	4407	6171	3630	2837	800	2650	2400	520	53400
OMOEE LEL			190	560	220		750	490	320	340	240	370	200	60	170			4000

Code for PAHs: Acy=Acenaphthylene; Ace=Acenaphthene; Fle=Fluorene; Phe=Phenanthrene; Ant=Anthracene; Car=Carbazole; Fla=Fluoranthene; Pyr=Pyrene; Baa=Benz(a)anthracene; Cry=Chrysene; Bfa=Benzofluoranthene; Bap=Benzo(a)pyrene; Idp=Indeno(123-cd)pyrene; Dba=Dibenz(a,h)anthracene; Bgp=Benzo(g,h,i)perylene; Nap=Naphthalene; 2Mn=2-methylnaphthalene; TPAH=Total PAHs.

Total PAHs do not include nondetectable concentrations of PAH compounds.

Table 3-18. TOC-normalized PAH results for samples collected during September 1993, analyzed during October 1993. All measurements are reported as mg/kg oc dry weight. Concentrations exceeding the U.S. EPA SQC are given in italics.

Station	Acy	Ace	Fle	Phe	Ant	Car	Fla	Pyr	Baa	Cry	Bfa	Bap	Idp	Dba	Bgp	Nap	2Mn	TPAH
DSH 01	--	--	--	1.12	--	--	2.80	0.75	--	2.56	1.51	--	--	--	--	--	--	8.73
DSH 02	--	--	--	--	--	--	7.34	19.3	--	9.82	9.27	13.8	--	--	27.5	--	--	87.0
DSH 03	--	--	--	--	--	--	3.03	1.77	--	3.46	3.06	--	--	--	--	--	--	11.3
DSH 04	--	--	--	10.2	--	--	7.84	10.9	2.66	--	3.59	2.14	--	--	3.09	--	--	40.4
DSH 05	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 06	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	0
DSH 07	--	--	--	--	--	--	0	0	--	--	7.75	--	--	--	--	--	--	7.75
DSH 09	--	--	--	14.3	--	--	24.8	5.71	16.2	22.9	23.8	17.1	--	--	18.1	--	--	183
DSH 10	--	--	--	6.86	--	--	23.0	27.0	15.2	16.7	29.4	13.2	--	--	--	6.37	--	138
DSH 11	--	--	--	12.0	--	--	21.9	35.9	14.7	15.9	25.5	13.0	9.16	--	9.96	--	--	158
DSH 12	--	--	--	16.4	--	--	33.7	28.9	16.2	21.2	34.4	12.8	9.94	--	3.04	--	--	176
DSH 13	--	--	--	4.75	--	--	14.2	10.4	8.61	11.6	17.4	4.11	3.39	--	--	7.91	--	82.5
DSH 14	--	--	--	7.50	--	--	13.8	10.8	10.1	11.5	13.4	4.17	6.13	--	--	--	--	77.4
DSH 15	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 16	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	1.81	--	1.81
DSH 17	--	7.68	7.79	23.4	6.87	2.71	22.7	19.8	12.6	12.5	19.2	8.58	4.59	--	6.21	37.2	11.3	208
DSH 18	--	--	--	--	--	--	2.53	0	--	--	4.09	--	--	--	--	--	--	6.62
DSH 19	--	--	1.37	4.16	1.30	--	6.89	5.28	4.92	5.39	8.14	3.79	2.78	--	0.68	2.92	4.16	51.8
DSH 20	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 21	--	--	--	10.5	--	--	20.3	24.8	11.9	13.5	9.22	13.1	--	--	20.9	--	--	124
DSH 22	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 23	--	11.6	10.8	27.9	6.64	--	38.0	35.1	23.0	22.9	35.7	17.6	8.86	--	10.4	38.0	12.0	299

Table 3-18. Continued.

Station	Acy	Ace	Fle	Phe	Ant	Car	Fla	Pyr	Baa	Cry	Bfa	Bap	Idp	Dba	Bgp	Nap	2Mn	TPAH
DSH 24	32.4	10.1	95.3	*450*	119	15.6	540	540	234	234	362	173	144	36.0	101	180	23.4	3330
DSH 25	4.97	16.2	15.9	62.5	15.5	--	55.6	75.5	42.3	53.7	42.8	31.2	27.5	--	22.0	19.1	9.94	502
DSH 26	--	8.60	--	27.8	4.84	--	18.9	27.2	8.65	7.36	8.05	11.2	5.65	--	17.8	1.15	--	147
DSH 27	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 28	--	--	--	1.06	--	--	1.90	2.43	1.24	1.41	1.90	1.24	--	--	--	--	--	11.2
DSH 29	--	9.70	10.8	71.7	13.1	5.70	81.9	71.3	36.4	38.2	56.5	25.3	17.8	--	--	4.18	--	442
DSH 30	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--
DSH 31	--	--	3.23	23.8	5.33	--	21.0	37.9	15.4	19.6	27.1	13.5	12.6	--	10.8	--	2.53	193
DSH 32	--	--	--	19.2	--	--	27.5	48.1	17.9	18.9	29.6	14.4	10.3	--	--	--	--	186
DSH 33	--	--	--	--	--	--	9.52	12.1	--	5.71	8.89	6.67	--	--	--	--	--	42.9
DSH 34	--	--	--	21.0	--	--	32.5	47.3	20.4	26.9	47.0	21.9	--	--	--	8.88	6.81	233
DSH 35	--	--	--	10.4	--	--	27.3	29.8	13.2	14.9	29.0	12.9	--	--	9.93	--	--	147
DSH 36	--	--	--	42.2	6.69	--	66.9	91.6	38.7	49.3	86.6	42.2	30.6	--	33.8	--	--	489
DSH 37	--	4.92	5.71	41.3	7.48	--	35.4	76.8	27.6	27.6	38.2	18.9	14.6	--	--	5.51	4.72	309
DSH 38	--	--	9.09	43.6	--	--	37.0	54.6	21.2	21.8	23.6	15.2	--	--	--	15.2	12.1	253
DSH 39	--	--	--	130	--	--	--	140	--	--	--	--	--	--	--	--	--	270
DSH 40	--	26.0	20.1	164	42.4	20.7	226	225	12.1	123	172	101	79.2	22.4	74.0	67.0	14.5	1490
OMOEE SEL			160	950	370		1020	850	1480	460	1340	1440	320	130	320			10000
EPA SQC		130		180			620											

Code for PAHs: Acy=Acenaphthylene; Ace=Acenaphthene; Fle=Fluorene; Phe=Phenanthrene; Ant=Anthracene; Car=Carbazole; Fla=Fluoranthene; Pyr=Pyrene; Baa=Benz(a)anthracene; Cry=Chrysene; Bfa=Benzofluoranthene; Bap=Benzo(a)pyrene; Idp=Indeno(123-cd)pyrene; Dba=Dibenz(a,h)anthracene; Bgp=Benzo(g,h,i)perylene; Nap=Naphthalene; 2Mn=2-methylnaphthalene; TPAH=Total PAHs.

Table 3-19. PAH analysis on stored surficial (0-30 cm) Vibracore samples (collected September 1993 and analyzed July 1994). All PAHs are in μg/kg (ppb) dry weight. Samples exceeding the OMOEE LEL are given in bold print.

PAH	DSH 02	DSH 03	DSH 05	DSH 06	DSH 14	DSH 16	DSH 18	DSH 21	DSH 22	DSH 23	DSH 26	DSH 29	DSH 30	DSH 40
Acy	9.6	51	27	ND	22	46	15	ND	ND	150	ND	110	ND	240
Ace	ND	24	ND	ND	10	ND	ND	ND	ND	26	ND	420	ND	660
Fle	9.6	65	14	ND	29	37	17	ND	ND	120	ND	**500**	ND	**830**
Dbt	ND	41	ND	ND	10	12	ND	ND	ND	44	ND	220	ND	370
Phe	59	330	83	49	120	110	84	ND	ND	410	53	**3100**	32	**6800**
Ant	16	99	15	12	40	17	25	ND	ND	**270**	ND	**830**	ND	**1300**
Car	ND	30	ND	ND	ND	12	ND	ND	ND	26	ND	390	ND	840
Fla	130	740	110	97	300	150	190	ND	ND	**2400**	110	**4900**	66	**1300**
Pyr	110	**618**	98	73	230	94	180	ND	ND	**1600**	120	**3400**	72	**910**
Baa	74	**440**	54	51	150	20	110	ND	ND	**1400**	45	**2000**	29	ND
Cry	67	**390**	57	46	120	22	130	ND	ND	**1200**	74	**2000**	35	ND
5mc	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	30	ND	71
Bfa	150	**740**	110	92	220	17	**250**	ND	ND	**1800**	100	**2400**	64	**7300**
Bep	68	290	42	33	78	ND	91	ND	ND	780	47	930	37	2800
Bap	93	**440**	52	49	120	ND	110	ND	ND	**1200**	47	**1500**	28	**4200**
Per	130	520	110	170	210	ND	180	380	4200	480	390	400	290	1000
Idp	46	**200**	26	25	63	ND	58	ND	ND	**550**	24	**620**	14	**2100**
Dba	ND	47	ND	ND	17	ND	15	ND	ND	**170**	ND	ND	ND	**460**

Table 3-19. Continued.

PAH	DSH 02	DSH 03	DSH 05	DSH 06	DSH 14	DSH 16	DSH 18	DSH 21	DSH 22	DSH 23	DSH 26	DSH 29	DSH 30	DSH 40
Bgp	71	150	34	24	50	ND	58	ND	ND	**480**	36	**600**	27	**2100**
D1p	11	37	ND	ND	14	ND	17	ND	ND	160	ND	ND	ND	56
Dep	32	63	ND	ND	14	ND	27	ND	ND	150	ND	ND	ND	48
Dip	12	64	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	41
23bf	ND	ND	ND	ND	ND	57	ND	ND	ND	ND	ND	ND	ND	ND
23di	ND	33	ND	ND	25	14	ND	ND	ND	22	ND	15	ND	16
Ine	ND	33	ND	ND	29	96	ND	ND	ND	48	ND	29	ND	67
Nap	28	190	45	16	160	460	46	ND	ND	200	21	220	16	550
Bbt	ND	16	ND	ND	11	64	ND	ND	ND	ND	ND	ND	ND	17
Qnl	ND	ND	ND	ND	ND	68	ND	ND	ND	ND	ND	ND	ND	20
Ino	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	23
2mn	35	230	63	22	90	150	38	ND	ND	100	29	240	22	620
1mn	21	120	39	14	48	72	19	ND	ND	46	14	150	ND	400
Bph	ND	29	ND	ND	13	19	ND	ND	ND	28	ND	37	ND	96
TPAH	898	4780	788	556	1740	1140	1330	ND	ND	12102	659	23200	405	30200

ND = Not Detected

Code for PAHs: Acy = Acenaphthylene; Ace = Acenaphthene; Fle = Fluorene; Dbt = Dibenzothiophene; Phe = Phenanthrene; Ant = Anthracene; Car = Carbazole; Fla = Fluoranthene; Pyr = Pyrene; Baa = Benz(a)anthracene; Cry = Chrysene; 5mc = 5-methylchrysene; Bfa = Benzofluoranthenes; Bep = Benzo(e)pyrene; Bap = Benzo(a)pyrene; Per = Perylene; Idp = Indeno(1,2,3-cd)pyrene; Dba = Dibenz(a,h)anthracene; Bgp = Benzo(ghi)perylene; D1p = Dibenzo(a,1)pyrene; Dep = Dibenzo(a,e)pyrene; Dip = Dibenzo(a,i)pyrene; 23bf = 2,3-benzofuran; 23di = 2,3-dihydroindene; Ine = Indene; Nap = Naphthalene; Bbt = Benzo(b)thiophene; Qnl = Quinoline; Ino = Indole; 2mn = 2-methylnaphthalene; 1mn = 1-methylnaphthalene; Bph = Biphenyl; TPAH = total of 17 PAH compounds (i.e., same list as quantitated in the October 1993 analysis).

Table 3-20. Comparison of split analyses of sediment samples collected during June 1993 and analyzed during either October 1993 or July 1994. Total PAHs include the sum of 17 PAH compounds.

Site	Total PAHs (μg/kg dry wt.) Oct. 1993	July 1994	RPD (%)	CV (%)
DSH 02	948	898	5.4	3.8
DSH 03	448	4780	150	120
DSH 05	ND	788	200	140
DSH 06	ND	556	200	140
DSH 14	1860	1740	6.7	4.7
DSH 16	720	1140	45	32
DSH 18	131	1330	160	120
DSH 21	1900	ND	200	140
DSH 22	ND	ND	0	0
DSH 23	15,700	12,100	26	18
DSH 26	5140	659	150	110
DSH 29	23,300	23,200	0.43	0.30
DSH 30	ND	405	200	140
DSH 40	53,400	30,200	56	39

Table 3-21. Location and description of surficial sediment samples (0-15 cm) collected on June 11, 1994.

Site	Latitude	Longitude	Description
DSH 21	46°43'10.9"N	92°10'25.4"W	Silt mixed with heavy oil
DSH 22	46°43'01.6"N	92°10'17.5"W	Fibrous silt/sand mixture
DSH 23	46°42'37.8"N	92°11'41.8"W	Sandy silt
DSH 26	46°39'48.3"N	92°12'22.4"W	Mucky silt (plant material)
DSH 27	46°42'31.0"N	92°09'35.0"W	Sandy silt

Table 3-22. PAHs in surficial sediments (0-15 cm) from the Duluth/Superior Harbor collected during June 1994 and analyzed during July 1994. Concentrations are in μg/kg dry wt. Values exceeding the OMOEE LEL values for 12 PAH compounds are given in bold print.

PAH Compound	DSH 21	DSH 22	DSH 23	DSH 26	DSH 27
Acenaphthylene	2400	34	84	ND	17
Acenaphthene	650	ND	16	ND	ND
Fluorene	**1900**	24	80	ND	16
Dibenzothiophene	520	ND	28	ND	ND
Phenanthrene	**6800**	69	220	16	70
Anthracene	**7800**	**250**	190	ND	34
Carbazole	1000	28	16	ND	ND
Fluoranthene	**21000**	330	**1500**	41	230
Pyrene	**14000**	230	**1200**	35	180
Benz(a)anthracene	ND	**360**	**730**	26	150
Chrysene	ND	320	**580**	ND	170
5-methylchrysene	160	ND	96	22	18
Benzofluoranthenes	**15000**	**420**	**1600**	42	**250**
Benzo(e)pyrene	5400	140	490	33	97
Benzo(a)pyrene	**9800**	250	**910**	37	140
Perylene	2100	180	380	90	380
Indeno(123-cd)pyrene	**4900**	110	**510**	11	65
Dibenz(a,h)anthracene	**1300**	37	**110**	ND	19
Benzo(g,h,i)perylene	**4000**	96	**460**	26	72
Dibenzo(a,l)pyrene	1400	34	130	ND	29
Dibenzo(a,e)pyrene	1200	29	79	ND	17
Dibenzo(a,i)pyrene	ND	ND	240	ND	ND
2,3-benzofuran	ND	ND	ND	ND	ND
2,3-dihydroindene	110	ND	25	ND	ND

Table 3-22. Continued.

PAH Compound	DSH 21	DSH 22	DSH 23	DSH 26	DSH 27
Indene	590	ND	65	ND	ND
Naphthalene	750	42	180	ND	110
Benzo(b)thiophene	63	ND	20	ND	ND
Quinoline	17	ND	ND	ND	ND
Indole	24	ND	ND	ND	ND
2-methylnaphthalene	480	ND	110	ND	26
1-methylnaphthalene	210	ND	59	ND	13
Biphenyl	110	ND	25	ND	ND
Total PAHs*	90,300	2,570	8,370	208	1,520

*Total PAHs are based on the sum of: acenaphthene, acenaphthylene, anthracene, fluoranthenes, benzo(b)fluorene, benzo(a)anthracene, benzo(a)pyrene, benzo(g,h,i)perylene, chrysene, dibenzo(a,h)anthracene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene.

Table 3-23. PAH fluorescence screen results for Duluth/Superior Harbor sediments collected in September 1993. Core sections are listed in order from surface to bottom. Table 3-1 gives the sampling depths associated with each numbered core section. All concentrations expressed as μg/kg dry wt.

Site	Core section 1	2	3	4	5
DSH 01	4600	3200	10200	17100	13500
DSH 02	1150±71[1]	NO[2]	NO	NO	NO
DSH 03	3100±141[1]	32,900	700	NO	NO
DSH 04	7100	800	1400	600	600
DSH 05	1550±71[1]	8800 (Ponar)	NO	NO	NO
DSH 06	700±0[1]	600	600	NO	NO
DSH 07	6200	600	NO	NO	NO
DSH 08	19600 (Ponar)	NO	NO	NO	NO
DSH 09	577400	800	NO	NO	NO
DSH 10	18700	800	700	700	700
DSH 11	28200	900	800	800	NO
DSH 12	136700	11900	23600	39000	38800
DSH 13	30400	8600	800	600	500
DSH 14	1100±141[1]	18500	18500	NO	NO
DSH 15	1000	700	700	700	700
DSH 16	900	2000	1600	40700	1400
DSH 17	61000	7500	500	NO	NO
DSH 18	650	8000	24400	6200	6200
DSH 19	123800	223100	132400	55200	700
DSH 20	22000	700	700	700	NO
DSH 21	733±57[1]	700	NO	NO	NO
DSH 22	600	89000	1000	500	800
DSH 23	18550±353[1]	NO	NO	NO	
DSH 24	286800	5300	500	600	
DSH 25	2800	900	81300	15500	
DSH 26	2600	2500	6600	NO	
DSH 27	650	900	800	500	500
DSH 28	2400	13200	NO	NO	
DSH 29	114733±6610[1]	4300	2600	557700	2400
DSH 30	800±0[1]	15200	500	500	14300
DSH 31	148600	1900	NO	NO	
DSH 32	279800	49700	1800	900	
DSH 33	18900	800	14200	700	1600±0
DSH 34	153300	53900	1700	800	
DSH 35	25700	12900	600	NO	
DSH 36	399900	3900	84000	6800	301500
DSH 37	412300	332900	148200	NO	
DSH 38	360100	801800	72400	NO	
DSH 39	1500	1300	700	700	
DSH 40	21300±4700[1]	1700	2200	2600	18900

[1]Mean (± standard deviation) of two or more values
[2]NO: Section not obtained during coring

Table 3-24. Tributyltin (TBT), monobutyltin (1-BT), dibutyltin (2-BT), and tetrabutyltin (4-BT) concentrations in Duluth/Superior Harbor sediments.

Site	TBT	1-BT	2-BT	4-BT
DSH 01				
μg/kg Sn	1.3	2.1	1.7	ND
μg/kg Sn OC	24	39	32	ND
μg/kg TBT	3.3			
μg/kg TBT OC	60			
DSH 02				
μg/kg Sn	34.3	15.9	20.4	ND
μg/kg Sn OC	3150	1460	1870	ND
μg/kg TBT	86			
μg/kg TBT OC	7900			
DSH 08				
μg/kg Sn	16.3	18.6	17.8	ND
μg/kg Sn OC	815[1]	930[1]	890[1]	ND
μg/kg TBT	41			
μg/kg TBT OC	2000			
DSH 20				
μg/kg Sn	42.8	38.4	5.4	ND
μg/kg Sn OC	542	487	68	ND
μg/kg TBT	110			
μg/kg TBT OC	1400			
DSH 31				
μg/kg Sn	71.0	54.1	50.3	ND
μg/kg Sn OC	996	759	705	ND
μg/kg TBT	180			
μg/kg TBT OC	2500			
DSH 40				
μg/kg Sn	12.1	26.9	23.0	ND
μg/kg Sn OC	338	751	642	ND
μg/kg TBT	30			
μg/kg TBT OC	850			

[1]Total organic carbon not measured in this very sandy sample; TOC of 2% assumed.

Table 3-25. Sediment toxicity to *Hyalella azteca*, *Chironomus tentans*, *Photobacterium phosphoreum* (Microtox[R]), and *Vibrio fischeri* (Mutatox[R]).

Site	Percent Survival (%) *Hyalella azteca*	*C. tentans*	*P. phosphoreum* EC50[1]	*V. fischeri* Genotoxicity[2]
DSH 01	**63**	100	NT	D
DSH 02	**70**	93	39.8%	D
DSH 03	**77**	90	NT	D
DSH 04	**63**	87	NT	N
DSH 05	87	90	NT	N
DSH 06	**57**	97	NT	N
DSH 07	**63**	87	NT	D
DSH 08	**33**	100	54.1%	N
DSH 09	83	87	NT	N
DSH 10	93	90	48.0%	N
DSH 11	93	87	52.6%	N
DSH 12	**27**	90	90%[3]	D
DSH 13	**70**	93	74.4%	N
DSH 14	**87**	43*	NT	N
DSH 15	90	83	NT	S9
DSH 16	**60**	83	NT	N
DSH 17	**80**	90	NT	N
DSH 18	**50**	90	NT	D
DSH 19	**40**	77	90%[3]	D
DSH 20	**70**	60	90%[3]	D
DSH 21	**23**	90	NT	N
DSH 22	**77**	80	NT	N
DSH 23	**30**	97	NT	D
DSH 24	**60**	0*	23.7%	D
DSH 25	90	97	NT	D
DSH 26	**60**	83	NT	D
DSH 27	100	83	NT	D
DSH 28	97	93	NT	D
DSH 29	**37**	93	90%[3]	D
DSH 30	**53**	97	NT	N
DSH 31	90	73	NT	D
DSH 32	93	77	NT	N
DSH 33	**77**	53	95.9%	N
DSH 34	77	47*	90%[3]	D
DSH 35	77	93	90%[3]	N
DSH 36	**63**	73	90%[3]	D

Table 3-25. Continued.

Site	Percent Survival (%) *Hyalella azteca*	*C. tentans*	*P. phosphoreum* EC50[1]	*V. fischeri* Genotoxicity[2]
DSH 37	**60**	53	90%[3]	D
DSH 38	**57**	80	N/A	D
DSH 39	**63**	70	NT	N
DSH 40	**27**	83	90%[3]	D

[1]EC50: the sediment porewater concentration at which 50% reduction in bacterial luminescence was observed. NT = not toxic; N/A = sample not available for testing.

[2]In the Mutatox^{R} test, N = sample not genotoxic; D = sample caused direct mutation back to wild strain; S9 = S9 (hepatic-type) activation required for sample to be mutagenic.

[3]Indicates sample was toxic in initial 90% screen, but not in EC50 test run.

Table 3-26. Sedimentation rates for sediment cores collected from the Duluth/Superior Harbor, in cm/year.

	Sediment core				
Period	**DSH 36**	**DSH 38**	**DSH 11**	**DSH 20**	**DSH 28**
1954-1993	1.14 ± 0.13[1]	0.94 ± 0.10	0.15 ± 0.05	0.30 ± 0.05	?[2]
1954-1964	3.05 ± 0.51	2.03 ± 0.51	--[3]	--	?
1964-1993	0.48 ± 0.13	0.56 ± 0.15	--	--	?

[1]Estimated uncertainty in the deposition rate
[2]Not known; no ^{137}Cs was detected in any of the core sections
[3]Not known; no peak occurred in ^{137}Cs

CHAPTER 4

COMPOSITE SITE DESCRIPTIONS

4.1 RELATIVE CONTAMINATION FACTORS

This section provides a comprehensive picture of the relative contamination among 39 of the 40 sites evaluated in this survey. DSH 08 was excluded from the data set because the substrate was unsuitable for collecting a vibracore sample; butyltins were the only contaminant measured in a surficial sample collected from this site. For each contaminant measured that had a corresponding OMOEE LEL value, a relative contamination factor (RCF) was calculated as follows:

$$\text{RCF} = \frac{\text{Contaminant concentration (dry wt. units)}}{\text{OMOEE LEL (dry wt. units)}}$$

This normalization allows comparison of the surficial contamination at a site to that at other sites, with respect to a guideline that is biologically-based and widely utilized as a screening tool throughout the Great Lakes. The Wisconsin DNR has used a similar approach in evaluating relative contamination in Newton Creek and Hog Island Inlet in the Superior Harbor (Redman, 1994). The same units were used for the contaminant concentration and LEL value. Metals were given in mg/kg units, organic contaminants in μg/kg units, and TOC was expressed as a percentage.

Eighteen individual RCFs were calculated for each site (Table 4-1), one for each of the following contaminants: Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, TOC, aldrin, hexachlorobenzene (HCB), p,p'-DDD & o,p'-DDT, p,p'-DDE, dieldrin, endrin, lindane, total PCBs, and total PAHs. OMOEE LEL values were not available for ammonia, toxaphene, octachlorostyrene, some DDT metabolites, tributyltin, 2,3,7,8-TCDD, and 2,3,7,8-TCDD. Only total PAHs were included in the calculation of the total RCFs so as not to skew the results with individual PAH compounds. Individual RCF values which exceeded 1.0 (i.e., sediment concentration exceeded the OMOEE LEL value) are listed in bold typeface in Table 4.1. This table also indicates total RCFs for each site, calculated by adding the unweighted RCFs for each parameter. TOC was removed from the total RCF values because the LEL value appeared to be too low for the background TOC in the harbor. Sites with a total RCF (excluding TOC) value greater than 17 are given in bold typeface in Table 4-1 (i.e., this signifies sites with an average per contaminant RCF exceeding 1.0).

The sites evaluated in this survey showed a great degree of variability in overall level of contamination (Figure 4-1, Table 4-1). Based on the surficial chemistry results, the least contaminated site was DSH 05 (total RCF = 3.4), and the most contaminated site was DSH 25 (total RCF = 91). A number of sites exceeded the OMOEE LEL values for heavy metals, PCBs, and PAHs. Sites in the Superior Harbor generally had relatively fewer exceedances of the heavy metal, PCB, and PAH LELs than sites in the Duluth Harbor. Some of this difference may be due to different watershed inputs as the Nemadji River drains into the Superior Harbor and the St. Louis River drains into the Duluth Harbor. In addition, the Duluth Harbor watershed has a greater industrial/commercial/residential base than the Superior Harbor watershed. Thus, there is a greater probability of anthropogenic point and nonpoint sources of contamination in the Duluth portion of the harbor. The Duluth portion of the harbor is also impacted by two Superfund sites: USX and Interlake/Duluth Tar.

Two contaminated sediment deposits are located along the western shoreline of the USX Superfund site. One sediment delta is situated at the mouth of Unnamed Creek, and the other delta is located at the former outfall of the Wire Milling operation. As part of the Record of Decision (ROD) for this site, a remedial approach was chosen to remove contaminants and "cap" the contaminated material with clean material (Barr Engineering, 1985). This approach has not been successful because wave erosion along the shoreline of the two delta areas is disturbing contaminated sediments. Thus, a clean sediment layer has not been able to accumulate to naturally cap the sediments. The resuspension of contaminated sediments from the USX site is a potentially important source of contaminants to downstream portions of the St. Louis River and Duluth Harbor.

The Remedial Investigation/Feasibility Study (RI/FS) for the Interlake/Duluth Tar Superfund site found extremely elevated concentrations of coal tars, PAHs, and heavy metals in sediments near the eastern shore of Stryker Embayment (Malcolm Pirnie, 1991). Stryker Embayment is encompassed by this Superfund site. The RI/FS indicated there were elevated concentrations of contaminants within the bay near the mouth. From the sample (DSH 21) collected in the mouth of Stryker Embayment for this study, the surficial sediment appeared to be fairly "clean" (i.e., total RCF = 8.6). However, when the upper 15 cm of sediment was sampled from this site during June 1994, the sediment was highly contaminated with PAHs (i.e., 90,300 μg/kg total PAHs). This demonstrates that sediment-associated PAHs have been transported to the mouth of Stryker Embayment.

The consultants for Interlake have undertaken additional sediment sampling within the boundaries of the Superfund site, including Stryker Embayment and Docks 6 and 7; the results of sediment chemistry, toxicity, and benthos data have not been finalized yet. This

more recent study will provide additional information as to the potential for resuspended sediments to be transported and deposited downstream from the Interlake/Duluth Tar site. Some sediment remediation was conducted during the summer to winter of 1996 that resulted in the removal and incineration/landfilling of PAH contaminated sediments from the inland side of Dock 6. A number of other remediation options are being considered for containing or treating contaminated sediments from this Superfund site.

As mentioned in Section 3.2.3, the Duluth/Superior Harbor used to be a major port for the storage and transport of coal from the late 1800s to early 1900s. Several coal gasification plants, coal storage facilities, and coal-powered ships were historically found in the vicinity of the harbor. Today, coal is used to a lesser extent, and several technologies are employed to reduce dust emissions from coal piles. For example, the use of coal for generating electricity at the M.L. Hibbard/DSD No. 2 Plant ceased in 1973 (Lowell Neudahl, Minnesota Power, personal communication, 1996). Fuel oil was used from 1973 to 1981, and the plant was idle from 1981 to 1986. The plant currently burns a mixture of 85% wood and 15% coal to produce steam instead of electricity; this results in much lower fuel usage at the plant.

Contaminants associated with coal and coal combustion products include: PAHs, mercury, lead, and nickel. This study only examined the surficial (0-30 cm) level of these contaminants, except for the PAH screen. Since the PAH screen results did not correlate well with the PAH results by GC/MS, it is not possible to quantitatively assess the PAH contamination at depth. However, the general PAH screening results and field observations indicated that PAH-like compounds were associated with depth in some cores. This could be indicative of historical uses of coal in the harbor.

From Table 4-1, the RCFs for individual pesticides were fairly low except for DDT metabolites in the embayment bounded by the Lakehead Material Storage Facility on the west and Rices Point on the east. This bay has several suspected sources of contamination, including the discharge of WLSSD and the outfalls of Miller and Coffee Creeks. The WLSSD discharge encompasses the sum of the cities of Duluth, Proctor, and Cloquet's treated municipal and industrial effluents, and thus represents a significant potential source of current contamination. The bay also contains a shipping channel (the 21st Ave. W. Channel) which has not been dredged in 20 years. Recent work by the Natural Resources Conservation Service has shown that the channel has been filled-in by sediments since dredging was curtailed.

4.2 FIELD DESIGN CONSIDERATIONS

In order to ascertain whether it was likely for a site to be misidentified as uncontaminated (i.e., determine the likelihood of false negative results), sediment contamination was assessed at several sites in a spatially large area (the bay near WLSSD/Coffee Creek/Miller Creek outfalls) and several sites in a spatially small area (Slip C).

Six sites (DSH 11-12 and DSH 33-36) were selected in the bay to address the possibility of false negative results. With the possible exception of site DSH 33, the analysis of any one of the six sites would have pointed to the need for further assessment. Thus, while the sites varied slightly among themselves in degree of contamination, the pattern and magnitude of contamination throughout the area pointed to the need for further evaluation. This area should be of high priority for future sediment assessments because it represents an area where current point source loading of contaminants is occurring; thus, the status of the sediments could provide a valuable indicator of the success of current pollution prevention and control strategies in protecting sediment quality. The cesium-dating of the sediment cores in this bay indicated that either sedimentation rates were very slow near the WLSSD outfall (DSH 11), or that much scouring has occurred there. Therefore, it seems likely that contaminated sediments from this bay may be moving out into other parts of the harbor.

Four sites were evaluated in Slip C along a line emanating from the terminus of the slip to its outlet, with the sites approximately 50 m apart. The RCFs for DSH 29 and DSH 37-39, respectively, were 22, 19, 10, and 3.5. Therefore, overall surficial contamination decreased from the inland end to the outer end of the slip. The possibility of intrasite variability affecting the assessment of site contamination in Slip C was moderate. In two out of four cores, the slip would have been identified as a medium priority site for further investigation. The chances of successful identification can be improved by well planned site selection; that is, by selecting sites in the reconnaissance survey that are either closest to the suspected source, or that preliminary, cursory inspections indicate are contaminated. Possible sources of contaminants to this slip include the City of Duluth's stormwater overflow outfalls; at least one of these outfalls exists in the Cutler-Magner Slip which drains into Slip C. Additional historical sources include the industrial effluents that may have been released into this slip from the Superwood plant, Cutler Magner, and other (now defunct) industries on the north end of Rice's Point (including a coal gasification plant). It was fairly obvious in the field that the core at DSH 39 was less-contaminated than those at DSH 29, DSH 37, and 38. Thus, by carefully pre-selecting sites on a worst-case basis and using field observations to aid in site selection, the possibility of false negative contamination identification can be avoided.

4.3 COMPILATION OF RESULTS

Table 4-2 contains a compilation of the surficial sediment chemistry results for contaminants that had comparable OMOEE LEL values. A summary of the sediment toxicity tests resulting in significant toxicity is also given in Table 4-2. The sample sites are given in descending order according to their total RCF value. It is important to note that correlations cannot be made between the toxicity test results and sediment chemistry data; this is because the sediment chemistry measurements were based on the upper 30 cm of the vibracore samples, whereas the toxicity tests were run on approximately the top 0-20 cm of sediments obtained using a Ponar dredge.

For the sediment toxicity test results, there was little comparability between the *C. tentans* results and the Microtox^R and Mutatox^R results. Double "hits" with the Microtox^R and Mutatox^R tests only corresponded to significant toxicity in the *C. tentans* test in two out of ten occurrences. The results for the *H. azteca* tests were largely inconclusive due to control failure of several test runs. However, the results of other sediment investigations the MPCA is conducting in the harbor also indicate a low occurrence of significant toxicity to *H. azteca* and *C. tentans*. Thus, it may be implied for this study that the *H. azteca* results probably would have shown a low degree of significant acute mortality based on the results of the *C. tentans* tests.

Table 4-2 also lists the qualitative priority for conducting further sediment investigations at the sample sites. This ranking was based on the total RCF value and presence of bioaccumulative contaminants (e.g., mercury, PCBs) at depth in the core. In general, sites were ranked as follows:

- Total RCF = 0 - 10, Very Low
- Total RCF = 11 - 17, Low
- Total RCF = 18 - 29, Medium
- Total RCF = 30 - 48, High
- Total RCF = 49 - 91, Very High

Although DSH 21 (mouth of Stryker Embayment) had a low RCF value of 8.6, this site was highly contaminated with PAHs when it was resampled in 1994. Therefore, site DSH 21 was given high priority for further study.

The highest priority site for further study was the USX Superfund site. This site, along with the Interlake/Duluth Tar Superfund site, have been undergoing additional investigations as

part of the potentially responsible parties legal obligations. Other sites that were rated highly for further study included the bay surrounding the WLSSD and Coffee/Miller Creek outfalls, Fraser Shipyards, Minnesota Slip, area between the M.L. Hibbard Plant/DSD No. 2 and Grassy Point, and in the old 21st Ave. West Channel. Other areas, such as Slip C and off the Superior POTW outfall, were listed as medium priority. It is important to note that this study was limited in scope and was not meant to characterize large areas as to the extent of contamination.

The preliminary results of this investigation were used to select sites for a hotspot investigation the MPCA carried out in 1994. The hotspot areas included:

- Minnesota Slip
- Slip C
- WLSSD, Miller Creek, and Coffee Creek Embayment
- Bay south of the DM&IR Taconite Storage Facility
- Bay east of Erie Pier
- Area north of Grassy Point
- Howard's Bay
- Superior POTW
- Kimball's Bay (reference site)

The hotspot investigation included sediment chemistry measurements of different core segments, 10-day sediment toxicity tests with *H. azteca* and *C. tentans*, and an assessment of the benthological community structure. The results of this hotspot investigation are currently being evaluated by the MPCA Water Quality Division.

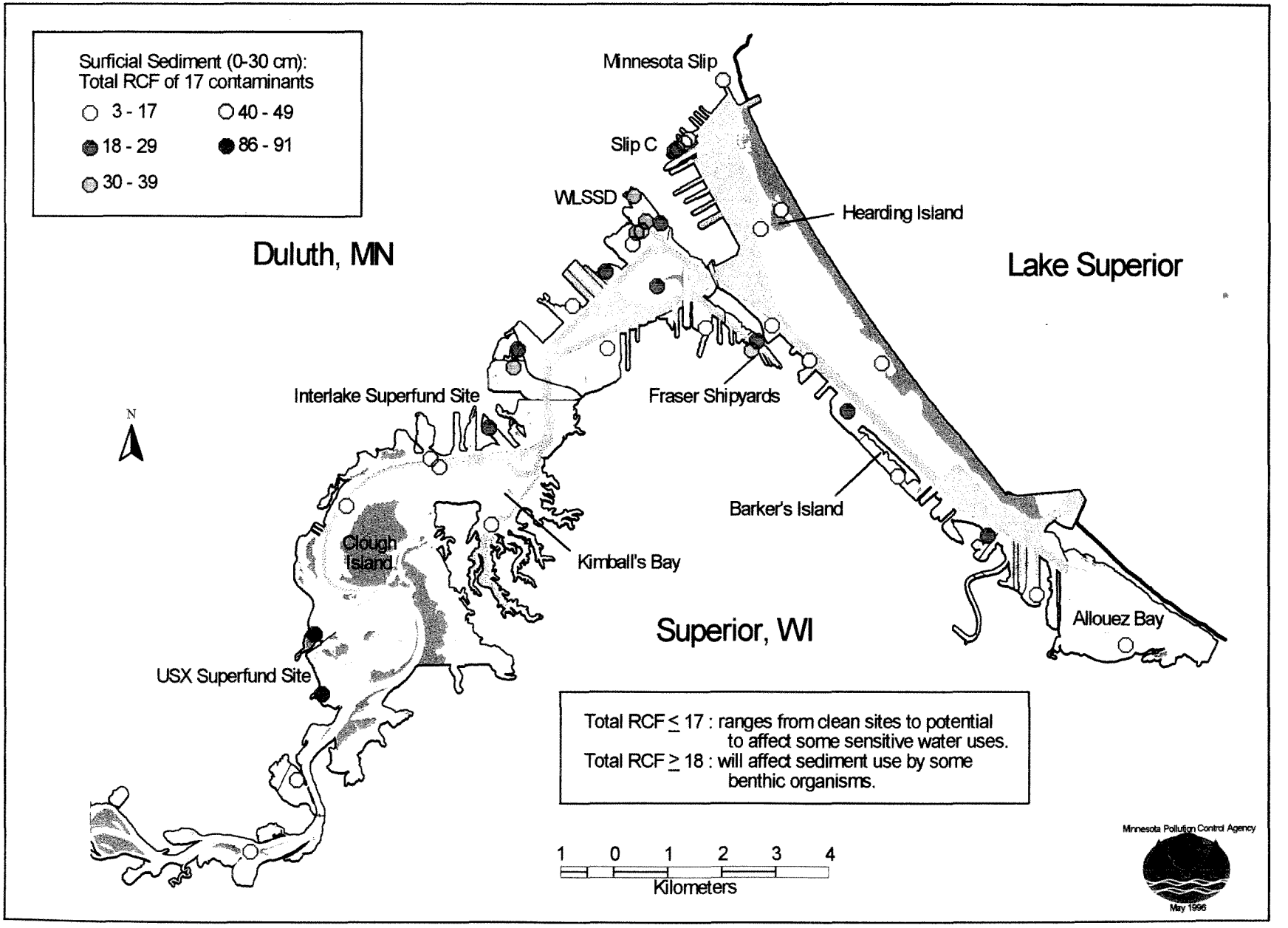

Figure 4-1. Map of total relative contamination factors (RCFs) for surficial sediments collected in the Duluth/Superior Harbor.

Table 4-1. Relative contamination factors (RCFs) for surficial sediments collected in the Duluth/Superior Harbor survey. Boldface RCFs are greater than 1 (i.e., the surface sediment concentration exceeds the OMOEE LEL).

Chemical	OMOEE LEL [1]	Sampling Location (DSH #)																		
		01	02	03	04	05	06	07	09	10	11	12	13	14	15	16	17	18	19	20
Hg	0.2	0.51	0.64	**2.6**	0.81	0.22	0.22	0.27	0.58	**1.6**	**4.2**	**2.7**	**1.9**	0.4	**1.1**	0.76	**2.3**	0.51	**1.3**	0.62
As	6	**4**	-	**1.8**	-	0.12	0.55	-	-	**2.9**	**2.8**	**2**	**1.9**	0.42	0.12	**2.4**	**3.9**	**3.6**	**1.1**	-
Cd	0.6	**3.1**	**1.1**	**3.6**	**2.1**	0.87	**2.5**	**1.9**	**1.8**	**4.8**	**6.3**	**4.4**	**4.0**	**1.9**	**3.4**	**5.0**	**6.1**	**4.9**	**7.6**	**2.5**
Cr	26	**1.9**	0.21	**2.0**	0.53	0.55	**1.1**	0.48	0.22	**2.1**	**2.2**	**2.1**	**1.9**	**1.2**	**1.2**	**1.2**	**2.4**	**2.1**	**1.7**	0.58
Cu	16	**2.4**	0.26	**2.6**	0.44	0.43	0.92	0.40	0.30	**2.0**	**3.0**	**3.8**	**1.9**	**1.1**	0.76	**1.9**	**3.3**	**2.1**	**2.3**	0.74
Pb	31	0.44	0.12	**1.5**	0.16	0.19	0.21	0.18	0.14	**1.3**	**1.6**	**3.0**	**1.1**	0.3	0.16	0.22	**2.4**	0.6	**1.4**	0.4
Ni	16	**1.7**	0.19	**1.7**	0.47	0.51	**1.0**	0.44	0.24	**1.7**	**1.9**	**1.8**	**1.6**	**1.0**	0.98	**1.7**	**2.6**	**1.8**	**1.7**	0.49
Zn	120	0.77	0.11	**1.4**	0.24	0.27	0.43	0.22	0.1	**1.5**	**1.6**	**1.6**	**1.4**	0.59	0.35	0.38	**2.2**	0.85	**1.5**	0.33
TOC	1	**5.4**	**1.1**	**4**	**4.2**	**1**	**2.6**	0.4	**1**	**4.1**	**5**	**3.3**	**3.2**	**2.4**	0.5	**4**	**8.9**	**2**	**16**	**7.9**
Aldrin	2	0.065	0.025	-	0.08	-	-	0.085	0.05	-	-	-	-	0.075	0	0.55	-	-	-	-
HCB	20	0.002	0	0.0065	0	0.0015	0	0.0005	0.0075	0.018	0.008	0.0085	0.016	0.006	0.006	0.036	-	0	0.012	0.026
p,p' -DDE	5	0.17	0.13	0.89	0.10	0.042	0.008	0.13	0.21	0.34	**1.7**	**1.3**	0.36	0.038	0.018	0.28	-	0.22	0.39	0.15
p,p'-DDD & o,p'-DDT	8	0.24	0.18	**1.3**	0.30	0.056	0.026	0.094	0.61	0.7	**1.5**	**1.3**	0.71	0.16	0.031	**1.0**	-	0.31	0.34	0.28
Dieldrin	2	-	-	-	-	-	-	-	0.03	-	**1.8**	0.21	-	0.07	0.03	0.5	-	-	-	-
Endrin	3	-	-	-	-	-	-	-	-	0.093	-	-	0.11	0.033	0.023	0.11	-	-	-	-
Lindane	3	0.023	0.003	0.07	0.03	0.0033	0.03	0.01	-	-	-	-	-	-	-	-	-	-	-	-
PCBs	70	0.48	**2**	**1.5**	0.24	0.18	0.14	0.46	0.86	**1.4**	**4.5**	**4.2**	0.81	0.41	0.17	**1.3**	-	0.97	**1.4**	0.23
PAHs	4000	0.12	0.24	**1.2***	0.42	0.20*	0.14	0.0078	0.48	**1.4**	**2**	**1.4**	0.65	0.46	-	0.28	**4.6**	0.33*	**2.1**	Lost
Total RCF		21	6.3	25	10	4.4	10	5.0	6.6	26	40	33	21	11	8.8	22	39	20	39	14
Total RCF excluding TOC		16	5	**21**	6	3	7	5	6	**22**	**35**	**30**	**18**	8	8	**18**	**30**	**18**	**23**	6

[1] Concentration units: metals (mg/kg), organic contaminants (μg/kg), TOC (%)

*PAH value taken from samples collected June 1993 and analyzed July 1994.

Table 4-1. Continued.

Chemical	OMOEE LEL [1]	Sampling Location (DSH #)																			
		21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40
Hg	0.2	0.14	0.2	2.1	3.5	2.1	1.4	0.06	0.27	1.1	1.2	1.6	1.4	0.99	11	3.6	2	2.2	0.43	0.025	1.1
As	6	0.8	1.2	-	5.6	3.4	1.4	-	2	0.23	0.7	1	1.9	1	0.067	0.87	0.97	0.17	0.13	-	0.57
Cd	0.6	3.2	2.5	1.5	12	9.2	4.9	1.9	3.6	4.0	3.0	5.1	3.5	2.9	6.8	6.0	5.2	3.2	1.5	1.7	4.4
Cr	26	1.3	1.4	0.33	2.1	3.6	1.7	0.96	1.6	0.80	1.6	2.1	1.6	1.5	1.7	1.7	1.7	0.73	0.37	0.58	1.9
Cu	16	0.96	1.6	0.46	4.0	31	1.6	0.72	2.8	2.3	1.6	4.7	2.1	1.6	4.4	2.4	4.0	2.0	0.80	0.36	5.2
Pb	31	0.08	0.16	0.62	18	9.3	0.43	0.13	0.17	1.7	0.3	9.2	1.5	0.5	3.0	1.2	3.5	1.8	1.6	0.05	6.6
Ni	16	1.1	1.5	0.24	1.4	7.3	1.5	0.75	0.99	0.74	1.6	1.6	1.6	1.5	1.6	1.4	1.6	0.66	0.39	0.35	1.9
Zn	120	0.46	0.63	0.23	32	14	1.0	0.34	0.59	1.0	0.83	2.4	2.0	0.78	2.5	1.3	1.3	0.83	0.49	0.17	1.8
TOC	1	1.5	10	5.3	5.6	5.2	3.5	1.3	23	5.3	3	7.1	2.9	3.1	3.4	4	2.8	5.1	1.6	0.1	3.6
Aldrin	2	-	-	-	-	-	-	0.11	-	-	-	1.7	0.45	-	-	-	-	-	-	0.045	-
HCB	20	-	-	0.01	0.006	0.05	0.004	-	0.012	0.01	0.005	0.02	0.01	0.0085	0.0095	0.012	0.01	0.019	0.028	0.0015	0.1
p,p'-DDE	5	-	0.012	0.52	0.66	2.4	0.22	0.018	0.098	0.64	0.15	1.3	0.36	0.16	4.8	0.96	1.5	0.64	0.36	-	0.9
p,p'-DDD & o,p'-DDT	8	0	0.024	0.39	0.21	0.18	0.26	0.013	0.028	1.2	0.12	4.5	0.81	0.25	3.9	1.0	6	1.1	0.45	0.019	1.3
Dieldrin	2	-	-	-	-	-	-	-	0.7	0.65	-	2	-	0.22	1.2	0.035	-	0.01	-	0.005	-
Endrin	3	-	-	-	-	-	-	-	-	-	0.067	-	-	0.087	-	0.0033	-	0.027	0.063	0.0067	-
Lindane	3	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
PCBs	70	0.12	0.16	1.5	2.7	1.6	0.97	0.12	0.38	2.2	0.44	2.2	1.0	0.8	6.3	2.9	3.5	2.0	1.9	0.061	1.9
PAHs	4000	0.48	-	3.9	4.6	6.6	1.3	-	0.63	5.8	0.10*	3.4	1.4	0.34	2.0	1.5	3.5	3.9	1.0	0.068	13
Total RCF		10	19	17	92	96	20	6.4	37	28	14	50	23	16	53	29	37	24	11	3.6	45
Total RCF excluding TOC		9	9	12	86	91	17	5	14	22	11	43	20	13	49	25	35	19	10	3	41

[1] Concentration units: metals (mg/kg), organic contaminants (μg/kg), TOC (%)

*PAH value taken from samples collected June 1993 and analyzed July 1994.

Table 4-2. Summary of contaminant and toxicology data for 40 sites in the Duluth/Superior Harbor. Note that the sediment chemistry results are not synoptic with the toxicity test results.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 25	91	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDE, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp	Cu, Pb, Ni, Zn	Incon.			X	Very High; high Hg and PCBs in 31-61 cm core segment
DSH 24	86	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Dba, Bgp	As, Pb, Zn	Incon.	X	X	X	Very High
DSH 34	49	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Dieldrin, p,p'-DDE, p,p'-DDD & o,p'-DDT, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap	Hg		X	X	X	Very High; high Hg in 31-61 cm core segment
DSH 31	43	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Aldrin, Dieldrin, p,p'-DDE, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp	Pb				X	High; higher PCBs than surface in 31-61 cm core segment
DSH 40	41	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDD & o,p'-DDT, Fle, Phe,Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Dba, Bgp		Incon.		X	X	High; high Hg in all deeper core segments, higher PCBs than surface in 36-66 cm core segment
DSH 11	35	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Dieldrin, p,p'-DDE, p,p'-DDD&o,p'-DDT, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp				X		High

Table 4-2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 36	35	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDE, p,p'-DDD & o,p'-DDT, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	High; high Hg in 122-216 cm core segment, high PCBs in most deeper core segments
DSH 17	30	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.				High; surficial PCB sample lost for this site and could not be included in total RCF calculation
DSH 12	30	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, p,p'-DDE, p,p'-DDD & o,p'-DDT, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp		Incon.		X	X	High; high Hg in 163-180 cm core segment, PCBs elevated in other core segments but less than surface
DSH 35	25	Hg, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp				X		Medium; high Hg in 31-61 cm core segment
DSH 19	23	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fle, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	Medium; high Hg in 31-61 cm core segment
DSH 29	22	Hg, Cd, Cu, Pb, Zn, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.		X	X	Medium; high Hg and PCBs in all deeper core segments
DSH 10	22	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Fla, Pyr, Baa, Cry, Bfa, Bap				X		Medium

Table 4-2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 03	21	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs		Incon.			X	Medium; higher PCBs than surface in 61-91 cm core segment
DSH 32	20	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, total PCBs, total PAHs, Phe, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp						Medium; higher Hg than surface in 31-61 cm core segment
DSH 37	19	Hg, Cd, Cu, Pb, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp		Incon.		X	X	Medium; higher Hg than surface in 31-61 cm and 61-91 cm core segments
DSH 13	18	Hg, As, Cd, Cr, Cu, Pb, Ni, Zn, Cry, Bfa		Incon.		X		Medium
DSH 18	18	As, Cd, Cr, Cu, Ni		Incon.			X	Medium
DSH 16	18	As, Cd, Cr, Cu, Ni, total PCBs, p,p'-DDD & o,p'-DDT		Incon.				Medium; higher Hg than surface in 81-122 cm core segment, higher PCBs than surface in 51-81 cm core segment
DSH 26	17	Hg, As, Cd, Cr, Cu, Ni, Zn, total PAHs, Phe, Pyr, Bfa, Bap, Bgp		Incon.			X	Low
DSH 01	16	As, Cd, Cr, Cu, Ni		Incon.			X	Low; higher PCBs than surface in 61-91 cm core segment
DSH 28	14	As, Cd, Cr, Cu, Ni, Pyr, Bfa					X	Low

Table 4-2. Continued.

Site	Total RCF Value	Surficial Chemical Contaminant Data[1]		Significant Toxicity Text Results?				Priority for Further Study/Comments
		Exceed LEL?	Exceed SEL?	*H. azteca*[2]	*C. tentans*	Microtox	Mutatox	
DSH 33	13	Hg, As, Cd, Cr, Cu, Ni		Incon.		X		Low
DSH 23	12	Hg, Cd, total PCBs, total PAHs, Fle, Phe, Ant, Fla, Pyr, Baa, Cry, Bfa, Bap, Idp, Bgp		Incon.			X	Low
DSH 30	11	Hg, Cd, Cr, Cu, Ni		Incon.				Low
DSH 38	10	Cd, Pb, total PCBs, total PAHs, Phe, Pyr, Baa, Cry, Bfa		Incon.			X	Medium; higher Hg and PCBs than surface in 31-61 cm core segment
DSH 22	9.4	As, Cd, Cr, Cu, Ni		Incon.				Very Low
DSH 21	8.6	Cd, Cr, Ni, Bpg		Incon.				High; high PAHs (RCF = 22) observed at this site when it was resampled in 1994
DSH 15	8.3	Hg, Cd, Cr					X	Very Low
DSH 14	8.2	Cd, Cr, Cu, Ni, Bfa		Incon.	X			Very Low
DSH 06	7.3	Cd, Cr, Ni		Incon.				Very Low
DSH 20	6.3	Cd		Incon.		X	X	Very Low
DSH 04	5.9	Cd		Incon.				Very Low
DSH 09	5.6	Cd, Bfa, Bgp						Very Low
DSH 02	5.2	Cd, total PCBs		Incon.		X	X	Low; high surficial PCBs, other core segments not analyzed for PCBs
DSH 27	5.1	Cd					X	Very Low
DSH 07	4.6	Cd		Incon.			X	Very Low
DSH 39	3.5	Cd		Incon.				Very Low
DSH 05	3.4			Incon.				Very Low
DSH 08	-	No vibracore sediment sample collected		Incon.		X		Insufficient information to evaluate

[1]Codes: Fle = Fluorene; Phe = Phenanthrene; Ant = Anthracene; Fla = Fluoranthene; Pyr = Pyrene; Baa = Benz(a)anthracene; Cry = Chrysene; Bfa = Benzofluoranthene; Bap = Benzo(a)pyrene; Idp = Indeno(123-cd)pyrene; Dba = Dibenz(a,h)anthracene; Bgp = Benzo(g,h,i)perylene

[2]Incon. = Inconclusive test results due to control failure

CHAPTER 5

RECOMMENDATIONS

This study filled a critical need for an estuary-wide sediment survey that assessed horizontal and vertical chemical concentrations, as well as determined potential toxicity to benthic organisms in the Duluth/Superior Harbor. By supporting the assessment goals of the Phase I sediment strategy for the RAP, this study formed the basis for three other sediment investigations the MPCA has been conducting in the St. Louis River AOC. In lieu of listing recommendations from this investigation that are already being carried out in ongoing MPCA sediment surveys, some general recommendations for the management of contaminated sediments in the harbor are given here.

- Determine background levels of contaminants in the St. Louis River AOC. The R-EMAP project the MPCA is conducting in collaboration with NRRI and the U.S. EPA will accomplish this for PAH compounds and mercury.

- Develop biologically-based sediment quality guidelines specific to the Duluth/Superior Harbor. A logistic modeling approach could be used to develop guideline values.

- Determine clean-up goals for remediation activities in the St. Louis River AOC.

- Implement proposed remediation options at the USX and Interlake/Duluth Tar Superfund sites. The remediation would be carried out by the potentially responsible parties in cooperation with the MPCA Site Response Section.

- Develop a GIS-based sediment database for the St. Louis River AOC that would include sediment chemistry, toxicity, benthological, and tissue residue data. This database could be expanded from the sediment database currently under development by GLNPO.

- Conduct hydrodynamic and sediment transport modeling in the Duluth/Superior Harbor to determine how susceptible hotspot sediments are to resuspension.

- Assess the bioaccumulation of contaminants in the Duluth/Superior Harbor by analyzing benthic fish tissue and conducting 28-day sediment bioaccumulation toxicity tests with the oligochaete, *Lumbriculus variegatus*.

- Develop sediment remediation options for non-Superfund sites in the Duluth/Superior Harbor. This could be accomplished by screening previously sampled site data with the MPCA's draft "Site Screening Evaluation Guidelines." Contaminated sites identified by this screening step could then be evaluated to identify a set of remedial options for each site.

- Monitor concentrations of 2,3,7,8-TCDD/TCDF in fish tissue in order to ascertain the risk to human and ecological health of fish consumers. In addition, it would be useful to analyze sediments and fish tissue for all seventeen 2,3,7,8 substituted congeners of dioxin and furans. Such assessment may also point out the need for continuing diligence in controlling point and nonpoint sources of dioxins and furans.

- Investigate the occurrence of toxaphene in the harbor.

- Increase public education efforts to communicate the results of the MPCA's sediment investigations in the St. Louis River AOC and goals for remediation.

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APPENDIX A

DATABASE OF SEDIMENT CHEMISTRY DATA

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DATABASE OF SEDIMENT CHEMISTRY DATA

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
GREAT LAKES NATIONAL PROGRAM OFFICE
77 WEST JACKSON BOULEVARD
CHICAGO, IL 60604-3590

January 16, 1997

Judy L.Crane, Ph. D.
Minnesota Pollution Control Agency
Water Quality Division
520 Lafayette Rd. N.
St. Paul, MN 55155-4194

SUBJECT: Electronic data for 1993 Mudpuppy sampling - Duluth/Superior Harbor

Dear Judy Crane:

Please find enclosed a diskette with data from the 1993 Mudpuppy project. The data has been formatted in MS Excel according to the GLNPO data reporting format, provided to you last August. All the files, with the exception of one, adhere to this format. The one exception is the station file (dsstatn.xls), which follows the Station Reporting Standard, a hard copy of which I have enclosed.

The Mudpuppy data contains three types of files. The station file (dsstatn.xls) contains station descriptions and location information. The field file (dsfield.xls) contains detailed sample information, and all the remaining files contain analytical results. Each result file represents a different analytical method (e.g., dspcb.xls and dspcbimm.xls contain PCB and PCB/immunoassay data, respectively).

Files containing the lists of allowable codes for the Station Reporting Standard are contained on a second diskette. Each file contains codes for a single column within the Station Reporting Standard.

A list containing short descriptions of file contents is enclosed. If you have any questions or comments, please call me at (312) 353-3565.

Sincerely,

Brian Stage

Brian Stage

Enclosures

cc: Callie Bolattino (letter only)

File Name	Description

93 Mudpuppy files

Note: 'ds' prefix stands for Duluth/Superior

dsdiox&f.xls	dioxin & furan
dsfield.xls	field file
dsmetals.xls	metals other than As and Hg
dsmetas.xls	arsenic (As)
dsmethg.xls	mercury (Hg)
dsmetxrf.xls	metals by x-ray fluorescence
dsnh3.xls	ammonia
dspahall.xls	PAH's
dspahflr.xls	PAH, by fluorescence
dspcb.xls	PCB's
dspcbimm.xls	PCB's by immunoassay
dspest.xls	pesticides
dsstatn.xls	station file
dstoc.xls	TOC

Station Reporting Standard files

(for use with dsstatn.xls)

alp_type.xls	absolute location point type
country.xls	country
county.xls	FIPS county
datum_h.xls	geopositioning horizontal datum
datum_v.xls	geopositioning vertical datum
dist_shr.xls	distance to shore
huc.xls	FIPS hydrologic unit code
native.xls	native american lands
poll_rel.xls	pollutant spatial relation
poll.src.xls	pollutant source
reln.shr.xls	relation to shore
stn_shap.xls	station shape
stn_typ.xls	station type

STATIC Reporting Standards

Station/Location Reporting Standard

This reporting standard includes two spreadsheet templates for entering station and location information. When entering data, you first should enter all data into the station spreadsheet template. Then, you will enter the data in the absolute location point template. You also need to link the data in the two spreadsheets by using the first column of both spreadsheets (*i.e.*, station GLNPO code).

Most importantly to submit data using this reporting standard, you should read through the following directions carefully *before entering any data* into either spreadsheet template.

Template Layout

The template includes all the information about the data model that you need to know to enter data. For example, the column headings denote the table and column names, the cardinality among the data in the template, and additional information that may be useful. The *presentation* of the column headings also is intended to provide you with useful information. For example, CAPITALIZATION denotes mandatory. Underlined entries specify whether you need to include a valid reference table code. These concepts are described in more detail below. The following descriptions also can be used as reference material until you become familiar with the general template layout.

Column Headings

Each template has several column headings. Each row of the column heading has a different purpose as described below.

1st row—*Logical Data Unit* = describes the group of columns that fall between the pair of dark black lines.

2nd row—*Cardinality Explanation* = describes how many rows should be included for the logical data unit (*i.e.*, the columns that fall between the pair of dark black lines).

3rd row—*Entity Type/Table Name* = references the entity type/table name where the data will be stored in the target database.

The reference tables that are included in the station spreadsheet template include:

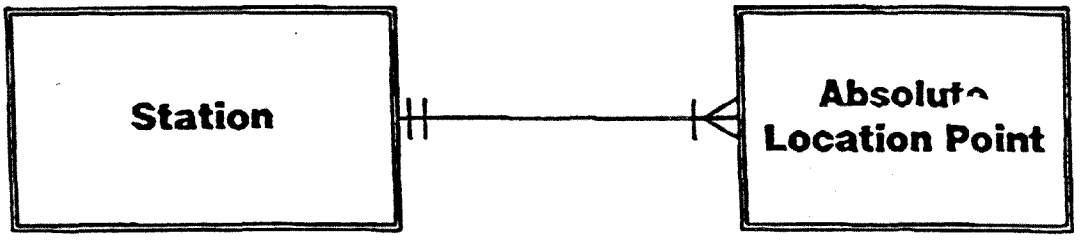
(1) Absolute Location Point Type
(2) Map or Photo
(3) Geopositioning Map or Photo Scale
(4) Geopositioning Horizontal Method
(5) Geopositioning Horizontal Datum
(6) Geopositioning Vertical Method
(7) Geopositioning Vertical Datum
(8) FIPS County
(9) USDA District (to be determined)
(10) FIPS HUC
(11) Native American Land
(12) EPA RF1 River Reach
(13) Unit of Measure

Reference tables with the valid code for data entry are attached to these instructions. *Do not enter codes that do not exist in the attached tables.* You also should not add entries and new codes to the attached reference tables. (If you absolutely need a code that is not listed, contact the project manager. He will research your request and provide an answer, usually within a few days.)

Linking Stations to Absolute Location Points

Although stations and absolute locations points are reported on separate spreadsheets, the data in both spreadsheets are related. In other words, a row in the station spreadsheet is related to a row(s) in the absolute location point spreadsheet. Therefore, when you use this reporting standard, you need to make link between the two spreadsheets so that the data can be related in the database.

The logical connection between the rows in the two spreadsheets are as follows:



A *STATION* must have one or more *ABSOLUTE LOCATION POINTs.*

An *ABSOLUTE LOCATION POINT* must have one and only one *STATION.*

For each logical unit, there is a pre-defined cardinality between station and the logical unit. In other words, each station could have many entries in a logical unit such as Station Pollutant Source information. For example, a station may be polluted by more than one type of pollutant source (*e.g.*, urban runoff, industrial discharge).

These cardinalities are described in the second row of the template. When there is ONE Entry per Station, the user should enter only one row of data for any given station. When this row states MANY Entries per Station, the user may enter one or more rows of data.

The following table provides a high-level example of how the template should be used. To simplify the explanation, this example does not include all the template columns.

Figure 3: Simplified Station Template

(In comparison to the real template, some columns and rows of column headings have been deleted in this simplified version.)

Primary Station Info.		**Station Description**		**Distance to Shore**		**Pollutant Source**	
GLNPO CODE	Establishment Date	TYPE	SHAPE	Distance to Shore	DIST TO SHORE TYPE	Pollutant Source Type	Pollutant Spatial Relation
1	081596	RVR	LN	5	LEFT	ID	CROSS
1				10	RIGHT		
2	081596	RVR	PT			ORU	IN
2						ID	IN
2						CSO	IN

To include data in the template, the user should begin in the left-most column (*i.e.*, station GLNPO code) and continue to the right. According to the entries in the simplified version of the template, there are two stations being reported. The stations are uniquely defined by GLNPO as 1 and 2. These two stations were established on 8/15/96, and they are both RVR (*i.e.*, river) stations. More specifically, station 1 is a LN (*i.e.*, line shaped station) that is 5 meters to the LEFT shore and 10 meters to the RIGHT shore. Station 2 is a PT (*i.e.*, point station) where the user decided not to measure the distance to shore. (This omission is acceptable because Distance to Shore is not mandatory based on the template convention that non-capitalized table names are optional). Finally, both stations are being polluted by an ID (industrial discharge). In addition, station 2 is effected by a CSO (combined sewer overflow) and an ORU (overland runoff, urban). For station 1, the station is located cross-stream from an industrial discharge. For station 2, the station is located in-stream (in the pollutant stream) of all pollutant sources listed.

In addition to the entries that should be included in specific cells, this example also shows how the cardinality rules work. In this case, a station can have only one set of station descriptions. Therefore, the description information is listed on the same row as the original station information. At the same time, the station can have many distances to shore and pollutant sources. When the user gets to the first logical unit that allows *many* entries per station (*i.e.*, distance to shore), the user can enter as many rows as necessary. The first row of entries must be in the same row as the related primary station information. After entering all rows for the current logical unit (*e.g.*, distance to shore), the user should move to the next logical unit

Like the station template, the spreadsheets are divided into logical units of data entry as denoted by the thick, solid black lines. For example in figure 6 above, the logical unit is standard location information. Figure 5 includes the logical units called latitude/longitude and geopositioning explanation. In this template, the cardinality among these logical units is one entry for every absolute location point.

To enter data in the template, the user should begin in the left-most column (*i.e.*, station GLNPO code) a continue to the right. On every row, you must not only enter a station GLNPO code in the first column, the code must match a GLNPO code that was provided in the station template. If this GLNPO code do not correspond to an entry in the station template, there is no way to relate the absolute location information to a station.

APPENDIX B

SEDIMENT TOXICITY TEST REPORTS FOR *HYALELLA AZTECA* AND *CHIRONOMUS TENTANS*

ACUTE TOXICITY TESTS WITH *HYALELLA AZTECA* AND *CHIRONOMUS TENTANS* ON SEDIMENTS FROM THE DULUTH/SUPERIOR HARBOR:

1993 Sampling Results - Batches # 1 and 2

Conducted by

Minnesota Pollution Control Agency
Monitoring and Assessment Section
520 Lafayette Road
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February 1997

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INTRODUCTION

As part of the 1993 survey of sediment quality in the Duluth/Superior Harbor, sediment toxicity tests were conducted to assess acute (survival) and chronic (growth) toxicity to benthic invertebrates. Acute effects were measured in separate 10-day toxicity tests to *Hyalella azteca* (*H. azteca*) and *Chironomus tentans* (*C. tentans*). Growth was measured at the end of the *C. tentans* test to assess chronic effects. Survival and growth endpoints were compared to organisms similarly exposed to a reference control sediment collected from West Bearskin Lake (Cook County, MN).

A total of 40 sediment samples were collected for toxicity testing. This report presents the results of nine of these sediment samples run in two separate batches with separate controls.

SAMPLE COLLECTION AND HANDLING

Between September 13-23, 1993, Minnesota Pollution Control Agency (MPCA) staff collected the nine sediments referred to in this report. The samples were collected from the harbor using a Ponar sampler and were taken to the University of Minnesota-Duluth Chemical Toxicology Research Laboratory. The samples were stored at 4°C until they were transported to the MPCA Toxicology Laboratory in St. Paul, MN on October 4, 1993.

METHODS

Nine sediment samples and two control sediment samples were subjected to the 10-day sediment toxicity tests using the modified procedures described in ASTM (1993). However, the specific test system used for these assays is not indicated in the methods. The test organisms (*H. azteca* and *C. tentans*) were exposed to sediment samples for ten days in a portable, mini-flow system described in Benoit et al. (1993). The test apparatus consists of 300 mL, glass-beaker test chambers held in a glass box supplied with water from an acrylic plastic headbox. The beakers have two, 1.5 cm holes covered with stainless steel mesh, to allow for water exchange, while containing the test organisms. The headbox has a pipette tip drain calibrated to deliver water at an average rate of 32.5 mL/min. The glass box is fitted with a self-starting siphon to provide exchange of overlying water.

The *H. azteca* used for this test were 1 to 3 mm long, and the *C. tentans* were approximately 14 days old. These organisms were supplied by Environmental Consulting and Testing in Superior, WI. On the day of the Batch #1 test set up, MPCA personnel picked up the organisms from the supplier and transported them to the MPCA Toxicology Laboratory. An insufficient number of *H. azteca* were received to set up the toxicity tests. Thus, another batch of *H. azteca* was received from the supplier the next day via Federal Express.

On October 4, 1993, four samples (DSH 08, DSH 12, DSH 21, and DSH 40) and the control sediment were separately homogenized by hand, and 100 mL of each sediment was placed in a test beaker (Batch #1). On October 5, 1993, five more samples (DSH 16, DSH 18, DSH 19,

DSH 23, and DSH 29) and another control sediment were homogenized and placed in beakers (Batch #2). Aerated, artesian well water was added to the beakers, and the sediments were allowed to settle for approximately two hours before the organisms were added. The sediment samples for DSH 18 and DSH 19 had accidentally frozen during storage. These sediment samples were thawed in a water bath the morning of October 5 before homogenizing them.

Each sediment test was set up with three replicates of *H. azteca* and three replicates of *C. tentans.* Ten organisms were placed in each of six beakers in a random fashion. The organisms were exposed to 16 hours of light and eight hours of darkness for the duration of the ten-day test. Each day, two liters of aerated water from the artesian well at Stroh Brewery in St. Paul were exchanged in each test chamber. On weekdays, this was done in two equal aliquots. On weekends, the two liters were passed through the chambers all at once. Water quality measurements (i.e., pH, temperature, and dissolved oxygen) of the overlying water were taken in one beaker of each of the triplicate sets of each of the sediments. The results, along with daily observations involving the physical appearance of the sediments and organisms, were recorded in a laboratory notebook.

The test was terminated on October 14, 1993 for Batch #1 and on October 15, 1993 for Batch #2. The sediments were sieved through 40 mesh screens, and the sieved material was sorted for organisms. The organisms found were counted, and the number of alive and dead organisms were recorded. Organisms not found were recorded as missing and presumed dead. The *C. tentans* that survived were placed in aluminum weighing dishes, dried at approximately 90°C for at least four hours, desiccated to room temperature, and weighed.

Growth (weight) of the *C. tentans* and survival of both organisms were used as the endpoints for these tests. The resulting survival data were analyzed using TOXSTAT (Gulley and WEST, Inc., 1994), a statistical software package obtained from the University of Wyoming; however, due to a quality assurance problem, the growth data were not analyzed.

A 96-hour, reference toxicant test with *H. azteca* in sodium chloride (NaCl) was run in conjunction with these toxicity tests to determine the acceptability of the *H. azteca* used. Four concentrations of NaCl solution (i.e., 5, 2.5, 1.25, and 0.625 g/L) and a control (aerated, artesian well water) were used in this test. Three replicates of five organisms each were set up per concentration.

RESULTS

Water Quality

Measurements of pH, dissolved oxygen concentration, and temperature in the overlying water of the test beakers were made daily. These measurements are summarized below and in Tables 1, 2, and 3, respectively, for both batches of tests.

Batch # 1 Water Chemistry

In Batch #1, the range of pH values in the beakers containing *H. azteca* was 7.2 to 7.7 (Table 1). The water in the *C. tentans* beakers had a pH range of 7.0 to 7.5 (Table 1). The pH fluctuations during these tests were acceptable since it did not vary more than 50% within each treatment (U.S. EPA, 1994).

The dissolved oxygen concentration ranged from 3.8 to 7.6 mg/L in the *H. azteca* beakers and from 1.6 to 7.2 mg/L in the *C. tentans* beakers (Table 2). It should be noted that on days 2, 3, 5, 6, and 9, the dissolved oxygen concentration in the DSH 40 sediment beaker containing *C. tentans* was less than 40% saturated, which is out of the acceptable test range for dissolved oxygen.

The temperature of the overlying water in each glass box was measured and ranged from 20.0°C to 22.5°C (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Batch # 2 Water Chemistry

In Batch #2, the range of pH values in the beakers containing *H. azteca* was 6.9 to 7.7 (Table 1). The water in the *C. tentans* beakers had a pH range of 6.8 to 7.7 (Table 1). These pH ranges were acceptable for these tests.

The dissolved oxygen concentration ranged from 4.4 to 6.9 mg/L in the *H. azteca* beakers and from 3.2 to 6.7 mg/L in the *C. tentans* beakers (Table 2). It should be noted that on day 5, the dissolved oxygen concentration in the DSH 19 sediment beaker containing *C. tentans* was less than 40% saturated. On day 9, sample DSH 29 and Control #2 also had low dissolved oxygen concentrations in the *C. tentans* tests.

The range of temperature values in the beakers was measured and ranged from 20.0°C to 22.5°C (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Test Endpoints

The mean percent survival of the test organisms is summarized below and in Table 4. The sediments for DSH 18 and DSH 19 had frozen during sample storage. Changes in the sample matrix that may have taken place during the freezing and thawing of these sediments could not be determined. Thus, it is not known whether similar survival data would have resulted from using unfrozen sediments for these toxicity tests.

The mean percent survival of *H. azteca* in Control #1 was 13% with a range of 0% to 30%. For Control #2, the mean percent survival was 33% with a range of 10% to 50%. Survival for both of these controls was less than 80% and, therefore, unacceptable. Thus, both test batches for *H. azteca* failed.

For the control sediment containing *C. tentans*, percent survival ranged from 90% to 100% with a mean of 93% for Control #1 and a range of 80% to 100% with a mean of 90% for Control #2. Mean percent survival of *C. tentans* in Batch #1 in the test sediments ranged from 83% in the DSH 40 sample to 100% in the DSH 08 sample. Mean percent survival of *C. tentans* in Batch #2 ranged from 77% in the DSH 19 sample to 97% in the DSH 23 sample.

Although the dried *C. tentans* were weighed, the balance on which they were weighed was not calibrated with standard weights; therefore, the data are suspect since the internal calibration of the balance may have drifted with time.

Data Analysis

Survival data for both batches of test sediments containing *C. tentans*, except DSH 08 (100% survival) and DSH 21 (90% survival), were transformed using an arc sine-square root transformation before being analyzed statistically using Dunnett's test. A one-tailed test was used to test the alternative hypothesis that sample survival was less than control survival. Thus, it was not necessary to include the sample survival data which exceeded the control survival in the Dunnett's test (e.g., survival data for DSH 08). For DSH 21, survival (90%) was within the variability of 30-50% necessary to see any significant difference between the control and any given sediment (T. Norberg-King, U.S. EPA, Duluth, MN, personal communication). Thus, it is reasonable to assume that the effect that DSH 21 had on the test organisms was not significantly less than that of the control.

For both batches of test, none of the test sediment survivals were statistically less than the control at $p=0.05$ (Appendix A). For test batch #2, all of the survival results were included in the Dunnett's test even though the survival in DSH 23 and DSH 29 exceeded the control survival. This was because the statistical analysis had been run prior to implementing a policy at the MPCA Toxicology Laboratory to exclude results exceeding the control survival.

Reference Toxicant Test with *Hyalella azteca* in Sodium Chloride Solution

The pH of the overlying water in the reference toxicant test ranged from 7.1 to 8.0. The dissolved oxygen ranged from 7.4 to 8.4 mg/L and the temperature was 21°C on the first day of the test (temperature was not measured during the remainder of the test). Mean percent survival of the organisms in the control was less than 90% (i.e., 40%) which was unacceptable. Thus, the health of the test organisms was suspect, and the test failed.

SUMMARY

Survival of *H. azteca* in the control sediments was unacceptable (i.e., less than 80%), and the reference toxicant test with *H. azteca* failed. Therefore, no conclusions can be drawn about the effect that the sediments had on *H. azteca*.

Control survival was acceptable in both batches of *C. tentans* tests, and the survival of organisms in the test sediments was not statistically less than the control sediments.

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TABLE 1. Daily Overlying Water pH Measurements

Batch # 1

Day	Control 1		DSH 08		DSH 12		DSH 21		DSH 40	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.1	7.2	7.5	7.4	7.3	7.3	7.5	7.5	7.2	7.2
1	7.2	7.3	7.4	7.5	7.2	7.2	7.4	7.5	7.3	7.2
2	7.1	7.2	7.4	7.4	7.3	7.3	7.3	7.3	7.3	7.2
3	7.3	7.4	7.5	7.6	7.3	7.3	7.5	7.5	7.2	7.4
4	7.3	7.3	7.4	7.5	7.3	7.4	7.4	7.5	7.3	7.3
5	7.3	7.3	7.5	7.5	7.3	7.3	7.3	7.3	7.4	7.4
6	7.2	7.2	7.3	7.3	7.4	7.4	7.3	7.2	7.3	7.4
7	7.2	7.4	7.5	7.7	7.4	7.4	7.5	7.5	7.2	7.4
8	7.2	7.4	7.5	7.7	7.3	7.4	7.4	7.7	7.3	7.3
9	7.0	7.5	7.3	7.5	7.3	7.3	7.3	7.6	7.1	7.2
Mean	7.2	7.3	7.4	7.5	7.3	7.3	7.4	7.5	7.3	7.3
Range	7.0-7.3	7.2 - 7.5	7.3 - 7.5	7.3 - 7.7	7.2 - 7.4	7.2 - 7.4	7.3 - 7.5	7.2 - 7.7	7.1 - 7.4	7.2 - 7.4

Checked all Day 1 SLC 1/31/97

Batch # 2

Day	Control 2		DSH 16		DSH 18		DSH 19		DSH 23		DSH 29	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.3	7.3	7.4	7.4	7.2	7.1	7.3	7.2	7.4	7.4	6.8	7.0
1	7.0	6.9	7.2	7.2	7.3	7.3	7.3	7.3	7.3	7.3	7.1	7.2
2	7.4	7.6	7.5	7.7	7.4	7.5	7.5	7.5	7.5	7.5	7.3	7.3
3	7.5	7.6	7.5	7.7	7.4	7.5	7.5	7.6	7.5	7.6	7.3	7.3
4	7.4	7.4	7.4	7.4	7.4	7.5	7.4	7.4	7.5	7.5	7.4	7.4
5	7.4	7.4	7.4	7.4	7.5	7.5	7.5	7.4	7.5	7.5	7.5	7.4
6	7.4	7.6	7.4	7.7	7.5	7.6	7.5	7.6	7.6	7.6	7.3	7.4
7	7.5	7.6	7.7	7.7	7.5	7.5	7.4	7.6	7.5	7.5	7.3	7.4
8	7.2	7.4	7.4	7.6	7.2	7.3	7.2	7.5	7.2	7.3	7.1	7.4
9	7.2	7.3	7.3	7.4	7.4	7.4	7.4	7.4	7.4	7.4	7.1	7.2
Mean	7.3	7.4	7.4	7.5	7.4	7.4	7.4	7.5	7.4	7.5	7.2	7.3
Range	7.0 - 7.5	6.9 - 7.6	7.2 - 7.7	7.2 - 7.7	7.2 - 7.5	7.1 - 7.6	7.2 - 7.5	7.2 - 7.6	7.2 - 7.6	7.3 - 7.6	6.8 - 7.5	7.0 - 7.4

Checked all Day 0 SLC 1/31/97

initial QA/QC review by PK 8/29/96
final 10% QA/QC review by SLC 1/31/97

TABLE 2. Daily Overlying Water Dissolved Oxygen Concentrations (mg/L)

Batch # 1

Day	Control 1		DSH 08		DSH 12		DSH 21		DSH 40	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	6.9	6.8	7.2	7.0	6.7	6.7	7.2	7.3	6.6	6.2
1	5.9	6.7	5.3	6.3	6.0	5.7	6.4	7.0	4.6	5.1
2	5.0	6.3	5.5	6.5	4.3	5.7	5.8	6.4	3.3	3.8
3	6.1	6.4	5.5	6.5	4.4	5.7	5.5	5.9	3.2	5.3
4	5.3	6.8	5.2	6.4	5.1	6.1	5.8	6.8	4.3	4.6
5	4.2	6.1	5.1	6.2	4.5	5.2	4.1	5.9	1.7	5.0
6	4.0	5.8	4.9	6.0	4.2	5.1	4.0	6.0	1.6	4.8
7	5.7	6.7	6.0	7.5	5.7	6.0	6.5	7.0	3.6	5.3
8	5.7	6.6	6.4	7.1	5.5	5.8	6.1	7.6	4.2	4.6
9	4.4	6.5	4.7	6.5	4.1	5.1	4.8	6.8	3.0	3.8
Mean	5.3	6.5	5.6	6.6	5.1	5.7	5.6	6.7	3.6	4.9
Range	4.0-6.9	5.8-6.8	4.7-7.2	6.0-7.5	4.1-6.7	5.1-6.7	4.0-7.2	5.9-7.6	1.6-6.6	3.8-6.2

Checked all Day 8 - JLC 1/31/97

Batch # 2

Day	Control 2		DSH 16		DSH 18		DSH 19		DSH 23		DSH 29	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	6.7	5.8	6.6	6.9	5.0	5.2	4.7	4.4	5.7	5.4	6.7	6.9
1	5.2	6.0	5.3	5.8	5.3	5.7	4.2	5.0	5.4	5.9	5.0	5.4
2	5.3	6.4	4.9	6.0	5.2	5.8	5.1	5.4	5.5	5.9	5.0	5.4
3	5.8	6.9	5.2	6.5	4.9	6.4	6.0	6.4	5.9	6.6	4.8	6.1
4	5.5	6.4	5.1	6.3	4.5	6.3	3.5	6.1	4.4	5.8	4.5	6.0
5	5.3	6.2	5.0	5.8	4.2	6.0	3.2	5.7	4.0	5.3	4.3	6.1
6	5.5	6.7	4.5	6.6	6.0	6.9	5.3	6.8	6.4	6.7	4.7	6.3
7	5.6	6.7	6.2	6.7	6.5	6.0	5.0	6.6	5.8	6.3	5.1	5.9
8	3.7	6.2	4.5	6.1	4.3	5.8	3.9	6.0	4.1	5.4	3.8	6.0
9	3.4	5.5	4.1	5.8	4.2	5.5	3.5	5.6	4.3	5.6	3.4	5.4
Mean	5.2	6.3	5.1	6.3	5.0	6.0	4.4	5.8	5.2	5.9	4.7	6.0
Range	3.4-6.7	5.5-6.9	4.1-6.6	5.8-6.9	4.2-6.5	5.2-6.9	3.2-6.0	4.4-6.8	4.0-6.4	5.3-6.7	3.4-6.7	5.4-6.9

Checked all Day 7 - JLC 1/31/97

Initial QA/QC review by PK 8/29/96

final 10% QA/QC review by JLC 1/31/97

TABLE 3. Daily Overlying Water Temperatures (Degrees Celsius)

Batch # 1

Day	Control 1		DSH 08		DSH 12		DSH 21		DSH 40	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
1	21.5	21.5	21.5	21.5	20.5	21.0	21.5	21.5	21.0	21.0
2	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
3	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
4	20.5	20.5	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
5	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
6	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
7	22.0	22.0	21.5	21.5	21.5	21.5	22.0	22.0	21.5	21.5
8	21.0	21.0	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
9	20.5	20.5	20.5	*	*	20.5	20.5	20.5	20.5	20.5
Mean	21.6	21.6	21.5	21.6	21.4	21.4	21.5	21.5	21.4	21.4
Range	20.5-22.5	20.5-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5

* Temperature was not recorded.

Checked all Day 4 -JLC 1/31/97

Batch # 2

Day	Control 2		DSH 16		DSH 18		DSH 19		DSH 23		DSH 29	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	22.0	22.0	21.5	21.5	21.5	21.5	21.5	21.5	21.0	21.0	21.5	21.5
1	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
2	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
3	20.0	20.0	20.0	20.0	20.5	20.5	20.5	20.5	20.0	20.0	20.0	20.0
4	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
5	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
6	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	21.5	22.0
7	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
8	20.5	20.5	20.5	20.5	21.0	21.0	20.5	20.5	21.0	21.0	20.5	20.5
9	21.0	21.0	21.0	21.0	21.5	21.5	21.5	21.5	21.5	21.5	21.0	21.0
Mean	21.5	21.5	21.5	21.5	21.6	21.6	21.6	21.6	21.5	21.5	21.4	21.5
Range	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.5	20.0-22.5	20.0-22.5	20.0-22.5	20.0-22.5

Checked -all Day 3 -JLC 1/31/97

initial QA/QC review by PK 8/29/96
final 100% QA/QC review by JLC 1/31/97

TABLE 4. Mean Percent Survival of *Hyalella azteca* and *Chironomus tentans*

	Mean Percent Survival	
	Hyalella azteca [1]	*Chironomus tentans*
Batch # 1		
CONTROL #1	13%	93%
DSH 08	33%	100%
DSH 12	27%	90%
DSH 21	23%	90%
DSH 40	27%	83%
Batch # 2		
CONTROL #2	33%	90%
DSH 16	60%	83%
DSH 18	50%	90%
DSH 19	40%	77%
DSH 23	30%	97%
DSH 29	37%	93%

[1] Controls were unacceptable (< 80% survival). Thus, the *Hyalella azteca* tests failed for both batches of samples.

initial QA/QC review by PK 8/2
final QA/QC review by JLC 8/3

APPENDIX A

TOXSTAT Analysis

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
4
3
3
3
3
CONTROL
1.00000000
0.90000000
0.90000000
DSH 12
0.80000000
1.00000000
0.90000000
DSH 40
0.80000000
0.70000000
1.00000000

QA/QC'd JLC 1/30/97

TITLE: 93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
FILE: 93mpr2CA.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 3

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	CONTROL	1	1.0000	1.4120
1	CONTROL	2	0.9000	1.2490
1	CONTROL	3	0.9000	1.2490
2	DSH 12	1	0.8000	1.1071
2	DSH 12	2	1.0000	1.4120
2	DSH 12	3	0.9000	1.2490
3	DSH 40	1	0.8000	1.1071
3	DSH 40	2	0.7000	0.9912
3	DSH 40	3	1.0000	1.4120

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	CONTROL	3	1.249	1.412	1.303
2	DSH 12	3	1.107	1.412	1.256
3	DSH 40	3	0.991	1.412	1.170

QA/QC'd JLC 1/30/97

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	CONTROL	0.009	0.094	0.054	7.22
2	DSH 12	0.023	0.153	0.088	12.15
3	DSH 40	0.047	0.217	0.126	18.58

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	2	0.027	0.014	0.517
Within (Error)	6	0.159	0.026	
Total	8	0.186		

Critical F value = 5.14 (0.05,2,6)
Since F < Critical F FAIL TO REJECT Ho: All equal

QA/QC'd JLC 1/30/97

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.159

W = 0.934

Critical W (P = 0.05) (n = 9) = 0.829
Critical W (P = 0.01) (n = 9) = 0.764

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 1.05

Table Chi-square value = 9.21 (alpha = 0.01, df = 2)
Table Chi-square value = 5.99 (alpha = 0.05, df = 2)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 4/30/97

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	CONTROL	1.303	0.933		
2	DSH 12	1.256	0.900	0.356	
3	DSH 40	1.170	0.833	1.003	

Dunnett table value = 2.34 (1 Tailed Value, P=0.05, df=6,2)

93 MUDPUPPY RUN #2A CHIRONOMIDS 10/4/93
File: 93mpr2CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	CONTROL	3			
2	DSH 12	3	0.229	24.5	0.033
3	DSH 40	3	0.229	24.5	0.100

QA/QC'd JLC 1/30/97

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
6
3
3
3
3
3
3
CONTROL
0.8
1.0
0.9
DSH 16
0.8
0.8
0.9
DSH 18
1.0
0.8
0.9
DSH 19
0.6
0.8
0.9
DSH 23
0.9
1.0
1.0
DSH 29
0.9
1.0
0.9

@A/QCD JLC 4/30/97

TITLE: 93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 6

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	CONTROL	1	0.8000	1.1071
1	CONTROL	2	1.0000	1.4120
1	CONTROL	3	0.9000	1.2490
2	DSH 16	1	0.8000	1.1071
2	DSH 16	2	0.8000	1.1071
2	DSH 16	3	0.9000	1.2490
3	DSH 18	1	1.0000	1.4120
3	DSH 18	2	0.8000	1.1071
3	DSH 18	3	0.9000	1.2490
4	DSH 19	1	0.6000	0.8861
4	DSH 19	2	0.8000	1.1071
4	DSH 19	3	0.9000	1.2490
5	DSH 23	1	0.9000	1.2490
5	DSH 23	2	1.0000	1.4120
5	DSH 23	3	1.0000	1.4120
6	DSH 29	1	0.9000	1.2490
6	DSH 29	2	1.0000	1.4120
6	DSH 29	3	0.9000	1.2490

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	CONTROL	3	1.107	1.412	1.256
2	DSH 16	3	1.107	1.249	1.154
3	DSH 18	3	1.107	1.412	1.256
4	DSH 19	3	0.886	1.249	1.081
5	DSH 23	3	1.249	1.412	1.358
6	DSH 29	3	1.249	1.412	1.303

QA/QC'd JLC 1/30/97

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	CONTROL	0.023	0.153	0.088	12.15
2	DSH 16	0.007	0.082	0.047	7.10
3	DSH 18	0.023	0.153	0.088	12.15
4	DSH 19	0.033	0.183	0.106	16.92
5	DSH 23	0.009	0.094	0.054	6.93
6	DSH 29	0.009	0.094	0.054	7.22

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	5	0.153	0.031	1.755
Within (Error)	12	0.209	0.017	
Total	17	0.362		

Critical F value = 3.11 (0.05,5,12)
Since F < Critical F FAIL TO REJECT Ho: All equal

QA/QC'd JLC 1/30/97

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.209

W = 0.958

Critical W (P = 0.05) (n = 18) = 0.897
Critical W (P = 0.01) (n = 18) = 0.858

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 1.79

Table Chi-square value = 15.09 (alpha = 0.01, df = 5)
Table Chi-square value = 11.07 (alpha = 0.05, df = 5)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 4/30/97

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	CONTROL	1.256	0.900		
2	DSH 16	1.154	0.833	0.943	
3	DSH 18	1.256	0.900	0.000	
4	DSH 19	1.081	0.767	1.628	
5	DSH 23	1.358	0.967	-0.943	
6	DSH 29	1.303	0.933	-0.439	

Dunnett table value = 2.50 (1 Tailed Value, P=0.05, df=12,5)

93 MUDPUPPY RUN #2B CHIRONOMIDS 10/5/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR2CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	CONTROL	3			
2	DSH 16	3	0.208	23.1	0.067
3	DSH 18	3	0.208	23.1	0.000
4	DSH 19	3	0.208	23.1	0.133
5	DSH 23	3	0.208	23.1	-0.067
6	DSH 29	3	0.208	23.1	-0.033

QA/QC'd JLC 1/30/97

ACUTE TOXICITY TESTS WITH *HYALELLA AZTECA* AND *CHIRONOMUS TENTANS* ON SEDIMENTS FROM THE DULUTH/SUPERIOR HARBOR: 1993 Sampling Results - Batches # 3 and 4

Conducted by

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INTRODUCTION

As part of the 1993 survey of sediment quality in the Duluth/Superior Harbor, sediment toxicity tests were conducted to assess acute (survival) and chronic (growth) toxicity to benthic invertebrates. Acute effects were measured in separate 10-day toxicity tests to *Hyalella azteca* (*H. azteca*) and *Chironomus tentans* (*C. tentans*). Growth was measured at the end of the *C tentans* test to assess chronic effects. Survival and growth endpoints were compared to organisms similarly exposed to a reference control sediment collected from West Bearskin Lake (Cook County, MN).

A total of 40 sediment samples were collected for toxicity testing. This report presents the results of thirteen of these sediment samples run in two separate batches with separate controls.

SAMPLE COLLECTION AND HANDLING

During September 14-23, 1993, Minnesota Pollution Control Agency (MPCA) staff collected the thirteen sediments referred to in this report. The samples were collected from the harbor using a Ponar sampler and were taken to the University of Minnesota-Duluth Chemical Toxicology Research Laboratory. The samples were stored at 4°C until they were transported to the MPCA Toxicology Laboratory in St. Paul, MN.

METHODS

Thirteen sediment samples and two control sediment samples were subjected to the 10-day sediment toxicity tests using the modified procedures described in ASTM (1993). However, the specific test system used for these assays is not indicated in the methods. The test organisms (*H. azteca* and *C. tentans*) were exposed to sediment samples for ten days in a portable, mini-flow system described in Benoit et al. (1993). The test apparatus consists of 300 mL, glass-beaker test chambers held in a glass box supplied with water from an acrylic plastic headbox. The beakers have two, 1.5 cm holes covered with stainless steel mesh, to allow for water exchange, while containing the test organisms. The headbox has a pipette tip drain calibrated to deliver water at an average rate of 32.5 mL/min. The glass box is fitted with a self-starting siphon to provide exchange of overlying water.

The *H. azteca* used for this test were 1 to 3 mm long, and the *C. tentans* were approximately 14 days old. These organisms were supplied by Environmental Consulting and Testing, Superior, WI and were shipped to St. Paul the night before the test was set up. The organisms arrived at 10 p.m. and were stored at the St. Paul bus depot until 9 a.m. the next morning. The organisms were then transported to the MPCA Toxicology Laboratory. The majority of the organisms were then placed in glass vessels and transferred to the test beakers by 1:30 p.m. The remaining organisms were aerated in these vessels until they were placed in the test beakers the following day.

On October 18, 1993, eight samples (DSH 01, DSH 02, DSH 06, DSH 07, DSH 14, DSH 22, DSH 26, and DSH 30) and the control sediment were separately homogenized by hand, and 100 mL of each sediment was placed in a test beaker (Batch #3). On October 19, 1993, five more samples (DSH 03, DSH 04, DSH 13, DSH 17, and DSH 24) and another control sediment were homogenized and placed in beakers (Batch #4). Each sediment test was set up with three replicates of *H. azteca* and three replicates of *C. tentans*. Aerated, artesian well water was added to the beakers, and the sediments were allowed to settle for approximately two hours before the organisms were added. For each toxicity test, ten organisms were placed in each beaker in a random fashion.

The organisms were exposed to 16 hours of light and eight hours of darkness for the duration of the ten-day test. Each day, two liters of aerated water from the artesian well at Stroh Brewery in St. Paul, MN were exchanged in each test chamber. On weekdays, 1-L was exchanged in the morning and 1-L in the afternoon. On weekends, the two liters were passed through the chambers all at once. Water quality measurements (i.e., pH, temperature, and dissolved oxygen) of the overlying water were taken in one beaker of each of the triplicate sets of each of the sediments. The results, along with daily observations involving the physical appearance of the sediments and organisms, were recorded in a laboratory notebook. This notebook is retained on file at the MPCA.

The test was terminated on October 28, 1993 for Batch #3 and on October 29, 1993 for Batch #4. The sediments were sieved through 40 mesh screens, and the sieved material was sorted for organisms. The organisms found were counted, and the number of alive and dead organisms were recorded. Organisms not found were recorded as missing and presumed dead. The *C. tentans* that survived were placed in aluminum weighing dishes, dried at approximately 90°C for at least four hours, desiccated to room temperature, and weighed.

Growth (weight) of the *C. tentans* and survival of both organisms were used as the endpoints for these tests. The resulting survival data were analyzed using TOXSTAT (Gulley and WEST, Inc., 1994), a statistical software package obtained from the University of Wyoming; however, due to a quality assurance problem, the growth data were not analyzed.

A 96-hour, reference toxicant test with *H. azteca* in sodium chloride (NaCl) was run in conjunction with these toxicity tests to determine the acceptability of the *H. azteca* used. Four concentrations of NaCl solution (i.e., 5, 2.5, 1.25, and 0.625 g/L) and a control (aerated, artesian well water) were used in this test. Three replicates of five organisms each were set up per concentration.

RESULTS

Water Quality

Measurements of pH, dissolved oxygen, and temperature in the overlying water of the test beakers were made daily. These measurements are summarized below and in Tables 1, 2, and 3, respectively, for both batches of tests.

Batch # 3 Water Chemistry

In Batch #3, the range of pH values in the beakers containing *H. azteca* was 6.0 to 7.9 (Table 1). The water in the *C. tentans* beakers had a pH range of 6.8 to 7.7 (Table 1). The pH fluctuation during this test was acceptable since it did not vary more than 50% within each treatment (U.S. EPA, 1994).

The dissolved oxygen concentration ranged from 4.3 to 7.8 mg/L in the *H. azteca* beakers and from 3.3 to 8.1 mg/L in the *C. tentans* beakers (Table 2).

The temperature of the overlying water in each glass box was measured and ranged from 19.5°C to 22.0°C (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Batch # 4 Water Chemistry

In Batch #4, the range of pH values in the beakers containing *H. azteca* was 7.2 to 8.0 (Table 1). The water in the *C. tentans* beakers had a pH range of 7.0 to 8.0 (Table 1). These pH ranges are acceptable for this test.

The dissolved oxygen concentration ranged from 3.6 to 6.9 mg/L in the *H. azteca* beakers and from 3.4 to 7.0 mg/L in the *C. tentans* beakers (Table 2).

The temperature of the overlying water in each glass box was measured and ranged from 20.5°C to 22.5°C (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Test Endpoints

The mean percent survival of test organisms is summarized below and in Table 4.

Batch #3 Survival Data

The mean percent survival of *H. azteca* in Control #3 was 73% with a range of 70% to 80%. For this test, the mean percent survival must be at least 80% in the controls for the test to pass. For the control sediment containing *C. tentans,* percent survival ranged from 80% to 100% with a mean of 90%. Survival for these controls was greater than 70% and, therefore, acceptable.

Mean percent survival of *H. azteca* in the test sediments of Batch #3 ranged from 53% in the DSH 30 sample to 87% in the DSH 14 sample. Mean percent survival of *C. tentans* in Batch #3 test sediments ranged from 43% in the DSH 14 sample to 100% in the DSH 01 sample.

Batch #4 Survival Data

For Control #4 containing *H. azteca*, the mean percent survival was 73% with a range of 60% to 90%. The control survival for this test was unacceptable (<80% survival). Therefore, all of the *H. azteca* tests for Batch #4 failed. Survival in the control sediment containing *C. tentans* ranged from 80% to 100% with a mean of 90%; this was acceptable, and the test passed.

Mean percent survival of *H. azteca* in Batch #4 ranged from 60% in the DSH 24 sample to 80% in the DSH 17 sample. Mean percent survival of *C. tentans* in Batch #4 ranged from 0% in the DSH 24 sample to 93% in the DSH 13 sample.

C. tentans Growth Data

Although the dried *C. tentans* were weighed, the balance on which they were weighed was not calibrated with standard weights; therefore, the data are suspect since the internal calibration of the balance may have drifted with time.

Data Analysis

Survival data for both batches of test sediments containing *C. tentans,* except DSH 01, 03, and 24, were transformed using an arc sine-square root transformation before being analyzed statistically using Dunnett's test. The aforementioned data were eliminated from the analysis because there was zero variance between replicates. Although nonparametric statistics can be used to analyze zero variance data, a minimum of four replicates per sediment is needed. Only three replicates per sediment were run in this toxicity test.

A one-tailed test was used to test the alternative hypothesis that sample survival was significantly less than control survival. Thus, it was not necessary to include the sample survival data which exceeded the control survival in the Dunnett's test [e.g., survival data for DSH 01 (100%) and DSH 03 (90%)]. Since it is assumed that variability of 30-50% is necessary to see any significant difference between the control and any given sediment (T. Norberg-King, U.S. EPA, Duluth, MN, personal communication), and since DSH 24 had 0% survival, it is reasonable to assume that survival in DSH 24 was significantly less than the control. The only other sample survival that was significantly less than the control was site DSH 14. Results of the statistical analysis of the data are included in Appendix A.

Reference Toxicant Test with *Hyalella azteca* in Sodium Chloride Solution

The pH of the overlying water in the reference toxicant test ranged from 7.1 to 8.2. The dissolved oxygen ranged from 7.8 to 8.7 mg/L, and the temperature ranged between 19.5°C and 22.0°C. Mean percent survival of the organisms in the control was less than 90% (i.e., 67%) which was unacceptable. Thus, the health of the test organisms was suspect, and the test failed.

SUMMARY

Survival of *H. azteca* in both of the control sediments was unacceptable (i.e., less than 80% survival), and the reference toxicant test failed. Therefore, no conclusions can be drawn about the effect that the sediments had on *H. azteca.*

Control survival was acceptable in both batches of samples containing *C. tentans*. The mean percent survival of *C. tentans* in the DSH 14 and DSH 24 samples was significantly less than their respective test controls. Survival of *C. tentans* in all other samples analyzed was not significantly different from the respective test controls

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TABLE 1. Daily Overlying Water pH Measurements

Batch #3

Day	Control 3		DSH 01		DSH 02		DSH 06		DSH 07		DSH 14		DSH 22		DSH 26		DSH 30	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.2	6.0	6.9	6.8	7.3	7.3	7.2	7.2	6.9	6.8	6.9	6.9	7.3	7.2	6.8	6.9	7.0	6.9
1	7.0	7.1	7.2	7.3	7.4	7.6	7.5	7.5	7.3	7.4	7.4	7.4	7.6	7.6	7.3	7.5	7.4	7.6
2	7.2	7.4	7.3	7.4	7.5	7.5	7.5	7.5	7.3	7.4	7.5	7.6	7.5	7.5	7.6	7.7	7.4	7.4
3	6.9	7.2	7.2	7.3	7.4	7.5	7.4	7.5	7.3	7.4	7.4	7.6	7.4	7.6	7.3	7.4	7.3	7.4
4	7.0	7.3	7.3	7.4	7.3	7.4	7.3	7.5	7.2	7.4	7.4	7.6	7.4	7.5	7.3	7.5	7.3	7.5
5	7.4	7.4	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5	7.5
6	7.4	7.5	7.3	7.3	7.4	7.5	7.4	7.7	7.3	7.4	7.5	7.6	7.5	7.6	7.5	7.5	7.3	7.6
7	7.4	7.5	7.5	7.6	7.4	7.6	7.2	7.5	7.5	7.6	7.4	7.7	7.4	7.6	7.5	7.6	7.4	7.6
8	7.2	7.3	7.3	7.4	7.3	7.5	7.4	7.5	7.3	7.5	7.3	7.4	7.4	7.6	7.4	7.5	7.3	7.4
9	7.7	7.7	7.2	7.4	7.4	7.6	7.2	7.5	7.5	7.7	7.6	7.9	7.5	7.6	7.2	7.3	7.4	7.6
Mean	7.2	7.2	7.3	7.3	7.4	7.5	7.4	7.5	7.3	7.4	7.4	7.5	7.5	7.5	7.3	7.4	7.3	7.5
Range	6.9-7.7	6.0-7.7	6.9-7.5	6.8-7.6	7.3-7.5	7.3-7.6	7.2-7.5	7.2-7.7	6.9-7.5	6.8-7.7	6.9-7.6	6.9-7.9	7.3-7.6	7.2-7.6	6.8-7.6	6.9-7.7	7.0-7.5	6.9-7.6

Checked all Day 9 JLC 1/31/97

Batch #4

Day	Control 4		DSH 03		DSH 04		DSH 13		DSH 17		DSH 24	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.4	7.3	7.3	7.2	7.5	7.4	7.5	7.3	7.7	7.6	7.8	7.8
1	7.0	7.4	7.3	7.3	7.5	7.6	7.5	7.5	7.5	7.6	7.7	7.8
2	7.3	7.5	7.3	7.3	7.5	7.5	7.5	7.6	7.5	7.7	7.8	7.8
3	7.3	7.4	7.3	7.3	7.4	7.5	7.5	7.6	7.6	7.6	7.7	7.7
4	7.4	7.4	7.4	7.4	7.5	7.5	7.5	7.5	7.4	7.4	7.5	7.5
5	7.1	7.4	7.3	7.4	7.3	7.5	7.5	7.6	7.4	7.6	7.6	7.6
6	7.4	7.5	7.4	7.6	7.5	7.7	7.5	7.7	7.5	7.7	7.6	7.7
7	7.4	7.4	7.3	7.5	7.3	7.5	7.5	7.6	7.5	7.6	7.6	7.7
8	7.7	7.9	7.7	7.9	7.9	8.0	7.9	8.0	7.9	8.0	8.0	8.0
9	7.2	7.3	7.3	7.4	7.8	7.9	7.8	7.9	7.9	7.9	7.7	7.8
Mean	7.3	7.5	7.4	7.4	7.5	7.6	7.6	7.6	7.6	7.7	7.7	7.7
Range	7.0-7.7	7.3-7.9	7.3-7.7	7.2-7.9	7.3-7.9	7.4-7-8.0	7.5-7.9	7.3-8.0	7.4-7.9	7.4-8.0	7.5-8.0	7.5-8.0

Checked all Day 8 JLC 1/31/97

original QA/QC review by PK 8/29/96
final 10% QA/QC review by JLC 1/31/97

TABLE 2. Daily Overlying Water Dissolved Oxygen Concentrations (mg/L)

Batch #3

Day	Control 3		DSH 01		DSH 02		DSH 06		DSH 07		DSH 14		DSH 22		DSH 26		DSH 30	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.5	6.8	6.3	6.6	6.9	6.8	6.9	7.0	6.7	6.1	4.1	4.3	7.0	6.9	8.1	7.7	6.2	7.8
1	6.3	6.7	6.0	6.5	6.2	6.9	6.6	6.6	6.1	6.5	5.4	5.8	6.6	6.2	6.0	7.0	6.2	7.0
2	5.4	5.0	5.3	6.2	5.2	6.3	6.1	6.7	5.1	5.7	5.3	6.1	5.8	6.4	6.4	6.9	5.8	6.3
3	5.3	6.8	4.3	5.9	5.2	6.2	5.4	6.6	4.1	5.5	5.0	6.2	5.4	6.7	4.9	6.4	4.6	6.5
4	4.7	6.7	4.8	6.0	4.7	6.2	4.9	6.4	4.4	5.9	4.7	6.2	4.8	6.5	4.7	6.9	4.6	6.4
5	4.5	6.0	4.1	5.6	4.5	5.9	4.5	5.8	3.8	5.1	4.2	5.8	4.3	5.0	4.2	6.0	4.0	5.0
6	5.0	6.0	4.9	5.4	3.7	5.7	4.2	6.7	3.5	4.4	5.4	5.2	5.0	6.0	5.4	6.0	4.4	5.9
7	5.2	6.2	4.1	6.3	4.0	6.8	4.7	6.2	4.7	6.3	5.0	6.1	4.2	6.6	3.9	6.2	4.5	6.3
8	5.5	6.0	4.5	6.0	3.9	5.6	4.1	5.9	4.0	6.3	3.5	5.2	4.0	6.1	5.3	5.9	4.4	5.7
9	5.4	6.2	3.3	6.2	5.0	6.0	4.0	6.5	4.5	6.4	4.0	5.9	5.3	6.7	5.5	6.2	4.0	6.4
Mean	5.5	6.2	4.8	6.1	4.9	6.2	5.1	6.4	4.7	5.8	4.7	5.7	5.2	6.3	5.4	6.5	4.9	6.3
Range	4.5-7.5	5.0-6.8	3.3-6.3	5.4-6.6	3.7-6.9	5.6-6.9	4.0-6.9	5.8-7.0	3.5-6.7	4.4-6.5	3.5-5.4	4.3-6.2	4.0-7.0	5.0-6.9	3.9-8.1	5.9-7.7	4.0-6.2	5.0-7.8

Checked all Day 3 JLC 4/31/97

Batch #4

Day	Control 4		DSH 03		DSH 04		DSH 13		DSH 17		DSH 24	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	6.8	6.5	6.6	5.7	6.7	6.3	6.7	6.0	7.0	6.6	6.4	6.3
1	6.3	6.6	5.8	5.9	6.0	6.4	6.2	6.3	6.0	6.7	5.7	6.2
2	5.6	6.9	4.9	5.4	5.7	6.2	6.3	6.3	6.0	6.4	5.4	6.1
3	5.2	6.6	5.1	5.6	5.3	6.3	6.1	6.7	6.1	6.7	5.1	5.7
4	4.3	5.9	3.7	5.5	4.0	5.3	5.0	5.2	4.8	5.1	4.8	3.6
5	4.8	6.3	4.9	5.8	3.7	6.0	6.0	5.0	4.4	5.8	4.3	4.3
6	4.7	5.9	4.6	6.4	4.2	6.5	4.9	5.6	4.3	6.0	3.4	5.0
7	4.5	5.7	4.8	6.2	3.8	5.9	5.1	6.7	5.1	6.2	4.3	5.1
8	4.4	6.4	3.5	6.0	4.5	6.8	4.5	6.9	5.5	6.0	4.5	4.5
9	4.7	6.6	3.6	5.5	4.8	6.5	5.5	5.9	5.8	6.1	3.6	4.3
Mean	5.1	6.3	4.8	5.8	4.9	6.2	5.6	6.1	5.5	6.2	4.8	5.1
Range	4.3-6.8	5.7-6.9	3.5-6.6	5.4-6.4	3.7-6.7	5.3-6.8	4.5-6.7	5.0-6.9	4.3-7.0	5.1-6.7	3.4-6.4	3.6-6.3

Checked all Day 2 JLC 1/31/97

original QA/QC review by PK 3/29/96
final 10% QA/QC review by JLC 1/31/97

TABLE 3. Daily Overlying Water Temperatures (Degrees Celsius)

Batch #3

Day	Control 3		DSH 01		DSH 02		DSH 06		DSH 07		DSH 14		DSH 22		DSH 26		DSH 30	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	19.5	19.5	19.5	19.5	21.0	21.0	21.0	21.0	20.0	20.0	20.0	20.0	21.0	21.0	19.5	19.5	20.0	20.0
1	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.0	21.0	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
2	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
3	20.5	20.5	20.0	20.0	20.5	20.5	20.5	20.5	20.0	20.0	20.0	20.0	20.5	20.5	20.0	20.0	20.0	20.0
4	20.5	20.5	20.5	20.5	20.5	NA	20.5	NA	20.5	20.5	20.5	NA	20.5	NA	20.5	20.5	20.5	20.5
5	22.0	22.0	22.0	NA	22.0	NA	22.0	22.0	NA	22.0	NA	22.0	22.0	NA	22.0	NA	NA	22.0
6	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
7	21.5	21.5	21.5	21.5	22.0	22.0	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
8	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
9	21.0	21.0	20.5	20.5	21.0	21.0	21.0	21.0	20.0	20.0	20.0	20.0	20.5	20.5	20.5	20.5	20.0	20.0
Mean	21.0	20.9	20.9	20.8	21.2	21.2	21.2	21.1	20.9	20.7	20.9	20.8	21.1	21.1	20.9	20.8	20.9	20.8
Range	19.5-22.0	19.5-22.0	19.5-22.0	19.5-22.0	20.5-22.0	20.5-22.0	20.5-22.0	20.5-22.0	20.0-22.0	20.0-22.0	20.0-22.0	20.0-22.0	20.5-22.0	20.5-22.0	19.5-22.0	19.5-22.0	20.0-22.0	20.0-22.0

checked all Days JLC 4/31/97

Batch #4

Day	Control 4		DSH 03		DSH 04		DSH 13		DSH 17		DSH 24	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
1	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
2	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
3	20.5	NA	20.5	NA	20.5	NA	20.5	NA	20.5	NA	20.5	NA
4	NA	22.0	NA	22.0	22.0	NA	22.0	NA	NA	22.0	NA	22.0
5	22.5	22.5	22.5	22.5	22.0	22.0	22.5	22.5	22.5	22.5	22.5	22.5
6	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0	22.0
7	21.5	21.5	21.0	21.0	21.0	21.0	21.0	21.0	21.5	21.5	21.0	21.0
8	21.0	21.0	21.0	21.0	21.5	21.5	21.0	21.0	21.0	21.0	21.0	21.0
9	21.0	21.0	21.0	21.0	21.0	21.5	21.0	21.0	21.0	21.0	21.0	21.0
Mean	21.4	21.4	21.3	21.3	21.3	21.4	21.3	21.3	21.4	21.4	21.3	21.3
Range	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.0	20.5-22.0	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.5	20.5-22.5

checked Days 3+4 JLC 4/31/97

NA = Not applicable, no measurement taken.

Original QA/QC review by PK 8/29/96
Final 10% QA/QC review by JLC 4/31/97

TABLE 4. Mean Percent Survival of *Hyalella azteca* and *Chironomus tentans*

	Mean Percent Survival	
	Hyalella azteca[1]	*Chironomus tentans*
Batch # 3		
CONTROL #3	73%	90%
DSH 01	63%	100%
DSH 02	70%	93%
DSH 06	57%	97%
DSH 07	63%	87%
DSH 14	87%	43% *
DSH 22	77%	80%
DSH 26	60%	83%
DSH 30	53%	97%
Batch # 4		
CONTROL #2	73%	90%
DSH 03	77%	90%
DSH 04	63%	87%
DSH 13	70%	93%
DSH 17	80%	90%
DSH 24	60%	0% *

[1] Controls were unacceptable (<80% survival). Thus, the *Hyalella azteca* tests failed for both batches of samples.

* Significantly different from the control, p = 0.05.

initial QA/QC review by PK 5
final QA/QC review by JLC 2

APPENDIX A

TOXSTAT Analysis

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
8
3
3
3
3
3
3
3
3
CONTROL
1.0
0.8
0.9
DSH 30
0.9
1.00000000
1.00000000
DSH 02
1.00000000
0.90000000
0.90000000
DSH 06
0.90000000
1.00000000
1.00000000
DSH 07
0.80000000
0.90000000
0.90000000
DSH 14
0.60000000
0.30000000
0.40000000
DSH 22
0.90000000
0.80000000
0.70000000
DSH 26
0.80000000
0.90000000
0.80000000

QA/QC'd JLC 2/1/97

TITLE: 93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 8

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	CONTROL	1	1.0000	1.4120
1	CONTROL	2	0.8000	1.1071
1	CONTROL	3	0.9000	1.2490
2	DSH 30	1	0.9000	1.2490
2	DSH 30	2	1.0000	1.4120
2	DSH 30	3	1.0000	1.4120
3	DSH 02	1	1.0000	1.4120
3	DSH 02	2	0.9000	1.2490
3	DSH 02	3	0.9000	1.2490
4	DSH 06	1	0.9000	1.2490
4	DSH 06	2	1.0000	1.4120
4	DSH 06	3	1.0000	1.4120
5	DSH 07	1	0.8000	1.1071
5	DSH 07	2	0.9000	1.2490
5	DSH 07	3	0.9000	1.2490
6	DSH 14	1	0.6000	0.8861
6	DSH 14	2	0.3000	0.5796
6	DSH 14	3	0.4000	0.6847
7	DSH 22	1	0.9000	1.2490
7	DSH 22	2	0.8000	1.1071
7	DSH 22	3	0.7000	0.9912
8	DSH 26	1	0.8000	1.1071
8	DSH 26	2	0.9000	1.2490
8	DSH 26	3	0.8000	1.1071

QA/QC'd JC 2/1/97

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	CONTROL	3	1.107	1.412	1.256
2	DSH 30	3	1.249	1.412	1.358
3	DSH 02	3	1.249	1.412	1.303
4	DSH 06	3	1.249	1.412	1.358
5	DSH 07	3	1.107	1.249	1.202
6	DSH 14	3	0.580	0.886	0.717
7	DSH 22	3	0.991	1.249	1.116
8	DSH 26	3	1.107	1.249	1.154

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	CONTROL	0.023	0.153	0.088	12.15
2	DSH 30	0.009	0.094	0.054	6.93
3	DSH 02	0.009	0.094	0.054	7.22
4	DSH 06	0.009	0.094	0.054	6.93
5	DSH 07	0.007	0.082	0.047	6.82
6	DSH 14	0.024	0.156	0.090	21.72
7	DSH 22	0.017	0.129	0.075	11.58
8	DSH 26	0.007	0.082	0.047	7.10

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.208

W = 0.952

Critical W (P = 0.05) (n = 24) = 0.916
Critical W (P = 0.01) (n = 24) = 0.884

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 1.74

Table Chi-square value = 18.48 (alpha = 0.01, df = 7)
Table Chi-square value = 14.07 (alpha = 0.05, df = 7)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd YJC 2/1/97

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	7	0.912	0.130	10.000
Within (Error)	16	0.208	0.013	
Total	23	1.120		

Critical F value = 2.66 (0.05,7,16)
Since F > Critical F REJECT Ho: All equal

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	CONTROL	1.256	0.900		
2	DSH 30	1.358	0.967	-1.091	
3	DSH 02	1.303	0.933	-0.508	
4	DSH 06	1.358	0.967	-1.091	
5	DSH 07	1.202	0.867	0.583	
6	DSH 14	0.717	0.433	5.787	*
7	DSH 22	1.116	0.800	1.506	
8	DSH 26	1.154	0.833	1.091	

Dunnett table value = 2.56 (1 Tailed Value, P=0.05, df=16,7)

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #3A CHIRONOMIDS 10/18/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	CONTROL	3			
2	DSH 30	3	0.180	20.0	-0.067
3	DSH 02	3	0.180	20.0	-0.033
4	DSH 06	3	0.180	20.0	-0.067
5	DSH 07	3	0.180	20.0	0.033
6	DSH 14	3	0.180	20.0	0.467
7	DSH 22	3	0.180	20.0	0.100
8	DSH 26	3	0.180	20.0	0.067

QA/QC ✓ JLC 2/1/97

```
93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
4
3
3
3
3
CONTROL
0.80000000
0.90000000
1.00000000
DSH 17
1.0
0.9
0.8
DSH 04
0.90000000
0.80000000
0.90000000
DSH 13
1.00000000
0.90000000
0.90000000
```

QA/QC'd JLC 2/1/97

TITLE: 93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 4

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	CONTROL	1	0.8000	1.1071
1	CONTROL	2	0.9000	1.2490
1	CONTROL	3	1.0000	1.4120
2	DSH 17	1	1.0000	1.4120
2	DSH 17	2	0.9000	1.2490
2	DSH 17	3	0.8000	1.1071
3	DSH 04	1	0.9000	1.2490
3	DSH 04	2	0.8000	1.1071
3	DSH 04	3	0.9000	1.2490
4	DSH 13	1	1.0000	1.4120
4	DSH 13	2	0.9000	1.2490
4	DSH 13	3	0.9000	1.2490

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	CONTROL	3	1.107	1.412	1.256
2	DSH 17	3	1.107	1.412	1.256
3	DSH 04	3	1.107	1.249	1.202
4	DSH 13	3	1.249	1.412	1.303

DA/QC ✓ JLC 2/1/97

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	CONTROL	0.023	0.153	0.088	12.15
2	DSH 17	0.023	0.153	0.088	12.15
3	DSH 04	0.007	0.082	0.047	6.82
4	DSH 13	0.009	0.094	0.054	7.22

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	3	0.016	0.005	0.333
Within (Error)	8	0.124	0.016	
Total	11	0.140		

Critical F value = 4.07 (0.05,3,8)
Since F < Critical F FAIL TO REJECT Ho: All equal

QA/QC JLC 2/1/97

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.124

W = 0.939

Critical W (P = 0.05) (n = 12) = 0.859
Critical W (P = 0.01) (n = 12) = 0.805

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 0.98

Table Chi-square value = 11.34 (alpha = 0.01, df = 3)
Table Chi-square value = 7.81 (alpha = 0.05, df = 3)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC JLC 2/1/97

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	CONTROL	1.256	0.900		
2	DSH 17	1.256	0.900	0.000	
3	DSH 04	1.202	0.867	0.534	
4	DSH 13	1.303	0.933	-0.465	

Dunnett table value = 2.42 (1 Tailed Value, P=0.05, df=8,3)

93 MUDPUPPY RUN #3B CHIRONOMIDS 10/19/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR3CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	CONTROL	3			
2	DSH 17	3	0.187	20.8	0.000
3	DSH 04	3	0.187	20.8	0.033
4	DSH 13	3	0.187	20.8	-0.033

QA/QC JLC 2/6/97

ACUTE TOXICITY TESTS WITH *HYALELLA AZTECA* AND *CHIRONOMUS TENTANS* ON SEDIMENTS FROM THE DULUTH/SUPERIOR HARBOR: 1993 Sampling Results - Batches # 5 and 6

Conducted by

Minnesota Pollution Control Agency
Monitoring and Assessment Section
520 Lafayette Road
St. Paul, Minnesota 55155-4194

February 1997

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INTRODUCTION

As part of the 1993 survey of sediment quality in the Duluth/Superior Harbor, sediment toxicity tests were conducted to assess acute (survival) and chronic (growth) toxicity to benthic invertebrates. Acute effects were measured in separate 10-day toxicity tests to *Hyalella azteca* (*H. azteca*) and *Chironomus tentans* (*C. tentans*). Growth was measured at the end of the *C. tentans* test to assess chronic effects. Survival and growth endpoints were compared to organisms similarly exposed to a reference control sediment collected from West Bearskin Lake (Cook County, MN).

A total of 40 sediment samples were collected for toxicity testing. This report presents the results of twelve of these sediment samples run in two separate batches with separate controls.

SAMPLE COLLECTION AND HANDLING

During September 22-27, 1993, Minnesota Pollution Control Agency (MPCA) staff collected the twelve sediments referred to in this report. The samples were collected from the harbor using a Ponar sampler and were taken to the University of Minnesota-Duluth Chemical Toxicology Research Laboratory. The samples were stored at 4°C until they were transported to the MPCA Toxicology Laboratory in St. Paul, MN.

METHODS

Twelve sediment samples and two control sediment samples were subjected to the 10-day sediment toxicity tests using the modified procedures described in ASTM (1993). However, the specific test system used for these assays is not indicated in the methods. The test organisms (*H. azteca* and *C. tentans*) were exposed to sediment samples for ten days in a portable, mini-flow system described in Benoit et al. (1993). The test apparatus consists of 300 mL, glass-beaker test chambers held in a glass box supplied with water from an acrylic plastic headbox. The beakers have two, 1.5 cm holes covered with stainless steel mesh, to allow for water exchange, while containing the test organisms. The headbox has a pipette tip drain calibrated to deliver water at an average rate of 32.5 mL/min. The glass box is fitted with a self-starting siphon to provide exchange of overlying water.

The *H. azteca* used for this test were 1 to 3 mm long, and the *C. tentans* were approximately 14 days old. These organisms were supplied by Environmental Consulting and Testing, Superior, WI on the day of the test.

On November 1, 1993, eight samples (DSH 05, DSH 09, DSH 10, DSH 11, DSH 25, DSH 27, DSH 31, and DSH 32) and the control sediment were separately homogenized by hand, and 100 mL of each sediment was placed in a test beaker (Batch #5). On November 2, 1993, four more samples (DSH 15, DSH 28, DSH 34, and DSH 35) and another control sediment were homogenized and placed in beakers (Batch #6). Each sediment test was set up with three replicates of *H. azteca* and three replicates of *C. tentans*. Aerated, artesian well water was added

to the beakers, and the sediments were allowed to settle for approximately two hours before the organisms were added. For each toxicity test, ten organisms were placed in each beaker in a random fashion.

The organisms were exposed to 16 hours of light and eight hours of darkness for the duration of the ten-day test. Each day, two liters of aerated water from the artesian well at Stroh Brewery in St. Paul, MN were exchanged in each test chamber. On weekdays, 1-L was exchanged in the morning and 1-L in the afternoon. On weekends, the two liters were passed through the chambers all at once. Water quality measurements (i.e., pH, temperature, and dissolved oxygen) of the overlying water were taken in one beaker of each of the triplicate sets of each of the sediments. The results, along with daily observations involving the physical appearance of the sediments and organisms, were recorded in a laboratory notebook. This notebook is retained on file at the MPCA.

The test was terminated on November 11, 1993 for Batch #5 and on November 12, 1993 for Batch #6. The sediments were sieved through 40 mesh screens, and the sieved material was sorted for organisms. The organisms found were counted, and the number of alive and dead organisms were recorded. Organisms not found were recorded as missing and presumed dead. The *C. tentans* that survived were placed in aluminum weighing dishes, dried at approximately 90°C for at least four hours, desiccated to room temperature, and weighed.

Growth (weight) of the *C. tentans* and survival of both organisms were used as the endpoints for these tests. The resulting survival data were analyzed using TOXSTAT (Gulley and WEST, Inc., 1994), a statistical software package obtained from the University of Wyoming; however, due to a quality assurance problem, the growth data were not analyzed.

A 96-hour, reference toxicant test with *H. azteca* in sodium chloride (NaCl) was run in conjunction with these toxicity tests to determine the acceptability of the *H. azteca* used. Four concentrations of NaCl solution (i.e., 5, 2.5, 1.25, and 0.625 g/L) and a control (aerated, artesian well water) were used in this test. Three replicates of five organisms each were set up per concentration.

RESULTS

Water Quality

Measurements of pH, dissolved oxygen, and temperature in the overlying water of the test beakers were made daily. These measurements are summarized below and in Tables 1, 2, and 3, respectively, for both batches of tests.

Batch # 5 Water Chemistry

In Batch #5, the range of pH values in the beakers containing *H. azteca* was 7.0 to 8.6 (Table 1). The water in the *C. tentans* beakers had a pH range of 6.8 to 8.6 (Table 1). The pH fluctuation

during these tests was acceptable since it did not vary more than 50% within each treatment (U.S. EPA, 1994).

The dissolved oxygen concentration ranged from 5.5 to 7.4 mg/L in the *H. azteca* beakers and from 2.3 to 7.3 mg/L in the *C. tentans* beakers (Table 2). The recommended dissolved oxygen concentration for these tests is greater than 40% saturation. The dissolved oxygen dipped below 40% saturation on day 6 in most of the *C. tentans* beakers (i.e., the control, DSH 9, 10, 11, 25, 27, 31, and 32) and in the control on days 8 and 9. Feeding of the organisms was suspended on these days. The chambers were not aerated.

The range of temperature values in the *H. azteca* beakers was 19.0°C to 21.0°C, whereas the range was 18.9°C to 21.0°C in the *C. tentans* beakers (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Batch #6 Water Chemistry

In Batch #6, the range of pH values in the beakers containing *H. azteca* was 7.8 to 8.4 (Table 1). The water in the *C. tentans* beakers had a pH range of 7.5 to 8.3 (Table 1). These pH ranges are acceptable for these tests.

The dissolved oxygen concentration ranged from 5.0 to 7.9 mg/L in the *H. azteca* beakers and from 2.2 to 8.0 mg/L in the *C. tentans* beakers (Table 2). The dissolved oxygen in some of the *C. tentans* chambers dropped below 40% saturation. Levels were lower than acceptable on day 5 in chambers holding sediments DSH 15, 28, and 35. On days 7, 8, and 9, levels were too low in DSH 35. Dissolved oxygen levels were unacceptable in the control on days 8 and 9. Feeding of the organisms was suspended on these days. The chambers were not aerated.

The range of temperature values in the *H. azteca* beakers was 18.9°C to 21.0°C, whereas the range was 18.9°C to 21.0°C in the *C. tentans* beakers (Table 3). The recommended temperature range for this test is 23 ± 1°C (U.S. EPA, 1994).

Test Endpoints

The mean percent survival of test organisms is summarized below and in Table 4.

Batch #5 Survival Data

The mean percent survival of *H. azteca* in Control #5 was 97% with a range of 90% to 100%. For the control sediment containing *C. tentans,* percent survival ranged from 70% to 80% with a mean of 77%. Survival for these controls was acceptable, and both tests passed.

Mean percent survival of *H. azteca* in the test sediments of Batch #5 ranged from 83% in the DSH 09 sample to 100% in the DSH 27 sample. Mean percent survival of *C. tentans* in Batch #5 test sediments ranged from 73% in the DSH 31 sample to 97% in the DSH 25 sample.

Batch #6 Survival Data

For Control #6 containing *H. azteca*, the mean percent survival was 87% with a range of 80% to 90%. For the control sediment containing *C. tentans*, the range was 90% to 100% with a mean of 97%. Both of these survival measurements were acceptable.

Mean percent survival of *H. azteca* in Batch #6 ranged from 77% in the DSH 34 and DSH 35 samples to 97% in the DSH 28 sample. Mean percent survival of *C. tentans* in Batch #6 ranged from 47% in the DSH 34 sample to 93% in the DSH 35 sample.

C. tentans Growth Data

Although the dried *C. tentans* were weighed, the balance on which they were weighed was not calibrated with standard weights; therefore, the data are suspect since the internal calibration of the balance may have drifted with time and no conclusions regarding chronic toxicity (growth) can be made.

Data Analysis

Survival data for all of the sediments tested, except DSH 05 containing *C. tentans* and DSH 15, 25 and 27 containing *H. azteca*, were transformed using an arc sine-square root transformation before being analyzed statistically using Dunnett's test. The aforementioned samples were eliminated from the analysis because there was zero variance between replicates. Although nonparmetric statistics can be used to analyze zero variance data, a minimum of four replicates per sediment is needed. Only three replicates per sediment were run in these toxicity tests. Since it is assumed that variability of 30-50% is necessary to see any significant difference between the control and any given sediment, and since survival of the organisms in the sediments in question was equal to or greater than 90%, it is reasonable to assume that the effect these sediments had on the organisms tested was not significantly less than that of their respective controls (T. Norberg-King, USEPA, Duluth, MN, personal communication).

The mean percent survival of *C. tentans* in the DSH 34 sample was significantly less than the control as determined by a 1-tailed Dunnett's test, $p=0.05$. The survival results of all other organisms in all other samples run in these tests were not significantly less than their respective controls. Results of the statistical analysis of the data are included in Appendix A.

Reference Toxicant Test with *Hyalella azteca* in Sodium Chloride Solution

The pH of the overlying water in the reference toxicant test ranged from 7.8 to 8.5. The dissolved oxygen ranged from 7.8 to 8.5 mg/L, and the temperature ranged between 19.0°C and 20.0°C. Mean percent survival of the organisms in the control was less than 90% (i.e., 73%) which was unacceptable. Thus, the reference toxicant test failed. The cause of this failure could not be determined. Since the control survivals in Batch #5 and Batch #6 were acceptable, the organisms appeared to be healthy.

SUMMARY

Survival of *H. azteca* in the control sediments was acceptable (greater than 80%), however, the reference toxicant test failed, leaving the health of the organisms suspect and, therefore, no conclusion can be drawn about the effect that the sediments had on *H. azteca.*

Control survival was acceptable in both batches of samples containing *C. tentans*. The mean percent survival of *C. tentans* in the DSH 34 sample was significantly less than the control ($p=0.05$). Survival of *C. tentans* in all other samples analyzed were not significantly different than the control.

TABLE 2. Daily Overlying Water Dissolved Oxygen Concentrations (mg/L)

Batch #5

Day	Control 5		DSH 05		DSH 09		DSH 10		DSH 11		DSH 25		DSH 27		DSH 31		DSH 32	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.0	6.5	7.3	7.1	7.3	6.9	7.0	6.3	6.9	6.5	6.9	6.8	7.3	6.7	6.7	6.3	6.7	6.2
1	6.1	6.8	6.6	6.9	6.6	6.8	6.2	6.1	6.0	6.5	6.3	6.8	6.9	6.6	6.3	6.3	6.4	6.5
2	5.2	6.3	5.4	6.4	4.3	6.7	5.3	6.2	4.6	6.1	4.0	6.0	5.7	6.1	5.7	6.2	4.6	6.9
3	4.3	6.9	4.6	6.7	4.9	6.9	4.5	6.6	4.5	6.6	4.0	6.5	5.4	6.4	4.3	6.1	4.2	6.1
4	4.6	6.8	4.7	6.4	4.4	7.0	4.5	6.8	4.3	6.8	4.9	6.3	5.8	6.6	4.8	6.4	5.2	6.4
5	4.5	6.9	4.6	6.7	3.9	7.0	5.2	6.7	4.3	6.5	3.6	6.0	4.9	6.9	4.3	6.4	4.5	6.3
6	2.9	6.3	3.5	6.8	2.4	6.6	2.8	5.8	2.9	6.5	2.3	5.5	3.1	6.6	2.6	5.9	2.9	5.9
7	3.6	6.8	3.4	7.1	3.4	7.1	3.4	6.4	3.4	7.0	4.4	6.4	4.3	6.7	4.7	6.6	4.0	6.7
8	3.1	6.4	4.4	7.4	3.4	7.0	4.0	6.5	4.0	7.0	3.6	6.4	4.5	7.0	4.5	6.1	4.6	6.8
9	2.9	6.3	4.0	7.3	5.7	7.0	3.4	6.5	4.5	6.9	3.9	6.5	4.0	7.0	3.6	5.9	4.8	6.6
Mean	4.4	6.6	4.9	6.9	4.6	6.9	4.6	6.4	4.5	6.6	4.4	6.3	5.2	6.7	4.8	6.2	4.8	6.4
Range	2.9-7.0	6.3-6.9	3.4-7.3	6.4-7.4	2.4-7.3	6.6-7.1	2.8-7.0	5.8-6.8	2.9-6.9	6.1-7.0	2.3-6.9	5.5-6.8	3.1-7.3	6.1-7.0	2.6-6.7	5.9-6.6	2.9-6.7	5.9-6.9

Checked all Days JLC 2/2/97

Batch #6

Day	Control 6		DSH 15		DSH 28		DSH 34		DSH 35	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.4	7.4	8.0	7.9	7.8	7.6	7.6	7.5	7.5	7.6
1	5.6	6.3	5.8	6.3	5.6	6.6	5.5	5.9	5.3	6.1
2	5.5	6.7	6.0	6.8	5.0	6.6	5.8	6.4	5.2	6.4
3	5.2	6.7	6.0	7.1	4.7	6.9	5.7	6.4	4.3	6.3
4	4.8	6.6	4.6	6.7	5.2	6.5	4.9	6.4	4.1	6.6
5	4.0	6.4	2.8	6.6	3.3	6.2	4.8	5.9	2.2	5.4
6	4.5	6.6	4.4	7.2	4.6	7.0	5.3	6.4	3.6	6.7
7	5.1	6.8	4.8	7.0	4.5	6.9	5.7	6.1	3.2	7.1
8	3.2	6.4	6.0	6.8	3.6	6.8	3.8	5.0	3.0	6.4
9	3.2	6.2	4.6	6.5	3.6	6.5	4.3	5.6	2.6	6.0
Mean	4.9	6.6	5.3	6.9	4.8	6.8	5.3	6.2	4.1	6.5
Range	3.2-7.4	6.2-7.4	2.8-8.0	6.3-7.9	3.3-7.8	6.2-7.6	3.8-7.6	5.0-7.5	2.2-7.5	5.4-7.6

Checked all Day 4 JLC 2/2/97

initial QA/QC reviewed by PK 8/30/96
100% final QA/QC reviewed by JLC 2/2/97

Table 3. Daily Overlying Water Temperatures (Degrees Celsius)

Batch #5

Day	Control 5		DSH 05		DSH 09		DSH 10		DSH 11		DSH 25		DSH 27		DSH 31		DSH 32	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0	20.0
1	21.0	21.0	20.5	20.5	20.5	20.5	21.0	21.0	21.0	21.0	20.5	20.5	20.5	20.5	20.5	20.5	20.5	20.5
2	21.0	21.0	21.0	20.5	20.5	20.5	21.0	21.0	21.0	21.0	20.5	20.5	21.0	21.0	20.5	20.5	20.5	20.5
3	19.9	19.9	19.8	19.8	20.1	20.1	19.9	19.9	20.1	20.1	20.1	20.1	19.9	19.9	19.6	19.9	20.4	20.4
4	19.2	19.2	19.4	19.4	19.5	19.6	19.3	19.2	19.8	19.2	19.5	19.5	19.4	19.4	19.5	19.5	19.5	19.5
5	20.5	20.5	20.5	20.5	21.0	21.0	20.5	20.5	20.5	20.5	21.0	21.0	20.5	20.5	20.5	20.5	20.5	20.5
6	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
7	19.3	19.3	19.3	19.5	19.5	19.5	19.5	19.5	19.7	19.7	19.5	19.5	19.5	19.5	19.5	19.5	19.3	19.4
8	19.0	19.0	19.0	19.0	19.1	19.3	19.1	19.1	19.3	19.3	18.9	19.0	19.1	19.1	19.0	19.1	19.1	19.0
9	19.2	19.2	19.3	19.3	19.3	19.6	19.3	19.3	19.5	19.5	19.2	19.4	19.1	19.3	19.3	19.4	19.2	19.4
Mean	20.0	20.0	20.0	20.0	20.1	20.1	20.1	20.1	20.2	20.1	20.0	20.1	20.0	20.0	19.9	20.0	20.0	20.0
Range	19.0-21.0	19.0-21.0	19.0-21.0	19.0-21.0	19.1-21.0	19.3-21.0	19.1-21.0	19.1-21.0	19.3-21.0	19.2-21.0	18.9-21.0	19.0-21.0	19.1-21.0	19.1-21.0	19.0-21.0	19.1-21.0	19.1-21.0	19.0-21.0

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Batch #6

Day	Control 6		DSH 15		DSH 28		DSH 34		DSH 35	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	20.5	20.5	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
1	20.5	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
2	19.5	20.2	20.5	20.5	20.5	20.5	20.2	20.6	20.0	20.3
3	19.6	19.6	19.8	19.9	20.0	20.0	19.8	19.7	19.6	19.8
4	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
5	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0	21.0
6	19.4	19.7	19.6	20.1	20.0	20.1	19.7	19.8	19.6	19.6
7	18.9	19.3	19.5	19.6	19.6	19.7	19.5	19.5	19.4	19.4
8	19.5	19.7	19.6	19.6	19.8	20.0	19.6	19.8	19.6	19.8
9	20.0	20.0	19.7	20.0	20.1	20.3	20.0	20.0	20.0	19.9
Mean	20.0	20.2	20.3	20.4	20.4	20.5	20.2	20.3	20.2	20.3
Range	18.9-21.0	19.3-21.0	19.5-21.0	19.6-21.0	19.6-21.0	19.7-21.0	19.5-21.0	19.5-21.0	19.4-21.0	19.4-21.0

checked all Day 9
JLC 2/2/97

initial QA/QC review by PK 8/30/96
final 10% QA/QC review by JLC 2/2/97

TABLE 4. Mean Percent Survival of *Hyalella azteca* and *Chironomus tentans*

	Mean Percent Survival	
	Hyalella azteca	*Chironomus tentans*
Batch # 5		
CONTROL #5	97%	77%
DSH 05	87%	90%
DSH 09	83%	87%
DSH 10	93%	90%
DSH 11	93%	87%
DSH 25	90%	97%
DSH 27	100%	83%
DSH 31	90%	73%
DSH 32	93%	77%
Batch # 6		
CONTROL #6	87%	97%
DSH 15	90%	83%
DSH 28	97%	93%
DSH 34	77%	47% *
DSH 35	77%	93%

* Significantly different from the control, p=0.05.

initial QA/QC review by PK 8/30/96
final QA/QC review by LC 2/1/97

APPENDIX A

TOXSTAT Analysis

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
8
3
3
3
3
3
3
3
3
CONTROL
0.8
0.7
0.8
DSH 09
0.7
0.9
1.0
DSH 10
0.9
1.0
0.8
DSH 11
0.8
1.0
0.8
DSH 25
0.9
1.0
1.0
DSH 27
0.9
0.7
0.9
DSH 31
0.8
0.6
0.8
DSH 32
0.7
0.8
0.8

QA/QC'd JLC 2/1/97

TITLE: 93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
FILE: 93MPR4CA.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 8

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	CONTROL	1	0.8000	1.1071
1	CONTROL	2	0.7000	0.9912
1	CONTROL	3	0.8000	1.1071
2	DSH 09	1	0.7000	0.9912
2	DSH 09	2	0.9000	1.2490
2	DSH 09	3	1.0000	1.4120
3	DSH 10	1	0.9000	1.2490
3	DSH 10	2	1.0000	1.4120
3	DSH 10	3	0.8000	1.1071
4	DSH 11	1	0.8000	1.1071
4	DSH 11	2	1.0000	1.4120
4	DSH 11	3	0.8000	1.1071
5	DSH 25	1	0.9000	1.2490
5	DSH 25	2	1.0000	1.4120
5	DSH 25	3	1.0000	1.4120
6	DSH 27	1	0.9000	1.2490
6	DSH 27	2	0.7000	0.9912
6	DSH 27	3	0.9000	1.2490
7	DSH 31	1	0.8000	1.1071
7	DSH 31	2	0.6000	0.8861
7	DSH 31	3	0.8000	1.1071
8	DSH 32	1	0.7000	0.9912
8	DSH 32	2	0.8000	1.1071
8	DSH 32	3	0.8000	1.1071

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	CONTROL	3	0.991	1.107	1.068
2	DSH 09	3	0.991	1.412	1.217
3	DSH 10	3	1.107	1.412	1.256
4	DSH 11	3	1.107	1.412	1.209
5	DSH 25	3	1.249	1.412	1.358
6	DSH 27	3	0.991	1.249	1.163
7	DSH 31	3	0.886	1.107	1.033
8	DSH 32	3	0.991	1.107	1.068

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	CONTROL	0.004	0.067	0.039	6.27
2	DSH 09	0.045	0.212	0.123	17.43
3	DSH 10	0.023	0.153	0.088	12.15
4	DSH 11	0.031	0.176	0.102	14.56
5	DSH 25	0.009	0.094	0.054	6.93
6	DSH 27	0.022	0.149	0.086	12.80
7	DSH 31	0.016	0.128	0.074	12.35
8	DSH 32	0.004	0.067	0.039	6.27

QA/QC'd GLC 2/1/97

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.311

W = 0.950

Critical W (P = 0.05) (n = 24) = 0.916
Critical W (P = 0.01) (n = 24) = 0.884

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 3.84

Table Chi-square value = 18.48 (alpha = 0.01, df = 7)
Table Chi-square value = 14.07 (alpha = 0.05, df = 7)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.311

W = 0.950

Critical W (P = 0.05) (n = 24) = 0.916
Critical W (P = 0.01) (n = 24) = 0.884

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 3.84

Table Chi-square value = 18.48 (alpha = 0.01, df = 7)
Table Chi-square value = 14.07 (alpha = 0.05, df = 7)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	7	0.257	0.037	1.888
Within (Error)	16	0.311	0.019	
Total	23	0.568		

Critical F value = 2.66 (0.05,7,16)
Since F < Critical F FAIL TO REJECT Ho: All equal

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT SIG
1	CONTROL	1.068	0.767	
2	DSH 09	1.217	0.867	-1.308
3	DSH 10	1.256	0.900	-1.648
4	DSH 11	1.209	0.867	-1.232
5	DSH 25	1.358	0.967	-2.540
6	DSH 27	1.163	0.833	-0.831
7	DSH 31	1.033	0.733	0.308
8	DSH 32	1.068	0.767	0.000

Dunnett table value = 2.56 (1 Tailed Value, P=0.05, df=16,7)

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN 34 CHIRONOMIDS 11/01/93
File: 93MPR4CA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	CONTROL	3			
2	DSH 09	3	0.277	36.1	-0.100
3	DSH 10	3	0.277	36.1	-0.133
4	DSH 11	3	0.277	36.1	-0.100
5	DSH 25	3	0.277	36.1	-0.200
6	DSH 27	3	0.277	36.1	-0.067
7	DSH 31	3	0.277	36.1	0.033
8	DSH 32	3	0.277	36.1	0.000

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
5
3
3
3
3
3
control
1.0
0.9
1.0
dsh 15
0.8
1.0
0.7
dsh 28
1.0
0.9
0.9
dsh 34
0.4
0.5
0.5
dsh 35
0.9
0.9
1.0

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.154

W = 0.942

Critical W (P = 0.05) (n = 15) = 0.881
Critical W (P = 0.01) (n = 15) = 0.835

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 3.45

Table Chi-square value = 13.28 (alpha = 0.01, df = 4)
Table Chi-square value = 9.49 (alpha = 0.05, df = 4)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd DLC 2/1/97

TITLE: 93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 5

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	control	1	1.0000	1.4120
1	control	2	0.9000	1.2490
1	control	3	1.0000	1.4120
2	dsh 15	1	0.8000	1.1071
2	dsh 15	2	1.0000	1.4120
2	dsh 15	3	0.7000	0.9912
3	dsh 28	1	1.0000	1.4120
3	dsh 28	2	0.9000	1.2490
3	dsh 28	3	0.9000	1.2490
4	dsh 34	1	0.4000	0.6847
4	dsh 34	2	0.5000	0.7854
4	dsh 34	3	0.5000	0.7854
5	dsh 35	1	0.9000	1.2490
5	dsh 35	2	0.9000	1.2490
5	dsh 35	3	1.0000	1.4120

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	control	3	1.249	1.412	1.358
2	dsh 15	3	0.991	1.412	1.170
3	dsh 28	3	1.249	1.412	1.303
4	dsh 34	3	0.685	0.785	0.752
5	dsh 35	3	1.249	1.412	1.303

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	control	0.009	0.094	0.054	6.93
2	dsh 15	0.047	0.217	0.126	18.58
3	dsh 28	0.009	0.094	0.054	6.93
4	dsh 34	0.003	0.058	0.034	7.73
5	dsh 35	0.009	0.094	0.054	7.22

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	4	0.784	0.196	12.701
Within (Error)	10	0.154	0.015	
Total	14	0.939		

Critical F value = 3.48 (0.05,4,10)
Since F > Critical F REJECT Ho: All equal

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	control	1.358	0.967		
2	dsh 15	1.170	0.833	1.849	
3	dsh 28	1.303	0.933	0.000	
4	dsh 34	0.752	0.467	5.972	*
5	dsh 35	1.303	0.933	0.535	

Dunnett table value = 2.47 (1 Tailed Value, P=0.05, df=10,4)

93 MUDPUPPY RUN #4B CHIRONOMIDS 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4CB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	control	3			
2	dsh 15	3	0.155	16.1	0.133
3	dsh 28	3	0.155	16.1	0.000
4	dsh 34	3	0.155	16.1	0.500
5	dsh 35	3	0.155	16.1	0.033

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
7
3
3
3
3
3
3
3
control
1.0
0.9
1.0
DSH 05
1.0
0.8
0.8
DSH 09
0.9
0.9
0.7
DSH 10
1.0
0.9
0.9
DSH 11
0.9
0.9
1.0
DSH 31
0.8
0.9
1.0
DSH 32
0.8
1.0
1.0

QA/QC JLC 2/1/97

TITLE: 93 MUDPUPPY RUN #4A HYALELLA 11/01/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 7

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	control	1	1.0000	1.4120
1	control	2	0.9000	1.2490
1	control	3	1.0000	1.4120
2	DSH 05	1	1.0000	1.4120
2	DSH 05	2	0.8000	1.1071
2	DSH 05	3	0.8000	1.1071
3	DSH 09	1	0.9000	1.2490
3	DSH 09	2	0.9000	1.2490
3	DSH 09	3	0.7000	0.9912
4	DSH 10	1	1.0000	1.4120
4	DSH 10	2	0.9000	1.2490
4	DSH 10	3	0.9000	1.2490
5	DSH 11	1	0.9000	1.2490
5	DSH 11	2	0.9000	1.2490
5	DSH 11	3	1.0000	1.4120
6	DSH 31	1	0.8000	1.1071
6	DSH 31	2	0.9000	1.2490
6	DSH 31	3	1.0000	1.4120
7	DSH 32	1	0.8000	1.1071
7	DSH 32	2	1.0000	1.4120
7	DSH 32	3	1.0000	1.4120

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	control	3	1.249	1.412	1.358
2	DSH 05	3	1.107	1.412	1.209
3	DSH 09	3	0.991	1.249	1.163
4	DSH 10	3	1.249	1.412	1.303
5	DSH 11	3	1.249	1.412	1.303
6	DSH 31	3	1.107	1.412	1.256
7	DSH 32	3	1.107	1.412	1.310

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	control	0.009	0.094	0.054	6.93
2	DSH 05	0.031	0.176	0.102	14.56
3	DSH 09	0.022	0.149	0.086	12.80
4	DSH 10	0.009	0.094	0.054	7.22
5	DSH 11	0.009	0.094	0.054	7.22
6	DSH 31	0.023	0.153	0.088	12.15
7	DSH 32	0.031	0.176	0.102	13.43

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.268

W = 0.950

Critical W (P = 0.05) (n = 21) = 0.908
Critical W (P = 0.01) (n = 21) = 0.873

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 1.69

Table Chi-square value = 16.81 (alpha = 0.01, df = 6)
Table Chi-square value = 12.59 (alpha = 0.05, df = 6)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC JLC 2/1/97

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	6	0.081	0.013	0.703
Within (Error)	14	0.268	0.019	
Total	20	0.349		

Critical F value = 2.85 (0.05,6,14)
Since F < Critical F FAIL TO REJECT Ho: All equal

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	control	1.358	0.967		
2	DSH 05	1.209	0.867	1.318	
3	DSH 09	1.163	0.833	1.723	
4	DSH 10	1.303	0.933	0.481	
5	DSH 11	1.303	0.933	0.481	
6	DSH 31	1.256	0.900	0.900	
7	DSH 32	1.310	0.933	0.419	

Dunnett table value = 2.53 (1 Tailed Value, P=0.05, df=14,6)

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4A HYALELLA 11/01/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HA.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	control	3			
2	DSH 05	3	0.184	19.1	0.100
3	DSH 09	3	0.184	19.1	0.133
4	DSH 10	3	0.184	19.1	0.033
5	DSH 11	3	0.184	19.1	0.033
6	DSH 31	3	0.184	19.1	0.067
7	DSH 32	3	0.184	19.1	0.033

QA/QC ½ JLC 2/1

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
4
3
3
3
3
control
0.9
0.9
0.8
DSH 28
0.9
1.0
1.0
DSH 34
0.9
0.7
0.7
DSH 35
0.7
0.8
0.8

QA/QC'd JLC 2/1/97

TITLE: 93 MUDPUPPY RUN #4B HYALELLA 11/02/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 4

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	control	1	0.9000	1.2490
1	control	2	0.9000	1.2490
1	control	3	0.8000	1.1071
2	DSH 28	1	0.9000	1.2490
2	DSH 28	2	1.0000	1.4120
2	DSH 28	3	1.0000	1.4120
3	DSH 34	1	0.9000	1.2490
3	DSH 34	2	0.7000	0.9912
3	DSH 34	3	0.7000	0.9912
4	DSH 35	1	0.7000	0.9912
4	DSH 35	2	0.8000	1.1071
4	DSH 35	3	0.8000	1.1071

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	control	3	1.107	1.249	1.202
2	DSH 28	3	1.249	1.412	1.358
3	DSH 34	3	0.991	1.249	1.077
4	DSH 35	3	0.991	1.107	1.068

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	control	0.007	0.082	0.047	6.82
2	DSH 28	0.009	0.094	0.054	6.93
3	DSH 34	0.022	0.149	0.086	13.82
4	DSH 35	0.004	0.067	0.039	6.27

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	3	0.165	0.055	5.212
Within (Error)	8	0.084	0.011	
Total	11	0.249		

Critical F value = 4.07 (0.05,3,8)
Since F > Critical F REJECT Ho: All equal

QA/QC ✓ JLC 2/1/97

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.084

W = 0.855

Critical W (P = 0.05) (n = 12) = 0.859
Critical W (P = 0.01) (n = 12) = 0.805

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 1.23

Table Chi-square value = 11.34 (alpha = 0.01, df = 3)
Table Chi-square value = 7.81 (alpha = 0.05, df = 3)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 2/1/97

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	control	1.202	0.867		
2	DSH 28	1.358	0.967	-1.859	
3	DSH 34	1.077	0.767	1.486	
4	DSH 35	1.068	0.767	1.589	

Dunnett table value = 2.42 (1 Tailed Value, P=0.05, df=8,3)

93 MUDPUPPY RUN #4B HYALELLA 11/02/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR4HB.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	control	3			
2	DSH 28	3	0.163	18.8	-0.100
3	DSH 34	3	0.163	18.8	0.100
4	DSH 35	3	0.163	18.8	0.100

QA/QC'd JLC 2/1/97

EPA 905-R97-005
March 1997

ACUTE TOXICITY TESTS WITH *HYALELLA AZTECA* AND *CHIRONOMUS TENTANS* ON SEDIMENTS FROM THE DULUTH/SUPERIOR HARBOR: 1993 Sampling Results - Batch # 7

Conducted by

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Monitoring and Assessment Section
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February 1997

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INTRODUCTION

As part of the 1993 survey of sediment quality in the Duluth/Superior Harbor, sediment toxicity tests were conducted to assess acute (survival) and chronic (growth) toxicity to benthic invertebrates. Acute effects were measured in separate 10-day toxicity tests to *Hyalella azteca* (*H. azteca*) and *Chironomus tentans* (*C. tentans*). Growth was measured at the end of the *C. tentans* test to assess chronic effects. Survival and growth endpoints were compared to organisms similarly exposed to a reference control sediment collected from West Bearskin Lake (Cook County, MN).

A total of 40 sediment samples were collected for toxicity testing. This report presents the results of six of these sediment samples.

SAMPLE COLLECTION AND HANDLING

During September 27-28, 1993, Minnesota Pollution Control Agency (MPCA) staff collected the six sediments referred to in this report. The samples were collected from the harbor using a Ponar sampler and were taken to the University of Minnesota-Duluth Chemical Toxicology Research Laboratory. The samples were stored at 4°C until they were transported to the MPCA Toxicology Laboratory in St. Paul, MN.

METHODS

Six sediment samples and a control sediment sample were subjected to the 10-day sediment toxicity tests using the modified procedures described in ASTM (1993). However, the specific test system used for these assays is not indicated in the methods. The test organisms (*H. azteca* and *C. tentans*) were exposed to sediment samples in a portable, mini-flow system described in Benoit et al. (1993). The test apparatus consists of 300 mL, glass-beaker test chambers held in a glass box supplied with water from an acrylic plastic headbox. The beakers have two, 1.5 cm holes covered with stainless steel mesh, to allow for water exchange, while containing the test organisms. The headbox has a pipette tip drain calibrated to deliver water at an average rate of 32.5 mL/min. The glass box is fitted with a self-starting siphon to provide exchange of overlying water.

The *H. azteca* used for this test were 1 to 3 mm long, and the *C. tentans* were approximately 14 days old. These organisms were supplied by Environmental Consulting and Testing, Superior, WI on the day of the test.

On November 12, 1993, six samples (DSH 20, DSH 33, DSH 36, DSH 37, DSH 38, and DSH 39) and the control sediment were separately homogenized by hand, and 100 mL of each sediment was placed in a test beaker (Batch #7). Each sediment test was set up with three replicates of *H. azteca* and three replicates of *C. tentans*. Aerated, artesian well water was added to the beakers, and the sediments were allowed to settle for approximately two hours before the

organisms were added. For each toxicity test, ten organisms were placed in each beaker in a random fashion.

The organisms were exposed to 16 hours of light and eight hours of darkness for the duration of the ten-day test. Each day, two liters of aerated water from the artesian well at Stroh Brewery in St. Paul, MN were exchanged in each test chamber. On weekdays, 1-L was exchanged in the morning and 1-L in the afternoon. On weekends, the two liters were passed through the chambers all at once. Water quality measurements (i.e., pH, temperature, and dissolved oxygen) of the overlying water were taken in one beaker of each of the triplicate sets of each of the sediments. The results, along with daily observations involving the physical appearance of the sediments and organisms, were recorded in a laboratory notebook. This notebook is retained on file at the MPCA.

The test was terminated on November 22, 1993. The sediments were sieved through 40 mesh screens, and the sieved material was sorted for organisms. The organisms found were counted, and the number of alive and dead organisms was recorded. Organisms not found were recorded as missing and presumed dead. The *C. tentans* that survived were placed in aluminum weighing dishes, dried at approximately 90°C for at least four hours, desiccated to room temperature, and weighed.

Growth (weight) of the *C. tentans* and survival of both organisms were used as the endpoints for these tests. The resulting survival data were analyzed using TOXSTAT (Gulley and WEST, Inc., 1994), a statistical software package obtained from the University of Wyoming; however, due to a quality assurance problem, the growth data were not analyzed.

A 96-hour, reference toxicant test with *H. azteca* in sodium chloride (NaCl) was run in conjunction with these toxicity tests to determine the acceptability of the *H. azteca* used. Four concentrations of NaCl solution (i.e., 5, 2.5, 1.25, and 0.625 g/L) and a control (aerated, artesian well water) were used in this test. Three replicates of five organisms each were set up per concentration.

RESULTS

Water Chemistry

Measurements of pH, dissolved oxygen, and temperature in the overlying water of the test beakers were made daily. These measurements are summarized below and in Tables 1, 2, and 3, respectively.

The range of pH values in the beakers containing *H. azteca* was 7.5 to 8.2 (Table 1). The water in the *C. tentans* beakers had a pH range of 7.3 to 8.1 (Table 1). The pH fluctuation during these tests was acceptable since it did not vary more than 50% within each treatment (U.S. EPA, 1994).

The dissolved oxygen concentration ranged from 5.6 to 7.3 mg/L in the *H. azteca* beakers and from 4.1 to 7.2 mg/L in the *C. tentans* beakers (Table 2). The recommended dissolved oxygen concentration for these tests is greater than 40% saturation; therefore, these dissolved oxygen ranges were acceptable.

The range of temperature values in the beakers containing the *H. azteca* was 19.1°C to 22.0°C (Table 3). For the *C. tentans* test, the water temperature ranged from 18.9°C to 22°C (Table 3). The recommended temperature for this test is 23 ± 1°C (U.S. EPA, 1994).

Test Endpoints

The mean percent survival of *H. azteca* in the control was 37% which was unacceptable (Table 4). At least 80% survival in the control is necessary for the test to pass. Since the control survival of *H. azteca* in the 4-day reference toxicant test was acceptable at 93%, this would indicate that the culture was healthy. The reason for the poor control survival in the toxicity test could not be determined. For *C. tentans,* the mean percent survival in the control was 87% which was acceptable.

Mean percent survival of *H. azteca* in the test sediments ranged from 57% in the DSH 38 sample to 77% in the DSH 33 sample. Mean percent survival of *C. tentans* in the test sediments ranged from 53% in the DSH 33 and DSH 37 samples to 80% in the DSH 38 sample.

Although the dried *C. tentans* were weighed, the balance on which they were weighed was not calibrated with standard weights; therefore, the data are suspect since the internal calibration of the balance may have drifted with time.

Data Analysis

All *C. tentans* survival data were transformed using an arc sine-square root transformation before being analyzed statistically using Dunnett's test. The mean percent survival of *C. tentans* in all the samples was not significantly different from the control as determined by a 1-tailed Dunnett's test, p=0.05. Results of the statistical analyses of the data are included in Appendix A.

Reference Toxicant Test with *Hyalella azteca* in Sodium Chloride Solution

The pH of the overlying water in the reference toxicant test ranged from 8.2 to 8.7. The dissolved oxygen ranged from 7.5 to 8.6 mg/L, and the temperature ranged between 18.0°C and 22.0°C. The mean percent survival of the control was 93% which met quality assurance requirements (i.e., ≥ 90% control survival). The LC_{50} value for this test was 3.2 g/L NaCl as determined by the Trimmed Spearman-Karber method. A control chart will be developed for this test once five data points are obtained.

SUMMARY

Survival of *H. azteca* in the control sediment was unacceptable (less than 80%). Therefore, no conclusions can be drawn about the effect that the sediments had on *H. azteca.* The reference toxicant test for *H. azteca* was acceptable, and a LC_{50} value of 3.2 g/L NaCl was determined for this test.

Control survival was acceptable in the control containing *C. tentans*. The mean percent survival of *C. tentans* in the sediment samples was not significantly different from the control.

REFERENCES

ASTM. 1993. Standard guide for conducting sediment toxicity tests with freshwater invertebrates. E1383-93. In *Annual Book of ASTM Standards, Vol. 11.04*. American Society for Testing and Materials, Philadelphia, PA. pp. 1173-1199.

Benoit, D.A., G. Phipps, and G.T. Ankley. 1993. A sediment testing intermittent renewal system for the automated renewal of overlying water in toxicity tests with contaminated sediments. Water Research 27:1403-1412.

Gulley, D.D. and WEST, Inc. 1994. TOXSTAT 3.4. WEST, Inc., Cheyenne, WY.

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

TABLE 1. Daily Overlying Water pH Measurements

Day	Control #7		DSH 20		DSH 33		DSH 36	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.7	7.7	7.7	7.8	7.9	7.8	7.9	7.8
1	7.6	7.8	7.5	7.6	7.5	7.6	7.4	7.5
2	7.3	7.5	7.6	7.6	7.6	7.7	7.5	7.6
3	7.8	7.9	7.7	7.7	7.7	7.8	7.7	7.7
4	8.1	8.1	7.9	7.8	7.8	7.8	7.8	7.9
5	7.8	8.0	7.8	7.9	7.9	7.9	7.8	7.8
6	7.9	8.0	7.8	7.9	7.8	7.9	7.7	7.8
7	7.8	7.9	8.0	8.0	7.8	7.9	7.7	7.8
8	7.7	8.0	8.0	8.0	7.8	8.0	7.7	7.9
9	7.8	7.9	8.0	8.0	7.9	8.0	7.8	7.9
Mean	7.8	7.9	7.8	7.8	7.8	7.8	7.7	7.8
Range	7.3-8.1	7.5-8.1	7.5-8.0	7.6-8.0	7.5-7.9	7.6-8.0	7.4-7.9	7.5-7.9

Day	DSH 37		DSH 38		DSH 39	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.8	7.7	7.8	7.9	8.0	7.7
1	7.5	7.5	7.6	7.7	8.1	8.0
2	7.4	7.5	7.6	7.7	7.7	7.7
3	7.7	7.7	7.7	7.8	7.8	8.0
4	7.8	7.8	7.8	7.8	7.8	7.9
5	7.8	7.8	7.8	7.9	7.9	8.1
6	7.8	7.8	7.9	8.0	7.9	8.2
7	7.8	7.8	7.8	7.9	7.7	8.0
8	7.7	7.8	7.8	8.0	7.8	8.2
9	7.8	7.9	8.0	8.0	8.0	8.1
Mean	7.7	7.7	7.8	7.9	7.9	8.0
Range	7.4-7.8	7.5-7.9	7.6-8.0	7.7-8.0	7.7-8.1	7.7-8.2

Full QA/QC review by DLC 2/12/97

TABLE 2. Daily Overlying Water Dissolved Oxygen Concentrations (mg/L)

Day	Control #7		DSH 20		DSH 33		DSH 36	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	7.0	7.2	7.2	7.2	7.1	7.2	7.2	6.9
1	6.3	6.5	5.8	6.0	5.7	5.8	5.8	5.8
2	5.5	6.6	5.8	6.3	5.6	6.3	5.2	6.0
3	4.5	6.4	5.5	6.0	4.4	6.0	4.4	5.8
4	5.9	6.8	6.2	6.5	5.5	6.5	5.5	6.3
5	5.3	6.7	5.8	6.6	5.3	6.3	5.1	6.2
6	5.0	6.6	5.9	7.3	5.2	6.9	4.6	6.7
7	5.6	6.3	6.0	7.0	5.3	6.7	4.6	6.6
8	5.4	6.3	5.8	6.5	5.3	6.9	4.6	6.4
9	4.6	6.2	5.8	6.3	4.9	6.6	4.4	5.6
Mean	5.5	6.6	6.0	6.6	5.4	6.5	5.1	6.2
Range	4.5-7.0	6.2-7.2	5.5-7.2	6.0-7.3	4.4-7.1	5.8-7.2	4.4-7.2	5.6-6.9

Day	DSH 37		DSH 38		DSH 39	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	6.7	6.0	7.0	7.3	7.2	6.6
1	5.9	6.0	6.0	6.0	6.6	6.4
2	5.5	6.2	5.8	6.3	6.2	6.8
3	4.7	5.6	4.7	6.0	5.1	6.6
4	5.6	6.2	5.7	6.4	4.9	6.6
5	5.7	6.1	5.4	6.7	5.9	6.9
6	6.0	6.1	6.0	6.9	6.1	7.0
7	6.0	6.2	6.5	6.7	5.3	7.0
8	4.1	6.0	6.3	6.2	4.7	6.8
9	4.7	6.3	6.0	6.0	4.8	6.9
Mean	5.5	6.1	5.9	6.5	5.7	6.8
Range	4.1-6.7	5.6-6.3	4.7-7.0	6.0-7.3	4.7-7.2	6.4-7.0

full QA/QC review by DLC 2/2/97

TABLE 3. Daily Overlying Water Temperatures (Degrees Celsius)

Day	Control #7		DSH 20		DSH 33		DSH 36	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	19.6	19.5	19.2	19.2	19.1	19.1	19.0	19.1
1	21.4	21.3	20.5	20.7	20.7	20.6	20.8	20.9
2	21.7	21.6	21.3	21.3	21.1	21.2	21.3	21.4
3	20.5	20.5	19.7	19.6	19.6	19.5	19.5	19.8
4	20.0	19.8	19.5	19.5	19.5	19.5	19.6	19.6
5	20.1	20.0	19.6	19.6	19.6	19.6	19.5	19.5
6	20.2	20.1	19.6	19.6	19.6	19.6	19.6	19.6
7	19.8	19.8	19.5	19.6	19.6	19.6	19.6	19.6
8	21.2	21.1	20.8	20.7	20.6	20.6	20.9	20.9
9	21.5	21.5	21.4	21.4	21.3	21.2	21.4	21.4
Mean	20.6	20.5	20.1	20.1	20.1	20.1	20.1	20.2
Range	19.6-21.7	19.5-21.6	19.2-21.4	19.2-21.4	19.1-21.3	19.1-21.2	19.0-21.4	19.1-21.4

Day	DSH 37		DSH 38		DSH 39	
	C. tentans	*H. azteca*	*C. tentans*	*H. azteca*	*C. tentans*	*H. azteca*
0	19.3	19.3	19.2	19.3	18.9	19.1
1	21.0	21.0	21.0	21.0	22.0	22.0
2	21.2	21.3	21.3	21.3	21.2	22.0
3	20.5	20.5	19.7	19.7	19.6	19.7
4	19.5	19.5	19.5	19.5	19.5	19.7
5	19.7	19.7	19.5	19.5	19.2	19.1
6	19.9	19.9	19.7	19.7	19.2	19.6
7	19.8	19.8	19.7	19.7	19.7	19.8
8	21.0	21.0	20.9	20.9	20.9	21.0
9	21.5	21.5	21.5	21.5	21.3	21.3
Mean	20.3	20.4	20.2	20.2	20.2	20.3
Range	19.3-21.5	19.3-21.5	19.2-21.5	19.3-21.5	18.9-22.0	19.1-22.0

full QA/QC review by JLC 2/2/9

TABLE 4. Mean Percent Survival of *Hyalella azteca* and *Chironomus tentans*

Batch #7	Mean Percent Survival	
Sample	***Hyalella azteca***[1]	***Chironomus tentans***
CONTROL #7	37%	87%
DSH 20	70%	60%
DSH 33	77%	53%
DSH 36	63%	73%
DSH 37	60%	53%
DSH 38	57%	80%
DSH 39	63%	70%

[1] Control survival was unacceptable (<80% survival). Therefore, the test failed.

full QA/QC review by JC 2/2

APPENDIX A

TOXSTAT Analysis

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
7
3
3
3
3
3
3
3
control
0.9
0.7
1.0
dsh 37
0.5
0.6
0.5
dsh 36
0.7
0.7
0.8
dsh 33
0.8
0.3
0.5
dsh 38
0.7
0.8
0.9
dsh 20
0.3
0.9
0.6
dsh 39
0.8
0.7
0.6

QA/QC'd JLC 2/2/97

TITLE: 93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
FILE: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT
TRANSFORM: ARC SINE(SQUARE ROOT(Y)) NUMBER OF GROUPS: 7

GRP	IDENTIFICATION	REP	VALUE	TRANS VALUE
1	control	1	0.9000	1.2490
1	control	2	0.7000	0.9912
1	control	3	1.0000	1.4120
2	dsh 37	1	0.5000	0.7854
2	dsh 37	2	0.6000	0.8861
2	dsh 37	3	0.5000	0.7854
3	dsh 36	1	0.7000	0.9912
3	dsh 36	2	0.7000	0.9912
3	dsh 36	3	0.8000	1.1071
4	dsh 33	1	0.8000	1.1071
4	dsh 33	2	0.3000	0.5796
4	dsh 33	3	0.5000	0.7854
5	dsh 38	1	0.7000	0.9912
5	dsh 38	2	0.8000	1.1071
5	dsh 38	3	0.9000	1.2490
6	dsh 20	1	0.3000	0.5796
6	dsh 20	2	0.9000	1.2490
6	dsh 20	3	0.6000	0.8861
7	dsh 39	1	0.8000	1.1071
7	dsh 39	2	0.7000	0.9912
7	dsh 39	3	0.6000	0.8861

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 1 of 2

GRP	IDENTIFICATION	N	MIN	MAX	MEAN
1	control	3	0.991	1.412	1.217
2	dsh 37	3	0.785	0.886	0.819
3	dsh 36	3	0.991	1.107	1.030
4	dsh 33	3	0.580	1.107	0.824
5	dsh 38	3	0.991	1.249	1.116
6	dsh 20	3	0.580	1.249	0.905
7	dsh 39	3	0.886	1.107	0.995

@A/QC'd JLC 2/2

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

SUMMARY STATISTICS ON TRANSFORMED DATA TABLE 2 of 2

GRP	IDENTIFICATION	VARIANCE	SD	SEM	C.V. %
1	control	0.045	0.212	0.123	17.43
2	dsh 37	0.003	0.058	0.034	7.10
3	dsh 36	0.004	0.067	0.039	6.50
4	dsh 33	0.071	0.266	0.154	32.26
5	dsh 38	0.017	0.129	0.075	11.58
6	dsh 20	0.112	0.335	0.193	37.03
7	dsh 39	0.012	0.111	0.064	11.12

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

ANOVA TABLE

SOURCE	DF	SS	MS	F
Between	6	0.399	0.067	1.759
Within (Error)	14	0.530	0.038	
Total	20	0.929		

Critical F value = 2.85 (0.05,6,14)
Since F < Critical F FAIL TO REJECT Ho: All equal

QA/QC'd JLC 2/2/97

File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Shapiro - Wilk's test for normality

D = 0.530

W = 0.968

Critical W (P = 0.05) (n = 21) = 0.908
Critical W (P = 0.01) (n = 21) = 0.873

Data PASS normality test at P=0.01 level. Continue analysis.

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

Bartlett's test for homogeneity of variance
Calculated B1 statistic = 7.74

Table Chi-square value = 16.81 (alpha = 0.01, df = 6)
Table Chi-square value = 12.59 (alpha = 0.05, df = 6)

Data PASS B1 homogeneity test at 0.01 level. Continue analysis.

QA/QC'd JLC 2/2/97

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 1 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	TRANSFORMED MEAN	MEAN CALCULATED IN ORIGINAL UNITS	T STAT	SIG
1	control	1.217	0.867		
2	dsh 37	0.819	0.533	2.509	
3	dsh 36	1.030	0.733	1.181	
4	dsh 33	0.824	0.533	2.477	
5	dsh 38	1.116	0.800	0.640	
6	dsh 20	0.905	0.600	1.968	
7	dsh 39	0.995	0.700	1.402	

Dunnett table value = 2.53 (1 Tailed Value, P=0.05, df=14,6)

93 MUDPUPPY RUN #5 CHIRONOMIDS 11/12/93
File: S:\MA\CHUBBAR\TSD\93MUD\93MPR5C.DAT Transform: ARC SINE(SQUARE ROOT(Y))

DUNNETT'S TEST - TABLE 2 OF 2 Ho:Control<Treatment

GROUP	IDENTIFICATION	NUM OF REPS	Minimum Sig Diff (IN ORIG. UNITS)	% of CONTROL	DIFFERENCE FROM CONTROL
1	control	3			
2	dsh 37	3	0.350	40.4	0.333
3	dsh 36	3	0.350	40.4	0.133
4	dsh 33	3	0.350	40.4	0.333
5	dsh 38	3	0.350	40.4	0.067
6	dsh 20	3	0.350	40.4	0.267
7	dsh 39	3	0.350	40.4	0.167

QA/QC'd JLC 2/2/97