PHASE IV GIS-BASED SEDIMENT QUALITY DATABASE FOR THE ST. LOUIS RIVER AREA OF CONCERN—WISCONSIN FOCUS

Overview of Sediment Quality Conditions in the St. Louis River Area of Concern

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FORWARD

The Phase IV geographic information system (GIS)-based sediment quality database for the St. Louis River Area of Concern (AOC)—Wisconsin focus represents a collaborative project between the St. Louis River Citizens Action Committee (CAC), Minnesota Pollution Control Agency (MPCA), Wisconsin Department of Natural Resources (WDNR), and Exa Data & Mapping Services, Inc. in conjunction with their subconsultants from Premier Environmental Services, Inc. and Searay Environmental. This project was funded by the Wisconsin Coastal Management Program (WCMP) and the National Oceanic and Atmospheric Administration (NOAA), Office of Ocean and Coastal Resource Management under the Coastal Zone Management Act, Grant # NA05NOS4191067, through a grant agreement with the St. Louis River CAC. In addition, the MPCA contributed over 60% of state matching funds to this project.

This report was prepared by Dr. Judy Crane (MPCA). Dr. Crane's time was used as part of the state match to the St. Louis River CAC's grant under award number WCMP 86003-006.07 from NOAA, U.S. Department of Commerce. The statements, findings, conclusions, and recommendations are those of the author and do not necessarily reflect the views of NOAA, the Department of Commerce, the MPCA, WDNR, or St. Louis River CAC.

WISCONSIN COASTAL MANAGEMENT PROGRAM

Minnesota Pollution Control Agency

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The Phase IV sediment quality databases include new sediment quality data for the Wisconsin side of the St. Louis River AOC, as well as data that were assembled from three earlier phases of the GIS-based sediment quality database project conducted by Dr. Crane (MPCA) and her consultants. These earlier projects were funded as follows:

- Phase I (completed September 30, 2003): Grant number GL97536301-1 ($81,000) from the U.S. Environmental Protection Agency's (EPA) Great Lakes National Program Office

(GLNPO) plus a 5% state match from the MPCA. MacDonald Environmental Sciences Ltd. (MESL) provided contractual assistance on this project.

- Phase II (completed December 22, 2004 as one component of a MPCA-Duluth grant to develop a comprehensive sediment management plan for the lower St. Louis River AOC): Grant number GL97540401-2 ($40,000 of funds for the Phase II project) from GLNPO plus a 5% state match from the MPCA. MESL provided contractual assistance on this project.

- Phase III (completed December 31, 2005): Grant number MLSCP 306-28-06 ($50,000) from Minnesota's Lake Superior Coastal Program (MLSCP) plus a 50% state match from the MPCA. MESL and Exa Data & Mapping Services, Inc. provided contractual assistance on this project.

Work products from Phases I through IV are either available on the MPCA's Contaminated Sediment Web page at: http://www.pca.state.mn.us/water/sediments/studies-stlouis.html#assessment or by contacting Dr. Crane at:

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LIST OF ABBREVIATIONS AND ACRONYMS

AOC	Area of Concern
BC	British Columbia
CAC	Citizens Action Committee
DM&IR	Duluth, Missabe, and Iron Range
DSD	Duluth Steam District
EPA	Environmental Protection Agency
FL	Florida
F/P	Fluoranthene to Pyrene Ratio
FTP	File Transfer Protocol
GIS	Geographic Information System
GLNPO	Great Lakes National Program Office
ID	Identification
IJC	International Joint Commission
LMW	Low Molecular Weight
MESL	MacDonald Environmental Sciences Ltd.
MLE	Maximum Likelihood Estimation
MLSCP	Minnesota's Lake Superior Coastal Program
MN	Minnesota
MPCA	Minnesota Pollution Control Agency
MS™	Microsoft™
MT	Montana
NA	Not Available
ND	Not Detected
NOAA	National Oceanic and Atmospheric Administration
P/A	Phenanthrene to Anthracene Ratio
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PEC	Probable Effect Concentration
PEC-Q	Probable Effect Concentration Quotient
P.O.	Post Office
QAPP	Quality Assurance Project Plan
RAP	Remedial Action Plan
R-EMAP	Regional Environmental Monitoring and Assessment Program
SD	Standard Deviation
SEH	Short Elliott Hendrickson
SEM	Simultaneously Extractable Metals
SLRIDT	St. Louis River Interlake/Duluth Tar
SQG	Sediment Quality Guideline
SQT	Sediment Quality Target
TMDL	Total Maximum Daily Load
TOC	Total Organic Carbon

LIST OF ABBREVIATIONS AND ACRONYMS

TR	Training Site
U.S.	United States
USS	U.S. Steel
UV	Ultraviolet
WA	Washington
WCMP	Wisconsin Coastal Management Program
WDNR	Wisconsin Department of Natural Resources
WI	Wisconsin
WLSSD	Western Lake Superior Sanitary District

ACKNOWLEDGMENTS

A number of individuals assisted with the preparation of earlier phases of the GIS-based sediment quality database. These individuals have been acknowledged in the documentation that accompanied each phase of the database. The Phase IV project team members that assisted with other project tasks have been acknowledged in other report and database documentation.

Kate Angel was the WCMP Program Liaison to the St. Louis River CAC for this grant. Lynelle Hanson and Phil Monson were the respective grant managers from the St. Louis River CAC. The funding acknowledgments for this project were provided in the Forward of this report.

Jan Eckart and Julie Lendway (MPCA) provided word processing and report production support. Todd Biewen (MPCA) provided useful supervisory assistance and was instrumental in securing state match funding for Dr. Crane's position.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

The lower St. Louis River provides an important coastal resource to western Lake Superior. In particular, this transboundary waterway provides critical habitat to invertebrate, fish, and waterfowl species, and it also provides an economic venue for Great Lakes shipping and business in the Duluth-Superior Harbor. The lower estuary and harbor are bisected by the Minnesota-Wisconsin state line (Figure 1). Contaminated sediments have contributed to several use impairments in the lower St. Louis River and were a factor in the International Joint Commission's (IJC) decision to designate the lower St. Louis River as one of 43 Areas of Concern (AOCs) in the Great Lakes basin (IJC 1989). As such, contaminated sediments are an important nonpoint source of pollution to the St. Louis River AOC, especially in the Duluth-Superior Harbor. Consequently, several sediment quality and fish tissue studies have been conducted in the lower St. Louis River AOC, particularly since 1990, to delineate the extent and magnitude of contaminants of potential concern and to assess the potential for ecological effects (Figure 1).

As part of the remedial action plan (RAP) process for the St. Louis River AOC, the Minnesota Pollution Control Agency (MPCA) and the Wisconsin Department of Natural Resources (WDNR), along with citizen and technical stakeholders, identified the need to compile sediment quality data collected from the AOC in a database format for mapping and evaluation purposes (MPCA/WDNR 1995). This need was the basis for securing funding to conduct earlier phases of a Geographic Information System (GIS)-based sediment quality database (see Forward), as well as this Phase IV project. The updates of this database will support the assessment, preservation, and restoration of the St. Louis River AOC. The primary applications of the Phase IV GIS-based sediment quality database are to:

- Allow users to access sediment quality data for the AOC;
- Allow users to view the data spatially, along with GIS-watershed data;
- Assist agencies and stakeholders with implementing the three-phase sediment strategy of the Stage II St. Louis River RAP (MPCA/WDNR 1995), along with newer sediment management efforts;
- Further the goals of the Lake Superior Lakewide Management Plan by tracking the occurrence of critical pollutants; and
- Allow analysis of sediment quality data in conjunction with the detailed habitat evaluation and mapping accomplished through the St. Louis River Habitat Plan (St. Louis River CAC 2002). Most of the GIS data from the Habitat Plan are available in the ArcMap 9.1 map documents available for this project.

Sediment quality issues in the St. Louis River AOC are of interest to local and state agencies in Minnesota and Wisconsin, as well as to federal agencies, tribal groups, responsible parties, nonprofit organizations, and other concerned stakeholders. The St. Louis River RAP (MPCA/WDNR 1992, 1995), as well as a number of sediment investigations, have identified several areas of elevated sediment contamination (i.e., hot spot sites) within the Minnesota side of the lower estuary, including the:

- St. Louis River Interlake/Duluth Tar (SLRIDT) Superfund site;
- USS Superfund site;
- Minnesota Slip;
- Slip C;
- Embayment encompassing the old Duluth sewage treatment plant near the Western Lake Superior Sanitary District (WLSSD) and the confluence with Coffee and Miller Creeks;
- Embayment encompassing the M.L. Hibbard plant/DSD No. 2, north of Grassy Point;
- Bay near the DM&IR taconite storage facility; and
- Dakota Pier.

Contaminated hot spot sites within the Wisconsin side of the St. Louis River AOC include the:

- Kopper's Industries Inc. site;
- Howard's Bay; and
- Area near the City of Superior wastewater treatment plant.

Final sediment remediation of the Hog Island Inlet and Newton Creek site in Superior, WI was completed during November 2005 through the use of Great Lakes Legacy Act funding (http://www.epa.gov/glnpo/sediment/legacy/hogisland/index.html). Sediment remediation of the SLRIDT Superfund site began in June 2006 and is targeted for completion during 2009.

1.2 PROJECT OVERVIEW

The Phase IV GIS-based sediment quality database for the St. Louis River AOC—Wisconsin focus represents a collaborative project between the St. Louis River Citizens Action Committee (CAC), WDNR, MPCA, and Exa Data & Mapping Services, Inc. in conjunction with their subconsultants from Premier Environmental Services, Inc. and Searay Environmental. For this phase of the database, additional sediment quality data from the Wisconsin side of the AOC were added to the database based on the procedures documented in the Phase III Quality Assurance Project Plan (QAPP; Crane 2005a), as well as in the Phase IV project team roles and responsibilities report (Crane 2005b). These data consisted of mostly benthic invertebrate community data from throughout the Wisconsin side of the St. Louis River AOC, as well as some pre-remediation sediment chemistry data from Hog Island Inlet and Newton Creek in Superior, WI. Post-remediation sediment chemistry data from this site were not available in time to add to the Phase IV database.

The Phase IV sediment quality database is available to users in three different formats, which are available on the MPCA's ftp site at: ftp://files.pca.state.mn.us/pub/sedimentDB/. Each format is available as a zipped file, and users will need to unzip the file(s) before using them. The file options are as follows:

- **Microsoft™ (MS™) Access '97 sediment quality database file name:** STLR_SED_DB_PH4_97.zip. Only a few stakeholders lacking MS™ Access 2000 software will need to use this version of the database.

- **MS™ Access 2000 sediment quality database file name:** STLR_SED_DB_PH4_Finalb.zip.

- **Query Manager-compatible database files:** PhIV_STLR_SEDB_QM_Final.zip. See the instructions in Chapter 4 of the Phase III Addendum to the Phase II Help Section for Database Users (Crane and Myre 2005a) for how to use these files with the National Oceanic and Atmospheric Administration's (NOAAs) free Query Manager 2.56 software. NOAA's software is available at: http://response.restoration.noaa.gov/topic_subtopic_entry.php?RECORD_KEY%28entry_subtopic_topic%29=entry_id,subtopic_id,topic_id&entry_id(entry_subtopic_topic)=375&subtopic_id(entry_subtopic_topic)=5&topic_id(entry_subtopic_topic)=2.

A new feature of the MS™ Access 2000 version of the Phase IV database is that it contains a user-friendly Query Interface that facilitates retrieval of sediment chemistry, sediment toxicity, and benthic invertebrate community data. In addition to the interface, there are a series of pre-defined queries that allow the more experienced user to edit the queries directly. A Help Section (Crane and Myre 2006) for using the database products is available at: http://www.pca.state.mn.us/publications/tdr-fg06-02.pdf.

Since most of the sediment quality data have geopositional coordinates (i.e., latitude and longitude) for where the sediment samples were collected, the data can be displayed on maps along with GIS watershed data. This mapping process allows users to visualize the data results and to view watershed data that may help users interpret the results (e.g., location of current and historical industries, wastewater treatment plants, landfills, marinas, and navigational channels, as well as information on watershed soils, aquatic and nearshore habitats, and hydrological features). As part of the scope of work of this project, the MPCA completed an internal update of the Phase II ArcMap 8.3 map documents (Smorong *et al*. 2004a) to ArcMap 9.1 map documents. A Quick Guide (Crane 2006a) for using the ArcMap 9.1 map documents is available at: http://www.pca.state.mn.us/publications/tdr-fg06-01.pdf.

A twelve page pamphlet that provides a summary of sediment quality conditions in the St. Louis River AOC (Crane 2006b) is available at: http://www.pca.state.mn.us/publications/tdr-fg06-03.pdf. This pamphlet was an extra task not originally included in the list of work products for this grant. The MPCA was required to provide a 60% state match for this project, which amounted to 1264 hours of Dr. Crane's work time through her salary, fringe, and indirect expenses. The 60% state match requirement was met on June 19, 2006, and the MPCA has contributed additional state match time to this project through Dr. Crane's time.

1.3 SCOPE OF REPORT

This report provides an overview of sediment quality conditions in the St. Louis River AOC. Due to the resource limitations and time constraints of this project, more time went into the analysis of sediment quality data and preparation of tables and figures than in the preparation of text for this report. While this report examines sediment quality issues in a holistic basis throughout the St. Louis River AOC, it is not intended to be an exhaustive evaluation of how sediment quality data can be analyzed. Agency staff and stakeholders are encouraged to explore the databases for additional features they wish to plot on GIS maps of interest to them.

Web links to additional project documentation cited in this report are provided in the References section.

Note: Sediment remediation of the Hog Island Inlet/Newton Creek site in Superior, WI was completed during the fall of 2005. The data analyses and preparation of GIS maps in this report include pre-remediation sediment quality data from this area in order to provide a baseline to compare to in the future as post-remediation sediment quality data are collected.

CHAPTER 2

METHODS

2.1 FALL 2005 STAKEHOLDER MEETINGS

MPCA staff and stakeholders were invited to attend two stakeholders meetings during the fall of 2005 in which an overview presentation of the Phase IV database project was given and input was sought on the development of a user-friendly query interface for the MS™ Access 2000 sediment quality database. In addition, input obtained from the same meeting on preparation of a sediment quality report for the Phase III sediment quality database project (Crane 2005c) was also pertinent towards preparation of this report. Five people participated in the meeting held on October 31, 2005 in St. Paul, MN, and approximately 20 people participated in a similar meeting held on November 1, 2005 in Duluth, MN. A copy of the Phase IV presentation given at these meetings is available at: http://www.pca.state.mn.us/water/sediments/slr-p4stakeholder-f05.pdf.

2.2 DATA ANALYSIS

2.2.1 Data Queries from Phase IV MS™ Access 2000 Sediment Quality Database

Several queries were run using the new drop-down menu of query options in the MS™ Access 2000 sediment quality database. Where appropriate for further data analysis, pertinent data were excluded from studies of the Koppers Industries Inc. facility (Study ID 32) and of lakes on the Fond du Lac Reservation (part of Study ID's 47 and 48) since these sites were not directly connected to the St. Louis River (Figure 1). The data queries included pre-remediation sediment quality data from Hog Island Inlet and Newton Creek to provide a baseline analysis that can be used in the future when post-remediation sediment quality data are available for this site.

As explained in the supplemental Phase IV Help Section for Database Users (Crane and Myre 2006), many of the queries in the MS™ Access 2000 sediment quality database are organized by depth intervals. Every sample is coded with one unique depth interval to allow for greater flexibility in conducting the queries. These intervals are pre-defined and include in order of priority:

- ≥0 to ≤5 cm,
- ≥0 to ≤15 cm,
- ≥15 to ≤30 cm,
- ≥0 to ≤30 cm,
- ≥30 to ≤45 cm,
- ≥30 cm, and
- Other depths (including samples where either the upper or lower depth was unknown).

Thus, a sample with a depth interval of 2 - 4 cm would only be assigned to the 0 - 5 cm depth interval. It would not be assigned to the 0 - 15 cm or 0 - 30 cm categories since it can only be assigned to one depth interval.

In order to obtain all of the sediment chemistry data that were inclusive of the 0-30 cm depth interval and ≥30 cm depth intervals, the following query depth intervals were selected:

- 0 – 30 cm, inclusive:
    - ≥0 to ≤5 cm,
    - ≥0 to ≤15 cm,
    - ≥15 to ≤30 cm, and
    - ≥0 to ≤30 cm.
- ≥30 cm, inclusive:
    - ≥30 to ≤45 cm, and
    - ≥30 cm.

The following queries were run to obtain data for this report:

Other Query Option
- Sample count by data type;
- Station count by area and location description;
- Probable Effect Concentration (PEC) chemical classes – sample count by depth interval;
- Matching chemistry/bioassay samples with test and toxicity data: the query results were exported to MS™ Excel and the data were divided into the following categories:
    - 10-day *Hyalella azteca* Growth or Survival,
    - 10-day *Chironomus dilutus* (formerly known as *C. tentans*) Growth or Survival,
    - 28-day *H. azteca* Growth or Survival,
    - All Non-ultraviolet (UV) Tests Combined, and
    - All UV Tests Combined.

Sediment Chemistry Query Option
- Select Chemistry Data
    - Added all locations except for the Koppers Industries Inc. site (Study ID 32) and Fond du Lac Band lakes (Study ID 47). In addition, the Fond du Lac lake data for Study ID 48 were excluded after the query results had been brought into a MS™ Excel file.
    - Selected depth intervals that were inclusive of the upper 30 cm of sediment and greater than 30 cm of sediment.
    - In separate query runs, selected chemical classes that included chemicals for which corresponding Level I and Level II sediment quality targets (SQTs) were available (Crane *et al*. 2000, 2002a), as well as total organic carbon (TOC) and three particle size classes. One-half the detection limit was used for nondetect data.
- Polycyclic aromatic hydrocarbon (PAH) Source Ratios Summary of phenanthrene/anthracene (P/A) and fluoranthene/pyrene (F/P)

  - Added all locations except for the Koppers Industries Inc. site (Study ID 32) and Fond du Lac Band lakes (Study ID 47).
- Mean probable effect concentration quotient (PEC-Q) Summary
  - The results of this query for the 0 - 5, 0 - 15, and 0 - 30 cm depth intervals were combined in Excel with a separate query of mean PEC-Qs for the 15 - 30 cm depth interval from the Select Chemistry Data query option.
  - The distribution of mean PEC-Qs for location descriptions that had at least 20 sediment samples was determined.

2.2.2 Data Queries from Query Manager-Compatible Database Files

Tissue residue data were queried from the Phase IV Query Manager-compatible database files using the standard drop down menu of queries developed by NOAA.

2.2.3 Processing of Data

The results of most of the queries were exported to MS™ Excel for further data processing.

The results from the surface and subsurface multiple chemical queries were processed further in MS™ Excel by:

- Creating worksheets for each chemical. Missing values were removed.
- The surface and subsurface data for each chemical were copied to a SigmaStat® 3.1 worksheet so that a new worksheet was created for each chemical (e.g., lead, zinc, anthracene). The descriptive statistics feature of SigmaStat® 3.1 was used to obtain summary statistics (e.g., count, average, standard deviation, minimum, median, maximum) and 10th and 90th percentiles, as well as measures of skewness, kurtosis, and normality. Skewness is a measure of how symmetrically the observed values are distributed about the mean. Kurtosis is a measure of how peaked or flat the distributions of observed values are, compared to a normal distribution. A nonparametric Mann-Whitney Rank Sum Test of the median values for each pair of surface and subsurface chemicals was run using SigmaStat® 3.1 to determine if the chemical concentrations were significantly different ($p = 0.05$).
- The descriptive statistics output for each chemical was copied into MS™ Excel spreadsheets to generate summary tables. The 10th and 90th percentile values, as well as median values were compared to the corresponding Level I and Level II SQT values to determine exceedances.

The PAH source ratios were evaluated further by:

- Exporting the query results to Excel. The PAH source ratios for each depth interval were copied into separate worksheets in Excel. The data were then copied into SigmaPlot®. Summary statistics for each P/A and F/P column of data were calculated for the following parameters: count, average, standard deviation, minimum, median, maximum, and 10th and 90th percentiles, as well as measures of skewness, kurtosis, and normality. The number of samples, mean, standard deviation, and median values for each P/A and F/P source ratio for each depth interval were compiled, entered into Excel, and proofed against the hard copy table. Next, a Mann-Whitney Rank Sum test was run in SigmaStat® 3.1 between the P/A groups of 0 - 30 cm and >30 cm, as well as between the

F/P groups of the same depth intervals. Significant statistical differences were noted at $p = 0.05$.

- The above procedures were also followed after removing pre-remediation P/A and F/P data for Hog Island Inlet and Newton Creek from the data set.

The distribution of mean PEC-Qs in surficial sediments (i.e., 0 – 30 cm inclusive) was evaluated further by:

- Creating new worksheets for locations that had at least 20 samples with mean PEC-Q data. The data for each area of interest were then copied into SigmaPlot® where the following summary statistics were calculated: count, average, standard deviation, minimum, median, maximum, and 10^{th} and 90^{th} percentiles, as well as measures of skewness, kurtosis, and normality. The location description, number of sediment samples, arithmetic mean, standard deviation, minimum, 10^{th} percentile, median, 90^{th} percentile, and maximum values were copied electronically into a MS™ Excel spreadsheet to generate the table used in this report.
- The mean PEC-Q data for each location of interest were sorted in the MS™ Excel spreadsheet from low to high values. The data were split into the following categories so that the frequency of low, moderate, and high risk samples at mean PEC-Q ranges of <0.1, 0.1 to 0.6, and >0.6, respectively, could be calculated. The results were hand-entered into an Excel spreadsheet and proofed for accuracy.

The incidence of sediment toxicity for several mean PEC-Q ranges was calculated by:

- Using the results of the matching sediment chemistry/toxicity query. The following mean PEC-Q ranges were used to be consistent with similar analyses done on earlier phases of the sediment quality database (Crane *et al*. 2000, 2004):
    - ≤0.10,
    - >0.10 to ≤0.50,
    - >0.50 to ≤1.0,
    - >1.0 to ≤5.0,
    - >5.0, and
    - Overall.
- The sediment toxicity data were treated as follows:
    - 10-day *H. azteca* Growth or Survival:
        - deleted data from UV light exposures,
        - removed 2 negative control samples,
        - removed data from sites 102-TR and 044-TR associated with the Regional Environmental Monitoring and Assessment Program (R-EMAP) project (Study ID 04); these known contaminated sediment sites had incomplete sediment chemistry data collected at them, resulting in underestimated mean PEC-Q values.
        - deleted two not determined (ND) results from Study ID 34, and
        - deleted stations with no calculable mean PEC-Q values.
    - 10-day *C. dilutus* Growth or Survival:
        - deleted data from UV light exposures,
        - removed 4 negative control samples,
        - removed data from site 102-TR (no value was available for 044-TR) from the R-EMAP project (Study ID 04),

    - deleted 6 ND toxicity results, and
    - deleted 5 stations with no calculable mean PEC-Q values.
  - 28-day *H. azteca* Growth or Survival:
    - deleted 2 negative control samples
  - All non-UV Tests Combined:
    - excluded bacteria (i.e., Microtox® and Mutatox®) tests,
    - deleted UV-exposed sediment toxicity data,
    - deleted 12 negative control samples,
    - deleted data from sites 102-TR and 044-TR from the R-EMAP project (Study ID 04);
    - deleted 7 stations with no calculable mean PEC-Q value, and
    - deleted 6 not available (NA) and 19 ND toxicity test results.
  - All UV Tests Combined:
    - deleted non-UV exposed test treatments, and
    - deleted 12 negative control samples.
- Stations that had more than one toxicity test result were deemed toxic if at least one endpoint was toxic, and stations were determined to be nontoxic if all of the endpoints were nontoxic.

2.3 PREPARATION OF GIS MAPS

ArcMap 9.1 map documents were prepared by running queries in either the MS™ Access 2000 sediment quality database or the Query Manager-compatible database files. Next, the directions given in the "Quick Guide to the Phase IV ArcMap 9.1 Map Documents" (Crane 2006a) were followed for linking the queries with the GIS applications. Since the query results in the MS™ Access 2000 database are set-up to be hidden, these queries could be viewed by going to the Tools menu, selecting Options and the View tab. On the top right of the 'Show' area, the 'Hidden Objects' choice was checked to show the hidden queries in gray font. The rationale for selecting GIS data for the maps was based on the professional judgment of the author and on stakeholder input regarding GIS data of high interest to them (e.g., St. Louis River aquatic habitat plan).

The following maps were prepared based on the following queries (all done in the MS™ Access 2000 database, except for the tissue residue query which was done in the Query Manager-compatible database files):

- Sediment Stations: linked GIS to the ptbl – STATION table and retained it in ArcMap 9.1 as a dbf file.
- Distribution of Mean PEC-Q Ranges (0 – 30 cm, inclusive): selected the Other query option, and then selected PEC chemical classes – all samples. In GIS, excluded the 30 – 45 cm, >30 cm, and other classes from being viewed on the maps and set the mean PEC-Q ranges as <0.1, 0.1 – 0.6, and >0.6. Maps were prepared for both the entire St. Louis River AOC and for the SLRIDT Superfund site.
- Distribution of Mercury: from the Sediment Chemistry query option, selected chemistry data, all studies, all locations, depth intervals of 0 - 5, 0 – 15, 0 – 30, and 15 – 30 cm, chemical class of metals, and selected the output table to provide chemicals as columns with one-half detection limits used for nondetected data.

- Distribution of TOC: from the Sediment Chemistry query option, selected chemistry data, all studies, all locations, depth intervals of 0 - 5, 0 – 15, 0 – 30, and 15 – 30 cm, conventional chemical parameters, and selected the output table to provide one sample and chemical per row. In GIS, selected CHEMCODE to select the TOC data to display on the map.
- Distribution of Mean PEC-Q Ranges Used in the Incidence of Sediment Toxicity Analyses: from the Other query option, selected matching chemistry/bioassay samples with test and toxicity data, saved the query and linked it to GIS.
- Matching Sediment Toxicity Data: from the Other query option, selected matching chemistry/bioassay samples with test and toxicity data, saved the query and linked it to GIS. For the map, only displayed toxic and not toxic samples.
- *C. dilutus* Survival (no UV-exposure): from the Bioassay Data query, selected bioassay results, all studies, all locations (except negative controls), selected species of *Chironomus tentans* (now called *C. dilutus*), and selected bulk sediment/percent survival which provided the results for both 10-day and 20-day toxicity tests.
- *H. azteca* Survival (no UV-exposure): from the Bioassay Data query, selected bioassay results, all studies, all locations (except negative controls), selected species of *H. azteca*, and selected bulk sediment/percent survival which provided the results for 10-day, 28-day, 35-day, and 42-day toxicity tests.
- Mean Percentage of Benthic Invertebrates: from the Benthic Data query, selected benthic metrics, all studies, all locations, selected metric [i.e., noninsect abundance, oligochaeta abundance, chironomidae abundance, and Ephemeroptera (mayfly) abundance], selected units of percent, and selected summary data (i.e., mean, standard deviation, and sum).
- Tissue Residue Stations: ran query in Query Manager-compatible database files to locate stations.
- Particle Size: from the Sediment Chemistry query, selected chemistry data, all studies, all locations (except NA), depth intervals of 0 - 5, 0 – 15, 0 – 30, and 15 – 30 cm, conventional chemical parameters, and selected the output table to provide one sample and chemical per row. In GIS, selected CHEMCODE to select the particle size ranges of interest [i.e., fine (silt + clay; <63 µm), medium sand (250 – 500 µm), and coarse sand (500 – 1000 µm)]. In GIS, sorted by CHEMNAME to map the particle size ranges of interest.

Once the queries were linked to the ArcMap 9.1 map document, they were saved as dbf files. For some sediment stations, more than one sample was available for the sediment chemistry, sediment toxicity, or benthic invertebrate community results. In those cases, either the highest concentration effect or toxic sample was plotted on top of other samples for that station that displayed a lower concentration effect or nontoxic effect.

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CHAPTER 3

RESULTS

3.1 STAKEHOLDER MEETINGS

Stakeholders did not provide much input on the development of a user-friendly query interface for the Phase IV MS™ Access 2000 sediment quality database. In addition, a strong consensus did not emerge from the stakeholder group regarding the type of sediment quality data they would like to have queried from the Phase III sediment quality database to include in the Phase III sediment quality report (Crane 2005c), or the type of GIS data they would like to have presented on maps with sediment quality data. Some suggestions from the attendees of the St. Paul and Duluth meetings included:

- Matching sediment chemistry data with ecological functions;
- Linking future land uses in the harbor with current contaminant data;
- Mapping physical parameters like particle size (e.g., to determine sites with suitable capping material for remediation options);
- Providing guidance on how to handle nondetect data;
- Mapping the distribution of mercury throughout the AOC, particularly for the benefit of the total maximum daily load (TMDL) workgroup for the St. Louis River; and
- Providing a holistic report on sediment quality conditions for the entire AOC, not just pertaining to the Minnesota or Wisconsin side of the AOC.

Due to the time constraints of the Phase III database project, it was not possible to address each of these suggestions in the preparation of the Phase III sediment quality report (Crane 2005c). However, these suggestions were incorporated into much of this report for the Phase IV database project.

Since the Phase IV database includes all of the sediment quality data previously included in the Phase I, II, and III databases, the entire data set was used in the analyses presented in the following sections. This data set provides good spatial coverage of the Minnesota and Wisconsin sides of the St. Louis River AOC (Figure 1). In addition, sediment chemistry data were compared to corresponding SQTs adopted by the MPCA for use in the St. Louis River AOC (Crane *et al*. 2000, 2002a). The WDNR has adopted similar consensus-based sediment quality guidelines (SQGs), as well as other SQGs for additional chemicals (WDNR 2003). The Wisconsin SQGs are available in the MS™ Access 2000 and Query Manager-compatible databases for those stakeholders interested in comparing sediment chemistry data to those values.

3.2 SEDIMENT QUALITY DATA ASSESSMENT

3.2.1 General Database Query Results

The Phase IV GIS-based sediment quality database contains sediment quality results from 59 sediment studies, comprising 1,635 stations (Table 1). The greatest amount of sediment quality data in the database is for sediment chemistry (97,155 records), followed by replicate data for benthic invertebrate community metrics (59,642 records), and mean values of benthic invertebrate community metrics (19,396 records; Table 1). Summary data are also available for tissue chemistry, sample tissue, sediment toxicity, mean PEC-Qs, and sediment sample information (Table 1).

The number of samples of common sediment quality indicators available in the database is provided in Table 2 for chemistry samples, sediment toxicity samples, and benthic invertebrate community samples. The R-EMAP study (Study ID's 04 and 06) provides the most comprehensive study of the entire St. Louis River AOC for which matching sediment chemistry and sediment toxicity samples were collected, as well as benthic invertebrate community samples. A number of studies have only emphasized sediment chemistry measurements, whereas some specialty studies (particularly of Newton Creek) have only emphasized benthic invertebrate community studies.

The most assessed area to date has been the SLRIDT Superfund site in terms of the quantity of stations sampled from this large contaminated area (Table 3). The sediment quality data from several creeks and lakes on the Fond du Lac Reservation were included in the database because they are within the St. Louis River watershed and may provide data for consideration as reference sites (Table 3).

3.2.2 Sediment Chemistry Results

The results of the sediment chemistry analyses are provided in the following tables:

- Table 4: Number of Chemical Classes Used in the Calculation of mean PEC-Qs for Sediment Samples Included in the Phase IV Sediment Quality Database;
- Table 5: Statistical Summary of Sediment Chemistry Values in Surficial Sediments (0 – 30 cm, inclusive) of the St. Louis River AOC;
- Table 6: Statistical Summary of Sediment Chemistry Values in Subsurface Sediments (>30 cm, inclusive) of the St. Louis River AOC;
- Table 7: Determination of Statistical Significance Between Median Chemical Values in Surface and Subsurface Sediments from the St. Louis River AOC;
- Table 8: Summary of Phenanthrene/Anthracene (P/A) and Fluoranthene/Pyrene (F/P) Ratios for Selected Depth Intervals in the St. Louis River AOC;
- Table 9: Distribution of Mean PEC-Qs in Surficial Sediments (i.e., upper 30 cm) of Selected Locations in the St. Louis River AOC; and
- Table 10: Frequency of Low, Moderate, and High Risk Samples in Surface Sediments (i.e., upper 30 cm) from the St. Louis River AOC.

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Due to the non-normal distribution and skewness of the sediment chemistry data, comparisons should be made with the median (i.e., "middle) values instead of the arithmetic average values. The geometric mean is also appropriate to use when there is a wide range of concentrations in the data set (e.g., for PAH compounds). However, geometric means could not always be calculated with the available software. When geometric means could be calculated, the values were usually similar to the median values.

Some of the major sediment chemistry results include:

- **Number of Chemical Classes Used to Calculate Mean PEC-Qs**
    - In the 0 – 30 cm, inclusive depth interval, 47% of the mean PEC-Q values were based on one chemical class, 45% on two chemical classes, and 8% on three chemical classes (Table 4). Total polychlorinated biphenyls (PCBs) were less likely to be measured at these sites than total $PAHs_{13}$ (based on the addition of 13 low molecular weight and high molecular weight PAHs) or reliable metals (i.e., arsenic, cadmium, chromium, copper, lead, nickel, and/or zinc). However, total PCBs are not always a contaminant of concern at sites within the St. Louis River AOC, and total $PAHs_{13}$ are not generally a contaminant of concern upstream from the USS Superfund site (e.g., within the reservoir sediments).
    - In the >30 cm, inclusive depth interval, 71% of the mean PEC-Q values were based on one chemical class, 25% on two chemical classes, and 4% on three chemical classes (Table 4).
    - In the other depths category, 36% of the mean PEC-Q values were based on one chemical class, 45% on two chemical classes, and 19% on three chemical classes (Table 4).

- **Descriptive Statistics**
    - Lead and zinc were the only conventional metals in this analysis for which the median value exceeded the corresponding Level I SQT value in the surface and subsurface sediments (Tables 5 and 6). At the 90^{th} percentile, all conventional metals and SEM cadmium, lead, and zinc exceeded the corresponding Level I SQT values in the surface sediments, with conventional lead exceeding the Level II SQT (Table 5). For subsurface sediments, all conventional metals and SEM cadmium, copper, lead, and zinc exceeded the corresponding Level I SQT values at the 90^{th} percentile, with conventional lead and zinc exceeding the corresponding Level II SQT values.
    - At the 10^{th} percentile, 2-methylnaphthalene and acenaphthylene exceeded the corresponding Level I SQT values in the surface sediments (Table 5), whereas acenaphthene and acenaphthylene exceeded the corresponding Level I SQT values in the subsurface sediments (Table 6). All of the median concentrations of PAHs in Tables 5 and 6 exceeded the corresponding Level I SQTs in the surface and subsurface sediments (Tables 5 and 6). In addition, median concentrations of 2-methylnaphthalene exceeded the Level II SQT in both the surface and subsurface sediments (Tables 5 and 6). The median concentrations of acenaphthene, naphthalene, and total $PAHs_{13}$ also exceeded the corresponding Level II SQT values in the subsurface sediments (Table 6). At the 90^{th} percentile, all PAHs exceeded the corresponding Level II SQT values in the surface and subsurface sediments (Tables 5 and 6).
    - PCB results were available in the database for four different calculation methods. Three of these calculation methods resulted in exceedances of the median PCB concentrations compared to the Level I SQT value for total PCBs for both the surface and subsurface sediments (Tables 5 and 6). In addition, the 10^{th} percentile results in the surface sediments for total PCBs based on the addition of Aroclors that excluded high nondetect values exceeded the corresponding Level I SQT

value (Table 5). At the 90th percentile, total PCBs by all four calculation methods exceeded the corresponding Level I SQT value in the surface and subsurface sediments (Tables 5 and 6).

- Median concentrations of four pesticides exceeded the corresponding Level I SQT values in the surface sediments (Table 5), whereas five pesticides exceeded the corresponding Level I SQT values in the subsurface sediments (Table 6). The pesticide data were based on a small data set (i.e., less than 10 samples for most pesticides) so more data are needed to examine distribution trends. Some of the pesticide data are available in the "Other" category of depth intervals.
- The median of the mean PEC-Q values exceeded the Level I SQT value in both the surface and subsurface sediments (Tables 5 and 6). At the 90th percentile, the median of the mean PEC-Q values exceeded the Level II SQT value in both the surface and subsurface sediments (Tables 5 and 6).
- The median of the TOC values in surface and subsurface sediments were nearly the same (3.3% and 3.4%, respectively; Tables 5 and 6).
- The median concentrations in the surface sediments were statistically less ($p<0.05$) than in the subsurface sediments for the following chemicals: lead, acenaphthene, acenaphthylene, anthracene, fluorine, naphthalene, phenanthrene, total $PAHs_{13}$, low molecular weight (LMW) PAHs, and lindane (Table 7).
- The median concentrations in the surface sediments were statistically greater ($p<0.05$) than in the subsurface sediments for the following chemicals: chromium, SEM cadmium, total PCBs - reported (can be recalculated), total PCBs – reported only, total Aroclor PCBs (excluded high ND values), and total congener PCBs (excluded high ND values) (Table 7).

- **PAH Source Ratios**

  - The median P/A source ratios ranged from 2.15 to 2.69 in the three depth intervals for the St. Louis River data set including pre-remediation data for Hog Island Inlet and Newton Creek, whereas the median F/P ratios ranged from 1.12 to 1.17 (Table 8). When the pre-remediation P/A and F/P data from the Hog Island Inlet/Newton Creek site were excluded from the data set, the median P/A source ratios ranged from 2.11 to 2.48 and the median F/P source ratios ranged from 1.14 to 1.23 (Table 8).
  - The pre-remediation median P/A source ratio in the 0 – 30 cm depth interval was statistically greater ($p = 0.024$) than in the >30 cm depth interval, whereas there was no statistical difference between P/A source ratios ($p = 0.353$) at these depth intervals in the post-remediation data set (Table 8).
  - There was no statistical difference ($p = 0.678$) between the median F/P source ratios for these two depth intervals in pre-remediation sediments, whereas the post-remediation data set had a significantly greater median F/P source ratio ($p = 0.003$) in the 0 – 30 cm depth interval than in the >30 cm depth interval (Table 8).

- **Distribution of Mean PEC-Qs in Surficial Sediments**
  - Eleven areas had sufficient data (i.e., ≥20 sediment samples) on the chemical characteristics of surficial sediments to support subsequent data analyses,

including the pre-remediation sediment chemistry data for Hog Island Inlet/Newton Creek, Howard's Bay, lower St. Louis River, Minnesota Slip, Slip C, SLRIDT Superfund site, Superior Bay, Thomson Reservoir, USS Superfund site, the embayment encompassing WLSSD, Miller Creek and Coffee Creek, and the entire St. Louis River AOC. Insufficient data were available to support the assessment of sediment quality conditions in several other areas of interest that are known or suspected to contain elevated levels of contaminants of potential concern, including the City of Superior wastewater treatment plant, area near Grassy Point, Fond du Lac Reservoir, and Forbay Reservoir.

- The summary statistics that were used to describe the distribution of mean PEC-Qs for the selected areas of interest within the St. Louis River AOC are presented in Table 9. These results show that, on average, the highest levels of sediment contamination occurred at the SLRIDT Superfund site (average and maximum mean PEC-Qs of 20.3 and 821, respectively; n = 214). Elevated levels of contaminants of potential concern were also observed at the USS Superfund site and Minnesota Slip [i.e., average mean PEC-Qs of 3.18 (n = 36) and 1.23 (n = 62), respectively]. Relatively lower average mean PEC-Qs were observed at the other areas of interest. Overall, the mean PEC-Qs for surficial sediments from the St. Louis River AOC averaged 5.15 and ranged from 0.000385 to 821 (n = 910). However, the median of the mean PEC-Q values for the entire AOC was 0.246 (Table 9).
- As indicated by the high standard deviation in the average mean PEC-Qs for the SLRIDT Superfund site (SD = 90.1) and for the entire St. Louis River AOC (SD = 44.5), contaminant concentrations vary substantially, both within and among locations. Accordingly, these high standard deviations may limit the value of the arithmetic mean as an accurate estimate of central tendency, particularly when multiple areas are being compared. In addition, average values of mean PEC-Qs may not necessarily provide an accurate estimate of the distribution of data when sediment chemistry data from stratified random and gradient-type designs are included in the data sets for these areas of interest. Therefore, comparisons between locations within the St. Louis River AOC will be based on the median of the mean PEC-Qs for each area.
- At the 10^{th} percentile level, the mean PEC-Qs exceeded the Level I SQT of 0.1 at Minnesota Slip, the SLRIDT Superfund site, and at Howard's Bay (Table 9).
- Based on median values of the mean PEC-Qs, the SLRIDT Superfund site and Minnesota Slip exceeded the Level II SQT of 0.6 (Table 9). All other sites exceeded the Level I SQT value.
- At the 90^{th} percentile level, the SLRIDT Superfund site, USS Superfund site, entire St. Louis River data set, Minnesota Slip, Slip C, WLSSD/Miller Creek/Coffee Creek embayment, and Howard's Bay exceeded the Level II SQT value (Table 9). The other four locations exceeded the Level I SQT value.

- **Frequency of Low, Moderate, and High Risk Samples in Surface Sediments**
  - Minnesota Slip and the SLRIDT Superfund site had the greatest proportion of surface sediments likely to present a high risk to benthic invertebrates (Table 10).

- Howard's Bay had the highest percentage of moderately contaminated surface sediments (Table 10). The pre-remediation data for Hog Island Inlet and Newton Creek also indicated this area had a high percentage of moderately contaminated sediments. Diesel range organics and alkylated PAHs were other contaminants of concern at this site that are not considered in the calculation of mean PEC-Qs.
- Sediments from Superior Bay presented the lowest risk to benthic invertebrates (Table 10).
- For the entire St. Louis River AOC data set, the majority (50.8%) of surficial sediment samples were associated with moderate risk to benthic invertebrates, whereas 21% were of low risk to benthic invertebrates and 28.2% of high risk to benthic invertebrates.

3.2.3 Sediment Toxicity Test Results

The Phase IV sediment quality database contains data on 1,464 toxicity test endpoints. The predictive ability of the mean PEC-Qs was evaluated using the information from the matching sediment chemistry and sediment toxicity query. For the 10-day *H. azteca*, 10-day *C. dilutus*, and all non-UV toxicity tests combined (excluding Microtox® and Mutatox®), the greatest number of matching sediment chemistry and toxicity samples were available for the two lowest mean PEC-Q ranges (i.e., ≤0.10 and >0.10 to ≤0.50). For the next three higher mean PEC-Q ranges, the minimum data requirements (i.e., 20 samples per category) were not met for the 10-day *H. azteca* and *C. dilutus* toxicity tests. As such, comparisons of the predictive ability of these two toxicity tests in the St. Louis River AOC for the three highest mean PEC-Q ranges should be made with caution. For the group of all non-UV toxicity tests combined, more than 20 samples were available for the middle two ranges of mean PEC-Qs (i.e., >0.50 to ≤1.0 and >1.0 to ≤5.0), but only 9 samples were available for mean PEC-Qs >5.0. For the 28-day *H. azteca* toxicity tests, all of the mean PEC-Q ranges had less than 14 samples. For the combination of all UV toxicity tests, only the mean PEC-Q range of >0.10 to ≤0.50 exceeded 20 stations. Nevertheless, overall trends in the incidence of sediment toxicity can be distinguished in Table 11 with the available data set.

The results of the predictive ability evaluation indicate that the incidence of acute toxicity to amphipods and midges tends to be low (i.e., 4.3% and 2.1%, respectively) when the concentrations of sediment-associated contaminants are low (i.e., as indicated by mean PEC-Qs of ≤0.1; Table 11). Importantly, the incidence of sediment toxicity in St. Louis River AOC sediments increased with increasing contaminant concentrations in the 10-day amphipod and midge tests, as well as with all non-UV tests combined (Table 11). For the 28-day *H. azteca* and all UV tests combined data sets, additional data are needed to evaluate trends in the incidence of sediment toxicity.

On an overall basis, the 10-day amphipod and midge tests had a similar incidence of sediment toxicity (i.e., 16.6% and 18.0%, respectively), although these tests often were not toxic to the same samples. The combination of all non-UV toxicity tests had a higher incidence of toxicity (30.8%). The overall toxicity observed for all UV tests combined (47.4%) and for 28-day *H. azteca* toxicity tests (58.6%) was even higher.

3.3 GIS MAPS

The following GIS maps were prepared for this project report:

- Figure 1: Location of sediment stations in the St. Louis River AOC in relation to future land uses along the Duluth, MN and Superior, WI waterfronts;
- Figure 2: Distribution of mean PEC-Q values in the surface sediments (i.e., upper 30 cm of the St. Louis River AOC);
- Figure 3: Distribution of mean PEC-Q values in the surface sediments (i.e., upper 30 cm) of the SLRIDT Superfund site;
- Figure 4: Distribution of mercury in surface sediments (i.e., upper 30 cm) of the St. Louis River AOC;
- Figure 5: Distribution of TOC (%) in surface sediments (i.e., upper 30 cm) of the St. Louis River AOC in association with general land uses;
- Figure 6: Distribution of mean PEC-Q ranges used in the incidence of sediment toxicity analysis of matching sediment chemistry and toxicity data from the St. Louis River AOC;
- Figure 7: Map of sediment toxicity results (i.e., toxic or not toxic) in the St. Louis River AOC for sediment stations with matching sediment chemistry results;
- Figure 8: Results of sediment toxicity tests in the St. Louis River AOC using the midge, *C. dilutus*, with an endpoint of survival;
- Figure 9: Results of sediment toxicity tests in the St. Louis River AOC using the amphipod, *H. azteca*, with an endpoint of survival;
- Figure 10: Mean percentage of noninsects in the St. Louis River AOC;
- Figure 11: Mean percentage of oligochaetes in the St. Louis River AOC;
- Figure 12: Mean percentage of chironomids in the St. Louis River AOC;
- Figure 13: Mean percentage of mayflies in the St. Louis River AOC;
- Figure 14: Location of tissue residue stations in the St. Louis River AOC;
- Figure 15: Percentage of fine (silt + clay; <63 µm) particle size classes in surface sediments (i.e., upper 30 cm) of the St. Louis River AOC;
- Figure 16: Percentage of medium sand (250 – 500 µm) in surface sediments (i.e., upper 30 cm) of the St. Louis River AOC; and
- Figure 17: Percentage of coarse sand (500 – 1000 µm) in surface sediments (i.e., upper 30 cm) of the St. Louis River AOC.

CHAPTER 4

DISCUSSION

The sediment quality data in the Phase IV GIS-based sediment quality database includes data from 59 studies that had varying data quality objectives. Many of these studies took place at either known or suspected contaminated areas. Only one large randomly designed study, the R-EMAP project (Breneman *et al*. 2000; Crane *et al*. 2005), has been conducted within the entire St. Louis River AOC. As such, the sediment quality data are skewed toward contaminated areas within the AOC. In particular, the SLRIDT Superfund site data set comprises the largest sediment quality data set for a hot spot area in the database. The Hog Island Inlet/Newton Creek site is the only contaminated site for which sediment remediation has been completed (as of fall 2005). As contaminated areas are remediated within the lower St. Louis River AOC and post-remediation data are collected, it would be useful to evaluate the pre- and post-remediation data to obtain a measure of improvement in sediment quality conditions within this AOC.

PAHs are widespread chemicals of potential concern in the lower St. Louis River AOC, particularly starting at the USS Superfund site and progressing downstream to the rest of the estuary. The mean P/A and F/P ratios are indicative of pyrogenic (combustion) sources of PAHs to the AOC (i.e., P/A ratio <10 and F/P ratio >1.0; Budzinski *et al*. 1997). Similar results were found in the random sampling done in the lower estuary during 1995 for the R-EMAP project (Crane *et al*. 2005).

Data evaluations conducted as part of the Phase III sediment quality database showed a lack of correlations between total $PAHs_{13}$ and TOC, lead, mercury, and zinc; these observations may be due to multiple sources of PAHs and metals to the lower St. Louis River watershed (Crane 2005c). In contrast, r^2 values exceeding 0.76 were observed in Slip C, Duluth Harbor, for total PAHs and TOC (at <10% TOC), lead, and mercury (Crane 1999). Slip C is a relatively small contaminated site that appears to have limited sources of contaminants. The findings of Crane (2005c), though, were supportive of similar regression analyses done for the R-EMAP project (Crane *et al*. 2005), except that lead, mercury, and zinc accounted for additional variance in total $PAHs_{12}$ from the R-EMAP study (Crane *et al*. 2005). The R-EMAP study also displayed stronger correlations between the metals (mercury, lead, zinc; Crane *et al*. 2005) than in the analysis of the entire surface sediment chemistry data set from the Phase III database (Crane 2005c). The R-EMAP study only included simultaneously extractable metals for cadmium, copper, lead, nickel, and zinc that were assumed to be equivalent to conventional metal concentrations when used with other metals data in the database; this assumption was based on studies done elsewhere (Crane *et al*. 2000). On an AOC-wide basis, mixing the metals data for the R-EMAP study with conventional metals data from other sites may introduce more uncertainty into the regression relationships.

The distribution of sediment contaminants can be very heterogeneous within a short distance in the St. Louis River AOC, such as between field replicates in Minnesota Slip (Crane *et al*. 2002b). In addition, sediment cores from the USS Superfund site that were split and analyzed by different labs have recently yielded widely different sediment chemistry results that were not attributable to any quality assurance/quality control issues; these split samples were added to the Phase III database as separate studies (Study ID's 54 and 55; Crane and Myre 2005b). The heterogeneity of sediments at some of the contaminated sites can result in increased difficulty with analytical laboratories being able to adequately extract the chemicals of interest from the sediment matrix. Database users are encouraged to view the Qualify look-up table in the Phase IV MS™ Access 2000 database to become familiar with the descriptions of qualifiers for sediment chemistry parameters.

In the Phase IV database, the 0 - 5 cm depth interval for sediment chemistry was comprised of the 1995/1996 R-EMAP data set, as well as a smaller number of samples collected elsewhere. The 0 – 15 cm depth intervals were generally collected from hot spot sites. Since most of the data that comprised the 0 - 5 cm depth interval is about 10 years old, cleaner sediments may have been deposited over these sites since that time (or been eroded, too). The MPCA does not have much data on sediment deposition rates in the Duluth-Superior Harbor, partly because radioisotope dating of sediment cores has not always been successful. Some sections of the harbor were shown to have a sediment deposition rate of 0.5 cm/year (Schubauer-Berigan and Crane 1997), which would result in the deposition of 5 cm of new sediments within a 10-year period. If the newly deposited sediments are cleaner (due to source control actions in the St. Louis River watershed), then this may improve the habitat for benthic organisms in the AOC.

The R-EMAP project demonstrated that physical habitat characteristics had the greatest influence on the benthic invertebrate community in the lower estuary (Breneman *et al*. 2000; Crane *et al*. 2005). The harbor area, in particular, is dominated by oligochaetes (aquatic worms) and chironomids (midges) that are more pollutant-tolerant organisms common to slower moving, less oxygenated waters (Figures 11 and 12, respectively). The Allouez Bay area is a pulse stable wetland that contains a better selection of invertebrates, such as mayflies (Figure 13).

The St. Louis River AOC includes a gradient of sediment chemistry concentrations in the surface sediments, including fairly clean sites that present a low risk to benthic invertebrates, moderately contaminated sites that present some risk of impairment to benthic organisms, and highly contaminated sites that are likely to result in impairments to benthic organisms (Table 10). The Phase III Addendum to the Phase II Help Section for Database Users (Crane and Myre 2005a) provided a section on interpreting mean PEC-Q data contained within the database, as well as on recommended applications for using numerical SQTs in the St. Louis River AOC and on the limitations of the use of the Level I and Level II SQTs and mean PEC-Qs in this AOC (as referenced in Crane *et al*. 2002a and Crane and MacDonald 2003). As shown in Tables 9 and 10, the mean PEC-Qs provide a screening-level indication of the risks benthic organisms may be exposed to from a mixture of contaminants in the surface sediments of the St. Louis River AOC.

In interpreting the distribution of mean PEC-Qs in surficial sediments (Table 9), one must consider whether other contaminants of concern contribute to risk and whether the extent and magnitude of contamination has been adequately characterized at a site. Diesel range organics and alkylated PAHs were other contaminants of concern in the pre-remediation sediments of the Hog Island Inlet/Newton Creek. Sediment remediation of this area was completed November 2005, and post-remediation sediment chemistry data were not available in time for inclusion in either the Phase IV sediment quality database or for the data analysis section of this report. At the USS Superfund site, the median PEC-Q value of 0.168 appears to underestimate the extent of contamination at this site, which has resulted in complete mortality of sediment toxicity test organisms in some tests. Some of the surficial sediment data for the USS Superfund site were from samples collected to delineate the outer edges of the site. Thus, these sediments are less contaminated than from areas sampled closer to the sources of contamination at this site.

For the Minnesota side of the St. Louis River AOC, the areas with mean PEC-Qs exceeding 0.6 (Figures 2 and 3) include the:

- SLRIDT Superfund site;
- USS Superfund site;
- Minnesota Slip;
- Slip C;
- Embayment encompassing the old Duluth sewage treatment plant near WLSSD and the confluence with Coffee and Miller Creeks;
- Dakota Pier; and
- One site near Grassy Point.

For the Wisconsin side of the St. Louis River AOC, the areas with mean PEC-Qs exceeding 0.6 (Figure 2) include the:

- Koppers Industries Inc. site;
- Howard's Bay; and
- pre-remediation data for Hog Island Inlet/Newton Creek.

While the statistical analyses of mean PEC-Qs provide a useful screening assessment of sediment quality conditions in the surficial sediments of the St. Louis River AOC, these analyses must be considered in the context of the following uncertainties:

- The Phase IV sediment quality database is not inclusive of all the surficial sediment chemistry data available for some areas of interest, but was nevertheless assumed to be representative of the available data. Therefore, these analyses should be updated as the database is updated and expanded.
- The mean PEC-Qs may not include all contaminants of potential concern for a particular area. For example, diesel range organics and alkylated PAHs contributed to ecological risk at the Hog Island Inlet/ Newton Creek site under pre-remediation conditions (SEH Inc. 2003a,b), and mercury is an important contaminant throughout the AOC.
- Use of the mean PEC-Qs should take into consideration variations in physical, chemical, and biological factors in the sediment environment that may complicate and introduce uncertainty into their use. For example, certain chemicals can be present in relatively unavailable forms (such as in slag, paint chips, and tar). Use of the mean PEC-Qs may not be applicable in depositional wetlands (due to high organic matter and sulfides), oil and gas production environments, in highly modified depositional systems, and in nondepositional and erosional systems (Wenning and Ingersoll 2002).
- Sediments are often heterogeneous, resulting in patchy distributions of contaminants, particle size, sulfide levels, and organic carbon type at varying levels of scale.

- Use of the mean PEC-Qs is enhanced when considered as part of a weight-of-evidence approach that includes other sediment quality indicators, such as sediment chemistry and geochemical characteristics, sediment toxicity, and benthic invertebrate community structure (Crane and MacDonald 2003).
- Due to uncertainties associated with bioavailability, there is not 100% certainty that samples with mean PEC-Qs exceeding 0.6 will actually be toxic to sediment-dwelling organisms. Rather, the probability of observing chronic toxicity to amphipods (*H. azteca*) in 28-day exposures is greater than 50% when mean PEC-Qs exceed a mean PEC-Q of 0.63 (USEPA 2000; Ingersoll *et al.* 2001). The results of this study and previous analyses (Crane *et al.* 2000, 2002a, 2004) indicate that the incidence of toxicity to amphipods and midges (conducted as separate 10-day sediment toxicity tests) was found to increase as the mean PEC-Q ranges increased.

None of the aforementioned factors, though, preclude the general application of mean PEC-Qs to the analyses conducted in this assessment.

Assessments of sediment quality in the St. Louis River AOC are best done using a weight-of-evidence approach since sediment chemistry alone does not address bioavailability and bioaccumulation issues. Thus, sediment toxicity data and tissue residue data are useful to collect on surface sediments with matching sediment chemistry data, especially for suspected contaminated areas.

Survival was the principal metric for the 10-d amphipod and midge toxicity tests that comprised most of the toxicity test data in the database (Table 11). The chronic 28- to 42-d *H. azteca* toxicity test is more sensitive than either the 10-d amphipod or midge tests (Ingersoll *et al*. 2001), and its use would reduce the potential for false negatives at low mean PEC-Qs. Because longer-term toxicity tests provide the most effective mean of discriminating among moderately contaminated sediment samples and because *in situ* benthic invertebrates are exposed to contaminated sediments for an extended period, it would be prudent in future investigations to evaluate sediment toxicity using the 28- to 42-d *H. azteca* test (endpoints: survival and growth) in sediments with mean PEC-Qs <5.0 (Crane *et al*. 2000, 2005). However, it would be more cost-effective to utilize acute toxicity tests to characterize the toxicity of highly contaminated sediments (i.e., mean PEC-Qs ≥5.0; Crane *et al*. 2000, 2005).

The treatment of nondetected data was discussed in Section 5.1 of the Phase II Technical Documentation (Smorong *et al*. 2004b). The GIS-based sediment quality database was designed with four data treatment options for censoring nondetected data:

- Substitute nondetected values with one-half the detection limit;
- Delete nondetected values;
- Substitute nondetected values with the detection limit; and
- Exclude nondetected values with high detection limits.

Nondetects are also labeled as left-censored data since their values lie somewhere to the left of the detection limit threshold. Users should be aware that bias may be introduced into the results when the above data treatment options are used. For example, the presence of several nondetect values in the PCB and some pesticide data should be examined further to assess whether the higher concentrations in the surface sediments compared to subsurface sediments are due to varying detection limits or real effects. Users interested in better approaches for analyzing censored data should consider using maximum likelihood estimation (MLE), imputation, or the Kaplan-Meier method (Helsel 2005a). MLE solves a "likelihood equation" to find the values for mean and standard deviation that are most likely to have produced both nondetect and detected data (Helsel 2005a). Imputation methods fill in values for censored or missing observations without assigning them all the same value (Helsel 2005a). Kaplan-Meier is a nonparametric method designed to incorporate data with multiple censoring levels and does not require specification of an assumed distribution (Helsel 2005a). Additional information about these methods is available in Helsel (2005a,b).

Agency staff and stakeholders are encouraged to use the Phase IV GIS-based sediment quality database to obtain data of interest to them and to utilize the companion ArcMap 9.1 map documents of GIS-watershed data for viewing the data. The major findings of this report are available in a sediment quality pamphlet (Crane 2006b) that can be obtained from the MPCA's web site at: http://www.pca.state.mn.us/publications/tdr-fg06-03.pdf. Questions regarding the Phase IV sediment quality database should be directed to:

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