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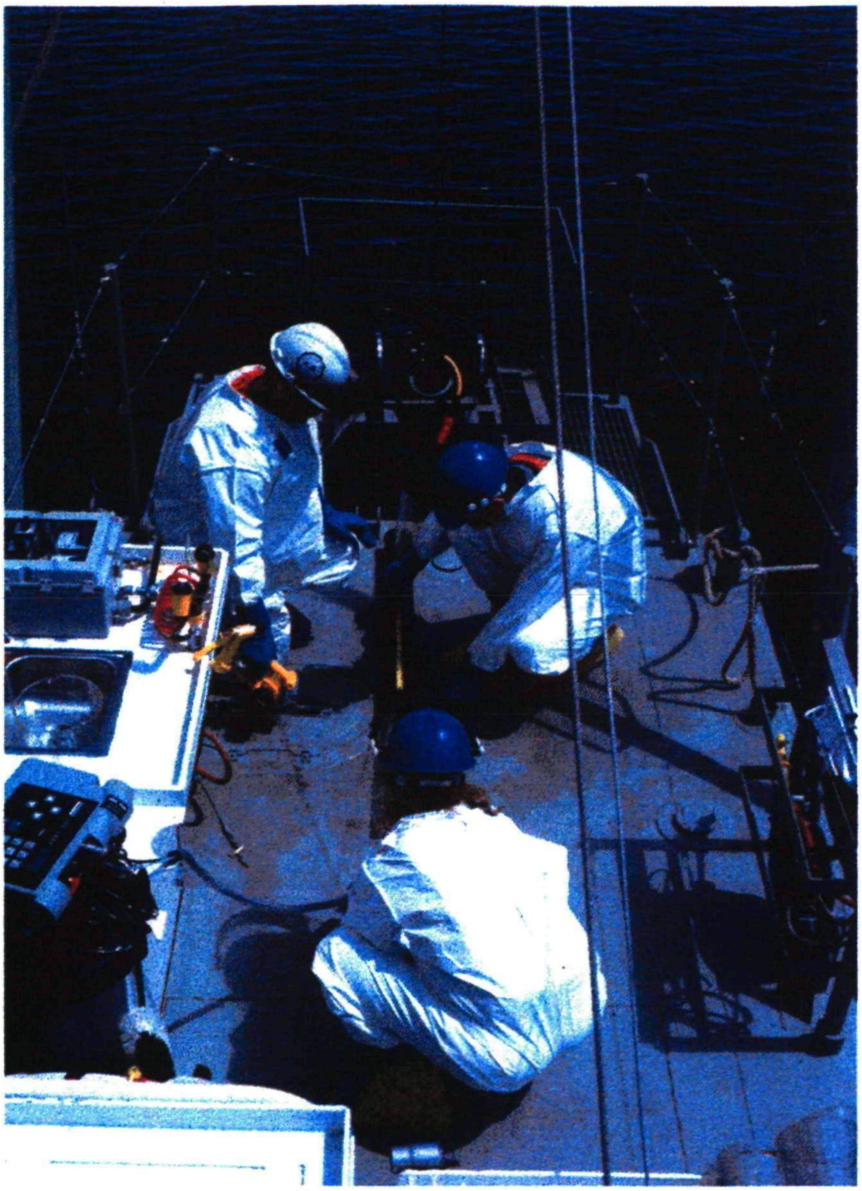
Development of a Framework for Evaluating Numerical Sediment Quality Targets and Sediment Contamination in the St. Louis River Area of Concern



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Development of a Framework for Evaluating Numerical Sediment Quality Targets and Sediment Contamination in the St. Louis River Area of Concern

Final Report

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LIST OF ACRONYMS AND ABBREVIATIONS

AET	Apparent Effects Threshold
Alk	Alkalinity
AOC	Area of Concern
ARAR	Applicable or Relevant and Appropriate Requirement
ARCS	Assessment and Remediation of Contaminated Sediments
As	Arsenic
ASTM	American Society for Testing and Materials
AVS	Acid Volatile Sulfide
BEDS	Biological Effects Database for Sediments
BKGD	Background
BSAF	Biota-to-Sediment Accumulation Factor
BTEX	Benzene, Toluene, Ethylbenzene, and Xylene
CAC	Citizens Action Committee
CCME	Canadian Council of Ministers of the Environment
CD	Compact Disk
CDF	Confined Disposal Facility
Co	Company
COCs	Chemicals of Concern (also referred to as contaminants of concern)
COD	Chemical Oxygen Demand
Cs	Cesium
DDD	Metabolite of DDT
DDE	Metabolite of DDT
DDT	Dichloro-diphenyl-trichloroethane
DO	Dissolved Oxygen
DQO	Data Quality Objective
DROs	Diesel Range Organics
DSI	Detailed Site Investigation
DW	Dry Weight
EC	Environment Canada
EC_{50}	Median Effective Concentration
EL	Effects Level
EPA	Environmental Protection Agency
EqP	Equilibrium Partitioning
ER	Effects Range
ERA	Ecological Risk Assessment
ERL	Effects Range-Low
ERM	Effects Range-Median
ESG	Equilibrium Partitioning Sediment Guideline
f_{oc}	Fraction of Organic Carbon in the Sediment
FCV	Final Chronic Value

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

FDA	Food and Drug Administration
FL	Florida
GIS	Geographic Information System
GLI	Great Lakes Initiative
GLNPO	Great Lakes National Program Office
H_2S	Hydrogen Sulfide
HA28	28-day *Hyalella azteca* Toxicity Test
Hg	Mercury
HTAC	Harbor Technical Advisory Committee
IJC	International Joint Commission
IT Corp.	International Technology Corporation
K_{oc}	Organic Carbon Partition Coefficient
K_{ow}	Octanol-Water Partition Coefficient
K_p	Sediment-Water Partition Coefficient
kg	Kilogram
km	Kilometers
L	Liter
LC_{50}	Median Lethal Concentration
LEL	Lowest Effect Level
LRM	Logistic Regression Modeling
MDH	Minnesota Department of Health
MDNR	Minnesota Department of Natural Resources
MENVIQ	Ministere de l'Envionnement du Quebec
MESL	MacDonald Environmental Sciences Ltd.
MET	Minimal Effect Threshold
mg	Milligram
MN	Minnesota
MPCA	Minnesota Pollution Control Agency
ND	No Data Available
NEC	No Effect Concentration
NG	Not Given
NH_3	Ammonia
NOAA	National Oceanic and Atmospheric Administration
NOECs	No Effect Concentrations
NPDES	National Pollutant Discharge Elimination System
NRCS	Natural Resources Conservation Service
NSTP	National Status and Trends Program
NYSDEC	New York State Department of Environmental Conservation
OC	Organic Carbon
PAET	Probable Apparent Effects Threshold

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

PAHs	Polycyclic Aromatic Hydrocarbons
Pb	Lead
PCBs	Polychlorinated Biphenyls
PCOCs	Potential Chemicals of Concern
PEC	Probable Effect Concentration
PEC-Q	Probable Effect Concentration Quotient
PEL	Probable Effect Level
PEL-28	Probable Effect Level for *Hyalella azteca*, 28-day Test
PEL-Q	Probable Effect Level Quotient
PRPs	Potentially Responsible Parties
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
RA	Risk Assessment
RAP	Remedial Action Plan
RDA	Redundancy Analysis
R-EMAP	Regional Environmental Monitoring and Assessment Program
SECs	Sediment Effect Concentrations
SEDTOX	Sediment Toxicity Database
SEL	Severe Effect Level
SEM	Simultaneously Extractable Metal
SETAC	Society of Environmental Toxicology and Chemistry
SLC	Screening Level Concentration
SMS	Sediment Management Strategy
SOLEC	State of the Lakes Ecosystem Conference
SQAL	Sediment Quality Advisory Levels
SQG	Sediment Quality Guideline
SQRT	Sediment Quality Remediation Target
SQT	Sediment Quality Target
SSLC	Species Screening Level Concentration
TCDD	2,3,7,8-Tetrachlorodibenzo-p-dioxin
TCDF	2,3,7,8-Tetrachlorodibenzo-p-furans
TEC	Threshold Effect Concentration
TEL	Threshold Effect Level
TEL-28	Threshold Effect Level for *Hyalella azteca*, 28-day Test
TEQ	Toxic Equivalent
TET	Toxic Effect Threshold
TIE	Toxicity Identification Evaluation
TOC	Total Organic Carbon
TMDL	Total Maximum Daily Load
TR	Tissue Residue

LIST OF ACRONYMS AND ABBREVIATIONS (continued)

TRG	Tissue Residue Guideline
TU	Toxic Unit
µg	Microgram
US	United States
USACOE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
UV	Ultraviolet
WDNR	Wisconsin Department of Natural Resources
WEA	Weight-of-Evidence Approach
WI	Wisconsin
WLSSD	Western Lake Superior Sanitary District

GLOSSARY OF TERMS

Acute toxicity - The immediate or short-term response of an organism to a chemical substance. Lethality is the response that is most commonly measured in acute toxicity tests.

Aquatic ecosystem - All the living and nonliving material interacting within an aquatic system (e.g., pond, lake, river, ocean)

Aquatic organisms - All of the species that utilize habitats within aquatic ecosystems (e.g., aquatic plants, invertebrates, fish, and amphibians).

Area of Concern - One of 43 Areas of Concern designated in the Great Lakes basin by the International Joint Commission. Each AOC must go through a multi-stage remedial action plan process.

Autotrophic organisms - The organisms (e.g., algae, bryophytes, and aquatic macrophytes) that are able to synthesize food from simple inorganic substances (e.g., carbon dioxide, nitrogen, and phosphorus) and the sun's energy.

Benthic invertebrate community - The assemblages of various species of sediment dwelling organisms that are found within an aquatic ecosystem.

Bioaccumulation - The net accumulation of a chemical substance by an organism as a result of uptake from all environmental sources.

Bioaccumulative substances - The chemicals that tend to accumulate in the tissues of aquatic organisms.

Bulk sediment - Sediment and associated porewater.

Chemical benchmark - Guidelines for water or sediment quality which define the concentration of contaminants that are associated with high or low probabilities of observing harmful biological effects, depending on the narrative intent of the guideline.

Chronic toxicity - The response of an organism to long-term exposure to a chemical substance. Among others, the responses that are typically measured in chronic toxicity tests include lethality, decreased growth, and impaired reproduction.

Consensus-based PECs - The probable effect concentrations that were developed from published sediment quality guidelines of similar narrative intent.

GLOSSARY OF TERMS (continued)

Consensus-based TECs - The threshold effect concentrations that were developed from published sediment quality guidelines of similar narrative intent.

Contaminants of concern - The chemical substances that occur in sediments at levels that could harm sediment-dwelling organisms, wildlife, or human health (also called chemicals of concern).

Contaminated sediment - Sediment containing chemical substances at concentrations that pose a known or suspected threat to environmental or human health.

Demersal fish species - Fish that are associated with bottom sediments, such as carp or sculpins.

Ecocentric approach - A view that considers the broader implications of human activities in the ecosystem.

Ecosystem - All the living (e.g., plants, animals, and humans) and nonliving (rocks, sediments, soil, water, and air) material interacting within a specified location in time and space.

Ecosystem-based management - An approach that integrates the management of natural landscapes, ecological processes, physical and biological components, and human activities to maintain or enhance the integrity of an ecosystem. This approach places equal emphasis on concerns related to the environment, the economy, and the community (also called the ecosystem approach).

Ecosystem goals - Are broad management goals which describe the long-term vision that has been established for the ecosystem.

Ecosystem metrics - Identify quantifiable attributes of the indicators and defines acceptable ranges, or targets, for these variables.

Ecosystem objectives - Are developed for the various components of the ecosystem to clarify the scope and intent of the ecosystem goals. These objectives should include target schedules for being achieved.

Egocentric approach - A way of viewing the external environment only in terms of human uses.

Endpoint - The response measured in a toxicity test.

Epibenthic organisms - The organisms that live on the surface of bottom sediments.

GLOSSARY OF TERMS (continued)

Exposure - Co-occurrence of, or contact between, a stressor (e.g., chemical substance) and an ecological component (e.g., aquatic organism).

Heterotrophic organisms - The organisms (e.g., bacteria, epibenthic and infaunal invertebrates, fish, amphibians, and reptiles) that utilize, transform, and decompose the materials that are synthesized by autotrophic organisms.

Hot spot site - An area of elevated sediment contamination.

Indicators - Provide a sign of ecosystem health. Indicators should adequately represent the ecosystem goals and objectives that have been established.

Infaunal organisms - The organisms that live in bottom sediments.

Level I SQT - Chemical concentrations which will provide a high level of protection for designated water uses in the St. Louis River Area of Concern.

Level II SQT - Chemical concentration which will provide a moderate level of protection for designated water uses in the St. Louis River Area of Concern.

Population - An aggregate of individuals of a species within a specified location in time and space.

Porewater - The water that occupies the spaces between sediment particles.

Potential chemicals of concern - The concentrations of chemical substances that are elevated above anthropogenic background and for which sources of these chemicals can be identified in the watershed (also called chemicals of potential concern).

Priority Substances - The chemicals that occur in sediments at concentrations sufficient to injure sediment-dwelling organisms, wildlife, or human health.

Sediment - Particulate material that usually lies below water.

Sediment-associated contaminants - Contaminants that can be or are present in sediments, including bulk sediments and/or porewater.

Sediment chemistry data - Information on the concentrations of chemical substances in bulk sediments or porewater.

GLOSSARY OF TERMS (continued)

Sediment-dwelling organisms - The organisms that live in, on, or near bottom sediments, including both epibenthic and infaunal species.

Sediment injury - The presence of conditions that have injured or are sufficient to injure sediment-dwelling organisms, wildlife, or human health.

Sediment quality guideline - Chemical benchmark that is intended to define the concentration of a sediment-associated contaminant that is associated with a high or a low probability of observing harmful biological effects or unacceptable levels of bioaccumulation, depending on its purpose and narrative intent.

Sediment quality target - Site-specific chemical benchmarks for the St. Louis River AOC. See Level I SQT and Level II SQT.

Targets - Provide measurable values for ecosystem metrics.

Toxic substances - The chemicals that have the potential to harm sediment-dwelling organisms, wildlife, or human health.

Wildlife - The reptiles, amphibians, birds, and mammals that are associated with aquatic ecosystems [e.g., piscivorous (fish eating) wildlife].

CHAPTER 1

INTRODUCTION

The St. Louis River Area of Concern (AOC) is an important transboundary waterway between northeastern Minnesota and northwestern Wisconsin (Figure 1). This AOC contains several sites where concentrations of metals, mercury, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and/or dioxins and furans are elevated in the sediments compared to reference areas. In areas where these chemical substances occur at concentrations that pose a known or suspected threat to environmental or human health, the sediments are designated as contaminated. Restrictions on dredging, fish advisories, and habitat impairments to bottom feeding organisms are just a few of the use impairments resulting from contaminated sediments in this Great Lakes AOC. Since the St. Louis River constitutes the second largest tributary to Lake Superior, the potential transport of sediment-derived contaminants to Lake Superior is of additional concern to many stakeholders. For general background information on sediment quality issues, see Appendix A.

The Minnesota Pollution Control Agency (MPCA) has taken the lead on a number of sediment assessment studies in the St. Louis River AOC, particularly since 1992 when more funding opportunities became available for contaminated sediment studies at Great Lakes AOCs. The MPCA utilizes a number of sediment quality assessment tools to characterize the sediments on both a random and site-specific basis. These tools include sediment chemistry measurements, physical measurements (e.g., particle size), sediment toxicity tests (acute and chronic tests), benthic (i.e., bottom-dwelling) community surveys, and bioaccumulation studies (see Appendix B for additional information about these sediment quality tools). The information gained from these studies is evaluated, using a weight-of-evidence approach, for making management decisions about contaminated areas.

Sediment quality guidelines (SQGs) provide another sediment quality assessment tool. The SQGs are chemical benchmarks that are intended to define the concentration of sediment-associated contaminants that are associated with a high or low probability of observing harmful biological effects, or unacceptable levels of bioaccumulation, depending on the purpose and narrative intent of the SQGs. The MPCA does not have SQGs, sediment criteria, or sediment standards promulgated for its use in Minnesota's Water Quality Rule (Minn. Rules Chapter 7050). The Water Quality Rule contains a general, narrative provision that no sewage, industrial waste, or other wastes shall be discharged from either point or nonpoint sources into any waters of the state so as to cause any nuisance conditions, such as aquatic habitat degradation (Minn. Rules Chapter 7050; http://www.revisor.leg.state.mn.us/arule/7050/). Sediment contamination is briefly discussed in the Minnesota Rule for total maximum daily loads (TMDLs) for the Lake Superior basin. This rule specifies that where sufficient data are available to quantify the transport of Great Lakes Initiative (GLI) designated pollutants to sediments, TMDLs must account for and prevent such accumulations that preclude attainment of specified designated uses (Minn. Rules Chapter 7052; http://www.revisor.leg.state.mn.us/arule/7052/). Without having numerical SQGs in place in Minnesota, MPCA staff have made benchmark comparisons of their sediment quality data to SQGs derived from other jurisdictions [e.g., Ontario's Ministry of Environment and Energy SQGs that define three levels of ecotoxic effects to benthic organisms (Persaud *et al.* 1993)].

The Wisconsin Department of Natural Resources (WDNR) has also utilized Ontario's SQGs in addition to the National Oceanic and Atmospheric Administration (NOAA) guidelines (Long and Morgan 1991), for assessing sediment quality at sites in Wisconsin. More recently, WDNR staff have been including the effects-based concentrations from other published guidelines and integrating them into a consensus-based approach in establishing lower and upper effect levels (Tom Janisch, WDNR, personal communication, 2000). WDNR staff start out using the Ontario and NOAA guidelines on the lower tiers of a site assessment in order to obtain a general idea of the potential extent and degree of contamination at a site. From this point, decisions are made about what the next steps in the tiered assessment should be (e.g., additional sampling for characterization, collect samples for toxicity testing, and/or conduct a screening level risk assessment). For some small sites, the WDNR has recently taken the approach of adopting the SQGs for several metals as the sediment quality remediation targets (SQRTs) for the sites. Thus, they have recommended moving immediately into remediation design without the need for further studies. However, the degree and extent of contamination at the site must have already been adequately characterized by the potentially responsible parties (PRPs).

Other government, academic, and tribal researchers, as well as consultants for the PRPs, have conducted localized sediment assessment studies in the St. Louis River AOC during the past ten years. In combination with the MPCA-led sediment studies, a number of high quality data sets of matching sediment chemistry and toxicity test results have been generated. The MPCA was interested in using these data sets to determine if site-specific sediment quality targets (SQTs) could be developed for potential chemicals of concern (PCOCs) and chemicals of concern (COCs) in the St. Louis River AOC. If so, the MPCA was also interested in determining how comparable the site-specific SQTs were with other regionally and nationally derived SQGs. The

MPCA obtained a grant from the United States Environmental Protection Agency's (U.S. EPA) Great Lakes National Program Office (GLNPO) to achieve the following objectives:

- Assemble a database of matching freshwater sediment chemistry and toxicity data for the St. Louis River AOC;
- Develop a biologically-based approach for deriving site-specific SQTs for PCOCs and COCs in the St. Louis River AOC; and,
- Evaluate the comparability of the site-specific SQTs with other published SQGs that represented regional and national geographic areas.

Through a competitive process, the MPCA selected MacDonald Environmental Sciences Ltd. (MESL) to assist the agency with this effort. In turn, MESL used EVS Environment Consultants as a subconsultant for a portion of the database work. The scope of work was revised due to MESL's input and collaborative work with the U.S. Geological Survey (USGS) and NOAA on two similar projects:

- NOAA's development of a matching sediment chemistry and toxicity database (SEDTOX) for North America (Jay Field, Principal Investigator); and
- USGS's prediction of sediment toxicity using consensus-based SQGs (Chris Ingersoll, Principal Investigator).

Based on the terms of reference that were established for the project, a work plan was developed. This work plan focused on the development of guidance on ecosystem-based management of contaminated sediments within the St. Louis River AOC that, in-turn, formed the basis for developing SQTs. A flow chart of the study team is given in Figure 2. The work plan consisted of the following elements (responsible team members are given in parentheses):

- Presentation of background information on commercial, industrial, and urban development of the St. Louis River watershed that has contributed to contamination of the aquatic ecosystem (MPCA and MESL);
- Description of historic and ongoing contaminant sources and the results of recent contaminated sediment investigations (MPCA);
- Collection, evaluation, and compilation of the existing matching sediment chemistry and sediment toxicity data for the study area (MPCA, MESL, EVS Environment Consultants, USGS, and NOAA);

- Description of an ecosystem-based approach to the management of the St. Louis River AOC, with an emphasis on contaminated sediment management (MESL and MPCA);
- Description of the designated water uses in the St. Louis River AOC (MPCA and MESL);
- Consultation with the Sediment Contamination Workgroup of the St. Louis River Citizens Action Committee (CAC) about implementation of the ecosystem-based management approach and development of sediment indicators (including specific metrics and target values). The workgroup is composed of volunteers, including private citizens and representatives from industries, nonprofit organizations, the Western Lake Superior Sanitary District (WLSSD), universities, the Fond du Lac Band of Lake Superior Chippewa, consultants, and government agencies (MPCA, MESL, and St. Louis River CAC Sediment Contamination Workgroup);
- Establishment of narrative ecosystem goals and objectives that articulate the long-term vision for managing contaminated sediments in the St. Louis River AOC (St. Louis River CAC Sediment Contamination Workgroup);
- Identification of candidate ecosystem health indicators that could be used to measure attainment of the ecosystem goals and objectives (including physical, chemical, and biological indicators) (MESL, MPCA, and USGS);
- Development of numerical SQTs that can be used as metrics and targets for the chemical indicators that were identified for the St. Louis River AOC (MESL, USGS, NOAA, and MPCA);
- Evaluation of the predictive ability of the numerical SQTs for the St. Louis River AOC data set (MESL, USGS, MPCA, NOAA, and EVS Environment Consultants);
- Recommendation of SQTs based on the results of these predictive ability evaluations (MESL, MPCA, and USGS); and,
- Development of a framework that provides guidance on the use of the numerical SQTs, in conjunction with other companion tools, for making decisions on the management of contaminated sediments (MESL, USGS, MPCA, NOAA, EVS Environment Consultants, Science Advisory Group on Sediment Quality Assessment, and GLNPO).

This report summarizes the results of the aforementioned study and provides a series of recommendations for advancing the assessment, management, and remediation of contaminated sediments in the St. Louis River AOC. Due to the technical nature of this report, a list of abbreviations and acronyms, as well as a glossary of terms are given in this report. The MPCA will also be utilizing other means (e.g., fact sheets, presentations) to communicate the results of this study to the public and other stakeholders.

As a caveat to this study, the authors wish to emphasize that the SQTs developed for the St. Louis River AOC are most applicable to soft sediments. These SQTs should not be applied to assessments of upland soils, land-applied sludge, or other land-based materials (e.g., gravel). These SQTs should be used with care for any sediments containing large amounts of gravel, coarse sand, tar, slag, metal ore (e.g., taconite pellets), paint chips, coal chunks, fly ash, or wood chips. The presence of the aforementioned materials may bind up some chemicals so that they are not bioavailable to aquatic organisms.

CHAPTER 2

BACKGROUND

2.1 DESIGNATION AS A GREAT LAKES AREA OF CONCERN

The St. Louis River estuary has been, and continues to be, of vital economic, environmental, and social importance to the area encompassing Cloquet, MN; Duluth, MN; and Superior, WI. The middle and lower portions of the estuary support a variety of industrial, residential, and recreational activities. In addition, these areas provide essential habitats for aquatic organisms and aquatic-dependent wildlife species. The lower estuary culminates in the Duluth-Superior Harbor, which is one of the most heavily used ports in the Great Lakes basin. Not surprisingly, historic and ongoing land use and water-related activities in the middle and lower portions of the estuary have contributed a variety of nutrients and chemicals to the St. Louis River.

In 1987, concerns over environmental quality conditions prompted the designation of the lower St. Louis River (i.e., from Cloquet, MN to its entrance to Lake Superior) as one of 43 Great Lakes AOCs [International Joint Commission (IJC) 1989]. Remedial Action Plans (RAPs) have been established as the principal mechanism for addressing concerns related to impaired uses in the most severely impacted geographic areas in the Great Lakes basin (i.e., AOCs). Specifically, the terms of the Great Lakes Water Quality Agreement necessitate the preparation of a RAP for each of the 43 AOCs. The RAPs are being prepared using a staged approach which includes:

- Stage I – Identify and assess use impairments, and identify the sources of the stresses from all media in the AOC;
- Stage II – Identify proposed remediation actions and their method of implementation; and,
- Stage III – Document evidence that impaired uses have been restored.

Importantly, the RAP process must embody a comprehensive ecosystem approach and include substantial citizen participation (MPCA and WDNR 1992). The IJC, through a formal protocol agreement between Canada and the United States, was charged with reviewing the RAPs for each AOC and assuring that they met these basic criteria. To facilitate effective citizen participation, the St. Louis River Citizen Advisory Committee became the independent, nonprofit Citizens Action Committee (CAC) in 1997. The CAC has played an essential role in the further development and implementation of the RAP process.

To support environmental quality assessments, the IJC developed a set of criteria for evaluating use impairments at Great Lakes AOCs. As part of the Stage I RAP, the existing information on environmental conditions in the St. Louis River was assembled and compared to the IJC's fourteen impaired use categories. The results of this assessment indicated that at least ten use impairments had occurred in the St. Louis River AOC (Table 1; MPCA and WDNR 1992). Additionally, two possible impairments were indicated; however, additional data were needed to confirm their presence in the AOC (MPCA and WDNR 1992). Many of the confirmed impairments were associated with sediment contamination in the St. Louis River watershed, including effects on sediment-dwelling organisms and other aquatic species, fish consumption advisories, and restrictions to dredging activities. For additional background information on the role of sediments in aquatic ecosystems and general sediment quality issues and concerns, see Appendix A.

2.2 DESCRIPTION OF THE STUDY AREA

The boundaries of the St. Louis River AOC range from Cloquet, MN to the Duluth and Superior entries to Lake Superior (Figure 1). Along much of its length, the St. Louis River flows through a landscape that is dominated by northern boreal forests. Upstream of the AOC boundaries, the river channel is characterized by shallow meanders and sandy gravel bars. Near Cloquet, MN, the character of the river changes abruptly as it starts its steep descent to Lake Superior (Fredrickson 1998). This portion of the watershed is characterized by deeply incised river channels and canyons. Five dams have been constructed on this reach of the river to take advantage of the hydroelectric power generation potential associated with the increased river gradient. These dams have resulted in the creation of six reservoirs downstream of Cloquet, including the Knife Falls, Potlatch, Scanlon, Thomson, Forbay, and Fond du Lac Reservoirs. While these reservoirs are relatively small and have limited water storage capacities, the flow and water level in the river downstream of the reservoirs are significantly affected by water releases from these facilities (MPCA and WDNR 1992).

As the river approaches Lake Superior, the current dissipates and the water body takes on the character of a lake (Fredrickson 1998). The St. Louis River estuary, which covers an area of roughly 12,000 acres, is comprised of numerous large bays, peninsulas, and islands. Some of the important natural features in the estuary include Spirit Lake, Pokegama Bay, Kimball's Bay, St.

Louis Bay, Duluth Harbor, Superior Bay, and Allouez Bay. Together, these areas support a wide variety of important fish, aquatic invertebrate, bird, and other wildlife species. Just prior to entering Lake Superior at the Duluth Ship Canal and the Superior Entry, the river forms a large embayment which is protected by two long sandbars (i.e., Minnesota and Wisconsin Points). These sandbars form the longest natural freshwater sandbars in the world. Two inner spits, Rices Point and Conners Point, divide the port into inner and outer harbors. This unique geomorphology has created a natural harbor which has been dredged and modified since the mid-1800s to accommodate shipping traffic and commerce (Walker and Hall 1976). The harbor waterfront is currently 79 km long, with 27 km of dredged channels (Duluth Seaway Port Authority Web Site: http://www.duluthport.com/seawayfactsmetric.html).

2.3 HISTORICAL DEVELOPMENT IN THE ST. LOUIS RIVER BASIN

The combination of abundant natural resources and easy access to markets through the Great Lakes waterway has supported a number of development activities in the Cloquet, MN and Duluth-Superior areas. For example, access to large tracts of virgin forest gave rise to a thriving forest products industry, including lumber, particle board, and pulp and paper production. Managed woodlands continue to support some of these activities today. Beginning in the 1870s, the Duluth-Superior Harbor became a conduit for the transport and milling of grains in the upper Midwest (Walker and Hall 1976). Bulk grain shipments currently constitute the ports third leading commodity after iron ore and coal (Duluth Seaway Port Authority Web Site: http://www.duluthport.com/seawaytonnagestats.html). Historically, the storage and shipping of taconite, limestone, coal, and iron ore were conducted at various locations within the Duluth-Superior Harbor (Walker and Hall 1976). The storage and transport of iron ore, coal, and limestone along the Duluth-Superior waterfront is still prevalent. Historically, smelting operations along the harbor have resulted in some of the most contaminated sediment sites in the harbor today (i.e., the USX and Interlake/Duluth Tar Superfund sites).

A significant amount of development along the St. Louis River was concentrated in the Duluth-Superior Harbor at Rices Point in Minnesota and Connors Point and Howard's Bay in Wisconsin (Kellner *et al.* 1999). These areas continue to be heavily utilized by waterfront businesses. The Harbor Technical Advisory Committee (HTAC) of the Duluth-Superior Metropolitan Interstate Committee has recommended that all waterfront commerce be moved to the outer harbor so that dredging of the inner harbor shipping channels can be reduced. The only company utilizing access to the waterfront in the upper part of the inner harbor is Hallet Dock Co. at Boat Slip 6.

Hallet's operations may be relocated in the next few years, depending on sediment remediation options selected for the nearby Interlake/Duluth Tar Superfund site.

Other important economic activities that are conducted in the lower portion of the basin include: residential and commercial development, hydroelectric power production, oil and gas storage, manufacturing, petroleum refining, gas and chemical production, and shipping. The tourism industry has increased substantially in the Duluth-Superior area since the mid-1980s. This has resulted in greater commercial development of the waterfront, particularly around Canal Park in Duluth, MN.

2.4 CONTAMINANT SOURCES IN THE ST. LOUIS RIVER BASIN

A number of point and nonpoint sources of nutrients and PCOCs in the St. Louis River AOC were identified in the Stage I RAP (MPCA and WDNR 1992). Prior to 1978, these sources included: National Pollutant Discharge Elimination System (NPDES) permitted dischargers, industrial discharges, and municipal sewage treatment plants. Since 1978, most of the Minnesota industries located in the lower portion of the watershed have sent their wastewater to WLSSD for treatment and disposal. Since 1985, WLSSD staff have worked with local companies to monitor industrial discharges. Major industrial contributors are regulated under the Industrial Pretreatment Program through a series of routine monitoring, self-monitoring and reporting, and on-site inspections (WLSSD 1995). The City of Superior also operates a waste water treatment plant by the Superior Harbor Basin. As a result of these actions to consolidate the treatment of sanitary and industrial effluent, the water quality and fisheries of the St. Louis River system greatly improved during the 1980s (MPCA and WDNR 1992). However, contaminated sediments remain as a major environmental problem in this AOC.

The nonpoint sources of nutrients and PCOCs to the St. Louis River AOC have not been fully documented. However, it is likely that the major nonpoint sources of environmental contaminants to the system include atmospheric deposition, landfills, storm water and urban runoff, unpermitted discharges, spills, and *in situ* contaminated sediments within the AOC. The release of PCOCs into the water column from nonpoint sources contributes to the load of these chemicals deposited in the sediments.

CHAPTER 3

AMBIENT SEDIMENT QUALITY CONDITIONS IN THE ST. LOUIS RIVER AREA OF CONCERN

While the sediment quality data given in the Stage I RAP provided some information on areas of elevated sediment contamination (i.e., hot spot sites), as determined by exceedances of the Ontario SQGs (Persaud *et al.* 1993), most of the historic data were generated to support assessments of the quality of dredged materials and evaluation of appropriate disposal options. As such, little information was available on the sediment quality of the reservoirs around Cloquet, MN and on the many shallow, biologically productive areas throughout the lower portion of the river. For this reason, the MPCA and WDNR agreed to cooperatively implement a sediment strategy under the Stage II RAP (MPCA and WDNR 1995), which includes:

- *Phase I: Assessment* - The assessment phase of the strategy involves reviewing the existing information on sediment quality in the St. Louis River AOC, conducting sampling to identify and determine the relative size of sediment hot spots, determining background concentrations of sediment-associated chemicals in the AOC, and establishing the current status of sediment quality in the AOC to support subsequent trend assessment.

- *Phase II: Hot Spot Management Plan* - The development of a hot spot management plan involves identifying the PRPs for each site and developing community and clean-up goals for each site. Subsequently, the extent of sediment contamination will be mapped, a feasibility study with developed remediation scenarios (with costs) will be conducted, and the necessary funds to complete the remediation will be solicited.

- *Phase III: Implementation* - During the implementation phase, the most suitable remediation scenario will be completed at each site, monitoring will be conducted at each site to evaluate success, and periodic sampling will be conducted to determine if sediment quality conditions are improving.

The sediment data assembled to support Stage I of the RAP, and those data collected thereafter (Table 2), indicate that several areas in the St. Louis River AOC are contaminated by a variety of PCOCs and COCs. These assessments of sediment quality involved comparing the sediment quality data in the St. Louis River AOC with guidelines used by other jurisdictions (Persaud *et al.* 1993; Smith *et al.* 1996). Sediment assessment projects in the reservoirs downstream of Cloquet, MN, and in the lower estuary, have been conducted to determine the spatial extent of contamination and to assess impacts to benthic biota and fish. The data that have been collected to date show a range of biological impacts and presence of COCs in the reservoirs and lower estuary of the St. Louis River AOC. The most important COC found in surficial sediment in the Thomson, Forbay, and Fond du Lac Reservoir sediments is mercury (Glass *et al.* 1990, 1998; Schubauer-Berigan and Crane 1996), while historical contamination by PCBs and 2,3,7,8-TCDD (dioxin) can be found in deeper sediments in these reservoirs (Schubauer-Berigan and Crane 1996). This determination of COCs was based on the usage of these chemicals in the immediate watershed and exceedances of the Ontario SQGs for mercury and PCBs (Persaud *et al.* 1993). The Ontario Ministry of Environment and Energy has not derived any SQGs for 2,3,7,8-TCDD.

Mercury and PAHs are widespread PCOCs in depositional areas of the lower St. Louis River estuary, whereas metals, PCBs, dioxins and furans, organochlorine pesticides, tributyltin, and diesel range organics (DROs) tend to be more localized PCOCs (MPCA and WDNR 1992; Redman and Janisch 1995; Schubauer-Berigan and Crane 1997; Crane *et al.* 1997; Crane 1999a,b,c; Breneman *et al.* 2000). The sediments with the highest concentrations of COCs occur at two Superfund sites (i.e., USX and Interlake/Duluth Tar) in the inner Duluth Harbor (Schubauer-Berigan and Crane 1997; IT Corporation 1997). Other areas with elevated concentrations of PCOCs and COCs in the Duluth-Superior Harbor include Hog Island Inlet/Newton Creek in Superior, WI (Redman and Janisch 1995), as well as several boat slips, areas adjacent to wastewater treatment plants, and other areas with historical sources of COCs (Figure 3) (Schubauer-Berigan and Crane 1997; Crane *et al.* 1997; Crane 1999a). The data from these sediment studies will be included in the next update of the U.S. EPA's National Sediment Inventory; this inventory will provide comparisons of the national incidence and severity of sediment contamination (USEPA 1997a).

Sediments from several hot spot sites in the AOC have been shown to be toxic to sediment-dwelling organisms and/or associated with alterations of benthic invertebrate community structure (Prater and Anderson 1977; Redman and Janisch 1995; Schubauer-Berigan and Crane 1996, 1997; Crane *et al.* 1997; Crane 1999b,c; Breneman *et al.* 2000; USEPA In prep.). A wide-scale assessment of the relationship between surficial sediment characteristics and benthic community structure in the St. Louis River AOC was conducted in 1995 as part of a Regional Environmental Monitoring and Assessment Program (R-EMAP) project (Breneman *et al.* 2000). For the R-EMAP study, taxa richness was variable (i.e., 1 to 25 taxa) among randomly sampled sites within two habitat classes (i.e., <5.5 m and >5.5 m water depth). Oligochaetes were the most abundant taxa, whereas Chironomidae larvae provided a majority of the taxa richness with 43 genera. For the entire data set, the majority of variation in benthic community structure was attributed to water depth and longitudinal location from the headwaters (Breneman *et al.* 2000).

Fish consumption advisories are in effect for selected fish species in the St. Louis River AOC because of elevated concentrations of mercury found in the tissue of the fish. Most of these advisories limit fish consumption to one meal per week for the protection of human health (MDH 1999); more restrictive advisories are in effect for women of child bearing age and young children. In addition, health advisories are also in effect for the consumption of carp and lake sturgeon due to elevated concentrations of PCBs found in the tissue of the fish (MDH 1999).

Action is currently being taken by the MPCA and WDNR to implement source control measures and remediate contaminated sediments at several contaminated hot spot areas in the lower St. Louis River estuary. Two Superfund sites, on the Minnesota side of the border, comprise the most contaminated sediment areas in the lower estuary. At the Interlake/Duluth Tar Superfund site, the Feasibility Study has been re-opened in accordance with the February 22, 2000 agreement between the MPCA, the Interlake Corporation, Honeywell International Inc., and Domtar, Inc. The following remediation options are being considered at this site:

- the no action alternative;
- dredging and in-water containment in Boat Slip 6;
- capping in place; and
- dredging, upland dewatering, and off-site disposal.

During a two-year process, data gaps will be identified and additional information will be collected to evaluate the remediation options at the Interlake/Duluth Tar Superfund site. Certain modifications to the remedial alternatives under consideration may be made. At the USX Superfund site, natural recovery was implemented as the remediation option in the 1989 Record of Decision. However, this option has not worked due to the slow deposition rate of new sediments, and areas of erosion, within the Superfund site. Other remediation options will be considered after more sediment quality data are collected for the USX site.

Additional assessment and remediation work is being done at several smaller contaminated sites. At the Hog Island Inlet/Newton Creek site in Superior, WI, the WDNR has worked with Murphy Oil Co. to dredge contaminated sediments out of both the Newton Creek impoundment and up to

800 feet downstream from the impoundment. The sediments were placed in a designated landfill, which was formerly a lagoon on the Murphy Oil property, as the first phase of the clean-up efforts. In the Duluth Harbor, a sediment remediation scoping project has been completed at one boat slip, Slip C (Crane 1999a), and a similar project is underway at another boat slip, Minnesota Slip, to further delineate the extent of contamination and to develop a short-list of potential remediation options (Crane 1999c).

The results of some of these recent sediment investigations (i.e., Schubauer-Berigan and Crane 1997; Crane *et al.* 1997; Breneman *et al.* 2000) have shown that several areas within the St. Louis River AOC are relatively clean. These determinates were based on comparing sediment chemistry data from sample sites to reference areas, in addition to Ontario's Lowest Effect Level (LEL) SQGs. For example, the areas located in the estuary upstream of the USX Superfund site in Morgan Park, MN and Allouez Bay in Superior, WI, have low concentrations of PCOCs compared to reference areas in the lower estuary and to available SQGs (MPCA and WDNR 1992; Schubauer-Berigan and Crane 1997; Breneman *et al.* 2000). These clean areas provide important fisheries and wildlife habitat. These clean sites also represent reference areas for determining background levels of anthropogenic contaminants in the lower estuary. In addition, the Duluth-Superior Harbor shipping channels contain substantial quantities of relatively clean materials that pass land-based application guidelines. Dredged materials from the shipping channels are washed at the Erie Pier confined disposal facility (CDF) in Duluth, MN and the sand-sized particles are re-used for beach nourishment, habitat development, highway construction, and other beneficial uses [U.S. Army Corps of Engineers (USACOE) 1997].

A number of ancillary studies, relating to contaminated sediments, provide additional information on nonpoint sources of pollutants to the St. Louis River, including:

- Miller Creek (Duluth, MN) storm water study (MPCA 1994);
- Nemadji River (Superior, WI) basin project [Natural Resources Conservation Service (NRCS) 1998];
- St. Louis River pollutant loading study (King 1999a); and
- Development of a TMDL for mercury in the St. Louis River AOC (MPCA, in progress).

The information generated in the aforementioned investigations is being used to identify nonpoint pollutant sources and to develop strategies for mitigating releases of toxic chemicals into the St. Louis River AOC. Reduction or elimination of contaminant discharges is an important element of the overall sediment management strategy (SMS) for the AOC (i.e., to prevent further degradation of sediment quality conditions).

CHAPTER 4

ECOSYSTEM-BASED MANAGEMENT IN THE ST. LOUIS RIVER AREA OF CONCERN

4.1 BACKGROUND

The sediment strategy that was developed under the Stage II RAP (MPCA and WDNR 1995) provided some general guidance on conducting phased sediment studies in the St. Louis River AOC. In order to achieve successful implementation of this strategy, though, the strategy needs to be framed within the context of an ecosystem-based management approach. Ecosystem-based management has been defined as the integrated management of natural landscapes, ecological processes, physical and biological components, and human activities to maintain or enhance the integrity of an ecosystem (Ecosystem Management Task Force 1992). It places equal emphasis on concerns related to the environment, the economy, and the community. This approach recognizes that it is the human interactions with ecosystems, rather than the ecosystems themselves, that must be managed (Environment Canada 1996; Thomas *et al.* 1988). Additional background information on the historical development of the ecosystem approach, benefits of the ecosystem approach, and framework for ecosystem-based management are given in Appendix C.

4.2 ECOSYSTEM-BASED SEDIMENT QUALITY MANAGEMENT IN THE ST. LOUIS RIVER AREA OF CONCERN

Under the Great Lakes Water Quality Agreement, a comprehensive ecosystem approach is to be used to address concerns related to environmental quality conditions at each of the 43 Great Lakes AOCs. The development and implementation of ecosystem-based RAPs has been established as the primary mechanism for restoring the beneficial uses of the aquatic ecosystem in these areas. The MPCA, Minnesota Department of Natural Resources (MDNR), WDNR, Fond du Lac Band, and the St. Louis River CAC are key partners in the remedial action planning process in the St. Louis River AOC. Successful adoption of the framework for ecosystem-based management will require a long-term commitment from all stakeholders and a willingness to explore new decision-making processes. In terms of ecosystem-based sediment quality management, the key elements in the implementation process include (Figure 4):

- conduct a preliminary assessment of existing information on sediment quality conditions and identify key sediment-related management issues;
- develop ecosystem goals and objectives that relate to sediment quality;
- identify and evaluate candidate indicators of sediment quality conditions in the St. Louis River AOC (including physical, chemical, and biological indicators of sediment quality conditions);
    - select a suite of key sediment-related indicators of ecosystem health;
    - establish metrics and targets for each key sediment-related indicator;
- conduct directed research and monitoring;
    - identify data gaps and research needs;
    - incorporate key sediment-related indicators, metrics, and targets into watershed management plans and decision-making processes;
    - design and implement focused environmental research and monitoring programs;
    - re-evaluate key sediment-related indicators to assess effectiveness of decisions (i.e., to evaluate progress towards the ecosystem goals and objectives); and,
    - refine key sediment-related indicators, metrics, and targets, if necessary.

The St. Louis River Stage I and II RAPs have been developed cooperatively by a wide variety of individuals representing government agencies, tribal organizations, academic institutions, community and environmental groups, private citizens, and industrial interests. These various interests are participating in several technical advisory committees of the St. Louis River CAC. In accordance with the terms of reference for the RAP, the participants involved in the management of the St. Louis River AOC have agreed to adopt the ecosystem approach to environmental management. The first step in this process involves identification of key management issues and a preliminary assessment of the knowledge base. This assessment is intended to provide stakeholders with a common basis for identifying management issues and priorities in the system under consideration. In the case of the St. Louis River basin, the existing information on the status of the physical, chemical, and biological components of the ecosystem was compiled during Stage I of the RAP (MPCA and WDNR 1992). This information provided stakeholders with a general understanding of the structure and function of the ecosystem and, therefore, a common basis for establishing broad management goals and ecosystem objectives.

Next, ecosystem goals and objectives need to be developed. Ecosystem goals are broad management goals which describe the long-term vision that has been established for the ecosystem. These goals must reflect the importance of the ecosystem to stakeholder groups, such as the St. Louis River CAC. The ecosystem goals for the St. Louis River AOC are further described in Section 4.2.1. Objectives are developed for the various components of the ecosystem to clarify the scope and intent of the ecosystem goals. These objectives should include target schedules for being achieved. The ecosystem objectives for the St. Louis River AOC are further described in Section 4.2.2.

Next, candidate indicators of ecosystem health need to be identified and evaluated to determine their applicability to the St. Louis River ecosystem. Indicators need to be meaningful and relevant to the community at large, as well as to scientists. Participants of the 1998 State of the Lakes Ecosystem Conference (SOLEC) prepared an overarching set of indicators which objectively represent the condition of the Great Lakes ecosystem (Bertram and Stadler-Salt 1998). The MPCA has its own programs to develop representative indicators in waters of the state. The selection criteria for choosing suitable indicators should consider attributes such as biological and social relevance, sensitivity to stressors, broad applicability, measurability, ease of interpretation, and cost effectiveness (Council of Great Lakes Research Managers 1991). However, local experience should also be employed to establish a suite of indicators that adequately reflects the goals and objectives that have been established. The Science Advisory Group on Sediment Quality Assessment has recommended that the MPCA adopt many of the sediment quality indicators they recommended for Tampa Bay, FL (MacDonald 1995; 1997a). The MPCA has solicited input from the St. Louis River CAC Sediment Contamination Workgroup, and other RAP participants, to review these recommendations and to provide input on the selection of a final suite of indicators.

Ecosystem metrics are also required to support the implementation of ecosystem-based management. These metrics identify quantifiable attributes of the indicators and define acceptable ranges, or targets, for these variables. If all of the measured metrics fall within acceptable ranges, as determined by the MPCA through consultations with interested stakeholders, then the narrative goals and objectives for the ecosystem would be considered to have been met. The information collected during the selection of metrics and targets will also provide a basis for identifying data gaps and research needs to support implementation of the ecosystem approach.

A key element of the implementation process will involve incorporation of the management goals, ecosystem objectives, indicators, and metrics into management plans and decision-making processes that coordinate the decisions and activities of all participants (i.e., the RAP). In addition, focused environmental research and monitoring programs need to be developed to evaluate the status and trends of the key indicators. The results of these research and monitoring programs provide a basis for further evaluating the relevance of the indicators, refining the ecosystem metrics, and determining if the goals and objectives for the watershed are being achieved. This implementation process is consistent with the environmental strategies the MPCA adopted in 1998 as part of an agency-wide reorganization (MPCA 1998). The MPCA initiated an agency-wide performance management system which will be used to track progress on achieving goals and objectives. If the goals and objectives are not met within a designated time period, then the MPCA and stakeholders will need to reassess the technical and financial feasibilities of implementing the goals and objectives.

The ecosystem-based management approach has already been employed at other areas in the St. Louis River watershed [e.g., Miller Creek watershed project (MPCA 1994) and the St. Louis River management plan (Mueller 1997)] and in the greater Lake Superior area (Jordan and Uhlig 1994; MPCA 1997a). The MDNR is committed to using an ecosystem-based framework for setting natural resource management priorities throughout the state (MDNR 1997). Thus, effective community, government, tribal, and business partnerships have already been established, which will further implementation of the sediment-related ecosystem-based management approach in the St. Louis River AOC.

Successful implementation of the ecosystem-based management approach, on a wide-scale basis in the St. Louis River AOC, could potentially take several years to decades to achieve. Examples of how the ecosystem approach is being used at another Great Lakes AOC (i.e., Toronto, Ontario) can provide a useful case study for stakeholders in the St. Louis River AOC. The ecosystem-based management approach has been particularly successful in the regeneration of the Toronto waterfront, especially for brownfields redevelopment and the creation of a Waterfront Trail (Royal Commission on the Future of the Toronto Waterfront 1992; Waterfront Regeneration Trust 1998). However, the Metropolitan Toronto and Region RAP encountered some initial difficulties with implementing an ecosystem approach, partly due to the enormous size of the AOC (Royal Commission on the Future of the Toronto Waterfront 1991; 1992). The Waterfront Regeneration Trust in conjunction with the Toronto and Region Conservation Authority implemented a watershed-based approach after completion of the Stage II RAP to make implementation of the ecosystem approach more manageable. With six major watersheds in the Toronto RAP area, the principle avenues for public involvement, project initiation, and priority setting are now with watershed and waterfront groups (Metro Toronto and Region Remedial Action Plan Web Site:

http://www.cciw.ca/glimr/raps/ontario/toronto/intro.html#implementation). Similarly, the St. Louis River AOC also encompasses a large area (i.e., 72 nautical kilometers of which the last section fans out into a 12,000-acre estuary), and efforts began approximately fifteen years ago to revitalize the Duluth waterfront. A long-term commitment from the MPCA, partnering agencies, and stakeholders is needed to ensure enough resources are dedicated to implement the ecosystem-based management approach in the St. Louis River AOC.

4.2.1 Ecosystem Goals for the St. Louis River Area of Concern

Ecosystem goals are broad narrative statements that define the management goals that have been established for a specific ecosystem. The development of ecosystem goals requires input from a number of sources to ensure that societal values are adequately represented. Open consultation with the public should be considered a primary source of information for defining these goals. Government agencies, nonprofit organizations, industries, tribal groups, and other stakeholders should also be consulted during this phase of the process.

A number of public consultation processes have already been conducted in the St. Louis River basin to support the development of a long-term vision for the future. For example, the City of Duluth led a visioning process that identified goals for the city for the year 2001 and beyond. Similarly, the Lake Superior Binational Forum has developed a broader vision for the Lake Superior basin, which includes the St. Louis River watershed. While the visions that have emerged from these processes vary, the citizens and communities in the vicinity of the St. Louis River generally share the following ecosystem goals:

- to create economic opportunities for residents;
- to preserve the St. Louis River and Lake Superior ecosystems;
- to protect open space and wild lands;
- to preserve the area's rich and colorful history;
- to create affordable housing;
- to support education;
- to maintain safe and friendly neighborhoods; and,
- to promote the arts and cultural activities.

Of the above goals, the preservation of the St. Louis River and Lake Superior ecosystems relates the most closely with contaminated sediment issues. However, the other goals also apply after a hot spot site is cleaned up. As part of any sediment remediation action, nearshore sources of COCs must be controlled and/or cleaned up. Economic opportunities can be created for residents that start businesses on newly cleaned-up nearshore land or operate recreational services on the water (e.g., charter fishing, kayaking, sailboat, and scuba diving services). Alternatively, open space and forested areas near the former hot spot site can be preserved and used for educational, artistic, or cultural activities, such as festivals. The incorporation of boardwalks that contain adjacent sculptures and/or sign posts of historical information could also be incorporated into waterfront development activities by former hot spot areas. Similar boardwalks have already been created in the Canal Park area of Duluth. For nearshore areas that could be zoned residential, affordable housing could be created. The formation of neighborhood block groups could increase the safety and sense of community in the neighborhood. Finally, any residential, commercial, or industrial development of nearshore areas would most likely increase the value of the property. Thus, increased property taxes on the land could be used to support education.

While these ecosystem goals provide a long-term vision for the area, they are too general to support the development of specific planning, research, and management initiatives for the St. Louis River watershed. Thus, ***ecosystem objectives***, that are more closely linked with ecological science (Harris *et al.* 1987), need to be developed to further clarify and add detail to the broad ecosystem goals. In turn, the ecosystem objectives will support the identification of indicators and metrics that provide direct information for assessing the health and integrity of the ecosystem.

4.2.2 Ecosystem Objectives for the St. Louis River Area of Concern

In recognition of the central role that communities play in the implementation of ecosystem management principles, the IJC has indicated that community vision statements are essential elements of the RAP process. For this reason, the MPCA and WDNR facilitated broad public involvement in the creation and implementation of the Stage I and II RAPs (MPCA and WDNR 1992, 1995). The participants involved in this process collectively developed a vision to protect and restore the St. Louis River AOC. This vision was articulated in a series of ecosystem objectives that are intended to guide the implementation of the RAP and other management processes in the St. Louis River basin (Table 3).

Many of these ecosystem objectives provide guidance on the desired future state of sediment quality conditions in the St. Louis River AOC. These ecosystem objectives make it clear that participants in the RAP process agree that sediment quality in the St. Louis River basin should be maintained and/or restored to protect benthic communities and, where necessary, restore and/or enhance the community. Another important ecosystem objective is to protect and restore fish and wildlife habitat. Thus, concentrations of bioaccumulative substances in benthos, fish, and wildlife tissues need to be reduced to a level protective of ecological and human health. Protection of recreational values and facilitation of dredged material management are also key elements of the overall vision.

In order to achieve the ecosystem objectives for the St. Louis River AOC, specific indicators must be established to determine the status of sediment quality conditions. A process for establishing such key indicators (including specific metrics and targets) is discussed in the following section.

4.2.3 Selection of Ecosystem Health Indicators for Sediment Quality Conditions in the St. Louis River Area of Concern

It is difficult to directly measure the level of attainment of various ecosystem goals and objectives that have been established for the St. Louis River AOC. For this reason, it is desirable to establish a suite of ecosystem health indicators that can be used to determine if the designated uses of the aquatic ecosystem are being protected and, where necessary, restored. In the St. Louis River AOC, indicators of aquatic ecosystem health are required to facilitate the assessment of water quality conditions, the hydrological regime, sediment quality conditions, fish tissue quality, contaminant loadings, and the status of aquatic habitats, wetlands, and biological communities. The present study is intended to contribute to this effort by identifying a suite of ecosystem health indicators that can be used for assessing ambient sediment quality conditions in the St. Louis River AOC.

A wide variety of tools have been recommended for assessing sediment quality conditions in freshwater ecosystems (Appendix B). The Science Advisory Group on Sediment Quality Assessment has evaluated a variety of tools and identified a suite of aquatic ecosystem health indicators for assessing sediment quality conditions in Tampa Bay, FL (MacDonald 1995; 1997a). This suite of indicators included sediment chemistry, sediment toxicity, benthic invertebrate community structure, sediment quality triad, physical characteristics of sediments, water chemistry, tissue chemistry, and biomarkers in fish. Ingersoll and MacDonald (1999) further evaluated these tools to identify the most relevant indicators of sediment quality conditions in freshwater ecosystems. This refined list of ecosystem health indicators included:

- sediment chemistry (i.e., relative to background levels and to effects-based and bioaccumulation-based SQGs);
- status of physical habitats;
- sediment toxicity (i.e., acute mortality and chronic endpoints, such as, growth, reproduction, and abnormal development in fish and invertebrates);
- benthic invertebrate community structure;
- status of fish populations;
- fish health (i.e., including tumor incidence, organ morphology, and other measures of health); and,
- fish tissue quality (i.e., including contaminant concentrations in fish tissue and the taste, odor, and consistency of the tissue).

The results of this evaluation provided important information for recommending a suite of candidate ecosystem health indicators for the St. Louis River AOC. Most of the aforementioned ecosystem health indicators were presented to the St. Louis River CAC Sediment Contamination Workgroup at a meeting that was convened in November 1998. Some Workgroup members also thought the presence of wild rice stands and hydrological factors could be used as sediment-related indicators. Additional comments were solicited from the entire Workgroup on a draft paper on this topic (MacDonald and Crane In review). The comments that were received by this diverse Workgroup provided a basis for selecting a final suite of indicators that would provide the necessary information on sediment quality conditions in the St. Louis River AOC. This suite of indicators include:

- sediment chemistry;
- sediment toxicity tests;
- benthic community assessments; and,
- bioaccumulation assessments (e.g., tissue chemistry).

The relationship between these indicators and the narrative objectives that have been established for the St. Louis River AOC is presented in Table 4. These indicators could be used to determine if various water uses are being protected by the sediment management strategies that are implemented in the St. Louis River AOC. These water uses include:

- aquatic life;
- aquatic-dependent wildlife;
- human health;
- recreation and aesthetics; and,
- navigation and shipping.

See Appendix D for additional information about the aforementioned water uses in the St. Louis River AOC.

Ecosystem health indicators are most effective when accompanied by metrics and quantitative targets. Metrics may be defined as any measurable characteristic of an ecosystem health indicator. For example, the dry weight concentration of mercury in sediments might be identified as an important metric relative to sediment chemistry. While metrics provide information that can be used to directly assess trends in environmental conditions, numerical targets are also needed to provide more direct linkages to the ecosystem objectives. In the case of sediment chemistry, such targets define the range of chemical concentrations necessary to protect the benthic community and/or assure that problematic levels of bioaccumulation do not occur.

There is a need to establish metrics and numerical targets for each of the priority ecosystem health indicators that have been recommended for the St. Louis River AOC. The first step in this process involves the identification of candidate metrics for each indicator. Subsequently, the candidate metrics for each priority indicator needs to be evaluated in terms of the utility of the information that they are likely to generate. This evaluation is likely to provide a basis for identifying the most appropriate metrics for each ecosystem health indicator.

Targets are also required for the metrics that apply to each indicator. Such targets may vary depending on the desired management actions to take place at a particular site. For example, a target that would trigger further investigations at a site would be set at a lower level than a target intended to trigger sediment remediation. In addition, targets for areas that are subjected to periodic or frequent physical disturbances (e.g., shipping channels) may differ from those that are established for areas that are seldom disturbed. For this reason, multiple targets may be set for many of the metrics. A listing of the metrics that are recommended for assessing sediment quality conditions in the St. Louis River AOC is presented in Table 5. Of these metrics, only SQTs for PCOCs and COCs in the St. Louis River AOC will be developed in this report.

It should be noted that the indicators that are recommended for assessing sediment quality conditions represent important components of the overall suite of indicators that is needed for evaluating environmental conditions within the St. Louis River AOC. Such a suite of indicators would include those that relate to water quality conditions, hydrological conditions, and other key environmental compartments. For example, the number and areal extent of wild rice stands could be used as an indicator of water quality conditions, since the presence of wild rice stands increases as water quality approves. In addition, discharge and stage height could be used as indicators of hydrological conditions. In the future, it would be advantageous to establish a full suite of indicators (including metrics and targets) and incorporate them into environmental monitoring programs that are conducted within the St. Louis River AOC.

CHAPTER 5

DEVELOPMENT OF A MATCHING SEDIMENT CHEMISTRY AND TOXICITY DATABASE FOR THE ST. LOUIS RIVER AREA OF CONCERN

5.1 ACQUISITION OF MATCHING SEDIMENT CHEMISTRY AND TOXICITY DATA

An extensive search of the scientific literature was conducted by MESL and the MPCA to acquire matching sediment chemistry and toxicity data for the St. Louis River AOC. More specifically, an effort was made to acquire all of the relevant information on the concentrations of PCOCs and COCs in sediments from the St. Louis River AOC (i.e., trace metals, PCBs, PAHs, certain organochlorine pesticides, such as toxaphene, and several other classes of organic contaminants, such as dioxins and furans), as well as associated data on the toxicity of those sediments to sediment-dwelling organisms. The process that was used to identify and acquire candidate data sets included:

- Collating the documents and electronic data sets for the studies that have been conducted by the MPCA and WDNR in the St. Louis River AOC (this information was compiled by MPCA staff and forwarded to MESL);
- Accessing the information contained in MESL's extensive database on the effects of sediment-sorbed contaminants on aquatic organisms [i.e., Biological Effects Database for Sediments (BEDS)];
- Conducting on-line searches of a number of commercial bibliographic databases to obtain recently published articles from peer-reviewed journals;
- Reviewing recent volumes of peer-reviewed journals that routinely publish papers on the effects of sediment-associated contaminants to access recently published data (e.g., *Chemosphere*; *Environmental Toxicology and Chemistry*; *Water, Air, and Soil Pollution*; *Toxicology*; *Archives of Environmental Contamination and Toxicology*; *Environmental Science and Technology*; *Ecotoxicology*, etc.);
- Contacting various experts in the sediment quality assessment field, by either letter or phone, to obtain published and unpublished data sets relevant to this project;

- Publishing general requests for matching sediment chemistry and toxicity data sets in the Society of Environmental Toxicology and Chemistry's *SETAC News* and the U.S. EPA's *Contaminated Sediments Newsletter*.

The matching sediment chemistry and toxicity data that were acquired during this study were used to support the development of a sediment toxicity database for the St. Louis River AOC. These matching sediment chemistry and sediment toxicity data were also used to support the development of a broader sediment toxicity database (i.e., SEDTOX). Development of the SEDTOX database is part of a larger cooperative effort between MESL, EVS Environment Consultants, NOAA, and the USGS to develop and evaluate tools for assessing sediment quality conditions in freshwater, estuarine, and marine ecosystems. Participation in this cooperative effort ensured that MPCA would be able to access information from the SEDTOX database to support evaluations of the predictive ability of the numerical SQTs in the St. Louis River AOC and in other areas within the Great Lakes. This broader perspective was considered to be an essential part of the overall SQT evaluation process due to the limitations on matching sediment chemistry and toxicity data from the St. Louis River AOC.

5.2 REVIEW AND EVALUATION OF CANDIDATE DATA SETS

All of the data sets and associated documents that were retrieved during the course of this study were critically evaluated to determine their scientific and technical validity. To support this critical evaluation, a comprehensive set of screening criteria were developed in cooperation with the Science Advisory Group on Sediment Quality Assessment (Appendices E and F). These screening criteria provided a means of consistently evaluating the methods that were used in each study, including the procedures that were used to collect, handle, and transport sediment samples, the protocols that were applied to conduct sediment toxicity tests, the methods that were used to determine the concentrations of PCOCs and COCs in sediments, and the statistical tests that were applied to the study results. In many cases, additional communications with investigators and professional judgement was needed to determine if the screening criteria had been satisfied. The data sets which met the screening criteria were incorporated into spreadsheets in Microsoft Excel format, printed, and verified against the original data sources. Overall, application of these quality assurance (QA) procedures were intended to ensure that only high quality and fully verified data were incorporated into the project database.

5.3 DEVELOPMENT OF THE PROJECT DATABASE

All of the matching sediment chemistry and toxicity data assembled from the St. Louis River AOC, which met the screening criteria, were incorporated into the project database in Microsoft Access (Table 6). These data were captured on a per sample basis. Each record in the resulting database included the citation, a brief description of the study area (i.e., by water body and reach), a description of the sampling locations (including georeferencing data, if available), information on the toxicity tests that were conducted (including species tested, endpoint measured, test duration, etc.), type of material tested (i.e., whole sediment, porewater, or elutriate), the total organic carbon (TOC) concentrations (if reported), and the chemical concentrations (expressed on a dry weight basis). Other supporting data, such as simultaneously extractable metal (SEM) concentrations, acid volatile sulfides (AVS), particle size distribution, and water temperature were also included in the individual data records, as available.

As a conservative estimate, SEM concentrations were assumed to be equivalent to total metal concentrations in the database. Most of the SEM entries in the database were from the R-EMAP study conducted in the St. Louis River AOC (Breneman *et al.* 2000).

EVS Environment Consultants and MESL were responsible for transferring St. Louis River AOC data into the SEDTOX database format and for generating ascending data tables for each PCOC in the St. Louis River AOC (Appendix G). Additional QA procedures were taken to verify that no translation problems had occurred with incorporating data into the project database (i.e., data entries were compared to the original data sources). In addition, the ascending data tables produced from the database were spot checked to insure that data quality objectives (DQOs) were met. Finally, the MPCA project manager conducted a QA review of the draft database. MESL incorporated final revisions into the database. This database is available, upon request, from Judy Crane (MPCA) at the contact address given in the acknowledgments.

CHAPTER 6

SEDIMENT QUALITY TARGETS FOR THE ST. LOUIS RIVER AREA OF CONCERN

6.1 INTENT AND APPLICATION OF SEDIMENT QUALITY TARGETS

Participants in the development of the RAP identified five water uses that need to be protected and/or restored in the St. Louis River AOC. These designated water uses include fish and aquatic life, wildlife, human health, recreation and aesthetics, and shipping and navigation. While it is generally agreed that these water uses should be protected, it may not be possible to provide an uniform level of use protection throughout the St. Louis River AOC. In particular, physical disturbances resulting from seiches, wind-induced waves, ice scour, navigational dredging, prop wash, and other factors can reduce the potential for maintaining productive benthic communities in certain locations. In addition, ongoing nonpoint sources of chemical releases (e.g., upland industrial and commercial activities, spills) have the potential to reduce the long-term effectiveness of any sediment clean-up activities. The TMDL program is one mechanism through which nonpoint sources of COCs (e.g., mercury) will be identified and controlled in the future. Other regulatory efforts by the MPCA and WDNR are needed to ensure that sources of chemical contamination to the St. Louis River will be identified, quantified, and controlled.

In recognition of the challenges that are associated with sediment management in this area, two types of SQTs are recommended. The Level I SQTs identify chemical concentrations which will provide a high level of protection for designated water uses, specifically for aquatic life. By comparison, a lower level of protection for designated water uses will be provided by the Level II SQTs. Higher chemical concentrations are likely to occur at sites that are provided with this level of protection, potentially affecting one or more of the designated water uses at the site. However, substantial off-site migration of PCOCs and COCs should not be permitted in areas that have chemical concentrations approaching the Level II SQTs. The bioaccumulation-based SQTs for the protection of wildlife and human health are intended to provide a high level of protection for these water uses.

The numerical SQTs developed for the St. Louis River AOC are most applicable to soft sediments. These SQTs should not be applied to assessments of upland soils, land-applied sludge, or other land-based materials (e.g., gravel). These SQTs should be used with care for any sediments containing large amounts of gravel, coarse sand, tar, slag, metal ore (e.g., taconite pellets), paint chips, coal chunks, fly ash, or wood chips. The presence of the aforementioned materials may bind up some chemicals so that they are not bioavailable to aquatic organisms. In addition, the SQTs were derived in units of dry weight sediments; therefore, they do not directly account for the potential effects of geochemical factors in sediments that may influence contaminant bioavailability (Long and MacDonald 1998). Guidance on the applications of using SQTs for assessing sediment quality conditions in the St. Louis River AOC is provided in the next chapter.

6.2 SEDIMENT QUALITY TARGETS FOR THE PROTECTION OF SEDIMENT-DWELLING ORGANISMS

The ecosystem objectives that have been established indicate that sediment quality conditions in the St. Louis River AOC should be maintained such that the benthic community, including epibenthic and infaunal species, is protected and, where necessary, restored. Evaluation of the extent to which this objective is being met necessitates the identification of ecosystem health indicators and their associated metrics and targets. The priority indicators of sediment quality conditions in the St. Louis River AOC include sediment chemistry (i.e., for PCOCs and COCs), sediment toxicity, and benthic invertebrate community structure (see Section 4.2.3). While these primary indicators provide a basis for evaluating effects on sediment-dwelling organisms, they do not provide a comprehensive basis for assessing sediment quality conditions. For this reason, a number of additional indicators are needed to support sediment quality assessments in the St. Louis River AOC, including bioaccumulation (i.e., as measured using 28-day laboratory bioaccumulation tests on the oligochaete, *Lumbriculus variegatus*, and on analyses of fish tissues collected in the field), habitat status, porewater and water column toxicity tests, and fish community characteristics.

SQTs provide an important sediment quality assessment tool that can be used to screen sediment chemistry data and evaluate the need to collect additional data on the various indicators to fully assess sediment quality conditions. For the St. Louis River AOC, the narrative objectives for the Level I and Level II SQTs are designated as such for the protection of sediment dwelling organisms:

- ***Level I SQTs*** are intended to identify contaminant concentrations below which harmful effects on sediment dwelling organisms are unlikely to be observed.

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

These narrative objectives recognize that water-based economic activities (i.e., such as shipping, operation of small craft marinas, waterfront development, tourism-related activities, etc.) are essential to the health and integrity of the communities (especially Duluth, MN and Superior, WI) that are located in the vicinity of the St. Louis River AOC. While these activities contribute significantly to the local economy, they also have the potential to degrade water quality conditions (i.e., through spills or stormwater runoff) and/or reduce the stability of sediments (i.e., through navigational dredging or prop wash). Therefore, the potential for maintaining an unaltered benthic invertebrate community is likely reduced in these areas, even in the absence of chemical contamination in the sediments.

6.2.1 Strategy for Establishing Numerical Sediment Quality Targets

Both theoretical and empirical approaches have been used to derive numerical SQGs for freshwater ecosystems (see Appendix H). A total of seven distinct approaches were evaluated to support the selection of procedures for deriving numerical SQTs for the St. Louis River AOC (Table 7). At the time that this project was initiated, insufficient data were available on the relationships between sediment chemistry and sediment toxicity in freshwater ecosystems to evaluate regional differences in the responses of sediment-dwelling organisms to contaminated sediments. For this reason, it was thought that the logistic regression modeling (LRM) approach (Field *et al.* 1999), applied to the matching sediment chemistry and toxicity data from the St. Louis River AOC, would provide the most effective means of establishing SQTs. That is, the LRM approach provides a means of utilizing matching sediment chemistry and toxicity data to determine the concentrations of sediment-associated contaminants that correspond to specific probabilities of observing adverse biological effects. Additionally, it was thought that this approach would facilitate the derivation of SQTs that would be directly applicable to the St. Louis River AOC (i.e., by utilizing site-specific data in the development of the logistic regression models and associated T20 and T50 values for each chemical substance). However, the results of preliminary analyses conducted using the entire North American freshwater database revealed that insufficient data were available to generate reliable logistic regression models for any of the toxicity test endpoints that were represented in the database (e.g, *Hyalella azteca* growth or survival in 10-14 day tests). As such, it was apparent that it would not be possible to develop logistic regression models using a portion of the database only (i.e., the data from the St. Louis River AOC).

In recognition of the potential limitations of the LRM approach for deriving SQTs for the St. Louis River AOC, a number of alternative approaches were considered to support the establishment of numerical SQTs (see Appendix H). The following strategy was used to recommend numerical SQTs for the protection of sediment-dwelling organisms in the St. Louis River AOC:

- adopt the consensus-based SQGs that were derived by MacDonald *et al.* (2000a); and,
- adopt the most reliable of the other effects-based freshwater SQGs that have been published in the scientific literature for those chemicals for which consensus-based SQGs are not available [i.e., Canadian Council of Ministers of the Environment (CCME) 1999 and New York State Department of Environmental Conservation (NYSDEC) 1999].

This strategy was developed to provide a consistent basis for establishing reliable and regionally-applicable SQTs for PCOCs and COCs in the St. Louis River AOC. The consensus-based SQGs, that were derived by MacDonald *et al.* (2000a) and evaluated by USEPA (2000a), appeared to be the most relevant for establishing numerical SQTs for the St. Louis River AOC for several reasons. According to Swartz (1999) and MacDonald *et al.* (2000a,b), consensus-based SQGs provide a unifying synthesis of the existing SQGs, reflect causal rather than correlative effects, and account for the effects of contaminant mixtures. Therefore, the consensus-based SQGs are likely to provide useful tools for assessing sediment quality conditions in the St. Louis River AOC.

The consensus-based SQGs have additional features that make them relevant for establishing numerical SQTs for the St. Louis River AOC. First, the consensus-based SQGs consist of both threshold effect concentrations (TECs) and probable effect concentrations (PECs), thereby satisfying the need to provide SQTs that allow two levels of protection for sediment-dwelling organisms (i.e., Level I and Level II SQTs). In addition, numerical consensus-based SQGs are available for most of the PCOCs and COCs in the St. Louis River AOC, including metals, PAHs, PCBs, and organochlorine pesticides. The consensus-based SQGs have been evaluated for reliability using matching sediment chemistry and toxicity data from field studies conducted throughout the United States (excluding the St. Louis River AOC data set; MacDonald *et al.* 2000a). The results of this evaluation indicated that most of the TECs (i.e., 21 of 28) provide an accurate basis for predicting the absence of sediment toxicity, whereas over half of the PECs (i.e., 16 of 28) provide an accurate basis for predicting sediment toxicity (MacDonald *et al.* 2000a). Importantly, these SQGs facilitate the evaluation of sediments that contain complex mixtures of contaminants [i.e., through the calculation of mean PEC quotients (PEC-Qs); see Section 6.2.2]. Finally, evaluations of the information in the entire North American freshwater database have facilitated the determination of relationships between sediment chemistry and sediment toxicity such that it is possible to identify the concentrations of contaminants that are associated with specific probabilities of observing adverse biological effects. As such, the consensus-based SQGs were considered to directly support the establishment of numerical SQTs for the St. Louis River AOC.

Effects-based SQGs from other published sources also represent relevant tools for conducting sediment assessments in freshwater ecosystems. For this reason, such SQGs were considered for adoption as numerical SQTs in the St. Louis River AOC for those substances for which consensus-based SQGs were not available. Among the freshwater SQGs that have been established in other jurisdictions, the threshold effect levels (TELs) and probable effect levels (PELs), that have been promulgated by the CCME (1999), were considered to be the most relevant for several reasons. First, the TELs and PELs represent numerical SQGs that provide two levels of protection for sediment-dwelling organisms that are comparable to the levels of protection that are afforded by the consensus-based TECs and PECs (MacDonald *et al.* 2000a). In addition, TELs and PELs are available for key PCOCs and COCs in the St. Louis River AOC for which consensus-based SQGs were not available. In contrast to the SQGs that were derived by Environment Canada (EC) and the Ministere de l'Envionnement du Quebec (MENVIQ) (1992) and Long and Morgan (1991), the TELs and PELs are intended to be directly applicable to the Great Lakes region. Finally, the TELs and PELs were derived using information on the effects of contaminated sediments on a wide variety of aquatic organisms and endpoints. Together, these features make the TELs and PELs the most relevant of the other published SQGs for establishing SQTs for the St. Louis River AOC. Therefore the TELs and PELs were selectively identified as candidate SQTs for chemicals lacking consensus-based SQG values.

Neither a consensus-based SQG or a CCME-derived SQG value was available for use as a Level II SQT for toxaphene. However, the NYSDEC has developed a sediment criterion for toxaphene that was protective of acute toxicity (NYSDEC 1999). The NYSDEC used the equilibrium partitioning (EqP) approach, along with established water quality criteria, to develop sediment criteria for nonpolar organic compounds. The NYSDEC (1999) sediment criterion for toxaphene was recommended as a Level II SQT for the St. Louis River AOC.

This strategy for identifying SQTs yielded candidate Level I and Level II SQTs for eight trace metals, 13 individual PAHs, total PAHs, total PCBs, and 10 organochlorine pesticides (Table 8).

In the next two sections, the candidates SQTs were evaluated to determine their relevance to the St. Louis River AOC.

6.2.2 Evaluation of Individual Candidate Sediment Quality Targets

Following the identification of candidate SQTs, these sediment management tools were evaluated to determine their ability, when used alone, to correctly classify sediment samples as toxic and non-toxic, based on the measured concentrations of chemical contaminants alone (MacDonald *et al.* 2000a). The predictive ability of the candidate SQTs was evaluated using a three-step process.

In the first step of the SQT evaluation process, the St. Louis River AOC sediment toxicity database was used to obtain matching sediment chemistry and toxicity data from the study area. The studies contained in the database provided eight data sets (168 sediment samples; Table 6) with which to evaluate the predictive ability of the candidate SQTs. These studies represented a broad range of sediment toxicity results for which sediment chemistry data were widely available for metals and PAHs. There was little matching sediment chemistry and toxicity data available for total PCBs, and no such data for pesticides. The database included broad geographic coverage of the St. Louis River AOC, as exemplified by the R-EMAP study (110 matching sediment chemistry and toxicity samples; Breneman *et al.* 2000) and by an assessment of hot spot areas in the Duluth/Superior Harbor (38 matching sediment chemistry and toxicity samples; Crane *et al.* 1997).

In the second step of the evaluation, the measured concentrations of metals, PAHs, and/or total PCBs in each sediment sample were compared to the corresponding SQTs for those substances. Sediment samples were predicted to be not toxic if the measured concentration of a chemical substance was lower than the corresponding Level I SQT value. Similarly, samples were predicted to be toxic if the corresponding Level II SQT values were exceeded in field-collected sediments. Samples with contaminant concentrations between the Level I and Level II SQTs were neither predicted to be toxic nor non-toxic (i.e., the individual SQTs are not intended to provide guidance within this range of concentrations). The comparisons of measured concentrations to the candidate SQTs were conducted for a total of 23 PCOCs in the St. Louis River AOC (Table 9).

Finally, the accuracy of each prediction was then evaluated by determining if the sediment sample actually was toxic to one or more aquatic organisms, as indicated by the results of various sediment toxicity tests. The following toxicity test endpoints were used as indicators of toxicity in this assessment (i.e., sediment samples were designated as toxic if one or more of the following endpoints were significantly different from the responses observed in the reference or control sediments):

- amphipod (*Hyalella azteca*) survival or growth;
- midge (*Chironomus tentans*) survival or growth;
- oligochaete (*Lumbriculus variegatus*) survival;
- daphnid (*Ceriodaphnia dubia*) survival; and,
- fathead minnow (*Pimephales promelas*) survival.

Microtox® was not included as an indicator of toxicity in this assessment because it failed to improve our ability to discriminate amongst sediment samples in the St. Louis River AOC (Table 10). Sediment samples were designated as non-toxic if no significant responses were found in any of the test endpoints.

Since most of the candidate Level I and Level II SQTs were adopted from the consensus-based TECs and PECs, respectively, the published reliability of the TECs and PECs were used in the evaluation of individual candidate SQTs. Based on reliability analyses that were carried out on a nation-wide database (which did not include the St. Louis River data set), the individual consensus-based TECs were considered to provide a reliable basis for assessing the quality of freshwater sediments if more than 75% of the sediment samples were correctly predicted to be non-toxic (MacDonald *et al.* 2000a). In addition, the individual consensus-based PECs were considered to be reliable if greater than 75% of the sediment samples were correctly predicted to be toxic (MacDonald *et al.* 2000a). Consequently, the target levels of both false positives (i.e., samples incorrectly classified as toxic) and false negatives (i.e., samples incorrectly classified as not toxic) were 25% using the TEC and PEC values (MacDonald *et al.* 2000a). The consensus-based SQGs were considered to be reliable only if a minimum of 20 samples were included in the predictive ability evaluation (CCME 1995). Consensus-based SQGs that were determined to be reliable by MacDonald *et al.* (2000a), and recommended for use as SQTs, are noted in Table 9.

With having two types of candidate SQTs for the St. Louis River AOC, three ranges of concentrations can be defined for each chemical substance as follows:

- ≤ Level I SQT;

- > Level I SQT to ≤ Level II SQT; and
- > Level II SQT.

The degree of concordance that exists between chemical concentrations and the incidence of sediment toxicity (MacDonald *et al.* 1996) can be assessed by determining the ratio of toxic samples to the total number of samples within each of these three ranges of concentrations for each substance (Table 9). In the St. Louis River AOC, the incidence of sediment toxicity generally increased with increasing concentrations of individual metals and PAHs (Table 9).

For individual chemical concentrations less than or equal to the corresponding Level I SQTs, the incidence of toxicity was low (i.e., ≤16%) for those metals and PAHs with reliable TECs (Table 9). In particular, sediment samples containing PAHs with reliable TECs had a lower incidence of toxicity (i.e., 0 to 12%; n= 9) than sediments containing metals with reliable TECs (i.e., 9 to 16%; n = 4) at concentrations less than or equal to the Level I SQTs (Table 9). The somewhat higher incidence of toxicity for sediment samples containing metals with reliable TECs may be due to other classes of chemicals (e.g., PAHs) associated with toxicity. For the other chemicals that had more than 20 samples at ≤ Level I SQTs, the incidence of toxicity ranged from 10 to 17% for metals (i.e., mercury and nickel) and from 3.1 to 6.5% for PAHs [i.e., dibenz(a,h)anthracene, acenapthene, and fluorene] (Table 9). These results indicate that the Level I SQTs provide an accurate basis for predicting the absence of sediment toxicity in the St. Louis River AOC.

The results of this analysis indicates that the incidence of sediment toxicity is higher above the Level II SQTs than it was at or below the Level I SQTs. For those metals and PAH compounds with reliable PECs, the incidence of toxicity was generally high for metals (i.e., 60 to 100%; n = 7) and moderate for PAHs (i.e., 36 to 45%; n = 7) (Table 9). While the observed incidence of toxicity was lower than expected for PAHs, the data that were used in this evaluation were primarily based on acute endpoints for short-term toxicity tests. The results of a more comprehensive evaluation of North American data indicate that the incidence of toxicity would have been higher (i.e., >75%) had the results of chronic toxicity tests been used in the assessment (USEPA 2000a).

6.2.3 Evaluation of Grouped Candidate Sediment Quality Targets

Although the results of evaluations of the predictive ability of individual SQTs are informative, they do not provide the most relevant basis for assessing the applicability of these sediment assessment tools. Because sediments in the St. Louis River AOC are known to contain complex mixtures of contaminants (Schubauer-Berigan and Crane 1996, 1997; Crane *et al.* 1997; Glass *et al.* 1998; Breneman *et al.* 2000), the predictive ability of these sediment quality assessment tools is likely to increase when the SQTs are used together to classify these sediments. For this reason, a second evaluation was conducted to determine the incidence of toxicity within the following ranges of mean PEC-quotients (PEC-Qs): ≤0.1, >0.1 to ≤0.5, >0.5 to ≤1.0, >1.0 to ≤5.0, and >5.0. These ranges were analogous to the mean PEC-Q ranges used by Ingersoll *et al.* (USEPA 2000a) and Long *et al.* 1998a to evaluate the predictive ability of freshwater and marine SQGs, respectively. In this evaluation, mean PEC-Qs were calculated using the methods that were recommended by USEPA (2000a) and outlined in the box below.

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

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

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

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

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

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

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

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

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

The predictive ability of the candidate SQTs, when used together, was evaluated using the information contained in the St. Louis River AOC sediment toxicity database (Table 10). For each type of toxicity test category given in Table 10, the greatest number of matching sediment chemistry and toxicity samples were available for the two lowest mean PEC-Q ranges (i.e., $\leq$0.1 and >0.1 to $\leq$0.5). For the next three higher mean PEC-Q ranges, the minimum data requirements (i.e., 20 samples per category) were not met (Table 10). As such, comparisons of the predictive ability of different toxicity tests in the St. Louis River AOC should be made with caution. Nevertheless, overall trends in the incidence of sediment toxicity can be distinguished in Table 10 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., 6.8% and 6.5%, respectively) when the concentrations of sediment-associated contaminants are low (i.e., as indicated by mean PEC quotients of $\leq$0.1; Table 10). Importantly, the incidence of sediment toxicity in St. Louis River AOC sediments increased with increasing contaminant concentrations. For all toxicity tests combined (excluding Microtox®), the incidence of toxicity was 53% in sediments with mean PEC-Qs of >1.0 (i.e., 10 of 19 samples). The incidence of sediment toxicity was even higher for this combination of toxicity tests (i.e., 100%; 5 of 5 samples) when the mean PEC-Qs exceeded 5. While these results are useful for assessing the applicability of the SQTs in the St. Louis River AOC, this evaluation was limited by the absence of data at higher contaminant concentrations and from longer-term toxicity tests. This represents an important data gap because the acute toxicity data do not provide an adequate basis for identifying chronic toxicity thresholds for sediment-associated contaminants (USEPA 2000a). Consideration of the results of the Microtox® tests in this analysis failed to improve our ability to discriminate amongst sediment samples in the St. Louis River AOC (Table 10).

Ingersoll *et al.* (USEPA 2000a) assembled matching sediment chemistry and toxicity data from a variety of geographic locations in North America in order to evaluate the predictive ability of the consensus-based SQGs. For this study, the incidence of toxicity in the St. Louis River AOC data set was compared to the Great Lakes and North American data sets for amphipods and midges (USEPA 2000a). This comparison was done to evaluate whether the mean PEC-Qs predicted a similar incidence of sediment toxicity in the St. Louis River AOC as for the Great Lakes region and the rest of North America.

The St. Louis River AOC amphipod and midge data comprised a substantial portion of the Great Lakes data set (49% and 32%, respectively) and about 24% of the North American data set (Table 11). The contribution of the St. Louis River AOC data set was even more pronounced at mean PEC-Qs ≤0.1 (Table 11). For example, the St. Louis River AOC data comprised 88% of the Great Lakes amphipod data set and 47% of the Great Lakes midge data set at mean PEC-Qs ≤0.1 (Table 11). Thus, in making comparisons of the incidence of toxicity between the St. Louis River AOC, Great Lakes, and North American data sets, it is also important to make these comparisons to the portions of the larger geographic data sets that exclude the St. Louis River AOC data. In addition, the Great Lakes amphipod and midge data comprised 47% and 75%, respectively, of the North American data set. This preponderance of Great Lakes sediment toxicity data in North America may be attributed to the IJC's listing of 43 AOCs around the Great Lakes area and subsequent assessments of contaminated sediments in these AOCs, the successful implementation of sediment assessment recommendations from the U.S. EPA's Assessment and Remediation of Contaminated Sediments (ARCS) program (USEPA 1994a), and an increase in funding of sediment-related projects by GLNPO during the 1990s.

The predictive ability of the mean PEC-Qs for 10-14 day amphipod tests is given in Table 12. The incidence of toxicity was calculated for the following freshwater geographic areas:

- St. Louis River AOC;
- Other Great Lakes sites (excluding the St. Louis River AOC data);
- Other North American sites (excluding the St. Louis River AOC data);
- Non-Great Lakes sites in North America;
- All Great Lakes sites (including the St. Louis River AOC data); and
- All North American sites (including the St. Louis River AOC data).

The above categories enabled comparisons of the St. Louis River AOC data set to be made with both independent data sets and with data sets inclusive of the St. Louis River AOC data. These comparisons were most appropriate for the two lowest mean PEC-Q ranges (i.e., ≤0.1 and >0.1 to ≤0.5), because the minimum data requirements (i.e., 20 samples) were met for the St. Louis River AOC. Any comparisons of the three higher mean PEC-Q ranges must be made with caution due to the small number of sediment samples from the St. Louis River AOC (i.e., ≤11 samples; Table 12). The incidence of toxicity calculations for the geographic areas described above are given in Appendix I (Tables I-1 and I-2) and are summarized in Table 12. For the two lowest mean PEC-Q ranges, 95% confidence intervals were calculated by using the binomial distribution (i.e., choice of toxic or non-toxic) and applying the Bonferroni correction (Table 12).

Based on the results of the 10-14 day toxicity tests with the amphipod, *Hyalella azteca*, the incidence of toxicity tended to increase with greater mean PEC-Q ranges for the St. Louis River AOC, all Great Lakes, and all North American data sets (Table 12). This pattern was also observed for the other Great Lakes sites, except at mean PEC-Qs ≤0.1 where the incidence of toxicity was 50%. This number was based on a small sample size (i.e., n = 6), and all of the toxic hits came from the Sheboygan River, WI data set (USEPA 2000a). The Sheboygan River samples had high control survival (i.e., 97%), resulting in samples with 88% survival being designated as toxic. As more records are entered into the North American freshwater database, it may be possible to evaluate other ways of designating samples as toxic or non-toxic (i.e., in addition to significance only).

The 95% confidence intervals for the St. Louis River AOC overlapped with the 95% confidence intervals for all the other geographic areas for mean PEC-Q ranges of ≤0.1 and >0.1 to ≤0.5, thus implying no significant difference in the incidence of toxicity to amphipods. As more matching sediment chemistry and toxicity endpoint data are added to the St. Louis River AOC and North American databases, the 95% confidence intervals can be expected to decrease in size for various geographic areas. Consequently, the ability to discriminate between and within geographic areas will be improved with a larger matching sediment chemistry and toxicity database. Considering the limited number of St. Louis River AOC samples available at mean PEC-Qs >5.0 (n = 4), there appears to be good agreement in the incidence of amphipod toxicity (i.e., 64 to 77%) amongst all geographic areas for this category (Table 12).

The incidence of toxicity in the St. Louis River AOC for short-term amphipod tests can also be compared to the incidence of toxicity in North America for long-term amphipod toxicity tests [i.e., 28- to 42-day survival, growth, or reproduction tests with amphipods (*Hyalella azteca);* Table I-2]. Ingersoll *et al.* (USEPA 2000a) reported that mean PEC quotients of ≤0.1 and >0.1 to ≤0.5 were associated with a low incidence of sediment toxicity (i.e., 10% and 17%, respectively; Table I-2), based on the results of 28- to 42-day tests. In comparison, the incidence of toxicity from these long-term tests was similar to the results from short-term tests (i.e., 6.8 to 11%; Table 12) from the St. Louis River AOC. Survival was the principal endpoint for the short-term amphipod tests. The incorporation of growth as a chronic endpoint is recommended for future 10-day amphipod tests of St. Louis River sediments (Table 5). For St. Louis River sediments with mean PEC-Qs ≤0.5, short-term amphipod tests provide a cost-effective metric for assessing the incidence of toxicity when compared to long-term amphipod tests. As the level of sediment contamination increases above mean PEC-Qs of 0.5, more matching sediment chemistry and toxicity data (for acute and chronic endpoints for short-term tests) will need to be collected to more fully assess the predictive ability of these tests in the St. Louis River AOC. By comparison, long-term tests in North America showed a relatively high incidence of toxicity (i.e., 56%; 15 of 27 samples) to amphipods at mean PEC-Qs of >0.5 to ≤1.0, while mean PEC-Qs of >1.0 to ≤5.0 and >5.0 were usually toxic to amphipods (i.e., 96% and 100%, respectively; Table I-2) (USEPA 2000a). Therefore, long-term amphipod toxicity tests would be a favored metric to use in sediments with mean PEC-Qs >0.5.

The predictive ability of the mean PEC-Qs for 10-14 day midge tests is given in Table 13. The incidence of toxicity was calculated for the same freshwater geographic areas as for the amphipod, *Hyalella azteca* (see Tables I-3 and I-4). For the St. Louis River AOC, the incidence of toxicity in the midge tests increased exponentially from 6.5% at mean PEC-Qs ≤0.1 to 100% at mean PEC-Qs >5.0 (Table 13). As for the amphipod tests, 95% confidence intervals were calculated for the two lowest mean PEC-Q ranges (i.e., ≤0.1 and >0.1 to ≤0.5). At mean PEC-Qs ≤0.1, the incidence of toxicity to midges was significantly less in the St. Louis River AOC (i.e., 6.5%) than for the non-Great Lakes sites (i.e., 50%). Most of the toxicity at the non-Great Lakes sites was attributed to a study of the Tennessee portion of the lower Mississippi River (USEPA 2000a); this data set was not evaluated to determine possible factors contributing to sediment toxicity. For the other geographic areas at mean PEC-Qs ≤0.1 and >0.1 to ≤0.5, there was no statistical difference in the incidence of toxicity between these areas and the St. Louis River AOC (Table 13). In addition, the incidence of toxicity for midges and amphipods was virtually the same in the St. Louis River AOC for these lower mean PEC-Q ranges (Tables 12 and 13). Thus, for some sediment studies, it may be more cost effective to do either the short-term amphipod or midge tests at sites with mean PEC-Qs ≤0.5 (i.e., sites that have already had the spatial extent of contamination characterized or are suspected to be relatively clean). The minimum data requirements (i.e., 20 samples per category) were not met for the three higher mean PEC-Q ranges in the St. Louis River AOC (Table 13). Thus, limited comparisons can be made to other geographic areas.

At mean PEC-Qs >5.0, 100% of the midge tests were toxic at the St. Louis River AOC sites; most of these sediment samples were collected from the Interlake/Duluth Tar Superfund site that was heavily contaminated with PAHs. For the other geographic areas in the mean PEC-Q range >5.0, a lower incidence of toxicity was observed at the other Great Lakes sites (63%), other North American sites (61%), all Great Lakes sites (68%), and all North American sites (66%) compared to the St. Louis River AOC (100%) (Table 13). The higher incidence of sediment toxicity to midges in the St. Louis River AOC appears to be associated with PAH contamination, based on this small sample size (n = 5). At the other geographic areas, there are likely to be other COCs (e.g., PCBs) associated with toxicity at mean PEC-Qs >5.0. For the St. Louis River AOC, the greater incidence of toxicity in the short-term midge tests (i.e., 100%; n = 5; Table 13) compared to the short-term amphipod tests (i.e., 75%; n = 4; Table 12) warrants further evaluation to see if this trend remains stable after the minimum data requirements (i.e., 20 samples per category) have been met. For highly contaminated sites (i.e., mean PEC-Q > 5.0), both types of short-term sediment toxicity tests should be used, with additional consideration given to using 28-42 day amphipod tests at these sites.

The results of these predictive ability evaluations indicate that, collectively, the mean PEC-Qs provide a reliable basis for classifying sediments as toxic or not toxic. At the two lowest mean PEC-Q ranges, the results for the St. Louis River AOC were generally similar to those that were generated for different geographic areas for 10-14 day amphipod tests (Table 12) and for 10-14 day midge tests (Table 13). Therefore, the Level I and Level II SQTs for PCOCs and COCs (especially trace metals, PAHs, and total PCBs) are likely to provide a reliable basis for assessing sediment quality conditions in the St. Louis River AOC. The recommended Level I and Level II SQTs for the protection of sediment-dwelling organisms in the St. Louis River AOC are listed in Table 14.

Sediments in the St. Louis River AOC generally contain complex mixtures of contaminants (Crane *et al.* 1997). For this reason, assessments of sediment quality conditions relative to the protection of sediment-dwelling organisms should be conducted using the SQTs together (i.e., through the calculation of mean PEC-Qs). Sediments with mean PEC-Qs of ≤0.1 should be considered to provide the highest level of protection for sediment-dwelling organisms (i.e., Level I); the probability of observing chronic sediment toxicity is <10% in sediments with these chemical characteristics (USEPA 2000a). Sediments with mean PEC-Qs of >0.1 to ≤0.6 should be considered to provide a moderate level of protection for sediment-dwelling organisms (i.e., Level II); the probability of observing chronic sediment toxicity is <50% in sediments with these chemical characteristics (USEPA 2000a). At mean PEC-Qs of >0.6, the probability of observing chronic sediment toxicity is higher (i.e., >50%), indicating that sediment-dwelling organisms would be afforded a relatively low level of protection.

6.3 SEDIMENT QUALITY TARGETS FOR THE PROTECTION OF WILDLIFE

Sediment-associated contaminants have the potential to adversely affect wildlife species in several ways. First, certain wildlife species can be exposed directly to contaminated sediments through dermal contact (e.g., demersal fish species, such as carp or sculpins) or through ingestion pathways (e.g., bottom-feeding fish species or birds that consume sediment-dwelling organisms), potentially resulting in direct toxicity. In addition, many wildlife species may be exposed to sediment-associated contaminants as a result of food web transfers and associated bioaccumulation. The accumulation of toxic substances in the tissues of these species can result in decreased growth, impaired reproduction, reduced survival, or other harmful effects. Finally, sediment-associated contaminants can be toxic to sediment-dwelling organisms and, in so doing, result in decreased abundance of food for higher trophic organisms.

Bioaccumulation-based SQTs represent important tools for conducting sediment quality assessments for several reasons. First and foremost, unlike the effects-based SQTs described in the previous section, the bioaccumulation-based SQTs explicitly consider the potential for bioaccumulation and effects on higher trophic levels in the food web. That is, the bioaccumulation-based SQTs provide a basis for interpreting sediment chemistry data in terms of the potential for harmful effects on wildlife. Because there were a limited number of bioaccumulation-based SQTs, and methods for evaluating the reliability of these SQTs are not readily available, it is recommended that the existing SQTs for the protection of wildlife (NYSDEC 1999; MacDonald 1994) be adopted directly as interim SQTs in the St. Louis River AOC. The available bioaccumulation-based SQTs for PCOCs and COCs in the St. Louis River AOC are presented in Table 15. These SQTs should be used in conjunction with tissue chemistry data and applicable tissue residue guidelines (TRGs) (such as Newell *et al.* 1987) to confirm that contaminated sediments pose a hazard to mammalian and/or avian wildlife species.

6.4 SEDIMENT QUALITY TARGETS FOR THE PROTECTION OF HUMAN HEALTH

While aquatic organisms can be exposed to bioaccumulative substances (such as mercury, benzo(a)pyrene, PCBs, organochlorine pesticides, and dioxins and furans) via a number of exposure pathways, ingestion of contaminated sediments represent the most important pathway for sediment-dwelling organisms (Cook *et al.* 1992). In turn, these bioaccumulative contaminants can biomagnify in the food web, including species consumed by humans. Accumulation of toxic substances in fish tissues beyond specified TRGs [e.g., Food and Drug Administration (FDA) Action Levels] can impair designated water uses (i.e., recreation and human health) through the issuance of fish consumption advisories. Therefore, the accumulation of toxic substances in the tissues of fish, and other aquatic organisms, is an important issue in areas that support subsistence, sport, or commercial fisheries. Subsistence fishing may occur in the St. Louis River AOC, particularly by members of the Fond du Lac Band for whom fish is an important component of their diet. The area is widely utilized for sport fishing (especially walleye). Commercial fishing no longer takes place in the St. Louis River AOC.

Numerical SQTs for the protection of human health have not been previously established in Minnesota. However, the NYSDEC has established criteria for the protection of human health (NYSDEC 1999). NYSDEC's criteria are intended to identify the maximum concentrations of sediment-associated contaminants to prevent harmful levels of bioaccumulation in fish and other aquatic organisms. The recommended SQTs for the protection of human health that are presented in Table 15 were adopted directly from the criteria that were established by NYSDEC (1999). This approach to the selection of SQTs was used because protection of human health is a high priority management goal in Minnesota and Wisconsin and the criteria from NYSDEC (1999) are likely to provide a high level of protection in the St. Louis River AOC. These SQTs should be used in conjunction with tissue chemistry data and applicable TRGs (such as FDA Action Levels; USEPA 1989a; 1997a) to confirm that contaminated sediments pose a risk to human health.

6.5 SEDIMENT QUALITY TARGETS FOR THE PROTECTION OF RECREATIONAL AND AESTHETIC WATER USES

Recreation and aesthetics represent important water uses in the St. Louis River AOC. While certain recreational and aesthetic uses of the aquatic ecosystem in the study area can be affected by sediment quality conditions, SQTs for the protection of recreational and aesthetic water uses have not been established in either Minnesota or Wisconsin. In addition, a comprehensive review of the published scientific literature failed to reveal any SQGs for these water uses (MacDonald *et al.* 1999). Therefore, it is not possible to establish site-specific SQTs for recreation and aesthetics in the St. Louis River AOC. Nevertheless, it is likely that the SQTs for the protection of aquatic life, wildlife, and human health are likely to be provide adequate protection for recreational and aesthetic water uses (CCME 1999).

6.6 SEDIMENT QUALITY TARGETS FOR THE PROTECTION OF SHIPPING AND NAVIGATION

A comprehensive review of the scientific literature failed to identify any SQGs that were specifically intended to protect shipping and navigation in the St. Louis River AOC (MacDonald *et al.* 1999). However, SQGs which define the maximum concentrations of sediment-associated contaminants for unrestricted open-water disposal of dredged materials have been established in certain jurisdictions (e.g., Environment Canada has adopted the Canadian TELs for the protection of aquatic life for this application; Porebski 1999). In addition, Environment Canada has established SQGs which, if exceeded, necessitate special handling of marine dredged materials (e.g., upland disposal; the PELs have been adopted for this application). In Canada, toxicity testing is required when contaminant concentrations fall between the TEL and PEL values.

Open water disposal of dredged materials is prohibited in Minnesota and Wisconsin. However, dredged material in the outer Duluth-Superior Harbor tends to be very sandy and is utilized for many beneficial uses, including beach nourishment, habitat development, and highway construction. The beneficial use of dredged material within the water should be done in such a manner as to not cause further chemical degradation of the environment. For example, chemical concentrations in dredged material should be less than the Level I SQTs if it is to be used for habitat enhancement. Land application of dredged material must comply with the chemical limits specified in the MPCA's rules for land application of biosolids. The WDNR does not have written policies regarding the land application of dredged material (Tom Janisch, WDNR, personal communication, 2000). In Wisconsin, use of dredged material as a topsoil replacement would be considered as a low hazard waste grant of exemption.

CHAPTER 7

APPLICATIONS OF SEDIMENT QUALITY TARGETS FOR ASSESSING SEDIMENT QUALITY CONDITIONS IN THE ST. LOUIS RIVER AREA OF CONCERN

7.1 OVERVIEW

The long-term vision that has been developed for the St. Louis River AOC articulates the importance of this transboundary watershed to the people who live in Duluth, MN; Superior, WI; and surrounding areas. Based on the ecosystem goals and objectives that have been developed for the St. Louis River AOC, maintaining a healthy, well-balanced ecosystem is an essential element of this vision. Protection of existing water uses and restoration of those uses that have been compromised due to environmental contamination have also been identified as central components of the RAP process. Making progress toward this long-term vision will require the successful implementation of a variety of environmental management initiatives, including those that are focused on the assessment, management, and remediation of contaminated sediments.

Effective management of contaminated sediments in the St. Louis River AOC will require the collection and interpretation of information on the quality of aquatic sediments. The applicability of the SQTs in sediment assessments is increased when used in conjunction with other tools that facilitate determinations of concentrations of PCOCs and COCs, sediment toxicity, bioaccumulation, and effects on *in situ* benthic invertebrates (Chapman *et al.* 1987). The numerical SQTs (i.e., Level I and Level II values) that are recommended in this document are intended to support sediment management initiatives by providing tools that can assist in the collection and interpretation of sediment chemistry data. More specifically, the SQTs provide a basis for classifying sediments relative to their potential to be toxic to sediment-dwelling organisms. The recommended applications of the numerical SQTs for assessing contaminated sediments within the study area include:

- designing monitoring programs;
- interpreting sediment chemistry data;
- assessing the risks to biotic receptors associated with contaminated sediments; and,
- developing site-specific sediment quality remediation targets (SQRTs).

Each of these potential uses of the SQTs are discussed in the following sections. An integrated framework was formulated to illustrate the applications of the various assessment tools in the sediment quality assessment process (see Appendix J). The framework provides guidance on the use of information on sediment chemistry, sediment toxicity, benthic invertebrate community status, and tissue chemistry for determining if sediments are contaminated, interpreting the implications of contamination, and identifying use impairments at a site. In addition, roles of remedial action planning and confirmatory monitoring and assessment were described. More detailed guidance on this sediment quality assessment framework is currently being developed for GLNPO.

7.2 MONITORING PROGRAM DESIGN

Monitoring is an integral component of environmental surveillance programs. While such programs may be undertaken for a number of reasons (e.g., trend assessment, impact assessment, compliance), limitations on available resources dictate that they must be conducted in an effective and efficient manner. For this reason, it is important for sediment quality monitoring programs to be well focused and to provide the types of information necessary to effectively manage contaminated sediments.

The numerical SQTs contribute to the design of environmental monitoring programs in several ways. First, comparison of existing sediment chemistry data with the SQTs provides a systematic basis for identifying high priority areas for implementing monitoring activities such as delineating the spatial extent of contamination and assessing biological effects through sediment toxicity tests, benthological community surveys, and/or bioaccumulation assessments. Second, when used in conjunction with existing sediment chemistry data, the SQTs may be utilized to identify PCOCs and COCs within a study area. By considering the potential sources of these contaminants, it may be possible to further identify priority sites for investigation. The SQTs can also assist in monitoring program design by establishing target detection limits for each substance (e.g., 0.5 x Level I SQT). Determination of the detection limits that are needed to support subsequent interpretation of sediment chemistry data should help to avoid many of the difficulties that have resulted from the use of standard, yet inappropriate, analytical methods (i.e., methods that achieve method detection limits that are greater than the Level I SQTs).

7.3 INTERPRETATION OF SEDIMENT CHEMISTRY DATA

Over the past decade, sediment chemistry data have been collected at a wide range of sites in the St. Louis River AOC. While these data can be used directly to assess the status and trends in environmental quality conditions, they do not, by themselves, provide a basis for determining if the concentrations of contaminants represent significant hazards to aquatic organisms. In this context, however, numerical SQTs provide practical assessment tools or 'scientific benchmarks' against which the biological importance of sediment chemistry data can be assessed. In this context, individual SQTs may be used as screening tools to identify areas of contaminated sediments within the St. Louis River AOC.

The numerical SQTs can be used to identify, rank, and prioritize PCOCs and COCs in freshwater sediments. In this application, the concentration of each chemical substance in each sediment sample is compared to the corresponding SQT value. Those substances that occur at concentrations below the Level I SQTs should be considered to be of relatively low priority. Those substances that occur at concentrations above the Level I SQTs but below the Level II SQTs should be considered to be of moderate concern, while those that are present at concentrations in excess of the Level II SQTs should be considered to be of relatively high concern. The relative priority assigned to each chemical substance can be determined by evaluating the magnitude and frequency of exceedance of the SQTs. Chemicals that exceed the Level II SQTs frequently, or by a large margin, should be viewed as the chemicals of greatest concern (Long and MacDonald 1998; MacDonald *et al.* 2000a; USEPA 2000a).

In conducting such assessments, it is important to remember that certain chemicals can be present in relatively unavailable forms (such as in slag, paint chips, tar). The SQTs are not meant to be used for sediment samples that contain a large proportion of these foreign materials. The SQTs can be used for soft sediment samples that have small quantities of these types of materials. Therefore, there is not a 100% certainty that samples with chemical concentrations in excess of the Level II SQTs will actually be toxic to sediment-dwelling organisms. The reliability of the SQTs should also be considered when conducting evaluations of sediment chemistry data, with the greatest weight assigned to those SQTs which have been shown to be reliable (Ingersoll *et al.* 1996; MacDonald *et al.* 2000a).

Collecting ancillary sediment quality information can increase the degree of confidence that can be placed in determinations of COCs. Specifically, data on regional background concentrations of sediment-associated contaminants can be used to identify substances of relatively low concern with respect to anthropogenic activities (i.e., those that occur at or below background levels). Data from toxicity tests can also be used to support the identification of COCs. More specifically, matching sediment chemistry and toxicity data provide a basis for evaluating the degree of concordance between the concentrations of specific contaminants and measured adverse effects. The degree of concordance between chemical concentrations and sediment toxicity can be evaluated using correlation analyses and regression plots (Carr *et al.* 1996). Those substances that are present at elevated concentrations (i.e., as indicated by exceedances of the Level II SQTs) in toxic samples should be identified as the chemicals of highest concern (Long and MacDonald 1998). Those chemicals that are not positively correlated to the results of toxicity tests should be viewed as relatively lower priority contaminants. These types of analyses need to be conducted on a site-specific basis for hot spot areas in the St. Louis River AOC.

The numerical SQTs can also be used to identify sites of concern with respect to the potential for observing adverse biological effects. In this application, the concentrations of sediment-associated contaminants should be compared to the corresponding SQTs. Sediments in which none of the measured chemical concentrations exceed the Level I SQTs should be considered to have the lowest potential for adversely affecting sediment-dwelling organisms and could be considered reference areas (Long and Wilson 1997). However, the potential for unmeasured contaminants to be present at levels of toxicological concern cannot be dismissed without detailed information on land and water uses within the water body or the results of sediment toxicity tests. Those sediments which have concentrations of one or more contaminants between the Level I and Level II SQTs should be considered to be of moderate priority, while those sediments with contaminant concentrations in excess of one or more Level II SQTs should be considered to be of relatively high concern. Once again, the magnitude and frequency of exceedances of the Level II SQTs provide a basis for assigning relative priority ratings to areas of concern with respect to contaminated sediments.

Importantly, the numerical SQTs provide consistent tools for evaluating spatial patterns in chemical contamination. More specifically, the SQTs can be used to compare and rank sediment quality conditions among sites located within the St. Louis River AOC. For example, maps showing the mean PEC-Q ranges for sites with matching sediment chemistry and toxicity data in the St. Louis River AOC are given in Figures 5 to 7. Sixteen sites could not be plotted due to a lack of geopositional data. The most contaminated areas included the Interlake/Duluth Tar Superfund site and the USX Superfund site (Figure 5 and 7). Minnesota Slip, Slip C, and the area encompassing WLSSD and the outlets of Miller and Coffee Creeks also rank highly for surficial sediment contamination (Figure 6). Other hot spot areas (e.g., Howards Bay) also have surficial sediments with elevated mean PEC-Q ranges (i.e., >0.11 to ≤ 0.6) (Figures 5 to 7). If Figure 5 was expanded to include all surficial sediment chemistry, then the Hog Island Inlet and Newton Creek area would rank highly for sediment contamination as well. Similar maps could be generated for deeper core segments to give an indication of the temporal distribution of chemical substances.

If a stratified random sampling design is used in a monitoring program, then the SQTs provide a basis for calculating the spatial extent of potentially toxic sediments. In hot spot areas, further investigations would typically be implemented to identify contaminant sources, assess the areal extent and severity of actual sediment toxicity, evaluate the potential for bioaccumulation, and/or determine the need for source control measures or other remedial measures. The SQTs could also be used to evaluate the efficacy of any regulatory actions that are implemented at the site.

While previous guidance has cautioned against using SQGs as stand alone decision tools, the results of recent evaluations of their reliability and predictive ability substantially increase the level of confidence that can be placed in the consensus-based SQGs. For example, there is a low probability of observing sediment toxicity (i.e., <10%) in North American sediments with mean PEC-Qs ≤0.1 (i.e., based on the results of 28- to 42-day toxicity tests with amphipods; USEPA 2000a) (Table I-2). In contrast, the probability of observing sediment toxicity increases at mean PEC-Qs of >0.5 to ≤1.0 (56% incidence of toxicity) and >1.0 (97% incidence of toxicity) (i.e., based on the results of 28- to 42-day toxicity tests with amphipods on North American sediments; USEPA 2000a) (Table I-2). Therefore, the MPCA and WDNR should consider whether Level II SQTs, when incorporated into mean PEC-Qs, could be used directly to support small-scale sediment management decisions (e.g., implementing source control measures, conducting sediment remediation for small sites such as boat slips). These tools are particularly efficient for evaluating sediment quality at relatively small sites, where the costs of further investigations could approach or exceed the costs of implementing remedial measures. For larger sites, SQTs should be used in a screening approach for preliminary assessments of data. For complex studies in which additional sediment assessment phases are conducted (e.g., the Interlake/Duluth Tar and USX Superfund sites), SQTs are used in conjunction with other tools (e.g., sediment toxicity tests, benthological surveys, bioaccumulation assessments) to make decisions about the spatial and temporal extent of contamination and the need for remediation.

7.4 ECOLOGICAL RISK ASSESSMENT

Risk assessment is the process of assigning magnitudes and probabilities to the adverse effects that may be associated with exposure to environmental contamination or other hazards. Ecological risk assessment (ERA) is an evolving process that is designed to provide science-based guidance for managing environmental quality, particularly at contaminated sites. Sediment quality guidelines can be used, with sufficient certainty, in ecological risk assessments (SETAC 1997).

Numerical SQGs can contribute directly to several stages of the ecological risk assessment process, including problem formulation, effects assessment, and risk characterization. During problem formulation, background information and preliminary sampling data are used to identify the problem and define the issues that need to be addressed at contaminated sites (Chapman *et al.* 1987). At the problem formulation stage, SQGs can be used in conjunction with existing sediment chemistry data to identify the chemicals and areas of concern with respect to sediment contamination (Long *et al.* 1998a). In turn, this information can be used to scope out the nature and extent of the problem and to identify probable sources of sediment contamination at the site. In addition, the SQGs provide a consistent basis for identifying appropriate reference areas that can be used in subsequent assessments of the contaminated site (Menzie 1997). Furthermore, the underlying data (i.e., the matching sediment chemistry and biological effects data) provide a scientific basis for identifying appropriate assessment endpoints (i.e., receptors and ecosystem functions to be protected) and measurement endpoints (i.e., metrics for the assessment endpoints) that can be used at subsequent stages of the assessment.

Numerical SQGs also represent effective tools that can be used to assess the effects of sediment-associated contaminants (i.e., during the effects assessment of the ERA). The goal of the effects assessment is to provide information on the toxicity or other effects that are likely to occur as a result of the sediment contamination. In this application, the SQGs provide an effective basis for classifying sediments as toxic or not toxic when used in conjunction with sediment chemistry data (MacDonald *et al.* 1996; Ingersoll *et al.* 1996; MacDonald *et al.* 2000a; USEPA 2000a). The applicability of the SQGs in effects assessments is increased when used in conjunction with other tools that facilitate determinations of background concentrations of contaminants such as, sediment toxicity, bioaccumulation, and effects on *in situ* benthic macroinvertebrates (Chapman *et al.* 1987).

The primary purpose of the risk characterization stage of an ERA is to estimate the nature and extent of the risk at a contaminated sediment site and to evaluate the level of uncertainty associated with that estimate (Chapman *et al.* 1987). The SQGs are particularly useful at this stage of the process because they provide a quantitative basis for evaluating the potential for observing adverse effects in contaminated sediments, for determining the spatial extent of unacceptable levels of sediment contamination (i.e., sediments that exceed prescribed limits of risk to sediment-dwelling organisms), and for estimating the uncertainty in the risk determinations (i.e., the potential for Type I and Type II errors). Importantly, calculation of the frequency of exceedance of the upper level SQGs and specified mean PEL quotients (PEL-Qs) enables risk assessors to estimate the probability that contaminated sediments will be toxic to sediment-dwelling organisms (Long and MacDonald 1998). When appropriate sediment chemistry data are available, these procedures facilitate the determination of the cumulative effects of contaminants arising from multiple sources (i.e., in addition to the contaminated site) and the evaluation of the potential for off-site impacts. The uncertainty associated with the application of the SQGs at this stage of the ERA can be effectively reduced by using the SQGs in conjunction with other measurement endpoints, such as results of toxicity tests and benthic invertebrate community assessments. For the St. Louis River AOC, the Level I and Level II SQTs can be applied in ERAs in the same manner that SQGs are used at other sites.

7.5 DEVELOPMENT OF SEDIMENT QUALITY REMEDIATION TARGETS

Sediment quality issues are rarely entirely the responsibility of one agency or one level of government. For this reason, it may be necessary to establish agreements between various levels of government to define their responsibilities with respect to the prevention, assessment, management, and remediation of sediment contamination. Multi-jurisdictional agreements may include accords on a number of issues; however, establishment of SQRTs is important because they provide a common yardstick against which the efficacy of a range of sediment management initiatives can be measured. These SQRTs should be based on chemical SQTs, as well as biological effects.

Numerical SQTs can be used in several ways to support the derivation of SQRTs. Specifically, SQTs are useful because they provide a means of establishing SQRTs that fulfill the narrative use protection objectives for the site. For example, SQRTs could be set at mean PEC-Qs ≤ 0.1 if the site management goal is to provide a high level of protection for sediment dwelling organisms. Alternatively, the SQRTs could be set at a mean PEC-Q of 0.6 if the immediate goal for the site is to reduce the potential for acute toxicity and permit natural recovery processes to further reduce contaminant concentrations. In addition, SQTs and evaluations of their predictive ability provide information that may be used to evaluate the costs and benefits associated with various remediation options.

For the Minnesota portion of the St. Louis River AOC, an internal MPCA group composed of technical, remediation, and policy and planning staff need to formulate a policy for using SQTs for sediment management activities. This policy should be developed with stakeholder input from the Natural Resource Trustees (which includes MPCA, MDNR, WDNR, NOAA, U.S. Fish and Wildlife Service, and Fond du Lac Band staff), St. Louis River CAC, Harbor Technical Advisory Committee, and concerned citizens. Discussions with the WDNR, and perhaps an interagency agreement with them, would be useful to ensure the SQTs are used in a consistent manner throughout the St. Louis River AOC. The MPCA Commissioner and the Citizens Board of the MPCA will make final decisions on the application of numerical SQTs as SQRTs, along the Minnesota side of the St. Louis River AOC.

For the USX and Interlake/Duluth Tar Superfund sites, the remediation requirements for these sites may involve the use of:

- an applicable or relevant and appropriate requirement (ARAR);
- a preliminary remedial action objective; and
- a preliminary remediation goal.

The Level I and Level II SQTs, as well as mean PEC-Qs and biological effects data, may be utilized by the MPCA and Natural Resource Trustees (with stakeholder input) to develop remediation requirements for these sites. Although ARARs have been established based on Minnesota Department of Health (MDH) drinking water criteria, surface water criteria, and acceptable human health carcinogenic risks of one person in 100,000 (i.e.,10^{-5}), ARARs have yet to be established for ecological risk. As discussed in the previous section, SQTs can be applied in the ERA framework and can contribute to the development of ARARs. In addition, the SQTs can be utilized with bioeffects and tissue residue data to develop preliminary remedial action objectives and remediation goals that are protective of aquatic life (i.e., benthic invertebrates). The process of developing remediation requirements for the Interlake/Duluth Tar Superfund site has recently begun. The ARARs are not negotiable with the PRPs unless they apply for a technical impracticability waiver (e.g., a waiver for meeting mixing zone requirements during remedy implementation). Any development of sediment-based ARARs for PAH compounds will need to take into consideration the phototoxicity of PAHs in shallow water areas.

CHAPTER 8

SUMMARY AND RECOMMENDATIONS

The St. Louis River AOC provides substantial social, economic, and cultural benefits to the residents of northeastern Minnesota and Superior, Wisconsin. The area also provides important habitats for a wide variety of aquatic organisms and aquatic-dependent wildlife species. Concerns over environmental quality conditions prompted the designation of the lower St. Louis River as one of 43 Great Lakes Areas of Concern, in part due to degraded sediment quality in portions of the watershed. In total, 12 confirmed and possible use impairments have been documented in the study area. Restoration of these beneficial uses will be expedited through the development and implementation of a three-phase RAP for the area.

To support the RAP process, an ecosystem-based approach to the assessment and management of sediment quality conditions is presented in this document. The recommended framework for ecosystem-based sediment quality management consists of four main elements, including:

- identification and assessment of issues and collation of the existing ecosystem knowledge base;
- development and articulation of ecosystem health goals and objectives;
- selection of ecosystem health indicators (including specific metrics and targets); and,
- implementation of directed research and monitoring.

This framework is intended to support sound management decisions to help protect, maintain, restore, and enhance ecosystem health. When applied to sediment quality management, this framework is intended to provide a basis for maintaining and restoring the conditions necessary to protect sediment-dwelling organisms, wildlife, and human health.

Numerical SQTs are required to support the assessment, management, and remediation of contaminated sediments in the St. Louis River AOC. In total, eight distinct approaches to the development of SQTs were evaluated during this investigation. The results of this evaluation were used to recommend a tiered strategy for establishing Level I and Level II SQTs for the protection of aquatic organisms. Using the tiered strategy, SQTs are derived preferentially using the consensus-based approach (MacDonald *et al.* 2000a,b). Sediment quality targets from other jurisdictions are utilized when insufficient site-specific data are available to support the consensus-based approach (CCME 1999 and NYSDEC 1999). These SQTs were evaluated and found to provide a reliable basis for classifying sediments as toxic and non-toxic in the St. Louis River AOC. SQTs for the protection of wildlife and human health were adopted from the state of New York (NYSDEC 1999).

Guidance on the uses of numerical SQTs was also developed as part of this investigation. The recommended applications of the numerical SQTs for assessing contaminated sediments in the study area include: designing monitoring programs; interpreting sediment chemistry data, conducting ecological risk assessments, and developing SQRTs. Each of these uses of the SQTs were described in this document.

Based on the results of this investigation, the following recommendations are offered to support sediment quality assessment activities in the St. Louis River AOC:

- Develop indicators, metrics, and targets for the other components (e.g., benthos) of the aquatic ecosystem to support full implementation of ecosystem-based management.

- Determine natural background concentrations of metals and PAHs in sediments from the study area. A reference element approach is recommended for determining background concentrations of total metals (after Schropp *et al.* 1990).

- Determine contemporary background concentrations of the substances that are subject to long-range transport in the atmosphere (i.e., PCBs, organochlorine pesticides, dioxins and furans, mercury, etc.) and in sediments (i.e., at unimpacted sites).

- Further evaluate the recommended SQTs for the protection of sediment-dwelling organisms using the results of longer-term toxicity tests (i.e., 28- to 42-day tests with the amphipod, *Hyalella azteca*), as the data become available for sites in the St. Louis River AOC.

- Conduct an evaluation of bioaccumulation-based SQTs that have been adopted from other jurisdictions.

- Establish tissue residue guidelines for the protection of wildlife and/or critical body burdens in sediment-dwelling organisms for bioaccumulative COCs.

- In consultation with the St. Louis River CAC, develop a geographic information system (GIS)-compatible database to support the compilation and use of all available sediment-related information for the study area. The MPCA has obtained GLNPO grant number GL975363-01 to develop a GIS-based contaminated sediment database for the St. Louis River AOC. This new project will be completed by September 30, 2002.

- Incorporate the effects-based and bioaccumulation-based SQTs, as well as the other indicators of sediment quality conditions, into the RAP and other decision-making processes to the St. Louis River AOC.

Implementation of the aforementioned recommendations will depend on MPCA, MDNR, WDNR, and Fond du Lac Band management priorities for the St. Louis River AOC, as well as on securing local, state, and/or federal funds to carry out these recommendations. In addition, input from two other natural resource trustees (i.e., U.S. Fish and Wildlife Service and NOAA) for two Superfund sites in the Duluth Harbor must be taken into consideration for sediment-related actions at these sites.

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