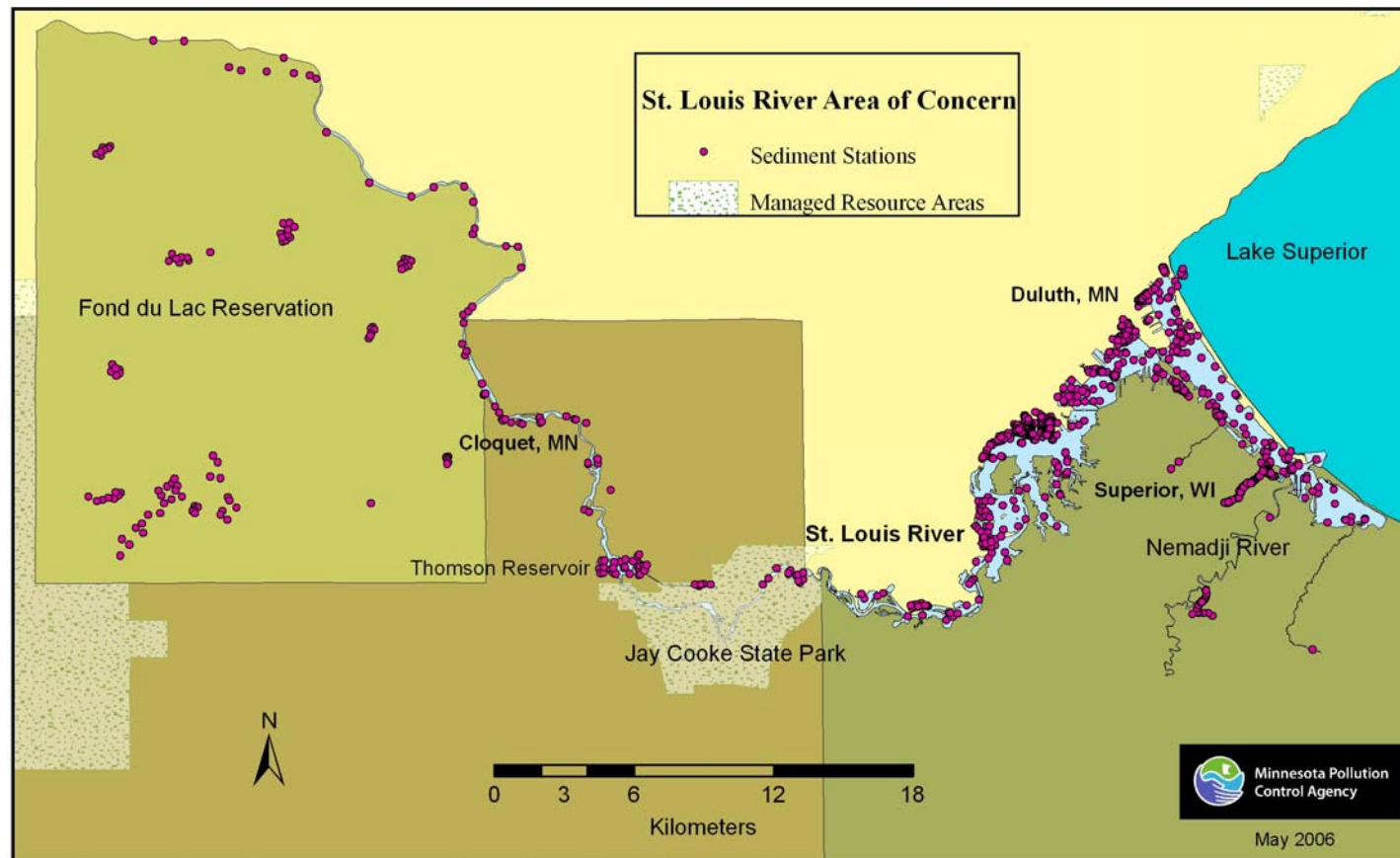


# Sediment Quality Conditions in the Lower St. Louis River, Minnesota/Wisconsin

June 2006

MPCA Document #  
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## Why Are We Concerned About Contaminated Sediments?

The lower St. Louis River has special significance due to its geographic boundary shared by Minnesota and Wisconsin, proximity to Lake Superior, and economic, social, and recreational importance to the area. In particular, this waterway provides critical habitat to benthic invertebrates (bottom-feeding organisms), fish, and waterfowl species and provides an economic venue for Great Lakes shipping and business in the Duluth-Superior Harbor. Economic development of this area over the past 130 years has contributed a mixture of contaminants to this waterway, including polycyclic aromatic hydrocarbons (PAHs), mercury and other metals, and polychlorinated biphenyls (PCBs). Some of these contaminants have accumulated in the sediments over time, resulting in concern about their potential ecological and human health effects.

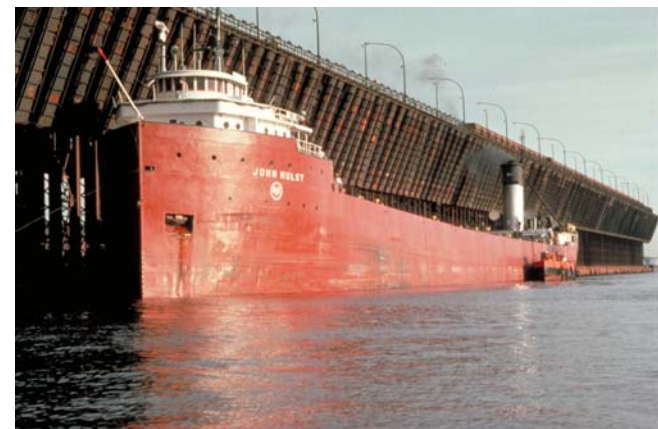
Contaminated sediments contribute to fish consumption advisories, restrictions on dredging, and habitat impairments to bottom-feeding organisms in the lower St. Louis River. These use impairments were a



The Duluth-Superior Harbor supports many recreational, commercial, and light industrial uses.

factor in the International Joint Commission's decision to designate this waterway as one of 43 Areas of Concern (AOCs) in the Great Lakes basin in 1987. The boundaries of this AOC include 72 nautical kilometers from Cloquet, Minnesota to the Duluth, Minnesota and Superior, Wisconsin entries to Lake Superior. Several sediment quality and fish tissue studies have been conducted to delineate the extent and magnitude of contaminants of potential concern and to assess the potential for ecological and human health effects. Sediment quality issues in this AOC are of interest to local and state agencies in Minnesota and Wisconsin, as well as to federal agencies, tribal groups, responsible parties, nonprofit groups, and concerned stakeholders.

A number of ecosystem health indicators have been selected to support the assessment of sediment quality conditions within the lower St. Louis River AOC, including sediment chemistry, sediment toxicity, benthic invertebrate community structure, tissue chemistry, sediment quality targets, physical parameters, and biomarkers in fish. Investigations conducted using data on multiple indicators provide a weight-of-evidence approach for assessing the effects of contaminated sediments on the beneficial uses of this aquatic ecosystem



In 2004, the principal cargoes from the Duluth-Superior Harbor included iron ore (43%), coal (41%), and grain (6%).

## Development of a Sediment Quality Database

As part of the International Joint Commission's Remedial Action Plan process for the St. Louis River AOC, stakeholders identified a need to compile sediment quality data collected from the lower St. Louis River in a database format for mapping and evaluation purposes. The Minnesota Pollution Control Agency (MPCA) and its collaborators developed an innovative set of tools to assemble several types of sediment quality data in a database and to plot features of these data on maps in relation to GIS-watershed data (e.g., contamination sources). Progress on the database has been made through several phases as grants were obtained to continue the database. Phase IV of the database, which emphasized adding data from the Wisconsin side of the AOC, was recently completed with the collaboration of the St. Louis River Citizens Action Committee, Wisconsin Department of Natural Resources, and Exa Data & Mapping Services, Inc.

## Assessment of Sediment Quality

The MPCA will complete a technical report on sediment quality conditions in the lower St. Louis River AOC by June 30, 2006. This pamphlet provides highlights of the technical report and shows how a weight-of-evidence approach can be used to identify regions of the lower St. Louis River AOC that present low, medium, and high risks to benthic invertebrates living in the sediments. These organisms are vital to the integrity of aquatic and nearshore ecosystems. In addition, they form part of the lower food chain for economically important species like sport fish and waterfowl.

Sediments in the lower St. Louis River AOC usually contain a mixture of contaminants (e.g., PAHs, PCBs, mercury, and other metals). These contaminants may not always be bioavailable to benthic invertebrates living in the surface sediments. In addition, contaminants in deeper sediments are permanently buried (i.e., cannot be resuspended due to wave action, currents, or bioturbation from aquatic worms), and benthic organisms are not exposed to them.



a)



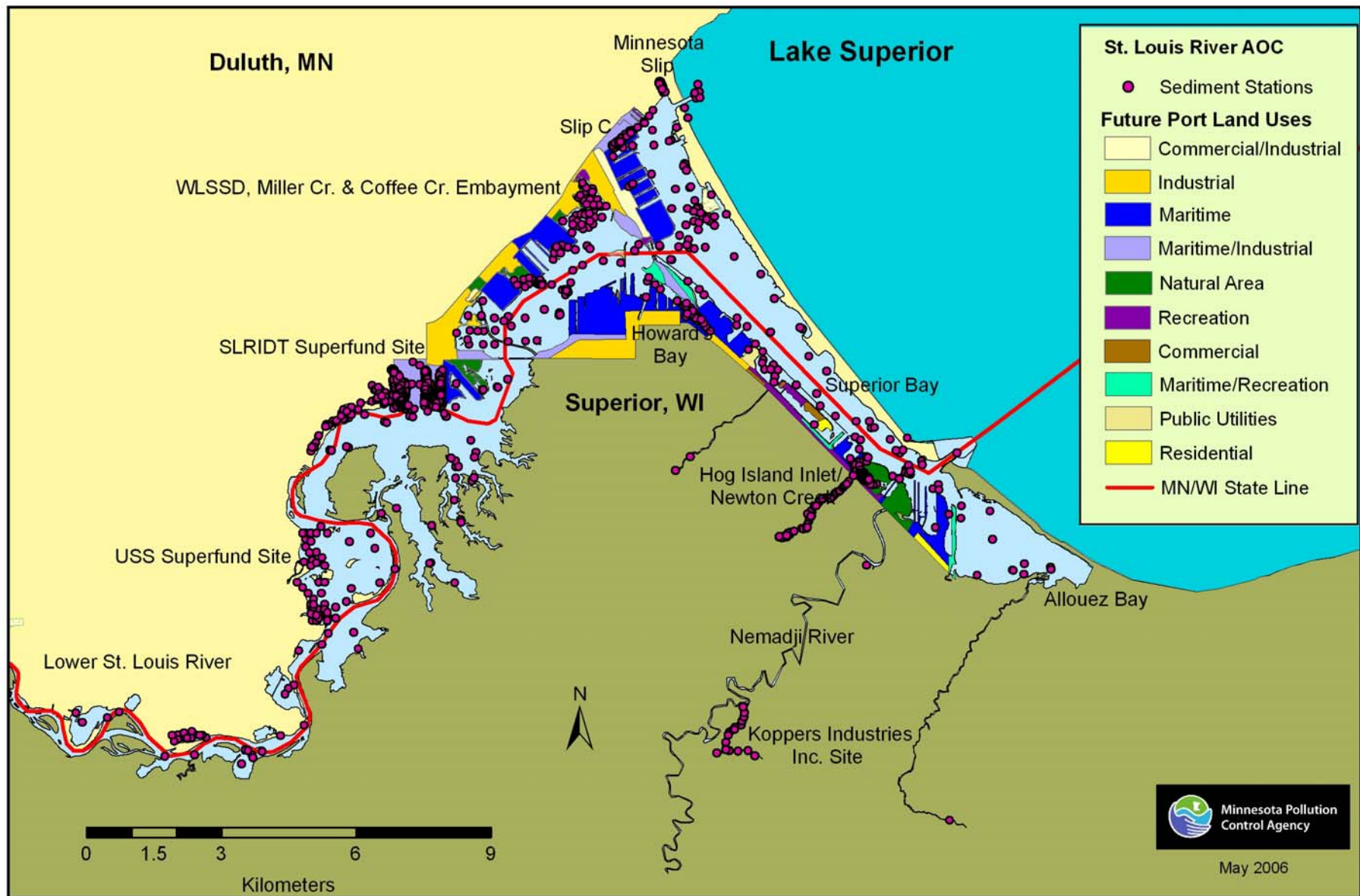
b)



c)

Collection of sediment samples from the Duluth Harbor: a) collection of a Vibrocorer sediment sample and b/c) processing of benthic samples.





This map shows sediment stations in the lower St. Louis River AOC in relation to future land uses along the Duluth, Minnesota and Superior, Wisconsin waterfronts. The Phase IV sediment quality database contains data from 1,635 stations, ranging from small lakes on the Fond du Lac Reservation (see cover page map) to the Duluth and Superior entries to Lake Superior. The Hog Island Inlet/Newton Creek site was cleaned up during fall 2005, and the sediment stations shown for this site were sampled prior to remediation.

## Use of Mean Probable Effect Concentration Quotients (PEC-Qs) for Assessing Sediment Quality

Mean PEC-Qs provide a sediment assessment tool that distills data from a mixture of contaminants into one unitless index. The table below shows the number of chemical classes used in the calculation of mean PEC-Qs for sediment samples in the Phase IV sediment quality database. At mean PEC-Q values less than 0.1, harmful effects on benthic invertebrates are unlikely to be observed. At mean PEC-Qs greater than 0.6, harmful effects on sediment-dwelling organisms are likely to be frequently or always observed.

### Number of Chemical Classes Used in the Calculation of Mean PEC-Qs for Sediment Samples Included in the Database

| Depth Interval     | Number of Chemical Classes |     |    |
|--------------------|----------------------------|-----|----|
|                    | 1                          | 2   | 3  |
| 0-30 cm, inclusive | 486                        | 468 | 83 |
| >30 cm, inclusive  | 495                        | 177 | 28 |
| Other Depths       | 144                        | 178 | 76 |

Chemical classes include mean metals (arsenic, cadmium, chromium, copper, lead, nickel, and zinc), total PAHs, and total PCBs

The mean PEC-Qs provide a way to compare sediment quality between sites (see below table). Due to the non-normal distribution of mean PEC-Qs in the data set, it is more appropriate to examine summary median values rather than arithmetic average values. In interpreting the below data, one must consider whether other contaminants of concern contribute to risk and whether the extent and magnitude of contamination has been adequately characterized at a site.

### Distribution of Mean PEC-Qs in Surface Sediments (i.e., upper 30 cm) of Selected Locations with More than Twenty Sediment Samples

| Location Description                     | N   | 10th Percentile | Median            | 90th Percentile    |
|--|-----|-----------------|-------------------|--------------------|
| Hog Island Inlet/Newton Creek*           | 189 | 0.054           | <i>0.19</i>       | <i>0.39</i>        |
| Howard's Bay                             | 30  | <i>0.14</i>     | <i>0.37</i>       | <b><i>0.61</i></b> |
| Lower St. Louis River                    | 46  | 0.051           | <i>0.16</i>       | <i>0.46</i>        |
| Minnesota Slip                           | 62  | <i>0.3</i>      | <b><i>1.1</i></b> | <b><i>1.9</i></b>  |
| Slip C                                   | 48  | 0.066           | <i>0.49</i>       | <b><i>1.2</i></b>  |
| SLRIDT Superfund Site                    | 214 | <i>0.19</i>     | <b><i>1.3</i></b> | <b><i>21.4</i></b> |
| Superior Bay                             | 41  | 0.013           | <i>0.11</i>       | <i>0.28</i>        |
| Thomson Reservoir                        | 23  | 0.082           | <i>0.15</i>       | <i>0.18</i>        |
| USS Superfund Site                       | 36  | 0.028           | <i>0.17</i>       | <b><i>4.8</i></b>  |
| WLSSD, Miller Cr. & Coffee Cr. Embayment | 42  | 0.021           | <i>0.33</i>       | <b><i>0.80</i></b> |
| St. Louis River AOC**                    | 910 | 0.052           | <i>0.25</i>       | <b><i>2.3</i></b>  |

\* Pre-remediation data for this site; sediment remediation was completed November 2005.

\*\* Includes pre-remediation data for Hog Island Inlet and Newton Creek.

PEC-Q = probable effect concentration quotient; AOC = Area of Concern; N = number of sediment samples; SLRIDT = St. Louis River Interlake/Duluth Tar; USS = U.S. Steel; Cr. = creek; WLSSD = Western Lake Superior Sanitary District.

Values in italics and yellow shading exceed the Level I sediment quality target (SQT) of 0.1; Values in bold italics and orange shading exceed the Level II SQT of 0.6 for mean PEC-Qs.

## Frequency of Low, Moderate, and High Risk Samples in Surface Sediments from the Lower St. Louis River AOC

| Location Description                     | N   | Percentage of Samples Within<br>Ranges of Mean PEC-Qs |                          |                |
|--|-----|---|--------------------------|----------------|
|  |     | <0.1<br>(Low)   | 0.1 to 0.6<br>(Moderate) | >0.6<br>(High) |
| Hog Island Inlet/Newton Creek*           | 189 | 19  | 78                       | 3              |
| Howard's Bay                             | 30  | 7   | 83                       | 10             |
| Lower St. Louis River                    | 46  | 33  | 61                       | 6              |
| Minnesota Slip                           | 62  | 2   | 11                       | 87             |
| Slip C                                   | 48  | 15  | 46                       | 39             |
| SLRIDT Superfund Site                    | 214 | 4   | 25                       | 71             |
| Superior Bay                             | 41  | 46  | 54                       | 0              |
| Thomson Reservoir                        | 23  | 30  | 70                       | 0              |
| USS Superfund Site                       | 36  | 30  | 42                       | 28             |
| WLSSD, Miller Cr. & Coffee Cr. Embayment | 42  | 24  | 55                       | 21             |
| St. Louis River AOC**                    | 910 | 21  | 51                       | 28             |

\* Pre-remediation data for this site; sediment remediation was completed November 2005.

\*\* Includes pre-remediation data for Hog Island Inlet and Newton Creek.

AOC = Area of Concern; N = number of sediment samples; PEC-Q = probable effect concentration quotient; SLRIDT = St. Louis River Interlake/Duluth Tar; USS = U.S. Steel; Cr. = creek; WLSSD = Western Lake Superior Sanitary District.

From the above table, Minnesota Slip and the SLRIDT Superfund site have the greatest proportion of surface sediments likely to present a high risk to benthic invertebrates. Sediment remediation of the SLRIDT Superfund site will begin June 2006 and is expected to be completed by 2009. A focused feasibility study of remediation options for Minnesota Slip was completed November 2005. Sediments from Superior Bay present the lowest risk to benthic invertebrates; part of this bay is regularly dredged to maintain the federal navigation channel. Howard's Bay has the highest percentage of

moderately contaminated surface sediments. The pre-remediation data for Hog Island Inlet and Newton Creek also indicates this site had a high percentage of moderately contaminated sediments. Diesel range organics and alkylated PAHs were other contaminants of concern at this site that are not considered in the calculation of mean PEC-Qs. Sediment remediation of Hog Island Inlet/Newton Creek was completed November 2005, and post-remediation sediment chemistry data were not available in time for inclusion in the Phase IV sediment quality database.



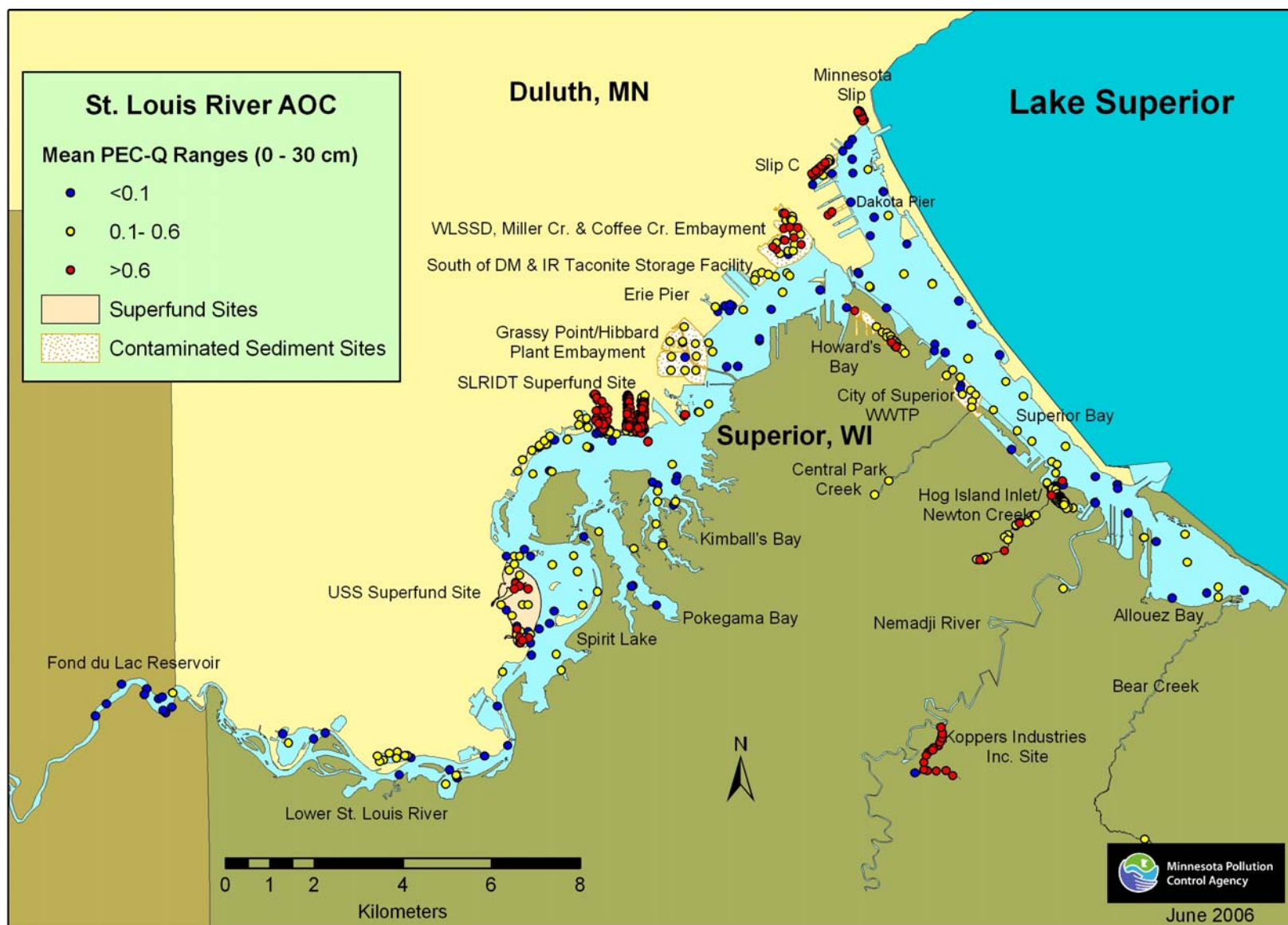
a)



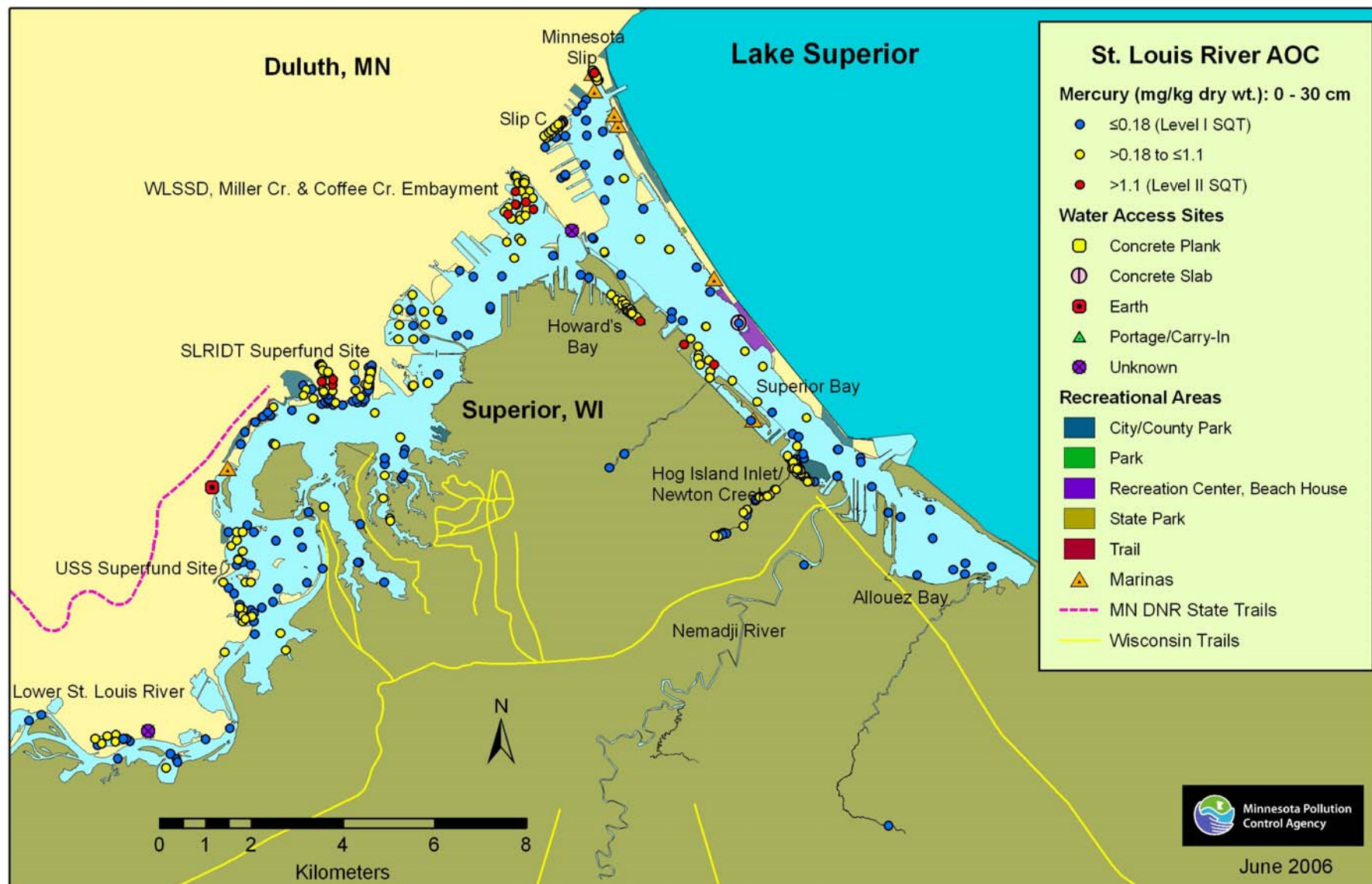
b)

Sediment remediation of (a) Hog Island Inlet and (b) Newton Creek in Superior, WI during the fall of 2005.





Distribution of mean PEC-Q values in the surface sediments of the lower St. Louis River AOC. The data for Hog Island Inlet and Newton Creek represent pre-remediation conditions (i.e., prior to fall 2005). The applicability of the mean PEC-Qs in sediment assessments is increased when used in conjunction with other tools that provide lines of evidence about sediment quality, including: sediment chemistry and geochemical characteristics, sediment toxicity, bioaccumulation tests, and benthic invertebrate community assessments.



Distribution of mercury in surface sediments of the lower St. Louis River AOC. Due to the unique chemical characteristics of mercury, it is not included in the calculation of mean PEC-Qs. Mercury is a potent neurotoxin, and one of the ways people can be exposed to it is through the consumption of contaminated fish. Fish consumption is restricted in the St. Louis River AOC because of mercury contamination. The Hog Island Inlet/Newton Creek site was cleaned up during fall 2005; the mercury data shown in this map were collected prior to remediation.



## Sediment Toxicity Tests

Sediment toxicity tests are used to demonstrate whether the sediment samples cause significant acute (e.g., survival) or chronic (e.g., growth, reproduction) toxicity to benthic organisms compared to reference or control sediments. These tests are usually done in a laboratory under controlled conditions using test organisms that have been cultured for this purpose. The amphipod, *Hyaletta azteca*, and the midge, *Chironomus dilutus* (formerly *tentans*) are common test organisms; amphipods and midges are also found in the native benthic invertebrate community of the St. Louis River AOC.



←*H. azteca*



←*C. dilutus*

The Phase IV sediment quality database contains data on 1,464 toxicity test endpoints. Data were queried from the database to obtain toxicity test data that had matching sediment chemistry results in the form of mean PEC-Qs. The term “matching” is used to mean the sediment sample was homogenized and split in the field so that part of the sample was used for sediment toxicity testing and the remainder for sediment chemistry analyses. Sediment samples were designated as toxic if one or more toxicity test endpoints were significantly depressed from the responses observed in the reference or control sediment.

The incidence of toxicity for the mean PEC-Q ranges shown in the accompanying table was calculated. The incidence of toxicity was low (i.e., 7.3%) when the concentrations of sediment-associated contaminants were low (i.e., as indicated by mean PEC-Qs of  $\leq 0.1$ ). Toxicity increased as the sediments became more contaminated with

the classes of chemicals used to calculate mean PEC-Q values. The incidence of sediment toxicity was 100% when the mean PEC-Qs exceeded five; however, these results should be evaluated with caution since this observation was only based on nine samples.

Sediments in the St. Louis River AOC generally contain complex mixtures of contaminants. The results of this evaluation indicate that, collectively, the mean PEC-Qs provide a reliable basis for classifying sediments as toxic or not toxic. For this reason, assessments of sediment quality conditions relative to the protection of sediment-dwelling organisms should be conducted using mean PEC-Qs.

### Incidence of Sediment Toxicity in the St. Louis River AOC for Selected Mean PEC-Q Ranges

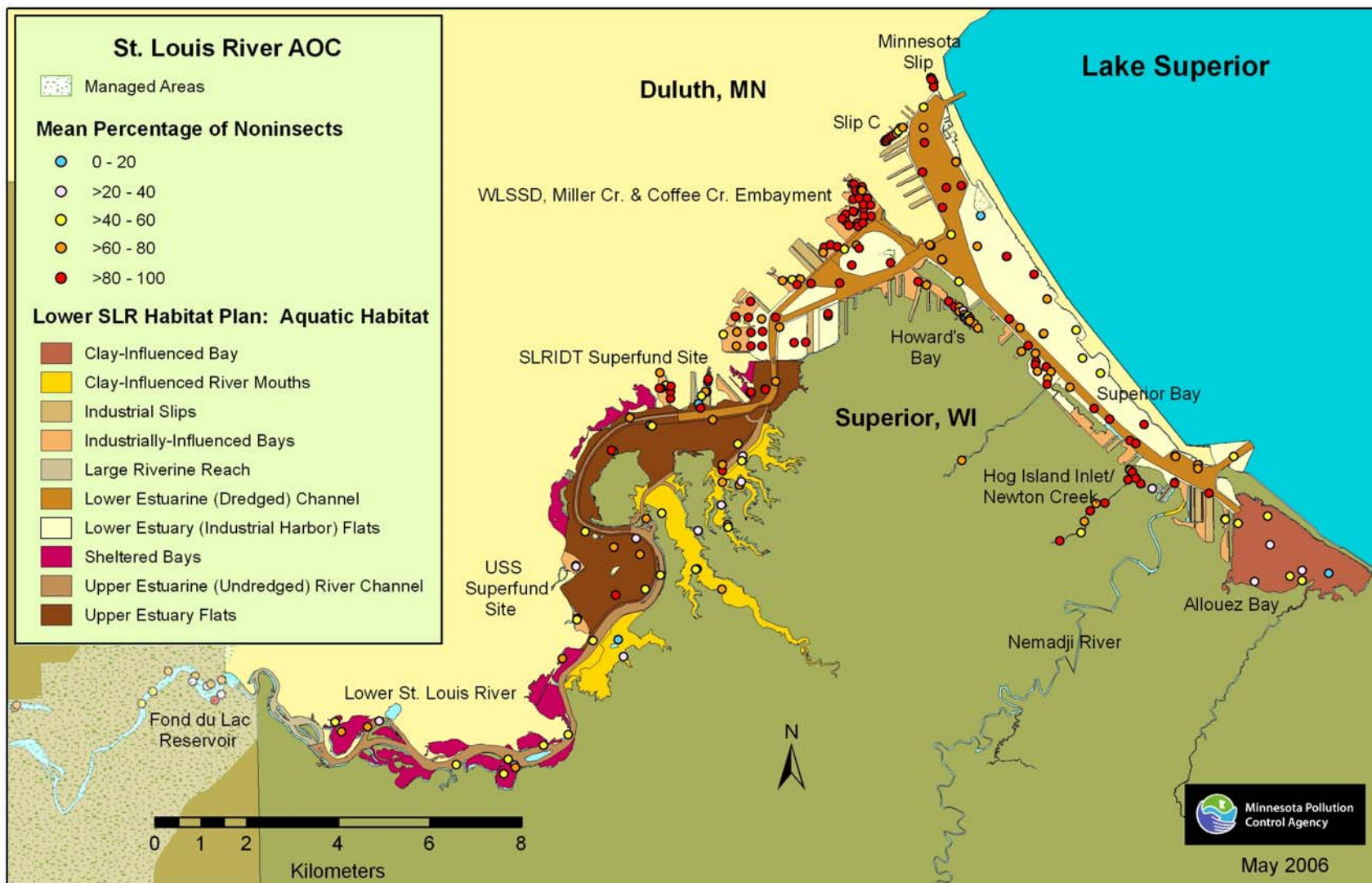
| Mean PEC-Q<br>Range     | N   | Incidence of Toxicity (%)                                 |
|-------------------------|-----|---|
|                         |     | All Standard Toxicity Tests<br>(Excluding Bacteria Tests) |
| $\leq 0.10$             | 55  | 7.3   |
| $> 0.10$ to $\leq 0.50$ | 126 | 27.0  |
| $> 0.50$ to $\leq 1.0$  | 24  | 45.8  |
| $> 1.0$ to $\leq 5.0$   | 26  | 61.5  |
| $> 5.0$                 | 9   | 100   |
| Overall                 | 240 | 30.8  |

PEC-Q = probable effect concentration quotient

N = number of stations



This map shows toxic and non-toxic sediments in the lower St. Louis River AOC for samples with matching sediment chemistry results. The most toxic sediments occurred at the two Superfund sites, resulting in the death of all test organisms in some cases. Sediments sampled from the federal navigation channel were not significantly toxic to test organisms. Dredge material from this channel is used for other beneficial uses, such as replenishing eroded beaches on the Lake Superior side of Minnesota Point. The sediment toxicity data for Hog Island Inlet and Newton Creek represent pre-remediation conditions (i.e., prior to fall 2005).



This map shows the percentage of noninsects in the lower St. Louis River AOC. Noninsects include benthic organisms such as pollutant-tolerant aquatic worms (oligochaetes), fingernail clams, and amphipods. Oligochaetes are especially prevalent in the sediments of Minnesota Slip, Slip C, the embayment near the Western Lake Superior Sanitary District (WLSSD) and under pre-remediation conditions at Hog Island Inlet and Newton Creek; these organisms also survive well under low oxygen conditions in slow moving water. On an AOC-wide basis, physical habitat factors affect the composition of the benthic invertebrate community the most. However, benthic invertebrates have been found to bioaccumulate PAHs in their tissues from several locations within the Duluth-Superior Harbor.



The technical report for this project will be completed by June 30, 2006. It will be available in PDF format on the MPCA's Contaminated Sediment Web page under the section heading for the Phase IV GIS-based sediment quality database project (see: <http://www.pca.state.mn.us/water/sediments/studies-stlouis.html#assessment>).

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**Photos:**

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Page 2: Judy Crane

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Page 8: left, U.S. Department of Agriculture; right, University of Wisconsin-Milwaukee Marine & Freshwater Biomedical Sciences Center

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