
Name of Organization: University of Minnesota - Duluth

Type of Organization: College or University

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Project Title: Mercury Speciation of Sediments: Lower St. Louis River

Project Category: Contaminated Sediments

Rank by Organization (if applicable): 0

Total Funding Requested (\$): 83,150 **Project Duration:** 1.5 Years

Abstract:

The University of Minnesota - Duluth proposes to conduct a survey of sediments from the lower St. Louis River for the purpose of analyzing them for mercury species present. The species of interest include Hg⁰, Hg⁺⁺, monomethyl, dimethyl, monophenyl, and diphenyl forms. Analyses will be performed on a subset of archived samples derived from a previous project supported by GLNPO and new samples that will be collected from areas of recent interest in the estuary. Existing knowledge, which is primarily for total mercury, is insufficient for assigning potential risks to toxicity/bioaccumulation. Information on mercury species will also provide a means to "fingerprint" the sediments for the purpose of identifying past (identifying original sources) and future contaminant movements within the estuary and out to Lake Superior. The lower St. Louis River offers an ideal case for demonstrating source identification because of the variety of historical mercury sources for that area.

Geographic Areas Affected by the Project

States:

<input type="checkbox"/> Illinois	<input type="checkbox"/>	New York
<input type="checkbox"/> Indiana	<input type="checkbox"/>	Pennsylvania
<input type="checkbox"/> Michigan	<input checked="" type="checkbox"/>	Wisconsin
<input checked="" type="checkbox"/> Minnesota	<input type="checkbox"/>	Ohio

Lakes:

<input checked="" type="checkbox"/> Superior	<input type="checkbox"/>	Erie
<input type="checkbox"/> Huron	<input type="checkbox"/>	Ontario
<input type="checkbox"/> Michigan	<input type="checkbox"/>	All Lakes

Geographic Initiatives:

<input type="checkbox"/> Greater Chicago	<input type="checkbox"/> NE Ohio	<input type="checkbox"/> NW Indiana	<input type="checkbox"/> SE Michigan	<input type="checkbox"/> Lake St. Clair
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Primary Affected Area of Concern: St. Louis River, MN

Other Affected Areas of Concern: Project concepts would be applicable to all Areas of Concern where mercury contamination has been identified as a problem

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

Several past studies have assessed total mercury levels in sediments of the lower St. Louis River where many "hot spots", both buried and surficial, have been identified (Sorensen et al., 1999; Crane, 1999; Shubauer-Berigan and Crane, 1997). However, virtually no data is available regarding mercury speciation in the sediments for that region. Knowledge of sediment mercury species in the lower St. Louis River, as well as in other Areas of Concern, would be beneficial for two reasons. The first is that the toxicity and bioaccumulation potentials of mercury in sediments depends on which mercury forms are present. For example, methylmercury is about 1,000 times more bioaccumulatable and toxic than elemental mercury (Hg⁰). High concentrations of methylmercury in sediments have been reported for well publicized contaminated sites such as Minimata Bay and others (Ebinhaus et al., 1999). Thus, priorities on which sediments to remediate, and to what degree, will likely change given an understanding of the toxic forms present. Data on total mercury is fine for defining areas of contamination but is of limited use in evaluating environmental consequences.

The second reason is that it would be very useful to provide a mechanism by which mercury contamination could be "fingerprinted". This could allow one to determine the mercury source(s), as it has been demonstrated that different industrial sources have contaminated sediments and soils with different mercury forms (Hintelmann et al., 1995). For example, in the past, phenylmercuric acetate was used as a slimicide in the paper products industry. Thus, the presence of the phenylmercuric form would indicate contributions from such a source. "Fingerprinting" would also allow future monitoring of mercury transport throughout the estuary as "hot-spots" release contaminated material by storm action or by man-induced disturbances. The lower St. Louis River offers an ideal case for demonstrating source identification because of the variety of historical mercury sources for that area.

Proposed Work Outcome:

This project will begin by selecting segments from archived cores for the analyses of mercury species. In 1995 approximately 80 sediment cores were taken from the lower reservoirs (Fond du Lac, Forbay, Thomson, Scanlon, Potlatch, and Knife Falls) of the St. Louis River (Sorensen et al., 1999). These cores were subdivided into 10 cm segments, analyzed for total mercury, and stored in ziploc bags at 4 degrees C. Approximately 800 segments are still available for further analyses. Approximately 200 core segments will be selected for mercury species analyses based on sampling location and existing data such as total mercury concentration, organic carbon content, and particle size distribution. Some new samples, taken at locations which overlap 1995 sampling sites, will be required to document effects of core storage on mercury species composition.

Sediments will be analyzed using methanolic KOH digestion/extraction followed by ethylation, gas chromatography

separation and atomic emission detection. The main species of interest include Hg⁰, Hg⁺⁺, monomethyl, dimethyl, monophenyl, and diphenyl forms, though other organic forms useful for "fingerprinting" are likely (Hintelmann et al., 1995) and will be documented. These species will be characterized in terms of location, strata, and relationships with other measured parameters (e.g. total mercury and organic carbon).

After assessing Hg-species data relating to archived cores, new cores will be collected primarily from areas not included in the archived core set. Locations for new sampling efforts will be in the St. Louis River estuary near areas of recent interest (e.g. the United States Steel site, Interlake Steel Iron site, and the Western Lake Superior Sanitary District discharge). In addition, "background" samples will be collected from a lake or lakes in the St Louis River watershed in order to characterize mercury species associated with precipitation derived contamination. Approximately 100 core segments (10 cm increments) will be analyzed for this effort.

The final report will include an assessment of which areas (and sediment strata) are more (or less) toxic than what existing total mercury data might suggest. Important species variations unique among contamination sources will also be documented.

Project Milestones:	Dates:
Project Start	10/2000
Methods Confirmation	12/2000
Analyses of Previously Collected Samples	06/2001
New Sample Collection	09/2001
Analyses of New Samples	02/2002
Draft Report	03/2002
Final Report	05/2002
Project End	05/2002

Project Addresses Environmental Justice

If So, Description of How:

Project Addresses Education/Outreach

If So, Description of How:

Results of this project will be used to educate those involved with the Sediment Contamination Work group of the St. Louis river Remedial Action Plan (RAP) and the Citizens Action committee of the RAP. Results will be published in peer review literature.

Project Budget:

	Federal Share Requested (\$)	Applicant's Share (\$)
Personnel:	46,281	6,200
Fringe:	11,711	1,700
Travel:	0	0
Equipment:	0	0
Supplies:	1,500	0
Contracts:	6,500	0
Construction:	0	0
Other:	0	0
Total Direct Costs:	65,992	7,900
Indirect Costs:	17,158	2,054
Total:	83,150	9,954
Projected Income:	83,150	9,954

Funding by Other Organizations (Names, Amounts, Description of Commitments):

The Fond du Lac Band will provide technical in-kind assistance in selecting samples of interest to be analyzed. They will also provide in-kind assistance in obtaining background sediment samples from a lake or lakes located within the reservation.

Description of Collaboration/Community Based Support:

Collaborators will be:

- 1) the University of Wisconsin - Superior, who will perform sampling within the estuary; and
- 2) the Fond du Lac Indian Band, who will assist in selecting archived samples for analyses and assist in sampling of a background lake or lakes. The Fond du Lac Band and the University of Minnesota - Duluth jointly hold responsibility for the archived sediment samples.