1993-1995 Research Project Abstract
For the period ending June 30, 1995
This project was supported by the Environment and Natural Resources Trust Fund.

Title: Mercury Reduction In Fish - Continuation
Program Managers: Drs. George R. Rapp Jr. and Gary E. Glass
Organization: University of Minnesota, Duluth
Legal Citation: M.L. 93 Chpt. 172, Sect. 14, Subd. 11(c)
Appropriation Amount: $200,000

STATEMENT OF OBJECTIVES: The goals of this project were to: 1) investigate mercury sources and bioavailability mechanisms in contaminated aquatic systems by identifying source-bioaccumulation relationships and measuring bioaccumulation effects of selected treatments in shoreline mesocosms; and, 2) conduct pilot studies to evaluate mechanisms for reducing mercury residue levels in fish and fish food chain organisms, and aid in developing future mitigative methods for reducing fish mercury contamination in lakes and rivers while long-term reductions in mercury usage and emissions are being accomplished.

RESULTS:
Mercury Source Identification. An investigation of mercury sources within the lower St. Louis River watershed revealed: 1) Several small streams entering the St. Louis River Estuary exhibited elevated mercury concentrations (5-12 ng/L); 2) high mercury concentrations (1- 2 ppm) were found in deeper sediment strata (up to 2m depth; corresponding to 1940s-1960s deposits) in five of the six lower St. Louis River reservoirs; 3) four of the six reservoirs exhibited areas with high mercury concentrations within surface sediment bioturbation strata; and 4) analyses of samples from a regional precipitation monitoring network showed a significant regional contribution, and wet deposition to be a major source of methylmercury inputs to aquatic ecosystems. Methyl mercury concentrations in rain were similar to those found in ambient water at the study sites.

Mercury Bioaccumulation Mechanism Studies. A total of 25 shoreline pilot test areas composed of 21 enclosed shoreline mesocosms (4m x 10m) and 4 nonenclosed adjacent zones, were maintained at two study sites: at Indian Point (70th Avenue West, Duluth) on the St. Louis River Estuary; and Sand Point/Crane Lake, SW end. Twenty-nine replicated pilot treatment tests were conducted over four years using mesocosms to measure mercury bioaccumulation effects and mechanisms for reducing mercury bioaccumulation. The experimental framework of the pilot studies followed two overall mechanisms for mercury reduction: 1) decreasing the exposure/bioavailability of the toxic form of mercury; and 2) reducing toxic contributions/loadings of mercury to the aquatic system.

Evaluations of results were assessed based on the hypothesis that mercury chemical activity was the controlling factor. The results observed included: 1) micronutrient additions of selenite could significantly reduce mercury concentrations in young-of-year (y-o-y) yellow perch (by about 72%) at Sand Point (Crane) Lake and y-o-y black crappie (22%) at the StLRE for additions at the 1 ppb level over 12 weeks; 2) Aquatic vegetation additions increased mercury concentrations in yellow perch and is a significant mechanism for transferring bioaccumulated mercury from one growing season to the next; and 3) An inverse relationship between mercury in forage fish and fish size was observed in some mesocosms, this is the opposite of what is observed for game fish. Further study of this inverse relationship may lead to better understanding mercury bioaccumulation mechanisms and have significant future application for residue reductions. Additional results were found for various mercury binding reagents (including compounds used for poison treatments, i. e. BAL); covering sediment with clean sand; water aeration; wet deposition changes (0x and 2x deposition); mesocosm isolation from ambient water; and water level and temperature variations.

These findings are useful in evaluating bioaccumulation mechanisms and assessing mitigative treatment alternatives for mercury contaminated hot-spots but also indicate that the solution to the wide spread problem is pollution prevention, through the reduction of mercury usage and emissions.

PROJECT RESULTS USE AND DISSEMINATION: Project results have been presented at workshops and conferences including: Heavy Metals Conf., Toronto, Ontario, Sept. 1993; Ecosystems Management Strategies Conf. for the L. Superior Region, Duluth, MN, May 1994; Internat. Conf. on Mercury as a Global Pollutant, Whistler, B. C., July 1994; and Mercury Pollution in the Upper Gt. Lakes Region Conf., Minneapolis, MN, June 1995. Results will be distributed among the following: MN Pollution Control Agency, U. of MN-Duluth, U.S. EPA, the Nat. Biological Survey, Voyageurs National Park, and others. Several journal publications are planned.

Date of Report: July 1, 1995

LCMR Final Report - Detailed for Peer Review - Research

I. Project Title: MERCURY REDUCTION IN FISH - CONTINUATION (PHASE II)

Program Managers: Drs. George R. Rapp Jr. and Gary E. Glass
Agency Affiliation: University of Minnesota, Duluth
Address: Archaeometry Laboratory
214 Research Laboratory Building
10 University Drive
Duluth, Minnesota 55812-2496
Phone: (218) 726-7957

A. Legal Citation: M.L. 93 Chpt. 172, Sect. 14, Subd. 11(c).

Total Biennial LCMR Budget: $200,000

Balance: $0

Appropriation Language as drafted 7/27/92: Subd. 11(c). This appropriation is from the trust fund to the commissioner of the pollution control agency for a contract with the University of Minnesota to complete pilot studies testing mercury reduction in fish for Minnesota waters. A Grant requests to supplement this appropriation must be submitted to the U.S. Environmental Protection Agency and the results reported to the legislative commission on Minnesota resources.

B. LMIC Compatible Data Language: Not applicable.

C. Status of Match Requirement: EPA will continue to provide salary support for Dr. Gary Glass, and ERL-D laboratory facilities including computer access.

II. Project Summary:

A. Fish from many of the lakes in Northeastern Minnesota are restricted from full utilization because of mercury (Hg) contamination in their flesh (up to 5 ppm in large fish). Minnesota is one of 40 states that have issued fish consumption advisories due to high levels of mercury in fish tissue. The sources of mercury contamination come primarily from atmospheric deposition, sediment hot-spots from historical usage, and watershed processes that accelerate the net methylation of mercury making it more bioavailable, and therefore, increasing concentrations up the food chain.

The goal of this project is to investigate mechanisms of mercury bioavailability and develop mitigative methods for reducing fish mercury contamination in lakes and rivers. These

mitigative methods will be used to evaluate the mercury activity or chemical potential hypothesis (Björnberg et al., 1988) and serve to enhance the quality of Minnesota's fish resources in high-use and high-value water bodies while long-term reductions of mercury usage and emissions are being accomplished. Relevant information will be summarized addressing mercury related problems to assist state agencies in determining research priorities.

Field measurements and testing of mercury reduction in fish will be conducted at actual sites showing high levels of mercury bioavailability and contamination. Monitoring mercury levels in biotic compartments (fish, vegetation, and plankton) in enclosed areas and adjacent areas as a function of various treatments applied to each enclosed area will demonstrate the mechanisms involved in the mercury cycle and the effectiveness of various treatments or changed conditions.

B. **Phase I summary**: The first phase of this project was from July 1, 1991 to June 30, 1993. The following is a summary of research completed in Phase I.

B.1. Develop and test methods and means for investigating mercury bioavailability mechanisms of reducing mercury residues in fish and fish food organisms:

Tests of assessment methodology. The testing of littoral (shoreline) enclosure designs necessary for assessing treatment effects on a mesocosm scale in a large lake (Sand Point Lake) and estuary (St. Louis River Estuary) setting was successful. Improved features incorporated in the mesocosm designs (Figure 2) were as follows: 1) commercial dock sections were used to provide a more stable and uniform perimeter for the littoral enclosures; 2) wave and wind barriers were designed and tested to effectively protect the enclosures from damage, and; 3) the Lake Superior seiche action which causes fluctuating water levels (up to 20 cm over an 8 hr period) in the St. Louis River Estuary was accommodated by leaving sufficient slack in enclosure walls so that the water volume in an enclosure remained nearly constant as the ambient water level changed.

Tests of materials. All materials used in the construction and repair of the enclosures, sampling equipment, and equipment used in the administration of experimental conditions were tested for mercury leaching to ensure against mercury contamination. Only those materials and supplies showing non-significant mercury concentration levels were selected for use.

Tests of exposure and assessment techniques. Tests of exposure design and impact assessment protocols yielded the following conclusions: 1) Full growing season tests are the most useful for uptake and growth endpoints. Original plans envisioned standard EPA 30-day testing periods for fish effects, however, a longer time period was needed to resolve responses to treatments when ambient mercury exposure levels are used. In addition, it was concluded that exposure of study fish to the full growing season mercury cycle was crucial toward understanding this phenomena; 2) test

endpoints should use indigenous young-of-year forage fish from the site to be studied. Original plans called for the use of laboratory reared fathead minnows with expectations that they would provide low initial mercury levels (optimal test results resolution). However, initial mercury concentrations for the minnows were higher, due to artificial food sources, than the indigenous forage fish; 3) biweekly water sampling was appropriate for monitoring seasonal fluctuations and the start, middle, and end of the test period were the most appropriate for sampling biota; 4) ecosystem health indicators were included by measuring water quality parameters, including chlorophyll and fish growth (length and weight) rate and condition; and 5) weekly reconnaissance was necessary to ensure enclosure integrity. This included maintaining the seal along the enclosure wall and sediment interface.

B.2. Mercury source identification:

Mercury sources within the lower St. Louis River watershed were characterized by surveys of mercury concentrations in small stream inputs and by mercury analyses of sediment depth profiles from sites in upstream reservoirs. Results (Figure 1a) revealed small stream inputs to the Upper Estuary from the South (WI) are significantly higher in mercury than most of those from the North (MN), and may warrant further investigation.

Sediment core analyses from the Thomson, Forbay, and Fond du Lac Reservoirs indicate substantial mercury contamination in deeper strata coinciding with historical discharges (1940s-1960s). Mercury concentrations were as high as 2000 ppb, 1400 ppb, and 1000 ppb, respectively for these reservoirs. This compares with an average of 174 ppb found in surface sediment from 77 lakes studied in 1990. A wide dispersion of mercury in sediment strata of the Fond du Lac Reservoir indicated that this contamination has undergone significant resuspension and redistribution throughout the years. It was concluded that more samples are needed from the lower St. Louis River reservoirs in order to determine if there are areas where the contaminated sediment is at or near the surface strata. This topic is addressed by additional research discussed under Phase II below.

A companion study managed by the Fond du Lac Indian Band, found mercury tissue residues in walleye taken from the lower reservoirs and immediately downstream are significantly higher than samples from walleyes collected from the Lower Estuary and Lake Superior. This suggested that upstream sources immediately up-river that were influencing fish contamination. Additional proposals to study this possibility were made and work is currently underway.

In recognition of wet deposition as a significant mercury source, monitoring of mercury in precipitation has continued (through other funding sources) at several Minnesota sites including Duluth and Voyageurs National Park, which are located near the two mesocosm testing sites (St. Louis River Estuary and Sand Point Lake). These stations

provide wet mercury deposition estimates for calculating atmospheric inputs to the mesocosms.

The isolation of a mesocosm from the ambient lake/river water provides a unique means of assessing the importance of upstream vs in-place and ground water sources of mercury contamination. Comparisons of mercury accumulations in biota between ambient and enclosed control areas (no other treatments) showed significantly higher concentrations for ambient areas.

B.3. Mitigative treatment tests results:

The hypothesis testing was based on the chemical activity framework described by Björnberg et al. (1988). Environmental conditions that result in the lowest mercury activity or chemical potential will result in the lowest mercury residue concentrations in fish tissue. There are two major mechanistic approaches to achieve low chemical activity. The first is through the additions of reactive substances or through changed conditions. The second is to lower the total inputs or speed up the total outputs of mercury in a given environmental system. We utilized the first approach mainly in Phase I of the program

Effects of the following six treatments or changed conditions on mercury accumulation in biota were determined for: 1) mercury chelator addition using a mercury complexing agent used for treating mercury poisoning in humans (2,3-dimercapto-1-propanol [BAL]; 2) a mercury chelator/precipitant addition using an agent designed for mercury recovery in air pollution wet scrubber systems (2,4,6-trimercapto-s-triazine-trisodium-salt); 3) a mercury absorption polymer addition using a polymer specifically designed for mercury recovery in industrial applications (a thiol functionalized chloromethylated copolymer of styrene and divinylbenzene); 4) a micronutrient addition using selenium (Se) which has been used successfully in Sweden and is the active component of a U.S. patented method for the treatment of lakes (Paulsson and Björnberg, 1988) (added as sodium selenite pentahydrate); 5) changed bioactive organic carbon content by changing the amount of plant material present; and 6) a water quality pH increase. These pilot studies (along with those for Phase II) are summarized in Table 3.

Results of these tests are discussed along with Phase II results presented under the Research Objectives Section given below.

B.4. Identification of operative mechanisms in the mercury cycle was suggested by the peer review as a focus for the Phase II (1993-1994) research program.

III. Statement of Objectives:

A. Identify mercury contamination sources and possible mechanisms for mitigation. Summarize relevant information addressing mercury related problems and assist state agencies to determine research priorities.

B. Implement field testing protocols for identifying mercury cycle mechanisms to reduce mercury residues in fish and fish food using enclosed shoreline (littoral) areas, conduct monitoring procedures, and sample media and biotic substrates for quantitative endpoints determination in selected study areas.

C. Conduct tests with treatments and changed conditions to identify mercury cycle mechanisms to reduce mercury contamination in fish and food chain organisms, investigate source types and mitigation mechanisms, and monitor ecosystem health.

IV. Research Objectives:

A. Identify mercury contamination sources for mitigation and characterization of testing areas within high use and high value water bodies. Summarize and provide relevant information addressing all mercury related problems and assist state agencies to determine research priorities.

A.1. Activity: Locate and identify mercury cycle mechanisms causing hot-spots and source transports (within the St. Louis River and Crane/Sand Point lakes) suitable for understanding and application of mitigative action for remediation of mercury contamination in fish and fish-food organisms. Conduct exploratory surveys/workshops to gather information in support of state agency research needs.

A.1.a. Context within the project: Mercury contamination data show a notable geographical variance within large watersheds. This is a result of significant historical point sources (in addition to atmospheric sources) and varying net transport and methylation processes in watersheds causing contamination of aquatic resources.

A.1.b. Methods: Methods for conducting surveys for identifying mercury contamination were developed and implemented during 1988-1992 and will continue through 1994. These surveys included major rivers, streams, and lakes in Minnesota and included several hundred sampling sites in three major watersheds: Lake Superior and Rainy and Mississippi Rivers. Precipitation and air monitoring were included in the earlier studies. Advances were made in the areas of analytical detection at the low ppt levels in water (Glass et al., 1990) and to lower levels by Bloom (1989). Environmental matrices including fish, plankton, aquatic plants, and sediments were analyzed and methods established and evaluated for precision and accuracy (Sorensen et al. 1990; Glass et al., 1992; Bloom, 1989, 1992). See details described in the LCMR Research Program 1993 - Detailed.

A.1.c. Materials: Materials needed for this activity are sampling and analysis equipment including maps, collection containers, boat and motor, lab glassware, reagents, an atomic absorption spectrometer system suitable for cold vapor mercury analysis, and a computer.

A.1.d. Budget: 10,000; balance $0

A.1.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
exploratory surveys/workshops began 7/88 ➡➡➡	xxx	xx	xx	xx	
study area selection	xx			xxx	

A.2. Status: (Identify sources, provide assistance, and request EPA funding)

Mercury Hot-Spot Identification.
A tributary stream to the St. Louis Bay, under consideration by the MNDNR for development as a recreational fishery at Twin Ponds, was surveyed for mercury in water and a hot-spot was found downstream from a municipal golf course.

Preliminary results from the new source sediment survey (funded by GLNPO) of six reservoirs on the Lower St. Louis River below Cloquet have indicated new information on mercury contamination sources from that media. Earlier work (1991-1993) based on one sediment core from the deepest part in three of the reservoirs showed that mercury contaminated sediment layers were buried by one to two meters of less contaminated deposits. Our latest data (78 analyzed cores), though, shows that high concentrations of mercury contamination exist in surface sediment layers of some reservoir areas (Figure 1b). This supports the assertion that local contamination hot-spots are influencing mercury concentrations in fish in the lower St. Louis River area.

A benthic organism population survey and mercury bioavailability assessment is underway. Samples from all six reservoirs were collected this spring and analyses should be completed by fall.

Methyl Mercury in Precipitation
Analysis of data from the 1993 research program field season and the regional precipitation monitoring network suggests a new and significant source of methyl mercury to the aquatic ecosystem. It has been generally accepted that the incorporation of methyl mercury in fish resulted only from in-lake or in-stream microbial processes forming methyl mercury. Following the lead of researchers in Sweden (Lindqvist, 1992) we have observed significant amounts of methyl mercury in rainfall at concentrations similar to those of surface waters in samples analyzed by L. Liang, Brooks Rand Ltd.. The sources of methyl mercury in wet deposition have yet to

be identified, but the ramifications of these observations are very significant. More research effort is needed to verify these observations and/or identify methyl mercury emission sources. A summary of these findings was presented at the International Conference on Mercury Pollution held in Whistler, B.C. July 11-14, 1994: "Airborne Methyl mercury Concentrations in Rain and Wet Deposition in the Upper Midwest".

Our recent studies in the Upper Midwest have shown significant amounts of mercury, (measured as total mercury) in the air, precipitation, surface waters, sediments, and biota (Glass et al., 1990, 1991, 1992; Sorensen et al., 1990, 1994). This report is based on measurements of methyl mercury in precipitation from nine wet deposition monitoring stations (MIC Type B Collectors) located in and around Minnesota near Lamberton, Bethel, Duluth, Finland, Ely, Tower, International Falls, Cavalier, ND, and Raco, MI using the analytical methods previously described (Glass et al., 1990; Liang et al., 1994).

The importance of the methyl form of mercury in the aquatic food chain bioaccumulation mechanisms and its toxicity is well established. However, the primary mechanisms and/or sources for the formation of methyl mercury(II) in the total environment are not well understood (Weber, 1993). A variety of reactions illustrate the potential importance and significance of abiotic mechanisms in the anthropogenic formation of organomercury compounds.

Our preliminary results show that methyl mercury and total mercury concentration means, std. dev., and ranges (in parentheses) were found to be 0.194 ± 0.091 ng/L (<0.04, 0.48) and 13.9 ± 7.6 ng/L (2.9, 34), respectively, for weekly samples of precipitation collected the 2nd or 3rd week of the months, June through September, 1993. Weekly averages for all sites from June to September were 0.15, 0.21, 0.22 and 0.17 ng/L methyl mercury, respectively, and the ratios of methyl mercury to total mercury were 0.015, 0.017, 0.018, and 0.013, respectively. Methyl mercury concentrations for 35 measurements correlated with total mercury concentrations (+0.35) and precipitation volume (-0.42), respectively.

The calculated weekly mean wet deposition values for the same sampling were 4.4, 5.5, 3.6, and 2.6 ng/m^2 methyl mercury, and 293, 335, 261, and 293 ng/m^2 total mercury, respectively, for all sites. Calculated weekly mean wet deposition for total mercury considering every week of the same months were 270, 292, 217, and 185 ng/m^2, respectively. Comparisons were made with other precipitation data, terrestrial and aquatic ecosystem data, and mechanisms of methyl mercury formation and cycling to evaluate the environmental significance of these observations.

Conferences and Workshops and Interlaboratory Comparisons.
American Chemical Society meeting held in Chicago in August of 1993. Kent Schmidt presented a paper on advances in low level mercury analyses using EPA methodology. This presentation won an award for best first paper given by the Division of Environmental Chemistry of ACS.

Heavy Metals Conference held in Toronto, Ontario during September, 1993. Gary Glass presented preliminary mercury bioaccumulation findings from our mesocosm research.

Mercury workshop for staff of Great Lakes States air quality agencies, held in Chicago November 9-10, 1993. Ed Swain presented a summary of a variety our mercury survey findings dealing with precipitation and Minnesota lakes and streams.

Mercury in fish monitoring workshop for Minnesota and surrounding state's Agencies held on December 10, 1993 in Minneapolis (Shoreview). Gary Glass presented our current findings on methodology for sampling and analyses.

Ecosystems Management Strategies for the Lake Superior Region held in Duluth during May 16-19, 1994. Gary Glass presented information on mercury contamination hot-spots within the St. Louis River watershed.

International Conference on Mercury as a Global Pollutant held in Whistler, British Columbia in July 1994. Gary Glass presented findings on total mercury and methyl mercury deposition and updated mercury bioaccumulation data from our mesocosm research.

A regional conference and workshop on mercury pollution sponsored by the New Jersey Department of Environmental Protection and Energy held on October 6, 1994. Gary Glass made a keynote address on "Airborne Mercury Deposition: Local Sources and Global Concern".

Mercury Pollution in the Upper Great Lakes Region Conference held on June 9, 1995. Gary Glass presented a paper titled "Airborne Mercury Species in Precipitation: Seasonal and Ecoregion Variations" and a poster titled "Mechanism Studies of Mercury Bioaccumulation in Aquatic Mesocosms".

John Sorensen, Kent Schmidt, and Gary Glass participated in an international mercury intercomparison study with other laboratories for the analyses of lake water. Very successful results were achieved (our result of 1.3 ppt vs overall mean result of 1.27 ppt for participating laboratories).

Related Funding from other Sources (as required by appropriation language).
Two applications for supplementary funding were made to EPA, Great Lakes National Program Office (GLNPO) during this study. The first request for funds was granted for further investigation of mercury hot-spots in the six reservoirs on the Lower St. Louis River below Cloquet. An extensive sediment survey and benthos screening was performed to specifically identify mercury hot-spot sources. This work is a joint effort conducted during 1994 and 1995 by the University of Minnesota-Duluth (UMD), the

University of Wisconsin-Superior (UWS), and the Fond du Lac Indian Band Department of Natural Resources (FDL), with analyses for mercury conducted at the USEPA Environmental Research Laboratory-Duluth.

The second application for funding to GLNPO, a request to develop a basin-wide mercury contamination model for Lake Superior using siscowet, its food chain, and deep-water sediments, was not funded, but other funding sources were identified.

Additional applications for funding through the USEPA Gt. Lakes National Program Office were made to perform mitigation research that would begin after July 1, 1995. Tentative approval of funding has been granted in both cases with both requests in the "quality assurance planning phase". These projects will be a cooperative effort between UMD, UWS, FDL and the USEPA.

B. Implement field testing for reducing mercury residues in fish and food organisms using enclosed littoral areas, conduct monitoring procedures, and sample media and biotic substrates for quantitative endpoints determination in selected study areas.

B.1. Activity: Reconstruct and expand enclosed shoreline testing areas and replace side wall material where needed.

B.1.a. Context within the project: This activity defines the extent of the natural substrates (mesocosms) in which treatments and changed conditions can be tested, and contamination mechanisms evaluated.

B.1.b. Methods: Shoreline enclosures have been successfully utilized in a number of studies involving effects and mechanisms (Hecky *et al.*, 1987; Rudd and Turner 1983a, 1983b; Rudd et al., 1983, 1980; Turner and Rudd, 1983; Turner and Swick, 1983; Turner *et al.*, 1992). For this study, up to twelve enclosed areas (shoreline littoral) will be constructed on Crane/Sand Point Lakes and the St. Louis River/Estuary. The basic design of the enclosed areas are similar to those developed by the U.S. Environmental Protection Agency, Environmental Research Lab.-Duluth (Siefert, 1989; Brazner, *et al.*, 1989; Brazner and Klein, 1990) and modified for use in rivers and lakes where currents, waves, and seiche activity are significant. These enclosed areas must be maintained and extended as the research continues. The enclosures are rectangular (4m x 10m), bordered with reinforced plastic sheeting covering slotted snow fencing walls on three sides and 4-m of natural shoreline on the fourth side. See details described in the LCMR Research Program 1993 - Detailed.

B.1.c. Materials: Materials needed for this activity are dock sections, snow fence, reinforced plastic, cedar posts, plywood, boards, various carpentry hardware and tools, waders, boat and motor, truck, and sampling gear.

B.1.d. Budget: $10,000 balance - $0

B.1.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
construct enclosures	xx		xxx		
stock with fish	x		x		

B.2. Activity: Maintain enclosed areas and monitor conditions.

B.2.a. Context within the project: Maintenance insures that the enclosures will not leak and compromise research results. Field monitoring documents important environmental conditions throughout the project.

B.2.b. Methods: Maintenance checks on the entire perimeters of the enclosed areas will be performed weekly above and below the water surface. Below water inspections (accomplished by diving) are required to check for and repair any erosion of sediment from the enclosure wall-sediment interface that may be caused by wave action or aquatic animals (muskrats, etc.). Field measurements will be made consisting of dissolved oxygen, temperature, and electrical conductivity. Photographs will be taken (to monitor area conditions including vegetation growth and water clarity) and the lake/river water level will be recorded. This activity will be performed concurrent (same personnel) with sampling activities described under research objective C.

B.2.c. Materials: Wet suit, conductivity/temperature meter, dissolved oxygen meter, camera, water level gauge.

B.2.d. Budget: $20,000 balance - $0

B.2.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
maintenance	xxxxxxxxx		xxxxxxxxx		
field measurements	xxxxxxxxx		xxxxxxxxx		

B.3. Status: (Implement mesocosm pilot studies)
Pilot studies were conducted using a total of 25 mesocosms areas (21 enclosed and 4 adjacent ambient) which were maintained during the 1993 and 1994 field seasons at the two study sites: At Indian Point (at about 70th avenue west, Duluth) on the St. Louis River Estuary and near the Mukooda Lake portage on Sand Point Lake. Mesocosm design and layout are depicted in Figure 2.

Extensive construction and maintenance efforts (e.g. wave barriers; weekly diving to secure eroded areas) resulted in the successful testing of fish effects in 47 of 50 mesocosms over the 1993 and 1994 field seasons.

The following are observations and advice for future use of mesocosms as a tool for testing bioaccumulation mechanisms:

1) Overall, the main features of the enclosure design were satisfactory as they provided: a) ease in sampling/monitoring; b) a "naturalness" of the system afforded by including the shoreline as a boundary; and c) the only way to separate water flows and inputs while maintaining a viable ecosystem and food chain. However, an effort should be made to locate the structures in areas with minimal wave activity, especially during storms.

2) Construction and maintenance of shoreline enclosures are very labor intensive activities for larger water bodies where wave action and water level fluctuations are a problem. However, because water levels dropped below the mesocosm test areas during winter draw down at Sand Point Lake, the superstructures could remain in place without fear of ice damage. This greatly reduced reconstruction demands at Sand Point for subsequent testing seasons.

3) The abundance of aquatic macrophytes within the mesocosms diminished with each study year. This was presumably from sampling activities and the presence of enclosure walls. Although vegetative samples were convenient to obtain, it was difficult to find consistent species across all mesocosms during the later study years.

C. Conduct tests with treatments and changed conditions to identify mechanisms of mercury cycling to reduce mercury contamination in fish and food chain organisms, investigate source types and mitigation approaches, and monitor ecosystem health.

C.1. Activity: Experimental treatment tests and conditions.

1) Perform additional qualitative tests for mercury reduction in fish and food organisms (magnitude of effect at one condition or concentration only) at mercury hot-spot sites using improved littoral enclosure design and test protocol, and the following treatments or changed conditions: sediment covering, water column degassing, reduction of plant growth accumulation, and alteration of bacterial growth (increased demethylation/methylation).

2) Perform multiple tests for identifying mechanisms of mercury reduction in fish and food organisms on the most appropriate treatments or combinations found for a particular mercury hot-spot source type identified in (1). This may encompass the use of several concentrations or test conditions for each mitigation method in order to determine the minimum requirements for a useful residue reduction result. In addition, the effects of the experimental treatment at concentrations or test conditions above anticipated target levels will be established to ensure against adverse ecosystem effects.

The approaches to residue reduction fall into two categories of mechanisms: 1) methods that decrease the net exposure to the toxic forms by reducing its bioavailability within a given watershed and 2) methods that reduce the total toxic chemical contributions and loadings to the watershed. These methods may yield site specific results and be dependent upon system characteristics of the local environment. Therefore, test method protocols

should be evaluated in that environment. Table I lists the individual approaches for residue reduction that could be evaluated for mercury reduction efficiency.

Table I. Mesocosm Studies and Mechanisms for Toxic Residue Reduction of Mercury

Mechanism	Approaches	Reference
Mechanism 1: Decrease exposure/bioavailability of the toxic form (mercury)		
1a	reduction of bioactive organic carbon content	Winfrey and Rudd (1990); Fischer *et al.* (1995)
1b	bacterial static/demethylation stimulation	Winfrey and Rudd (1990); Lexmond *et al.* (1976)
1c	addition of sequestering agents	Gottofrey and Tjälve, 1990; Huang *et al* (1990); Marchant (1974); Ritter and Bibler (1992)
1d	covering of contaminated sediments	Glass et al (in prep); Bongers et al. (1977)
1e	liming of sediments	Andersson and Borg (1990)
1f	changes in nutrient and micronutrient levels	Björnberg et al., 1988; Lindqvist et al., 1991; Paulsson and Lundburgh, 1991; Rudd and Turner (1983a, 1983b); Rudd et al. (1983, 1980); Turner and Rudd (1983); Turner and Swick (1983)
1g	reduction of water level changes (reservoir effect)	Bodaly *et al.* (1984)
1h	reduction of temperature	Winfrey and Rudd (1990)
Mechanism 2: Remove/reduce toxic chemical contributions/loadings (mercury)		
2a	contaminated sediment removal	Jernelov and Lann (1973); Jernelov *et al.* (1975)
2b	increase in water column flushing	Glass *et al.* (1990.)
2c	reduction/increase in plant growth (sed. to food link)	Glass *et al.* (in prep.)
2d	water column mercury degassing	Rudd and Hamilton (1978); Winfrey and Rudd (1990); Turner et al. (1992)
2e	reduction of incident mercury deposition	Sorensen *et al.* (1990)
2f	reduction of mercury from watershed runoff	Sorensen *et al.* (1990); Barkley (1991)

Not all of these treatment mechanisms may be cost effective on a large scale (whole lake system) but may be suitable for smaller areas of high bioavailability. The most promising and feasible are being tested first. Qualitative tests (magnitude of change at one condition or concentration, in duplicate, were evaluated during Phase I of the project. Phase II will include the following:

Crane/Sand Point Lake enclosed study areas.

1) Removing mercury in the bottom sediments from contact with the water column by covering the sediments with 5 cm of clean sand in two enclosures. This will require the addition of about 3 cubic yards of sand per enclosure.

2) Changing bioactive carbon inputs by removing most of the plant material from each enclosure at the beginning of the season.

3) Mercury in the gaseous form is supersaturated in natural waters. Removal from the water column by mechanical methods will reduce the chemical activity and could result in decreased methylation and lowered uptake. Surface water agitation will be used as a physical treatment to decrease dissolved gaseous mercury concentrations. This mechanism for mercury reduction could also be accelerated by adding a reducing agent such as Sn(II) as $SnCl_2$ (10025-69-1) in small quantities. Additional reaction mechanisms for demethylation of mercury are also possible using this reagent.

4) Changing the bioavailability of mercury in two enclosures by adjusting the concentration of the micronutrient selenium (Se) to about 1 ppb. This will require the addition of 80 mg of sodium selenite pentahydrate (26870-82-1). This compound was tested successfully in Phase I at 2 ppb with no adverse results noted and has also been tested in Sweden at higher concentrations for whole lakes (Paulsson and Björnberg, 1988). Several reaction mechanisms may contribute to the overall reduction of mercury bioavailability observed in fish.

5) Changing the bioavailability of mercury in two enclosures by adjusting the concentration of the element tellurium (Te) to about 0.5 ppb. About 40 milligrams of TeO_2 (7446-07-3) would be used for this purpose and the results would help evaluate the hypotheses concerning the mechanism of mercury uptake in biota.

Indian Point enclosed study areas.

1) Installation of enclosed areas similar to those on Sand Point (Crane) Lake but with design changes to accommodate lake seiche, river current, and lake level changes while maintaining the integrity of the test conditions.

2) Evaluation of the hypothesis that atmospheric deposition is a contributing source of biotic mercury contamination.

a. Decreasing mercury input to two enclosures by collecting the wet deposition (covering the enclosures to keep the precipitation out) while allowing air circulation and 90% of the sunlight to remain.

b. Increasing atmospheric mercury input to two enclosures, by diverting the rainwater runoff from the enclosures with covers and directing it to the adjacent enclosures.

3,4) Changing ambient mercury bioavailability by altering the metal chelation distribution in two sets of enclosures using about 30 µg/L of dimercaptopropane sulfonic acid sodium salt (4076-02-2) and dimercaptosuccinic acid (304-55-2), requiring about 1 gm per enclosure. These reagents could have similar mechanisms as the compound BAL that was tested in Phase I (1992).

For water quality change treatments (e.g. chelation, sequestering, and/or demethylator additions) the treatment will be administered on an as-needed basis to keep chemical concentrations within design specifications; 100 - 1000x mercury concentrations and loadings, but below any known or suspected toxicity endpoints. Monitoring the concentrations of chemical additions within the enclosed areas will be necessary in some cases.

Other test reagents and changed conditions for testing mercury residue reduction are planned for the field seasons in 1993 and 1994 and are summarized in Table II along with the work completed to date. The final selection of treatment conditions or changed conditions will be determined by May 1993 and May 1994 after a complete analysis and assessment of all available data and information is made.

Table II. Summary of Completed Mercury Mitigative Treatment and Cycling Mechanisms Tests Using Littoral (Shoreline) Enclosures on High Value Water Bodies.

Test treatments or changed conditions	St. Louis River[1]			Crane/Sand Point L.[2]		
	1991-1992	1993	1994	1991-1992	1993	1994
Evaluation of protocols and endpoints	√	-	-	√	-	-
Mechanism 1 approaches:						
chemical additions (sequestering agents)	√	√	√	√	√	√
bacterial static/demethylation stimulation	-	√		-	-	
covering contaminated sediments	-	-		-	√	-
change of bioactive organic carbon	-	-	√	√	√	√
Mechanism 2 approaches:						
reduction of incident mercury deposition	-	√		-	-	√
change in plant growth	-	-	-	√	√	-
water column mercury degassing		-	-	-	√	-
change in water column flushing	√	√	√	√	√	√

[1]Includes possible sites in Superior and St. Louis Bays, Indian Point, Fond du Lac, and stream mouth hot-spots.

[2]Includes possible sites on Thomson Reservoir, Island, Crane and Sand Point lakes

C.1.a. Context within the project: The study and evaluation of experimental test conditions and changed conditions is the main focus of this project.

C.1.b. Methods: Treatments will be tested in duplicate (under ambient mercury conditions) with a test period consisting of the entire summer growing season. A series of ten enclosed areas per site will thus allow four treatment tests per field season per site with two enclosed areas in addition to two non-enclosed, areas immediately adjacent used as controls.

C.1.c. Materials: test reagents, application equipment, balance, sample containers, mixing equipment, and enclosure covers.

C.1.d. Budget: $15,000 balance $0

C.1.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
apply and monitor treatments	xxxxxxx		xxxxxxxx		

C.2. Activity: Sampling and laboratory measurements of mercury test conditions and test endpoints, and other parameters in enclosures.

C.2.a. Context within the project: These measurements document and determine the effectiveness of the treatments, contribute data for determining the mechanisms involved, and assure quality of the test data and analytical measurements.

C.2.b. Methods:

Test Endpoints. The mercury concentrations and growth rates of yellow perch, other indigenous fish, and plankton will be used as the main endpoints for measuring mercury residue change/reduction and as an indicator of ecosystem health in each of the enclosed areas as well as outside of the enclosures. Water, plants, and sediments will be sampled as needed to measure mercury (total and methyl) and treatment exposure conditions.

Sampling. For each type of sampling, at least one sample will be taken from each enclosed area in addition to the area outside of the enclosures. Turbidity, pH, mercury (total) in water, and mercury in plankton will be sampled for at least once every two weeks. Total mercury in vegetation and sediments will be sampled for at least once during the test period and total mercury in fish and methyl mercury in water will be sampled for three times (start, middle, and end of test period). Sampling for methyl mercury in water is accomplished by immersing a precleaned teflon sample bottle below the water surface. A new pair of gloves are used by sampling personnel for each sample taken. Bottles are double bagged in plastic ziploc containers for storage and

transporting. HCl is added at the laboratory to preserve the samples until analyses. All other sampling methods will be the same as reported by Glass *et al.* (1990, 1992), Sorensen *et al.* (1990), and Bloom (1989, 1992).

Mercury Measurements. Mercury measurements (total and methyl forms in selected samples) in fish, water, plankton, sediments, vegetation, and precipitation will be made using atomic absorption spectrometry and will involve methods reported earlier (Glass *et al.* 1990, 1992; Sorensen *et al.* 1990; Bloom, 1989, 1992). The improved analytical analysis aspects for quantitative measurements of mercury at low levels have been addressed for samples, procedures and equipment, and will be used in this study. Split samples will be provided to other interested investigators and archived by freezing for quality assurance checks and for future analysis of other components. Water samples for mercury analysis will be preserved immediately with nitric acid/potassium dichromate. Cold vapor atomic absorption spectrometry will be the primary method of analyzing total mercury in environmental samples using a Perkin-Elmer Corp. Model 403 or 5000 instrument system. Selected samples will be analyzed both with and without a deuterium arc background correction to check for false positive interferences in various sample types. In addition, a gold gauze amalgam cell will be used to concentrate the mercury vapor to improve the level of detection and as an additional check for interferences.

Methyl mercury measurements in water will be made using methods described by Bloom (1989, 1992). Purchase orders for analyses were placed with Frontier Geosciences and Brooks Rand, Ltd. Methyl mercury measurements will also be made in our laboratory using infrared and Raman spectrometry (Ramalog spectrometer system, Spex Industry Inc. and CR-18 argon ion laser, Coherent Inc.) and the methods described in Sorensen *et al.* (1985) and Vo-Dinh *et al.* (1984), as well as by FT-NMR techniques (IBM NR/200AF) and by using an HP gas chromatograph equipped with an electron capture (Uthe *et al.*, 1972), atomic fluorescence (Bloom, 1989), atomic emission, or mass spectrometer detectors, as needed to verify standard compounds and to provide verification using a second independent method.

Other Measurements. Turbidity and pH will be measured using Hatch and Radiometer meters, respectively. Dissolved organic carbon will be measured by IR absorbance and chlorophyll will be measured spectrophotometrically.

For tests involving the micronutrient selenium, concentrations of selenium within and outside the enclosures will be measured (to insure levels do not exceed 2 ppb) by atomic absorption spectroscopy (Martin et al., 1975) using a Zeeman Perkin Elmer Model 5100.

The general status of ecosystem health in the littoral areas will be monitored using water quality indicators listed above and by measuring the abundance and growth of plants, plankton, and fish.

Quality Assurance. Accuracy of all measurements will be checked using spikes of known concentrations and NBS certified samples when available. Precision of all measurements will be checked by at least 10% replication of sample collection and 10% replication of laboratory measurements. Check samples for quality assurance will be analyzed and portions will be archived for possible future analysis as part of the integrated program of research with other investigators from the state and universities. These samples will include sediment, water, fish, and other biota. All data will be recorded on strip chart, magnetic tape, or in bound notebooks with complete identification and safety. Master copies of all original data will be kept in the possession of the principal investigators in UMD/ERLD-assigned rooms. Quality assurance checks and audits will be inventoried and kept current for ongoing review and corrective actions as deemed necessary.

Laboratory Screening Tests. Where field test conditions include the addition of mercury reactive agents, laboratory data and information will be gathered as a preliminary step to conducting the field test. These data and information will include studies reported in the literature, model calculations determining ranges of concentrations, and molecular interaction assay tests depending upon the availability of literature information, space, and equipment.

C.2.c. Materials: Atomic absorption spectrometers (Perkin-Elmer Corp. Model 403, 5000, and 5100) with gold gauze amalgam cell, infrared spectrometer (Beckman IR-12), Raman spectrometer (Ramalog spectrometer system, Spex Industry Inc. and CR-18 argon ion laser, Coherent Inc.), FT-NMR spectrometer (IBM NR/200AF), HP gas chromatograph (equipped with an electron capture, or atomic fluorescence detectors), mass spectrometer, turbidity meter, pH meter, colorimeter, reagents, and glassware.

C.2.d. Budget: $100,000 balance - $0

C.2.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
sampling	xxxxx		xxxxx		
lab. measurements	xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx				

C.3. Activity: Data base creation, quality assurance evaluation, mechanism identification, and interpretation and reporting of results.

C.3.a. Context within the project: This activity assembles and assures quality of all the data taken during this project in order that tests results may be interpreted. The interpretation of results will include the assessment of the effectiveness of each

treatment at reducing mercury in fish and other biotic compartments, cost comparison estimates, and possible implications for other environmental impacts.

C.3.b. Methods: Raw mercury analysis peak height data will be analyzed using a VAX computer. Results of those analyses as well as all other data will be entered on a Macintosh computer where statistical analyses (using correlations, regressions, analysis of variance, general statistical descriptions, and plots) will be performed using Systat. Reports will be written using a Macintosh computer and word processor software.

C.3.c. Materials: VAX terminals, Macintosh computer, laser writer, line printer, modem, and scanner.

C.3.d. Budget: $45,000 balance - $0

C.3.e. Timeline:

	7/93	1/94	6/94	1/95	6/95
assemble data base		xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx			
data quality assurance		xx	xx	xx	xx
interpret results		xxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxxx			
report results and recommendations					xxxxxxxxxxxxx

C.4. Status: (Continuation of the status report in Section B.3 for Phase I found on page 4.) The pilot studies testing the chemical activity hypothesis of Björnberg et al. (1988] proceeded along two major mechanistic themes as given in Table I on page 12.

A total of 29 replicated pilot treatments or changed conditions were applied to shoreline mesocosms during the Phase I (1991-1992) and Phase II (1993-1994) field seasons. Twenty-three of these tests were dynamic mesocosm treatments while 6 were passive treatments of "mesocosm isolation" (no treatment applied to enclosed mesocosm) and are identified as controls. See Table III for a summary listing of all pilot studies. The results of these tests are summarized by the various mechanisms for mercury residue reduction given below with references to treatments listed in Table III underlined for cross reference. Figures 3a and 3b show a graphical representation of treatment results on forage fish and Tables IVa and IVb present results for all other measured parameters.

Overall Mechanism 1: Decreased exposure/bioavailability of the toxic form, from Table I, listed by the various contributing submechanisms.

Mechanism 1a: reduction of bioactive carbon content. A high humic content in water is often linked with a high mercury content in biota indicating increased mercury chemical potential and methyl mercury production. Appreciable amounts of mercury were found to accumulate in aquatic plant tissue. This tissue forms the base of the food chain for some fish food chain organisms. At the end of the growing season, plant decomposition becomes an important source of mercury during the following season(s).

A direct test of this hypothesis was made by to applying the vegetative material to a test mesocosm and observe the results. Vegetation organic additions resulted in a statistically significant 66% increase in fish mercury concentrations (and an increase in body burden) in treated mesocosms as compared with controls. Other tests with different vegetation showed nonsignificant increases. Differences in results between tests may be attributed to the form of the vegetation added. The highest response was obtained by harvesting the vegetation immediately after the growing season rather than treatment wet detritus that had leached and decomposed over winter.

In comparison with fish, observed mercury levels in other mesocosm components, plankton, periphyton, and vegetation, showed no significant mercury concentration differences between treated and controls. This suggests a more direct rather than indirect link between vegetative input and yellow perch mercury concentrations.

Organic Removal. Dead vegetation was removed from the water and shore area of two mesocosms on the StLRE just before the growing season. Amounts removed from the shore area accounted for nearly all of the total removed. The removal of vegetative material from the shore area was intended to reduce inputs from terrestrial runoff. Results of mercury concentrations (and body burden) in fish showed treated to be higher (36% for concentration) than controls.

Shore area vegetation removal was intended to decrease the chemical potential of mercury, but it was noticed that there were numerous areas where removal exposed crevices between rocks (riprap) where decomposing vegetation had accumulated. An effort was made to remove this material but the extent of the crevices made this difficult. Disturbing the shore area in an effort to remove the vegetative material may have actually caused more decayed portions to runoff, thus causing increased mercury inputs to the mesocosm.

Mechanism 1b: bacterial static/demethylation stimulation. Bacterial activity has long been attributed to methyl mercury production and increasing methyl mercury chemical potential in aquatic systems. The most common stimulation comes from nutrient and substrate additions. Levels of humic material added to a system not only indicates increased sources of mercury associated directly with the vegetation from which it was derived, but also stimulates the amount of decay or bacterial activity which can affect methyl mercury concentrations in the water. Depending on the type of bacteria and conditions, both mercury methylation and demethylation can occur.

Specific tests altering and measuring microbial activity directly were not conducted. However, it was recognized that mesocosm functioning is dependent on microbial activity. and all tests probably involve some change in microbial response. The results of these changes are expressed through the various measurements of closely coupled environmental components.

In order to test the net methylation effects resulting from increased bacterial activity associated with vegetative decay, organic additions were applied to selected mesocosms. It was noted that methyl mercury concentrations in water, for 1992 and 1994 treatments, showed measurable but nonsignificant increases. Although the variability inherent with low level methyl mercury measurements reduced the statistical significances, the magnitude of the difference (88%, treated vs controls) for the 1992 test suggests further investigation of methylation activity associated with different forms (i.e. 1992 vs 1994 tests) of organic materials.

Mechanism 1c: addition of sequestering agents. Sequestering agents include complexing agents and precipitants which react directly with mercury in the water reducing its chemical activity. A precipitant is any reactive agent that binds with and removes mercury from solution, forming a colloid, particle, or becomes part of any solid surface such as the sediment. A mercury complexing agent is any agent that binds with mercury to reduce its chemical potential and bioavailability and/or promote mercury elimination by fish.

Precipitants (1, 2, and 3). Three compounds were tested to assess their effectiveness at removing mercury from the water column and affecting mercury bioaccumulation: precipitant 1) thiol functionalized chloromethylated copolymer of styrene and divinylbenzene; precipitant 2) 2,4,6-trimercapto-s-triazine, trisodium salt (TMT); and precipitant 3) tellurium (IV) added as tellurium tetrachloride. Precipitants 1 and 2 have been used in industrial applications for mercury removal from waste streams while precipitant 3 was selected because of its remarkably low solubility constant (10^{-70}) for the HgTe compound. The value of this solubility constant implies that nearly all mercury will be in the form of HgTe when Te is available.

For both total and methyl mercury concentrations in water, no significant reduction was observed in treated compared to controls for any of the three precipitants. Similarly for mercury concentrations in periphyton, plankton, and fish, no significant difference was found between treated and controls.

Complexors (1, 2, and 3). The three complexors tested were: 1) 2,3-dimercapto-1-propanol (BAL); 2) 2,3-dimercapto-1-propane sulfonic acid, sodium salt; and 3) meso-2,3-dimercaptosuccinic acid. Complexors 2 and 3 are close chemical derivatives of BAL, an agent used to detoxify humans of mercury poisoning.

For complexor 1, no significant differences were observed between treated and controls for total mercury in water (total and methyl), periphyton, or plankton. However, a 22% reduction ($p < 0.01$) in mercury was observed for fish.

For both complexor 2 and 3, total mercury concentrations in treated water were significantly less than that of controls. No significant difference was observed, however, for methyl mercury in water concentrations. Similarly, no significant differences were observed for mercury in periphyton or plankton. For mercury concentrations in fish, complexor 2 showed no difference between treated and controls, but complexor 3 resulted in slightly higher (18%, p=0.02) mercury concentrations in fish for treated compared to controls.

Micronutrient Addition (added as sodium selenite pentahydrate) may be considered as a sequestering agent due to the extremely small solubility constant of 10^{-58} for HgSe. The most direct measure of the sequestering effects of selenium is through mercury concentrations in water. Mercury concentrations in biota for micronutrient additions are discussed under mechanism 1f.

For the Sand Point tests, total mercury in water was lower in the selenium treated mesocosms than in controls during 1992 and 1993, but methyl mercury in water concentration differences were not significant. For tests at the StLRE no differences between total mercury or methyl mercury in water concentrations were found between treated and controls.

It would appear that selenium was the only tested sequestering agent that had a slight affect on mercury concentrations in water, however, these average differences were less than the precision of individual measurements. Plankton also showed an indication of decreased mercury levels. One reason why selenium and tellurium may exhibit different responses could be because the water solubility of sodium selenite pentahydrate is greater than that of tellurium tetrachloride.

Response differences of selenium between Sand Point and the StLRE are probably the same as those discussed for mercury in biota (see mechanism 1f).

Mechanism 1d: covering of contaminated sediments. High mercury contamination in surface sediments indicates high chemical potential of mercury in the interstitial water and elevated mercury concentrations in benthos and fish. Transport mechanisms result from 1) direct release of mercury species from the sediment to the water column or 2) incorporation of mercury into fish via the food chain (benthos). Covering the sediment treatment was intended to reduce the exchange of mercury between the water column and the surface sediment layer. The relative contribution of sediments to fish mercury contamination was evaluated for a system not characterized by high levels of mercury in the sediment. Results of this test revealed no significant differences between treated and controls for concentrations of mercury in water, periphyton, plankton, or fish. This indicates that sediment was not an important source of the mercury exposures for the time period at that pilot study site.

Mechanism 1e: liming of sediments. The purpose of liming sediments is to provide a mechanism by which water column and surface sediment pH will remain elevated over long periods of time. Increasing pH has the combined effect of reducing net mercury methylation and preserving sulfide concentrations which bind with mercury, thus reducing mercury activity. It has been suggested that the activity of mercury in any aquatic system is dominated by the availability of sulfide. Like selenium and tellurium, HgS has a very low solubility constant (10^{-52}) and can be effective at removing mercury from the water. However, the production of H_2S gas at lower pH levels sulfide concentrations in the system thus decreasing its effectiveness.

Because the mesocosm tests were over short periods of time (one growing season), pH Adjustment was accomplished by simply adding a sodium hydroxide solution at regular intervals. Because pH manipulation was tested as part of the 1991 Sand Point protocol development phase, short test periods and initial problems with wave erosion at the sediment/wall interface resulted in inconclusive results. Other tests were favored over pH manipulation for the following years, thus the experiment was not repeated using refined protocols. Calculations indicate that this treatment would be too costly to be applied to whole lake water body ecosystems.

Mechanism 1f: changes in nutrient and micronutrient levels.

The addition of selenium as sodium selenite pentahydrate (micronutrient addition) resulted in significantly lower mercury concentrations (and body burdens) in fish compared to controls at Sand Point. The treated averaged 72%, and 73% lower in concentration than the controls for 1992 (2 ppb Se) and 1993 (1 ppb Se), respectively. Because the same enclosures were used for both the 1992 and 1993 Se additions, there was some concern of possible Se carryover from one year to the next. To test for Se carryover, no additions were made in 1994 to those enclosures previously treated during 1992 and 1993. This test resulted in no significant difference with respect to controls, thus indicating carryover for Se effects was not appreciable. However, some elevated Se residues were observed.

Similar testing of micronutrient addition was done at the St. Louis River Estuary (StLRE) site using three concentration doses of Se at 0.5, 1, and 2 ppb. Fish mercury concentrations for the 0.5 ppb treatment were higher than the controls, however, this was based on a final population of two fish recovered from those two treated mesocosms. Fish mercury concentrations (and body burdens) for the 1 and 2 ppb treatments were 20% (p=0.12) and 24% (p=0.06) less than controls, respectively. This is somewhat consistent with results obtained at Sand Point but the magnitudes and statistical significances of the differences between treated and controls are less.

Possible explanations for the different responses observed for the two study sites could be related to: 1) fish at the StLRE were appreciably lower in mercury concentration than those at Sand Point. That is, control fish were approximately 75 ppb and 35 ppb at Sand

Point and the StLRE, respectively, for those years when Se was tested; and 2) responses of black crappies and yellow perch to Se may not be directly comparable.

Se concentration ratios, treated/controls, in selected mesocosm components for 1993 Sand Point were: periphyton ≈ 5x; plankton ≈ 4x; and fish ≈ 13x. For 1994 StLRE, considering those enclosures where Se addition goals were the same (1ppb Se in the water) as for 1993 Sand Point, these ratios were: periphyton ≈ 20x; plankton ≈ 7x; and fish ≈ 2x. These results seem to show a reversal in selenium uptake trends for Sand Point vs StLRE. That is, higher trophic levels show the most selenium uptake at Sand Point while at the StLRE relatively little selenium was incorporated into fish tissue. In fact, nearly 10 times the selenium was incorporated into fish at Sand Point than at the StLRE. This may explain why there was less mercury in fish reduction noticed in StLRE tests compared to Sand Point tests for micronutrient additions.

For both Sand Point Lake and StLRE tests, no significant mercury reduction was observed for mercury concentrations in plankton or periphyton in treated mesocosms. Similar results were obtained for macrophyte vegetation at Sand Point.

We conclude from these tests that selenite additions at low concentrations can be very effective in Minnesota waters at reducing mercury concentrations in fish but have negligible impacts on mercury levels in biota lower in the food chain. This suggests that selenium acts specifically upon the fish organism rather than indirectly through the food chain. Also, the concurrent slight reduction of total mercury in water observed at the Sand Point site suggests that reduced absorption of mercury by fish directly from water may be an important factor controlling mercury concentrations in fish. It is puzzling, though, that no corresponding reduction of methyl mercury in water was evident.

We also note that effects from selenium additions can vary markedly across different water bodies as is evident in comparing Sand Point and StLRE results. One explanation of these observations could be that the amount of macrophyte vegetation biomass in the StLRE mesocosms was much greater (about an order of magnitude, qualitative estimate) than that at Sand Point. The large amount of vegetative surface area at the StLRE may have dominated the system by acting as an absorption sink for selenium.

Mechanism 1g: reduction of water level changes (reservoir effect). Newly created reservoirs result in large increases of mercury concentrations in fish. This is the result of large quantities of terrestrial vegetative detritus that becomes part of the newly formed aquatic system. It has also been observed, though, that many reservoir systems continue to have high mercury concentrations in fish even decades after their formation; long after effects from initial flooding should have dissipated. One hypothesis explaining those observations is that large fluctuations in water levels associated with such systems may for a variety of reasons be responsible for the continued high mercury concentrations in fish.

During the studies at Sand Point Lake, a reservoir lake system, from 1991 to 1994, it was observed that mercury concentrations in ambient young-of-year yellow perch varied significantly from year to year, with 1992 exhibiting markedly lower concentrations than the other years. Average values for these fish sampled in October were 124, 67, 120, and 111 ppb for 1991, 1992, 1993, and 1994, respectively. Average weights for those fish for those same years were 1.3, 1.6, 1.5, and 1.8 g, respectively. As a first step toward investigating this peculiar phenomena, correlations were examined between those mercury concentrations and some dynamic variables associated with a reservoir system (summer discharge rate at dam, water level fluctuation range, temperature, and mean fish length). Of these variables it was found that water level fluctuation range and temperature (see mechanism 1h) were both strong correlates, however, the small number of data points yielded statistically nonsignificant results and will not be presented at this time.

Identifying the causative factors surrounding the yearly fluctuations of mercury concentrations in young-of-year yellow perch at the Sand Point Lake study site will be valuable in understanding mercury bioaccumulation. For this reason, we intend to continue monitoring ambient mercury concentrations in that species on a yearly basis in order to attain the statistical significance needed to explain the observed variations.

Mechanism 1h: reduction of temperature. Most chemical and biological reaction rates depend on temperature. In particular, the rates of mercury methylation and demethylation, as well as biologic uptake rates, change with temperature. Because the enclosed mesocosms averaged 1°C cooler than ambient water a comparison between control enclosed mesocosms to ambient areas could indicate effects from cooler temperatures.

Results for each testing season showed a reduction in mercury concentrations in fish for the enclosed (cooler) mesocosms as compared with ambient adjacent areas. This could be a combination of isolation from external mercury sources and temperature effects (see mechanism 2f).

Overall Mechanism 2: Remove/Reduce toxic chemical concentrations/ loadings of mercury.

Mechanism 2a: contaminated sediment removal. Contaminated sediment removal is designed to reduce mercury inputs to biota by reducing or removing a significant source of mercury from the rooted zone for plants and the bioturbation zone for benthos. This mechanism for reducing the chemical activity of mercury is reserved for sediment mercury hot-spots such as observed at some sites on the St. Louis River Estuary and the lower St. Louis River reservoirs. This is a most costly option.

Mechanism 2b: increase in water column flushing. For a flowage system, water column flushing means that the water column for any given area is continually renewed by upstream water which reflects mercury activities directly coupled to upstream sources. The rate of flushing in a given area then determines the influence that in-place sources of mercury activity have on the total chemical activity for that area. In this section we consider mercury effects in water and biota as a consequence of enclosure isolation from upstream sources (no water column flushing).

Mercury in Water. There are several factors which may cause mercury concentrations in enclosed water to be different than the ambient. First, mercury may be removed from the water column as it binds to biota or particulates that settle out. These mechanisms are likely to be different for shallow and deep water settings, and thus, different for enclosed and ambient. Second, the resuspension of fine particulates, which can contain appreciable amounts of mercury, can result in higher measured mercury-in-water concentrations. The average correlation (across all study years) between turbidity and mercury concentrations in water using data from all mesocosms was 0.34 and 0.39 ($p<0.03$ for each individual correlation) for the Sand Point and StLRE sites, respectively. Third, mercury inputs from runoff and groundwater can cause differences that will vary from site to site. This would especially be noticeable in a water body that has a mercury point source or sediment hot-spot area. For example, if a flowage system has an upstream sediment hot-spot, the leachate from the sediment could elevate the water concentrations and increase the chemical activity of mercury at all points downstream. If one isolates a portion of water downstream, natural processes discussed above may deplete mercury from the water column while the walls prevent reenrichment by the upstream sources.

During 1993 and 1994, statistically significant differences were observed for total mercury concentrations between ambient and controls at both study sites, while for 1992, only the StLRE exhibited differences approaching ($p=0.08$) statistical significance. At Sand Point, controls (3-yr mean = 3.0 ng/L) were higher than ambient (3-yr mean = 1.5 ng/L). This may be a result of turbidity differences between enclosed and ambient water.

For the StLRE, the mercury in water differences were opposite of that observed at Sand Point with ambient (3-yr mean = 4.4 ng/L) being higher than the controls (3-yr mean = 3.3 ng/L). This could be caused by upstream sources and enclosure isolation as discussed above. At 4.4 ng/L the average ambient total mercury concentration is higher than that observed for 94% of 77 Minnesota lakes studied previously.

For methyl mercury concentrations, it was observed that differences between ambient (3-yr mean = 0.21 ng/L) and controls (3-yr mean = 0.18 ng/L) were mostly nonsignificant at Sand Point for 1992, 1993, and 1994. At the StLRE site, however, methyl mercury behaved similar to total mercury, with controls (3-yr mean = 0.14 ng/L) being lower than ambient (3-yr mean = 0.30 ng/L). These differences at the StLRE had an average statistical significance of $p=0.10$ for the 3 study years.

Mercury in Lower Trophic Levels. Mercury in plankton exhibited higher ambient levels than controls at the StLRE site. This observation is consistent with observations for mercury in water at that site, discussed above. Other differences between ambient and controls for mercury levels in periphyton, or vegetation were nonsignificant.

Mercury in Forage Fish. Mercury concentrations in ambient fish at both study sites were significantly higher than controls. This indicates that mercury bioaccumulation in forage fish is mainly associated with mercury sources external to the enclosed littoral areas. In the case of the StLRE, observations in forage fish are consistent with the above discussion on mercury in water. That is, "upstream" mercury sources or open-lake processes are assumed to be responsible for the differences observed between ambient and control fish.

For Sand Point, the percentage differences (ambient greater than controls) are even greater than they are at the StLRE in spite of the lower mercury concentrations in ambient water.

Some of the observations discussed above may also be a result of the reduced temperatures noted for the enclosed mesocosms compared to ambient areas (see mechanism 1h).

Mechanism 2c: reduction/increase in plant growth. A change in the amount of aquatic plant growth has the potential of affecting mercury bioaccumulation in other biota in two ways: 1) Roots extending into mercury contaminated sediment can absorb mercury and incorporate it into the plant tissue. Thus, aquatic vegetation can "mine" mercury from beneath the sediment surface and return it to the water column as the plant decays. 2) Aquatic plant leaves can absorb mercury from water and act as a collector, thus reducing the pool of mercury available in the water column for accumulation by other organisms for that growing season. However, after the plant dies, the mercury once again becomes available to other organisms but this time at a much higher concentration as compared to ambient water. See discussion in Mechanism 1a.

It was observed that the amount of rooted vegetation in the enclosed mesocosms at each test site decreased with each testing season, especially at Sand Point. This provided an opportunity to assess the effects of varying amounts of vegetative growth by comparing mercury accumulations in fish between years for control enclosures. Results at Sand Point indicated that significant differences developed in fish mercury concentrations comparing ambient areas with control mesocosms after the first year of study.

Mechanism 2d: water column mercury degassing. Although volatile mercury components in the water represent only a small portion of the total mercury, continuous degassing of the volatile components results in continued production of these components through equilibrium reactions. This could have the eventual effect of depleting the mercury pool within the system.

The water aeration test was designed to continually remove volatile mercury components from the water by vigorously agitating the water surface. Statistically significant differences between treated and controls were observed for fish mercury body burdens with aerated mesocosms being 19% less than controls. However, fish concentrations were nearly the same for aerated vs controls. This indicates that 1) surface agitation was inefficient at removing mercury volatile compounds; and/or 2) the amount of Hg volatiles in the water was small and/or the rate of transformation to Hg volatiles from other Hg forms was not sufficiently rapid. Additional tests were planned using chemical reductants in combination with aeration, but approval could not be obtained for pilot testing without prohibited conditions attached.

Mechanism 2e: reduction of incident mercury deposition. In order to test the hypothesis that mercury in wet deposition was readily available to fish food chain organisms, the ratio of inputs to mesocosms were varied. In addition, precipitation has been shown to be an important source of mercury to Minnesota lakes we tested the seasonal response to wet deposition inputs by covering mesocosms (no wet deposition) and more inputs in mesocosms that received twice the normal wet deposition inputs (2x wet deposition). These tests were conducted at both the StLRE (1993) and Sand Point Lake sites (1994).

In order to roughly estimate the magnitude of potential impacts of deposition manipulation on mercury levels in the affected enclosures, data from mercury in precipitation monitoring stations at Duluth (near the StLRE) and International Falls (near Sand Point) were evaluated. Based on measured mercury depositions for these sites, enclosure surface areas and volumes, and average water mercury concentrations in controls, the theoretical change in water mercury concentrations for the affected enclosures could be calculated. Although these calculations are conservative (all mercury remains in the water column) they can give an upper boundary to the relative consequences of the "no deposition" and "2x deposition" treatments.

The average mercury in rain concentration at the Duluth monitoring station over the 1993 mesocosm testing period was 11.8 ng/L. The amount of precipitation depth for the same period was 18.6 cm. Using those numbers and an average (over the two affected enclosures) surface area (precipitation collection area) of 34 m^2 and water volume of 18 kL, the theoretical increase of water mercury concentrations of the "2x deposition" enclosures at the StLRE site would ultimately rise by 50% at the end of the test period.

For the StLRE site the no deposition mesocosms had the lowest total mercury concentrations in water of all enclosures, being significantly lower (45%, $p<0.01$) than controls. The 2x deposition mesocosms, though, showed no significant difference compared to controls. Wet deposition manipulation also appeared to have no significant effect on methyl mercury concentrations in water, or mercury concentrations in plankton

and fish. Mercury in periphyton appeared significantly higher in 2x deposition than in controls, but the small difference observed compared to the high variabilities in periphyton measurement across other mesocosms decreases the robustness of this comparison.

At the International Falls monitoring station the average mercury in rain concentration over the 1994 Sand Point testing period was 11.1 ng/L with a precipitation depth of 32.8 cm. Using an enclosure area of 34 m^2 and a volume of 22 kL the "2x deposition" enclosures at the Sand Point Lake site would ultimately rise by 150% at the end of the test period.

For the Sand Point Lake site, no significant differences were found between treated and controls for either total mercury or methyl mercury in water for the deposition manipulated mesocosms. The same was true for mercury in periphyton and vegetation. For fish however, mercury concentrations were significantly higher in "2x deposition" treated than in controls (59%, $p<0.01$). The "no wet deposition" treatment, though, showed no significant difference. One explanation for these results is that methyl mercury carryover from vegetation produced in the previous year and its production within the enclosure dominated over precipitation inputs.

Mechanism 2f: reduction of mercury from watershed runoff. Plant material (and increased mercury levels in an aquatic system) is associated with watershed runoff and serves as a mode of accumulation and transport for mercury inputs from terrestrial vegetation. We attempted to reduce this source of mercury input by removing all vegetative litter from the immediate watershed of selected mesocosms. These tests yielded slightly higher mercury concentrations in fish and may have been due to actual increases in mercury from watershed runoff. This may have resulted from disturbing humus during detritus removal (see mechanism 1a).

Other Bioaccumulation Observations. From 1992 to 1994 there were a total of 59 individual mesocosm studies where 5 or more young-of-year forage fish where sampled. Of these 59 mercury accumulation analyses groups, 17 showed a statistically significant ($p=0.10$) inverse relationship between mercury concentration and fish length (and weight) while only 4 groups showed a significant positive correlation between mercury concentration and fish length. This is an interesting observation because it is contrary to the consistent and strong positive correlation observed between mercury concentrations and size for game fish. Further study of this relationship may lead to a better understanding of mercury bioaccumulation mechanisms and have significant future application for residue reductions.

Summary. A total of 25 shoreline pilot test areas composed of 21 enclosed shoreline mesocosms (4m x 10m) and 4 nonenclosed adjacent zones, were maintained at two study sites: at Indian Point (70th Avenue West, Duluth) on the St. Louis River Estuary; and

Sand Point/Crane Lake, SW end. Twenty-nine replicated pilot treatment tests were conducted over four years using mesocosms to measure mercury bioaccumulation effects and mechanisms for reducing mercury bioaccumulation. The experimental framework of the pilot studies followed two overall mechanisms for mercury reduction: 1) decreasing the exposure/bioavailability of the toxic form of mercury; and 2) reducing toxic contributions/loadings of mercury to the aquatic system.

Evaluations of results were assessed based on the hypothesis that mercury chemical activity was the controlling factor. The results observed included: 1) micronutrient additions of selenite could significantly reduce mercury concentrations in young-of-year (y-o-y) yellow perch (by about 72%) at Sand Point (Crane) Lake and y-o-y black crappie (22%) at the StLRE for additions at the 1 ppb level over 12 weeks; 2) Aquatic vegetation additions increased mercury concentrations in yellow perch and is a significant mechanism for transferring bioaccumulated mercury from one growing season to the next; and 3) An inverse relationship between mercury in forage fish and fish size was observed in some mesocosms, this is the opposite of what is observed for game fish. Further study of this inverse relationship may lead to better understanding mercury bioaccumulation mechanisms and have significant future application for residue reductions.

Additional results were found for various mercury binding reagents (including compounds used for poison treatments, i. e. BAL); covering sediment with clean sand; water aeration; wet deposition changes (0x and 2x deposition); mesocosm isolation from ambient water; and water level and temperature variations.

These findings are useful in evaluating bioaccumulation mechanisms and assessing mitigative treatment alternatives for mercury contaminated hot-spots but also indicate that the solution to the wide spread problem is pollution prevention, through the reduction of mercury usage and emissions (MPCA 1994).

V. **Evaluation:** The success of the project may be evaluated by the ability to identify the mechanisms of mercury cycling and contamination and to quantify the effectiveness of a given treatment or changed condition. For example, one treatment may result in mercury concentrations in fish (or plankton) to be 50% lower than controls while another may show no statistically significant mercury reduction. Recommendations for sites with high mercury bioavailability and for whole water-body treatments will be made.

VI. **Context within field:** Environmental mercury contamination in Minnesota has been studied only recently to determine the extent, causes, and the bioaccumulation phenomena. The principal investigators and co-workers of this project have made major contributions to answering these questions since 1987 (Glass et al., 1990; Sorensen et al., 1990; Glass et al., 1991; Glass et al., 1992). This work has recently been recognized by the Science Advisory Board of the USEPA in receiving a 1991 Scientific and Technological Award .

The most notable work relating to the mitigation of mercury in water bodies has recently been attempted in Sweden with some success (Lindqvist, 1991). The only mercury mitigative work done in Minnesota, other than reducing mercury at the source(s), are those preliminary studies (using a micronutrient) described in Glass et al. (1992).

This project would test the most successful methods employed in Sweden and Canada to determine the applicability to Minnesota lakes. In addition, several other new methods applicable to many Minnesota lakes and streams would be evaluated by this project for the first time.

Dr. George Rapp (program manager), Dr. Gary Glass (co-program manager and principle investigator), John Sorensen (co-principle investigator), and Kent Schmidt (research chemist) have all worked together on various mercury studies since 1987. These studies have involved mercury research on over 100 Minnesota lakes, dozens of streams, and 7 precipitation monitoring sites with over 25,000 individual mercury analyses performed (total experience).

Dr. Stephen Hedman (professor of Biology) will supervise the UMD graduate work of Joe Austin on this project. Dr. Hedman's research interests include mercury incorporation in tissue and DNA molecules.

Larry Kallemeyn's (Research Biologist for Voyageurs National Park) involvement with this project stems from his interest in lowering mercury concentrations in fish within Voyageurs National Park in addition to his studies of changing water level impacts on fish and vegetation.

VII. **Benefits:** The results of this project could lead to a better understanding of the mercury cycle and to practical treatment methods (for both whole water bodies and localized hot-spot areas) that would reduce the mercury residue levels in fish. Mitigative treatments applied to the most contaminated and popular water bodies in Minnesota could reduce mercury levels in fish of those areas and, thus, reduce health hazards while promoting the full utilization of Minnesota's resources.

The permanent long-term solution to new mercury problems resides in the reduction of contamination at the source (e.g. reducing mercury in atmospheric deposition and historical hot-spots). However, this could take many years and does not address watershed and lake sediment hot-spot areas that have already been contaminated by industrial/municipal disposals. Thus, a near-term option is needed, especially for high-use and hot-spot areas.

VIII. **Dissemination:** Results of this project will be presented to Minnesota state agency staff and published in major peer-review journals. In addition, results will be distributed nationally and internationally as well as among cooperators from the following agencies/institutions: Minnesota Pollution Control Agency, University of Minnesota-Duluth, U.S. Environmental Protection Agency, and Voyageurs National Park.

IX. Time: Testing mitigative options using enclosures, data syntheses, conclusions, and recommendations should be finished by June 30, 1995.

X. Cooperation:

University of Minnesota, Duluth (UMD)

UMD will lead in project management (Dr. George Rapp, Jr), enclosure construction, sampling, analysis, quality assurance, and data interpretation with John Sorensen as a co-principal investigator. Dr. Stephen Hedman (Professor of Biology, 5-10% time) will supervise the graduate work of Joe Austin on this project. The north end of the Limnological Laboratory Building continues to be needed for office space, staging for field studies, and storing supplies, equipment, and materials.

Environmental Research Laboratory-Duluth (ERL-D)

This project will continue to be conducted under the direct supervision of co-project manager and principal investigator Dr. Gary Glass, Senior Research Chemist at ERL-D (greater than 50% time). Other ERL-D staff and cooperators who developed the shoreline enclosures are available as technical consultants on this project.

The equipment and space assigned to supporting the position of a Senior Research Chemist will continue including the ERL-D mercury clean laboratory room No. 233, a controlled temperature room and freezer space, and use of the mercury analysis glassware and the atomic absorption spectrometers (PE 403, 5000, & 5100) and other instruments. Access to the VAX computer is needed to compile and analyze the data.

Voyageurs National Park (VNP)

VNP will furnish supplies, a boat, and a cabin for maintaining the enclosure site at Sand Point Lake. VNP Research Biologist Larry Kallemeyn will assist in the design and interpretation of data for tests conducted in the Rainy River watershed area and contribute 5% time for field operations and logistical support. In addition, the Park Service is considering matching funds for work done in the VNP.

Minnesota Pollution Control Agency (MPCA):

MPCA will act as the project coordinator.

Contract Laboratories

Frontier Geosciences and Brooks Rand, Ltd. are providing analytical support for methyl mercury and other needed measurements. N. Bloom (formerly with Brooks Rand Ltd.), one of the original developers of ultra low level methyl mercury measurement techniques, is available up to 5% time on an as needed basis.

XI. Reporting Requirements: Semi-annual status reports will be submitted not later than Jan. 1, 1994, July 1, 1994, Jan. 1, 1995, and a final status report by June 30, 1995.

XII. Literature Cited:

Andersson, P. and Borg, H. June, **1990**. Effects of Liming on Mercury Concentration in Fish in a 10-Year Perspective. International Conference on Mercury as an Environmental Pollutant. Gävle, Sweden.

Barkley, N. **1991**. Extraction of Mercury from Groundwater Using Immobilized Algae. *J. Air Waste Manage. Assoc.* 41:1387-1393.

Björnberg, A., Häkanson, L., and Lundburg, K. **1988**. A Theory on the Mechanisms Regulating the Bioavailability of Mercury in Natural Waters. *Environ. Poll.* 49:53-61.

Bloom, N. S., **1992**. On the Chemical Form of Mercury in Edible Fish and Marine Invertebrates Tissue. *Can. J. Fish. Aquat. Sci.* 49:1010-1017.

Bloom, N. 1989. Determination of Picogram Levels of Methyl mercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. *Can. J. Fish Aquat. Sci.* 46:1131-1140.

Bodaly, R. A., Hecky, R. E., and Fudge, R. J. P. **1984**. Increases in Fish Mercury Levels in Lakes Flooded by the Churchill River Diversion, Northern Manitoba. *Can. J. Fish. Aquat. Sci.* 41: 682-691.

Bongers,L.H.and Khattak,M.N. **1977**. *Sand and Gravel Overlay for Control of Mercury in Sediments.* Report to Office of Research and Monitoring, United States EPA by Research Institute for Advanced Studies. Baltimore, MD.

Brazner, J. C. and Klein, E. R. **1990**. Effects of Chlorpyrifos on the Diet and Growth of Larval Fathead Minnows in Littoral Enclosures. *Can. J. Fish. Aquat. Sci.* 47: 1157-1165.

Brazner, J. C. *et al.* **1989**. A Littoral Enclosure for Replicated Field Experiments. *Environ. Toxicol. Chem.* 8: 1209-1216.

Fischer, R. G., Rapsomanikis, S., Andreae, M. O., and Baldi, F. **1995** Bioaccumulation of Methtylmercury and Transformation of Inorganic Mercury of Macrofungi. *Environ. Sci. Technol.* 29:993-999.

Glass, G. E., Sorensen, J. A., Schmidt, K. W., Rapp, G. R., Jr., Huber, J. K. Mercury Partitioning and Bioavailability in Minnesota Lakes and Rivers. in preparation.

Glass, G. E., Sorensen, J. A., Schmidt, K. W., Rapp, G. R., Jr., Huber, J. K. **1992**. Mercury in the St. Louis River, Mississippi River, Crane Lake, and Sand Point Lake: Cycling, Distribution, and Sources. *Report to the Legislative Commission on Minnesota Resources.* Minn. Pollut. Ctrl. Agency, 520 Lafayette Rd., St. Paul, MN. 55155.

Glass, G. E., Sorensen, J. A., Schmidt, K. W., and Rapp, G. R., Jr. **1991**. Mercury Deposition and Sources for the Upper Great Lakes Region. *Water, Air, and Soil Pollut.*, 56: 235-249.

Glass, G. E., Sorensen, J. A., Schmidt, K. W., and Rapp, G. R., Jr. **1990**. New Source Identification of Mercury Contamination in the Great Lakes. *Environ. Sci. Technol.*, 24: 1059.

Gottofrey, J. and Tjälve, H., June, **1990**. Effect of Some Chelating Agents on the Uptake and Distribution of Hg^{2+} and CH_3Hg^{+} in the Brown Trout. International Conference on Mercury as an Environmental Pollutant. Gävle, Sweden.

Hecky,R.E., Bodaly, R. A., Strange, N. E., Ramsey, D. J., Anema, C., and Fudge, R. J. P. **1987**. *Mercury Bioaccumulation in Yellow Perch in Limnocorrals Simulating the Effects of Reservoir Formation.* Central and Arctic Region Department of Fisheries and Oceans. Winnepeg, Manitoba. Canadian Data Report of Fisheries and Aquatic Sciences No. 628.

Huang, P. M., Wang, J. S., Liaw, W. K., and Hammer, U. T. June, **1990**. Kinetics of the Desorption of Mercury from Selected Freshwater Sediments as Influenced by Chloride. International Conference on Mercury as an Environmental Pollutant. Gävle, Sweden.

Jernelov, A., Landner, L., Larsson, T. **1975**. Swedish Perspectives on Mercury Pollution.*Journal WPCF* 47(4), 810.

Jernelov A. and Lann, H. **1973**. Studies in Sweden on Feasibility of Some Methods for Restoration of Mercury-Contaminated Bodies of Water. *Environ. Sci. and Tech.* 7(8): 712-718.

Lexmond, Th. M., de Haan, F. A. M., and Frissel, M. J. **1976**. On the Methylation of Inorganic Mercury and the Decomposition of Organo-Mercury Compounds - a Review. *Neth. J. Agric. Sci.* 24: 79-97.

Liang, L., M. Horvat, and N. S. Bloom. **1994** An Improved Speciation Method for Mercury by GC/CVAFS after Aqueous Phase Ethylation. *Talanta* 41:371-379.

Lindqvist, O. **1992**. Atmospheric Cycling of Mercury: An Overview. *Mercury Pollution, Integration and Synthesis*; Watras, C. J. and Huckabee, C. J.; Lewis Publishers: Boca Raton, Ann Arbor, London, and Tokyo, 1994.

Lindqvist, O. **1991**. Mercury in the Swedish Environment - Recent Research on Causes, Consequences and Corrective Methods. *Water, Air, and Soil Pollut.*, 55: 193-250.

Marchant,W. N. **1974**. Modified Cellulose Adsorbent for Removal of Mercury from Aqueous Solutions. *Environmental Science & Technology*. 8:993-996.

Martin, T., Kopp, J., and Ediger, R. **1975**. Determining Selenium in Water, Waste Water, Sediment, and Sludge by flameless atomic absorption spectroscopy. *Atomic Absorption Newsletter* 14(5): 109-116.

MPCA Mercury Task Force. **1994**. Strategies for Reducing Mercury in Minnesota. Edited by Edward B. Swain. 58 pp.

Paulsson, K. M. and Björnberg, A. **1988**. U.S. Patent Number 4,780,214.

Paulsson, K and Lundburgh, K. **1991**. Treatment of Mercury Contaminated Fish by Selenium Addition. *Water, Air, and Soil Pollut.* 56:833-841.

Ritter, J. A., and Bibler, J. P. **1992**. Removal of Mercury from Waste Water: Large-Scale Performance of an Ion Exchange Process. *Wat. Sci. Tech.* 25:165-172.

Rudd, J. W. M. and Hamilton, R. D. **1978**. Methane Cycling in a Eutrophic Shield Lake and its Effects on Whole Lake Metabolism. *Limnol. Ocean.* 23(2): 337-355.

Rudd, J. W. M. & Turner, M. A. **1983a**. The English-Wabigoon River System: II. Suppression of Mercury and Selenium Bioaccumulation by Suspended and Bottom Sediments. *Can. J. Fish. Aquat. Sci.* 40:2218-2227.

Rudd, J. W. M. and Turner, M. A. **1983b**. The English-Wabigoon River System: V. Mercury and Selenium Bioaccumulation as a Function of Aquatic Primary Productivity. *Can. J. Fish. Aquat. Sci.* 40: 2251-2259.

Rudd, J. W. M. , Turner, M. A., Furutani, A., Swick, A., and Townsend, B. E. **1983**. The English-Wabigoon River System: I A synthesis of Recent Research with a View Towards Mercury Amelioration. *Can. J. Fish. Aquat. Sci.* 40:2206-2217.

Rudd, J. W. M., Turner, M. A., Townsend, B. E., Swick, A., and Furutani, A. **1980**. Dynamics of Selenium in Mercury-Contaminated Experimental Freshwater Ecosystems. *Can. J. Fish Aquat. Sci.* 37:848-857.

Siefert, R. E, *et al.* **1989**. Effects of Chlorpyrifos on a Natural Aquatic System: Littoral Enclosures for Aquatic Field Testing of Pesticides. In: Using Mesocosms to Assess the Aquatic Ecological Risk of Pesticides: Theory and Practice, J. Reese Voshell, Jr. (Ed.). Entomological Society of America. MPPEAL 75: 57-73.

Sorensen, J. A., Glass, G. E., Schmidt, K. W., Huber, J. K., and Rapp, G. R., Jr. **1990**. Airborne Mercury Deposition and Watershed Characteristics in Relation to Mercury Concentrations in Water, Sediments, Plankton, and Fish of Eighty Northern Minnesota Lakes. *Environ. Sci. Technol.*, 24: 1716-1727.

Sorensen, J. A., G. E. Glass, K. W. Schmidt **1994**. Regional Patterns of Wet Mercury Deposition. *Environ. Sci. Technol.*, In Review.

Turner, R.R., Saouter, E., and Barkay, T. **1992**. *The Role of Biotic and Abiotic Mercury Reduction and Volatilization in the Removal of Mercury from a Contaminated Stream and Pond.* Paper presented at Internat. Conf. on Mercury as a Global Pollutant held at Monterey, CA.

Turner, M. A. & Rudd, J. W. M. **1983**. The English-Wabigoon River System: III. Selenium in Lake Enclosures: Its Chemistry, Bioaccumulation, and Ability to Reduce Mercury Bioaccumulation. *Can. J. Fish. Aquat. Sci.* 40:2228-2240.

Turner, M. A. & Swick, A.L. **1983**. The English-Wabigoon River System: IV. Interaction between Mercury and Selenium Accumulated from Waterborne and Dietary Sources by Northern Pike (*Esox lucius*). *Can. J. Fish. Aquat. Sci.* 40:2241-2250.

Uthe, J. F., Solomon, J., and Grift, B. **1972**. Rapid Semimicro Method for the Determination of Methyl Mercury in Fish Tissue. *J. of the AOAC* 55:583-589.

Vo-Dinh, T., Hiromoto, M. Y. K., Begun, G. M., and Moody, R. L. **1984**. Surface-Enhanced Raman Spectrometry for Trace Organic Analysis. *Anal. Chem.* 56:1667-1670.

Weber, J. H. **1993**. Rev. Abiotic Methylation of Hg(II) in Aqu. Environ. *Chemosph.* 26:2063.

Winfrey, M. R. and Rudd, J. W. M. **1990**. Review: Environmental Factors Affecting the Formation of Methylmercury in Low pH Lakes. *Environ. Toxicol. Chem.* 9: 853-869.

Table III. Summary of Pilot Tests, for the Reduction of Mercury in Fish, Conducted from 1991 through 1994 [a]

Enc. No.	Sand Point Lake				St. Louis River Estuary (at Indian Point)		
	1991 Protocol Development	1992 Mitigation Study	1993[b] Mechanism Study	1994 Mechanism Study	1992 Protocol Development	1993 Mechanism Study	1994 Mechanism Study
1	Ambient Lake Conditions	Ambient Lake Conditions	Ambient Lake Conditions	Ambient Lake Conditions	Ambient Estuary Conditions	Ambient Estuary Conditions	Ambient Estuary Conditions
2	pH Elevation	Micronutrient Addition, 2 ppb	Micronutrient Addition, 1 ppb	Micronutrient Carryover	Boundary Control Conditions	Boundary Control Conditions	Boundary Control Conditions
3	Control Conditions	Control Conditions	Control Conditions	Control Conditions	Precipitant 2	No Wet Deposition	Micronutrient Addition, 2 ppb
4	Hg Complexor 1	Hg Complexor 1	Covered Sediment	2X Wet Deposition	Interior Control Conditions	2X Wet Deposition	Organic Removal
5	pH Elevation	Precipitant 1	Aeration	No Wet Deposition	Precipitant 2	Interior Control Conditions	Interior Control Conditions
6	Control Conditions	Organic Additions	Precipitant 3	Organic Addition	Interior Control Conditions	No Wet Deposition	Micronutrient Addition, 0.5 ppb
7	Hg Complexor 1	Precipitant 1	Aeration	No Wet Deposition	Boundary Control Conditions	2X Wet Deposition	Micronutrient Addition, 1 ppb
8	pH Elevation	Micronutrient Addition, 2 ppb	Micronutrient Addition, 1 ppb	Micronutrient Carryover	Ambient Estuary Conditions	Hg Complexor 2	Micronutrient Addition, 0.5 ppb
9	Control Conditions	Organic Additions	Precipitant 3	Organic Addition		Hg Complexor 3	Micronutrient Addition, 1 ppb
10	Hg Complexor 1	Hg Complexor 1	Covered Sediment	2X Wet Deposition		Hg Complexor 2	Organic Removal
11	Control Conditions	Control Conditions	Control Conditions	Control Conditions		Hg Complexor 3	Micronutrient Addition, 2 ppb
12	Ambient Lake Conditions	Ambient Lake Conditions	Ambient Lake Conditions	Ambient Lake Conditions		Boundary Control Conditions	Boundary Control Conditions
13						Ambient Estuary Conditions	Ambient Estuary Conditions

[a]The following definitions are used: **Ambient Conditions** - The adjacent area outside of the enclosures; **pH Increase** - Adjustment of pH using .1M Sodium hydroxide; **Mercury Complexor 1** - 2,3-Dimercapto-1-propanol (BAL); **Mercury Complexor 2** - 2,3 dimercapto-1-propanesulfonic acid, sodium salt; **Mercury Complexor 3** - meso-2,3-Dimercaptosuccinic acid; **Micronutrient Addition** - Low concentrations of Sodium selenite pentahydrate; **Precipitant 1** - Thiol functionalized chloromethylated copolymer of styrene and divinylbenzene; **Precipitant 2** - 2,4,6-Trimercapto-s-triazine, trisodium salt; **Precipitant 3** - Tellurium (IV) tetrachloride; **Organic Additions** - aquatic vegetation collected from the shore introduced as dried (1992) and wet detritus (1994); **Organic Removal** - removed most of vegetative litter from within enclosure and up to 7 m onto the shore; **Covered Sediment** - Covering of the sediment with 5 - 7 cm of low in mercury sand; **Aeration** - Mechanical surface water agitation; **No Wet Deposition** - Enclosure covered to keep precipitation out; **2X Wet Deposition** - Runoff from covered enclosure directed into the selected enclosure.

[b]All vegetative litter was removed from each enclosure prior to testing.

Table IVa. Comparison of Water Quality Parameters between Ambient and Enclosed Control Areas

Parameter (units)	Site	Year	Control Mean	Control S.Dev.	Control n	Ambient Mean	Ambient S.Dev.	Ambient n	Mean Diff.[a]	T-Test Prob.[b]
Temperature (°C) [At 50 cm Depth]	Sand Point L.	92	16.7	2.9	28	17.7	2.7	28	1.0	<0.01
		93	17.7	4.5	32	18.6	4.3	32	0.9	<0.01
		94	18.9	2.9	42	20.2	2.6	42	1.3	<0.01
	St Louis R.	92	17.3	4.2	56	18.1	3.9	28	0.8	<0.01
		93	17.8	4.9	66	18.3	5.2	44	0.5	0.59
		94	19.6	2.0	96	20.3	2.1	64	0.7	<0.01
Conductivity (µS/cm) [Corrected to 25°C and at 50 cm Depth]	Sand Point L.	92	60.0	5.5	28	65.4	2.1	28	5.4	<0.01
		93	47.5	11.9	32	66.1	3.2	32	18.6	<0.01
		94	48.0	9.2	42	60.2	4.5	42	12.2	<0.01
	St Louis R.	92	168	22	56	159	25	28	-9	<0.01
		93	195	59	66	146	27	44	-49	<0.01
		94	218	96	96	147	27	64	-71	<0.01
Turbidity (NTU)	Sand Point L.	92	7.9	6.6	14	1.4	0.7	14	-6.5	<0.01
		93	10.4	14.3	16	2.5	2.9	16	-7.9	0.04
		94	9.5	8.4	16	2.4	0.9	16	-7.1	<0.01
	St Louis R.	92	12.3	7.1	36	15.0	12.1	18	2.7	0.31
		93	11.9	7.8	21	13.0	9.6	14	1.1	0.92
		94	18.2	17.3	21	9.9	6.1	14	-8.3	<0.01
Filtered Color (PT-Co)	Sand Point L.	92	47.1	10.9	14	53.6	2.3	14	6.5	0.03
		93	49.3	11.6	14	90.0	12.9	14	40.7	<0.01
		94	45.0	15.7	16	66.9	8.6	16	21.9	<0.01
	St Louis R.	92	143	36	36	146	36	18	3	0.79
		93	174	39	21	198	49	14	24	<0.01
		94	130	37	21	168	46	14	38	<0.01
Dissolved Oxygen (mg/L)	Sand Point L.	92	9.2	0.5	14	8.7	0.4	14	-0.5	0.02
		93	8.7	1.9	26	8.7	1.9	26	0.0	0.58
		94	9.3	2.0	12	9.8	2.2	12	0.5	<0.01
	St Louis R.	92	7.6	1.0	32	8.5	1.4	16	0.9	<0.01
		93	8.4	2.1	42	8.6	2.2	28	0.2	<0.01
		94	7.6	1.8	12	8.0	1.7	8	0.4	0.21
pH	Sand Point L.	92	7.57	0.27	14	7.42	0.16	14	-0.15	0.05
		93	7.09	0.40	14	7.42	0.09	14	0.33	<0.01
		94	7.38	0.21	16	7.26	0.30	16	-0.12	0.07
	St Louis R.	92	7.64	0.12	37	7.85	0.16	17	0.21	<0.01
		93	7.77	0.14	21	7.80	0.08	14	0.03	0.20
		94	7.93	0.22	21	7.67	0.24	14	-0.26	<0.01

Parameter (units)	Site	Year	Control Mean	Control S.Dev.	Control n	Ambient Mean	Ambient S.Dev.	Ambient n	Mean Diff.[a]	T-Test Prob.[b]
Total Organic Carbon (mg/L)	Sand Point L.	92	14.8	2.3	6	15.5	1.3	6	0.7	0.44
		93	14.3	2.3	6	17.4	1.7	6	3.1	0.08
		94	—	—	—	—	—	—	—	—
	St Louis R.	92	25.2	2.5	8	25.2	1.7	4	0.0	0.02
		93	25.9	3.7	9	28.9	4.9	6	3.0	0.17
		94	—	—	—	—	—	—	—	—
Chlorophyll-a (µg/L)	Sand Point L.	92	1.4	0.4	2	1.7	1.2	2	0.3	0.67
		93	1.8	0.6	6	3.0	2.5	6	1.2	0.24
		94	3.3	1.6	6	2.6	1.7	6	-0.7	0.41
	St Louis R.	92	4.9	1.1	4	9.8	0.5	2	4.9	0.04
		93	6.1	1.5	9	4.4	1.7	6	-1.7	0.07
		94	3.2	6.5	9	4.0	2.9	6	0.8	>0.99
Periphyton Density (mg/cm^2) [End Date Only and Wet Samples Only]	Sand Point L.	92	2.3	2.9	2	3.9	2.0	2	1.6	0.73
		93	3.2	3.5	2	7.8	2.8	2	4.6	0.07
		94	0.9	1.1	2	8.1	1.0	2	7.2	0.13
	St Louis R.	92	3.7	1.8	4	3.7	3.3	2	0.0	0.59
		93	4.5	2.8	3	3.1	2.8	2	-1.4	0.09
		94	4.7	2.3	3	2.6	1.2	2	-2.1	0.42
Plankton Density (µg/L)	Sand Point L.	92	12.8	7.9	14	12.2	7.6	14	-0.6	0.84
		93	7.1	4.9	14	6.8	6.7	14	-0.3	0.87
		94	21.0	10.8	6	15.6	12.0	6	-5.4	0.27
	St Louis R.	92	58.1	50.9	36	58.3	29.5	18	0.2	0.67
		93	191	287	21	219	409	14	28	0.78
		94	120	64	12	163	195	8	43	0.59
Fish Length (cm) [End Date Only]	Sand Point L.	92	4.62	0.41	15	5.53	0.39	10	0.91	<0.01
		93	4.86	0.29	10	5.68	0.42	10	0.82	<0.01
		94	6.44	1.10	5	5.76	0.43	10	-0.68	0.10
	St Louis R.	92	3.82	0.70	20	4.68	0.63	5	0.86	0.02
		93	4.25	0.59	13	5.07	0.41	10	0.82	<0.01
		94	4.65	0.57	13	6.01	1.14	10	1.36	0.03
Fish Mass (g) [End Date Only]	Sand Point L.	92	0.82	0.32	15	1.50	0.37	10	0.68	<0.01
		93	0.99	0.19	10	1.48	0.37	10	0.49	<0.01
		94	2.87	1.45	5	1.78	0.41	10	-1.09	0.04
	St Louis R.	92	0.63	0.38	20	1.08	0.43	5	0.45	0.03
		93	0.85	0.36	13	1.42	0.45	10	0.57	<0.01
		94	1.22	0.67	13	3.26	2.03	10	2.04	0.04

Table IVa (Continued)

Parameter (units)	Site	Year	Control			Ambient			Mean Diff.[a]	T-Test Prob.[b]
			Mean	S.Dev.	n	Mean	S.Dev.	n		
Fish Condition Factor ($100M/L^3$) [End Date Only]	Sand Point L.	92	0.81	0.07	15	0.87	0.04	10	0.06	0.06
		93	0.85	0.04	10	0.79	0.04	10	-0.06	<0.01
		94	1.00	0.06	5	0.92	0.07	10	-0.08	0.03
	St Louis R.	92	1.00	0.09	20	0.99	0.08	5	-0.01	0.94
		93	1.04	0.06	13	1.06	0.08	10	0.02	0.46
		94	1.17	0.02	2	1.39	0.09	2	0.22	0.15
Total Hg in Water (ng/L)	Sand Point L.	92	2.4	1.3	14	1.8	2.0	14	-0.6	0.40
		93	3.3	1.6	14	2.5	1.0	14	-0.8	0.02
		94	3.4	2.0	16	2.2	1.4	18	-1.2	0.03
	St Louis R.	92	3.3	1.2	36	3.9	1.4	18	0.6	0.08
		93	4.2	1.4	21	5.5	2.0	14	1.3	0.01
		94	2.4	1.5	23	3.9	2.2	16	1.5	0.02
Methyl Hg in Water (ng/L)	Sand Point L.	92	0.16	0.03	4	0.18	0.03	3	0.02	0.55
		93	0.15	0.06	6	0.22	0.05	6	0.07	<0.01
		94	0.24	0.11	6	0.23	0.07	5	-0.01	0.87
	St Louis R.	92	0.16	0.10	8	0.22	0.13	4	0.06	0.16
		93	0.19	0.07	9	0.29	0.13	6	0.10	0.05
		94	0.07	0.03	6	0.39	0.28	6	0.32	0.10
Hg in Periphyton (ng/g) [End Date Only and Wet Samples Only]	Sand Point L.	92	60.1	66.7	4	20.5	20.5	3	-39.6	0.39
		93	54.9	37.3	2	10.9	1.4	2	-44.0	0.33
		94	24.3	29.0	2	9.1	2.4	2	-15.2	0.57
	St Louis R.	92	27.9	10.0	4	25.2	18.8	2	-2.7	0.77
		93	20.7	6.5	3	51.4	37.7	2	30.7	0.42
		94	15.4	3.2	3	27.6	3.0	2	12.2	0.20
Hg in Vegetation[c] (ng/g) [Wet Leaf Samples and End Date Only]	Sand Point L.	92	66.3	28.6	2	57.7	12.2	2	-8.6	0.60
		93	—	—	—	—	—	—	—	—
		94	—	—	—	—	—	—	—	—
	St Louis R.	92	34.1	15.9	4	62.0	46.7	2	27.9	0.58
		93	18.4	1.7	3	33.4	6.2	2	15.0	0.25
		94	—	—	—	—	—	—	—	—
Hg in Plankton (ng/g)	Sand Point L.	92	294	309	14	298	367	14	4	0.97
		93	828	1470	14	571	542	14	-257	0.50
		94	267	185	6	190	173	6	-77	0.31
	St Louis R.	92	165	232	36	128	82	18	-37	0.35
		93	285	274	21	338	391	14	53	0.09
		94	167	125	12	296	265	8	129	0.07

Parameter (units)	Site	Year	Control			Ambient			Mean Diff.[a]	T-Test Prob.[b]
			Mean	S.Dev.	n	Mean	S.Dev.	n		
Hg in Fish (ng/g) [End Date Only]	Sand Point L.	92	65.6	12.9	15	66.8	9.2	10	1.2	0.81
		93	79.6	13.6	10	121.0	16.4	10	41.4	<0.01
		94	59.3	29.4	5	110.6	9.1	10	51.3	<0.01
	St Louis R.	92	39.0	5.6	20	53.2	15.7	5	14.2	<0.01
		93	57.8	5.4	13	65.2	6.7	10	7.4	<0.01
		94	34.9	6.6	13	49.1	8.6	10	14.2	0.01
Fish Body Burden (ng Hg per fish) [End Date Only]	Sand Point L.	92	55.3	17.3	15	100.9	32.4	10	45.6	<0.01
		93	76.9	11.8	10	176.7	45.8	10	99.8	<0.01
		94	140.1	31.8	5	198.7	54.4	10	58.6	0.03
	St Louis R.	92	23.0	11.8	20	60.1	30.2	5	37.1	0.02
		93	49.3	21.5	13	91.8	25.8	10	42.5	0.01
		94	38.6	11.5	13	149.7	66.2	10	111.1	<0.01
Hg in Sediment (ng/g) [End Date Only]	Sand Point L.	92	—	—	—	—	—	—	—	—
		93	9.2	8.2	2	6.0	1.6	2	-3.2	0.72
		94	2.8	0.1	2	7.4	.6.7	2	4.6	0.51
	St. Louis R.	92	—	—	—	—	—	—	—	—
		93	24.1	4.6	3	28.7	23.3	2	4.6	0.72
		94	21.3	2.4	3	23.5	6.9	2	2.2	0.58

[a] Average of ambient minus control values paired by sampling date.

[b] Probability that ambient and control sample means are from the same distribution.

[c] Sand Point: aquatic grass; St. Louis River: bull rush.

Table IVb. Comparison of Water Quality Parameters between Enclosed Treatment and Enclosed Control Areas

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Temperature (°C) [At 50 cm Depth]	Sand Point L.	92	16.7	2.9	28	Micronutrient, 2 ppb	16.8	3.0	28	0.1	0.02
						Mercury Complexor 1	16.7	2.9	28	0.0	0.09
						Precipitant 1	16.6	3.0	28	-0.1	0.05
						Organic Additions	16.6	3.0	28	-0.1	0.71
		93	17.7	4.5	32	Micronutrient, 1 ppb	17.8	4.7	32	0.1	0.11
						Covered Sediment	17.7	4.5	32	0.0	0.61
						Aeration, Water	17.7	4.7	32	0.0	0.39
						Precipitant 3	17.8	4.5	32	0.1	0.24
		94	18.9	2.9	42	Micronutrient Carryover	19.0	2.9	42	0.1	0.06
						Wet Deposition, 2X	18.8	3.0	42	-0.1	0.03
						No Wet Deposition	18.6	2.7	42	-0.3	<0.01
						Organic Addition	18.9	2.9	42	0.0	0.46
	St Louis R.	92	17.3	4.2	56	Interior Controls[d]	17.2	4.1	28	-0.1	0.07
						Precipitant 2	17.3	4.3	28	0.0	0.03
		93	17.8	4.9	66	Interior Controls[d]	17.8	4.9	22	0.0	0.41
						Wet Deposition, 2X	17.7	4.9	44	-0.1	0.22
						No Wet Deposition	17.8	4.8	44	0.0	0.46
						Mercury Complexor 2	17.8	4.8	44	0.0	0.86
						Mercury Complexor 3	17.7	4.9	44	-0.1	0.02
		94	19.6	2.0	96	Interior Controls[d]	19.5	2.0	32	-0.1	0.39
						Organic Removal	19.5	2.0	64	-0.1	0.03
						Micronutrient, 0.5 ppb	19.6	2.0	64	0.0	0.85
						Micronutrient, 1 ppb	19.6	2.0	64	0.0	0.49
						Micronutrient, 2 ppb	19.6	2.0	64	0.0	0.30
Conductivity (µS/cm) [Corrected to 25°C and at 50 cm Depth]	Sand Point L.	92	60.0	5.5	28	Micronutrient, 2 ppb	53.6	3.9	28	-6.4	<0.01
						Mercury Complexor 1	54.4	6.0	28	-5.6	<0.01
						Precipitant 1	54.3	5.4	28	-5.7	<0.01
						Organic Additions	59.7	4.4	28	-0.3	0.53
		93	47.5	11.9	32	Micronutrient, 1 ppb	47.5	12.2	32	0.0	0.99
						Covered Sediment	50.0	18.0	32	2.5	0.28
						Aeration, Water	49.2	9.9	32	1.7	0.03
						Precipitant 3	51.9	11.6	32	4.4	<0.01
		94	48.0	9.2	42	Micronutrient Carryover	38.9	6.7	42	-9.1	<0.01
						Wet Deposition, 2X	44.3	9.8	42	-3.7	<0.01
						No Wet Deposition	50.9	6.9	42	2.9	0.10
						Organic Addition	46.3	7.1	42	-1.7	0.02
	St Louis R.	92	168	22	56	Interior Controls[d]	169	22	28	1	0.07
						Precipitant 2	170	20	28	2	0.25
		93	195	59	66	Interior Controls[d]	158	23	22	-37	<0.01
						Wet Deposition, 2X	161	16	44	-34	<0.01
						No Wet Deposition	162	19	44	-33	<0.01
						Mercury Complexor 2	189	43	44	-6	<0.01
						Mercury Complexor 3	213	48	44	18	>0.99
		94	218	96	96	Interior Controls[d]	164	23	32	-54	<0.01
						Organic Removal	209	59	64	-9	<0.01
						Micronutrient, 0.5 ppb	171	26	64	-47	<0.01
						Micronutrient, 1 ppb	179	19	64	-39	<0.01
						Micronutrient, 2 ppb	203	57	64	-15	<0.01

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Turbidity (NTU)	Sand Point L.	92	7.9	6.6	14	Micronutrient, 2 ppb	3.8	2.9	14	-4.1	<0.01
						Mercury Complexor 1	4.5	4.0	14	-3.4	<0.01
						Precipitant 1	7.6	7.5	14	-0.3	0.79
						Organic Additions	7.7	5.8	14	-0.2	0.92
		93	10.4	14.3	16	Micronutrient, 1 ppb	4.5	3.0	16	-5.9	0.08
						Covered Sediment	9.1	4.2	16	-1.3	0.67
						Aeration, Water	9.2	6.5	16	-1.2	0.66
						Precipitant 3	6.2	5.9	16	-4.2	0.17
		94	9.5	8.4	16	Micronutrient Carryover	2.6	1.0	14	-6.9	<0.01
						Wet Deposition, 2X	3.8	2.2	14	-5.7	<0.01
						No Wet Deposition	4.2	1.9	14	-5.3	0.03
						Organic Addition	3.3	2.8	14	-6.2	<0.01
	St Louis R.	92	12.3	7.1	36	Interior Controls[d]	12.0	6.8	18	-0.3	0.07
						Precipitant 2	12.4	6.7	18	0.1	0.83
		93	11.9	7.8	21	Interior Controls[d]	9.2	2.2	7	-2.7	<0.01
						Wet Deposition, 2X	9.1	3.7	14	-2.8	<0.01
						No Wet Deposition	9.1	3.9	14	-2.8	<0.01
						Mercury Complexor 2	14.1	7.6	14	2.2	<0.01
						Mercury Complexor 3	18.0	10.2	14	6.1	0.07
		94	18.2	17.3	21	Interior Controls[d]	8.0	5.0	7	-10.2	<0.01
						Organic Removal	10.9	7.8	12	-7.3	<0.01
						Micronutrient, 0.5 ppb	5.8	2.5	12	-12.4	<0.01
						Micronutrient, 1 ppb	7.0	3.0	12	-11.2	<0.01
						Micronutrient, 2 ppb	13.7	11.4	12	-4.5	0.07
Filtered Color (PT-Co)	Sand Point L.	92	47.1	10.9	14	Micronutrient, 2 ppb	42.9	7.8	14	-4.2	0.12
						Mercury Complexor 1	40.4	11.2	14	-6.7	0.01
						Precipitant 1	41.8	9.5	14	-5.3	0.01
						Organic Additions	47.9	6.4	14	0.8	0.77
		93	49.3	11.6	14	Micronutrient, 1 ppb	43.6	9.1	14	-5.7	0.09
						Covered Sediment	43.6	10.5	14	-5.7	0.08
						Aeration, Water	49.3	7.0	14	0.0	>0.99
						Precipitant 3	53.6	4.6	14	4.3	0.12
		94	45.0	15.7	16	Micronutrient Carryover	38.6	6.0	14	-6.4	0.27
						Wet Deposition, 2X	24.6	5.4	14	-20.4	<0.01
						No Wet Deposition	50.7	3.9	14	5.7	<0.01
						Organic Addition	35.0	7.8	14	-10.0	0.01
	St Louis R.	92	143	36	36	Interior Controls[d]	142	35	18	-1	0.36
						Precipitant 2	141	35	18	-2	0.17
		93	174	39	21	Interior Controls[d]	176	46	7	2	0.41
						Wet Deposition, 2X	169	43	14	-5	0.22
						No Wet Deposition	183	40	14	9	0.46
						Mercury Complexor 2	174	40	14	0	0.83
						Mercury Complexor 3	168	43	14	-6	0.02
		94	130	37	21	Interior Controls[d]	153	48	7	23	0.04
						Organic Removal	145	37	12	15	0.04
						Micronutrient, 0.5 ppb	138	45	12	8	0.13
						Micronutrient, 1 ppb	117	19	12	-13	0.88
						Micronutrient, 2 ppb	135	46	12	5	0.18

Table IVb. Continued.

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Dissolved Oxygen (mg/L)	Sand Point L.	92	9.2	0.5	14	Micronutrient, 2 ppb	8.9	0.4	14	-0.3	0.02
						Mercury Complexor 1	9.1	0.4	14	-0.1	0.61
						Precipitant 1	9.0	0.4	14	-0.2	0.16
						Organic Additions	8.3	0.5	14	-0.9	<0.01
		93	8.7	1.9	26	Micronutrient, 1 ppb	8.7	1.9	26	0.0	0.76
						Covered Sediment	8.8	1.8	26	0.1	<0.01
						Aeration, Water	8.6	1.9	26	-0.1	0.87
						Precipitant 3	8.5	1.9	26	-0.2	0.05
		94	9.3	2.0	12	Micronutrient Carryover	9.3	2.1	12	0.0	0.65
						Wet Deposition, 2X	9.4	1.8	12	0.1	0.45
						No Wet Deposition	9.2	1.9	12	-0.1	0.34
						Organic Addition	9.2	1.7	12	-0.1	0.61
	St Louis R.	92	7.6	1.0	32	Interior Controls[d]	7.4	0.9	16	-0.2	<0.01
						Precipitant 2	7.5	1.0	16	-0.1	0.04
		93	8.4	2.1	42	Interior Controls[d]	8.4	1.9	14	0.0	0.81
						Wet Deposition, 2X	8.4	2.1	28	0.0	0.81
						No Wet Deposition	8.5	2.1	28	0.1	0.25
						Mercury Complexor 2	8.1	2.1	28	-0.3	0.02
						Mercury Complexor 3	8.0	2.1	28	-0.4	<0.01
		94	7.6	1.8	12	Interior Controls[d]	7.7	1.8	8	0.1	0.70
						Organic Removal	7.5	1.7	8	-0.1	0.56
						Micronutrient, 0.5 ppb	7.6	1.9	8	0.0	0.64
						Micronutrient, 1 ppb	7.4	1.7	8	-0.2	0.20
						Micronutrient, 2 ppb	7.5	1.8	8	-0.1	0.70
pH	Sand Point L.	92	7.57	0.27	14	Micronutrient, 2 ppb	7.39	0.36	14	-0.18	0.12
						Mercury Complexor 1	7.47	0.30	14	-0.10	0.29
						Precipitant 1	7.45	0.29	14	-0.12	0.19
						Organic Additions	7.39	0.40	14	-0.18	0.20
		93	7.09	0.40	14	Micronutrient, 1 ppb	7.03	0.32	14	-0.06	0.39
						Covered Sediment	7.16	0.37	14	0.07	0.25
						Aeration, Water	7.26	0.15	14	0.17	0.06
						Precipitant 3	7.09	0.29	14	0.00	>0.99
		94	7.38	0.21	16	Micronutrient Carryover	6.93	0.12	14	-0.45	<0.01
						Wet Deposition, 2X	7.45	0.40	14	0.07	0.23
						No Wet Deposition	7.24	0.11	14	-0.14	0.11
						Organic Addition	7.30	0.12	14	-0.08	0.15
	St Louis R.	92	7.64	0.12	37	Interior Controls[d]	7.60	0.11	18	-0.04	<0.01
						Precipitant 2	7.63	0.09	18	-0.01	0.05
		93	7.77	0.14	21	Interior Controls[d]	7.64	0.09	7	0.13	<0.01
						Wet Deposition, 2X	7.74	0.08	14	-0.03	<0.01
						No Wet Deposition	7.78	0.09	14	0.01	0.05
						Mercury Complexor 2	7.71	0.30	14	-0.06	0.14
						Mercury Complexor 3	7.85	0.10	14	0.08	0.65
		94	7.93	0.22	21	Interior Controls[d]	7.75	0.20	7	-0.18	<0.01
						Organic Removal	7.91	0.21	12	-0.02	<0.01
						Micronutrient, 0.5 ppb	7.96	0.23	12	0.03	0.06
						Micronutrient, 1 ppb	8.06	0.26	12	0.13	0.96
						Micronutrient, 2 ppb	8.00	0.36	12	0.07	0.46

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Total Organic Carbon (mg/L)	Sand Point L.	92	14.8	2.3	6	Micronutrient, 2 ppb	15.0	2.8	6	0.2	0.84
						Mercury Complexor 1	14.6	2.0	6	-0.2	0.78
						Precipitant 1	14.9	1.5	6	0.1	0.94
						Organic Additions	15.0	1.4	6	0.2	0.80
		93	14.3	2.3	6	Micronutrient, 1 ppb	14.4	1.8	6	0.1	0.96
						Covered Sediment	13.2	2.6	6	-1.1	0.25
						Aeration, Water	15.0	0.7	6	0.7	0.60
						Precipitant 3	16.5	2.6	6	2.2	0.18
		94	—	—	—	Micronutrient Carryover	—	—	—	—	—
						Wet Deposition, 2X	—	—	—	—	—
						No Wet Deposition	—	—	—	—	—
						Organic Addition	—	—	—	—	—
	St Louis R.	92	25.2	2.5	8	Interior Controls[d]	26.8	1.8	4	1.6	0.07
						Precipitant 2	27.3	2.6	4	2.1	0.07
		93	25.9	3.7	9	Interior Controls[d]	24.9	2.4	3	-1.0	0.33
						Wet Deposition, 2X	24.6	2.8	6	-1.3	0.29
						No Wet Deposition	26.9	4.2	6	1.0	0.71
						Mercury Complexor 2	25.6	3.4	6	-0.3	0.68
						Mercury Complexor 3	23.9	3.4	6	-2.0	0.03
		94	—	—	—	Interior Controls[d]	—	—	—	—	—
						Organic Removal	—	—	—	—	—
						Micronutrient, 0.5 ppb	—	—	—	—	—
						Micronutrient, 1 ppb	—	—	—	—	—
						Micronutrient, 2 ppb	—	—	—	—	—
Chlorophyll-a (µg/L)	Sand Point L.	92	1.4	0.4	2	Micronutrient, 2 ppb	2.1	1.1	2	0.7	0.64
						Mercury Complexor 1	1.5	0.0	2	0.1	0.78
						Precipitant 1	1.7	0.3	2	0.3	0.20
						Organic Additions	2.1	0.6	2	0.7	0.05
		93	1.8	0.6	6	Micronutrient, 1 ppb	3.9	2.8	6	2.1	0.10
						Covered Sediment	1.7	1.2	6	-0.1	0.93
						Aeration, Water	2.1	1.3	6	0.3	0.43
						Precipitant 3	4.2	3.3	6	2.4	0.11
		94	3.3	1.6	6	Micronutrient Carryover	6.0	3.1	3	2.7	0.07
						Wet Deposition, 2X	1.7	1.1	4	-1.6	0.48
						No Wet Deposition	4.1	4.2	4	0.8	0.43
						Organic Addition	2.2	2.3	4	-1.1	0.67
	St Louis R.	92	4.9	1.1	4	Interior Controls[d]	4.2	1.1	2	-0.7	0.51
						Precipitant 2	3.9	0.7	2	-1.0	0.37
		93	6.1	1.5	9	Interior Controls[d]	5.7	0.9	3	-0.4	0.39
						Wet Deposition, 2X	5.8	1.0	6	-0.3	0.74
						No Wet Deposition	5.5	2.0	6	-0.6	0.37
						Mercury Complexor 2	4.5	2.6	6	-1.6	0.13
						Mercury Complexor 3	3.1	0.6	6	-3.0	<0.01
		94	3.2	6.5	9	Interior Controls[d]	1.8	0.9	3	-1.4	0.55
						Organic Removal	3.7	2.0	4	0.5	0.65
						Micronutrient, 0.5 ppb	2.2	1.4	4	-1.0	0.47
						Micronutrient, 1 ppb	1.7	1.2	4	-1.5	0.42
						Micronutrient, 2 ppb	2.4	2.1	4	-0.8	0.57

Table IVb. Continued.

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Plankton Density (µg/L)	Sand Point L.	92	12.8	7.9	14	Micronutrient, 2 ppb	19.0	16.3	14	6.2	0.10
						Mercury Complexor 1	21.1	16.0	14	8.3	0.04
						Precipitant 1	12.3	10.6	14	-0.5	0.86
						Organic Additions	20.9	13.9	14	8.1	0.04
		93	7.1	4.9	14	Micronutrient, 1 ppb	10.1	10.9	14	3.0	0.40
						Covered Sediment	10.4	9.8	14	3.3	0.22
						Aeration, Water	8.8	10.3	10	1.7	0.70
						Precipitant 3	11.6	9.9	14	4.5	0.12
		94	21.0	10.8	6	Micronutrient Carryover	16.9	6.2	6	-4.1	0.41
						Wet Deposition, 2X	12.0	5.4	6	-9.0	0.02
						No Wet Deposition	9.4	3.6	6	-11.6	0.01
						Organic Addition	14.5	8.2	6	-6.5	0.13
	St Louis R.	92	58.1	50.9	36	Interior Controls[d]	52.6	40.5	18	-5.5	0.44
						Precipitant 2	52.4	55.2	18	-5.7	0.55
		93	191	287	21	Interior Controls[d]	119	179	7	-72	0.08
						Wet Deposition, 2X	154	232	14	-37	0.07
						No Wet Deposition	342	812	14	151	0.61
						Mercury Complexor 2	129	97	14	-62	0.15
						Mercury Complexor 3	118	113	14	-73	0.13
		94	120	64	12	Interior Controls[d]	116	78	4	-4	0.14
						Organic Removal	176	138	8	56	0.35
						Micronutrient, 0.5 ppb	153	105	8	33	0.20
						Micronutrient, 1 ppb	130	43	8	10	0.06
						Micronutrient, 2 ppb	113	85	8	-7	0.26
Periphyton Density (mg/cm^2) [End Date and Wet Samples Only]	Sand Point L.	92	2.0	2.5	2	Micronutrient, 2 ppb	3.9	3.1	2	1.9	0.72
						Mercury Complexor 1	4.5	0.8	2	2.5	0.29
						Precipitant 1	1.8	1.4	2	-0.2	0.82
						Organic Additions	2.5	1.0	2	0.5	0.89
		93	3.2	3.5	2	Micronutrient, 1 ppb	0.1	0.1	2	-3.1	0.43
						Covered Sediment	2.5	1.9	2	-0.7	0.67
						Aeration, Water	1.5	0.9	2	-1.7	0.53
						Precipitant 3	5.6	7.0	2	2.4	0.51
		94	0.9	1.1	2	Micronutrient Carryover	1.8	2.5	2	0.9	0.53
						Wet Deposition, 2X	2.6	3.5	2	1.7	0.50
						No Wet Deposition	0.8	0.4	2	-0.1	0.89
						Organic Addition	2.3	1.4	2	1.4	0.60
	St Louis R.	92	3.7	1.8	4	Interior Controls[d]	2.5	1.8	2	-1.2	0.49
						Precipitant 2	5.1	0.4	2	1.4	0.70
		93	4.5	2.8	3	Interior Controls[d]	2.6	—	1	-1.9	—
						Wet Deposition, 2X	6.8	1.3	2	2.3	0.49
						No Wet Deposition	6.3	0.7	2	1.8	0.71
						Mercury Complexor 2	1.2	1.3	2	-3.2	0.21
						Mercury Complexor 3	4.0	0.0	2	-0.5	0.66
		94	4.7	2.3	3	Interior Controls[d]	5.6	—	1	0.9	—
						Organic Removal	4.3	5.4	2	-0.4	0.99
						Micronutrient, 0.5 ppb	3.5	3.5	2	-0.2	0.24
						Micronutrient, 1 ppb	5.9	1.1	2	1.2	0.45
						Micronutrient, 2 ppb	5.9	1.2	2	1.2	0.69

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Fish Length (cm) [End Date Only]	Sand Point L.	92	4.62	0.41	15	Micronutrient, 2 ppb	5.37	0.29	7	0.75	<0.01
						Mercury Complexor 1	4.88	0.56	10	0.26	0.20
						Precipitant 1	4.66	0.48	10	0.04	0.83
						Organic Additions	4.93	0.49	15	0.31	0.02
		93	4.86	0.29	10	Micronutrient, 1 ppb	4.61	0.34	10	-0.25	<0.01
						Covered Sediment	4.49	0.22	8	-0.37	<0.01
						Aeration, Water	4.60	0.40	8	-0.26	<0.01
						Precipitant 3	4.96	0.47	5	0.10	0.14
		94	6.44	1.10	5	Micronutrient Carryover	6.24	0.58	10	-0.20	0.45
						Wet Deposition, 2X	5.52	1.02	10	-0.92	0.11
						No Wet Deposition	5.63	1.17	10	-0.81	0.74
						Organic Addition	5.62	0.77	10	-0.82	0.17
	St Louis R.	92	3.82	0.70	20	Interior Controls[d]	4.22	0.58	10	0.40	0.01
						Precipitant 2	3.87	0.50	10	0.05	0.08
		93	4.25	0.59	13	Interior Controls[d]	4.56	0.18	5	0.31	0.10
						Wet Deposition, 2X	3.50	0.68	10	-0.75	<0.01
						No Wet Deposition	3.02	0.58	15	-1.23	<0.01
						Mercury Complexor 2	4.34	0.66	10	0.09	0.14
						Mercury Complexor 3	3.46	0.46	15	-0.79	0.01
		94	4.65	0.57	13	Interior Controls[d]	4.42	0.27	5	-0.23	0.17
						Organic Removal	6.01	0.65	10	1.36	0.01
						Micronutrient, 0.5 ppb	4.25	0.07	2	-0.40	0.05
						Micronutrient, 1 ppb	4.71	0.74	8	-0.06	0.88
						Micronutrient, 2 ppb	5.33	0.98	10	0.68	0.17
Fish Mass (g) [End Date Only]	Sand Point L.	92	0.82	0.32	15	Micronutrient; 2 ppb	1.43	0.26	7	0.61	0.01
						Mercury Complexor 1	1.05	0.33	10	0.23	0.12
						Precipitant 1	0.91	0.35	10	0.09	0.71
						Organic Additions	1.05	0.35	15	0.23	0.01
		93	0.99	0.19	10	Micronutrient, 1 ppb	0.85	0.19	10	-0.14	<0.01
						Covered Sediment	0.72	0.14	8	-0.27	<0.01
						Aeration, Water	0.79	0.24	8	-0.20	<0.01
						Precipitant 3	1.07	0.38	5	0.08	0.34
		94	2.87	1.45	5	Micronutrient Carryover	2.26	0.81	10	-0.61	0.16
						Wet Deposition, 2X	1.92	1.10	10	-0.95	0.16
						No Wet Deposition	1.97	1.46	10	-0.90	0.78
						Organic Addition	1.83	0.79	10	-1.04	0.18
	St Louis R.	92	0.63	0.38	20	Interior Controls[d]	0.82	0.41	10	0.19	0.03
						Precipitant 2	0.59	0.27	10	-0.04	0.20
		93	0.85	0.36	13	Interior Controls[d]	1.01	0.15	5	0.16	0.21
						Wet Deposition, 2X	0.44	0.30	10	-0.41	0.02
						No Wet Deposition	0.29	0.18	15	-0.56	<0.01
						Mercury Complexor 2	0.90	0.42	10	0.05	0.54
						Mercury Complexor 3	0.39	0.16	15	-0.46	0.02
		94	1.22	0.67	13	Interior Controls[d]	0.88	0.18	5	-0.34	0.09
						Organic Removal	2.95	1.24	10	1.73	0.02
						Micronutrient, 0.5 ppb	0.80	0.03	2	-0.42	0.02
						Micronutrient, 1 ppb	1.07	0.62	8	-0.15	0.60
						Micronutrient, 2 ppb	1.88	1.07	10	0.44	0.31

Table IVb. Continued.

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Fish Condition Factor ($100M/L^3$) [End Date Only]	Sand Point L.	92	0.81	0.07	15	Micronutrient, 2 ppb	0.92	0.04	7	0.11	0.01
						Mercury Complexor 1	0.88	0.07	10	0.07	0.10
						Precipitant 1	0.86	0.07	10	0.05	0.31
						Organic Additions	0.85	0.04	15	0.04	0.04
		93	0.85	0.04	10	Micronutrient, 1 ppb	0.85	0.05	10	0.00	0.86
						Covered Sediment	0.78	0.07	8	-0.07	0.01
						Aeration, Water	0.79	0.05	8	-0.06	<0.01
						Precipitant 3	0.85	0.07	5	0.00	0.86
		94	1.00	0.06	5	Micronutrient Carryover	0.89	0.14	10	-0.11	0.03
						Wet Deposition, 2X	1.02	0.06	10	0.02	0.77
						No Wet Deposition	0.95	0.09	10	-0.05	0.37
						Organic Addition	0.97	0.07	10	-0.03	0.12
	St Louis R.	92	1.00	0.09	20	Interior Controls[d]	1.01	0.10	10	0.01	0.46
						Precipitant 2	0.95	0.07	10	-0.05	0.26
		93	1.04	0.06	13	Interior Controls[d]	1.06	0.04	5	0.02	0.45
						Wet Deposition, 2X	0.91	0.05	10	-0.13	<0.01
						No Wet Deposition	0.92	0.10	15	-0.12	<0.01
						Mercury Complexor 2	1.01	0.07	10	-0.03	0.03
						Mercury Complexor 3	0.90	0.09	15	-0.14	<0.01
		94	1.12	0.19	13	Interior Controls[d]	1.00	0.03	5	-0.12	0.05
						Organic Removal	1.27	0.19	10	0.15	0.35
						Micronutrient, 0.5 ppb	1.04	0.01	2	-0.08	0.18
						Micronutrient, 1 ppb	1.02	0.08	8	-0.10	0.11
						Micronutrient, 2 ppb	1.10	0.12	10	-0.02	0.10
Hg in Water (ng/L)	Sand Point L.	92	2.4	1.3	14	Micronutrient, 2 ppb	1.8	1.1	14	-0.6	0.09
						Mercury Complexor 1	2.2	1.3	14	-0.2	0.54
						Precipitant 1	2.4	1.4	14	0.0	0.95
						Organic Additions	2.1	1.1	14	-0.3	0.39
		93	3.3	1.6	14	Micronutrient, 1 ppb	2.5	1.0	14	-0.8	0.04
						Covered Sediment	3.2	2.3	14	-0.1	0.87
						Aeration, Water	2.7	1.1	14	-0.6	0.17
						Precipitant 3	3.1	1.3	14	-0.2	0.73
		94	3.4	2.0	16	Micronutrient Carryover	3.1	1.8	14	-0.3	0.91
						Wet Deposition, 2X	2.4	1.4	14	-1.0	0.16
						No Wet Deposition	2.1	1.2	14	-1.3	0.14
						Organic Addition	2.2	1.2	14	-1.2	0.20
	St Louis R.	92	3.3	1.2	36	Interior Controls[d]	3.3	1.2	18	0.0	>0.99
						Precipitant 2	3.4	1.5	18	0.1	0.73
		93	4.2	1.4	21	Interior Controls[d]	4.1	1.3	7	-0.1	0.70
						Wet Deposition, 2X	3.6	1.6	14	-0.6	0.16
						No Wet Deposition	2.3	1.3	14	-1.9	0.01
						Mercury Complexor 2	3.2	1.5	14	-1.0	<0.01
						Mercury Complexor 3	3.0	1.4	14	-1.2	<0.01
		94	2.4	1.5	23	Interior Controls[d]	2.2	1.0	7	-0.2	0.82
						Organic Removal	2.4	1.1	12	0.0	0.07
						Micronutrient, 0.5 ppb	2.5	1.3	12	0.1	0.09
						Micronutrient, 1 ppb	2.1	1.2	12	-0.3	0.44
						Micronutrient, 2 ppb	2.5	1.7	13	0.1	0.26

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Methyl Hg in Water (ng/L)	Sand Point L.	92	0.16	0.03	4	Micronutrient, 2 ppb	0.19	0.03	4	0.03	0.12
						Mercury Complexor 1	0.20	0.03	4	0.04	0.05
						Precipitant 1	0.15	0.04	4	-0.01	0.44
						Organic Additions	0.30	0.16	4	0.14	0.19
		93	0.15	0.06	6	Micronutrient, 1 ppb	0.19	0.08	6	0.04	0.18
						Covered Sediment	0.16	0.08	6	0.01	0.70
						Aeration, Water	0.20	0.07	6	0.05	0.13
						Precipitant 3	0.23	0.07	6	0.08	0.02
		94	0.24	0.11	6	Micronutrient Carryover	0.23	0.06	6	-0.01	0.87
						Wet Deposition, 2X	0.22	0.06	6	-0.02	0.63
						No Wet Deposition	0.20	0.07	6	-0.04	0.33
						Organic Addition	0.26	0.09	6	0.02	0.77
	St Louis R.	92	0.16	0.10	8	Interior Controls[d]	0.15	0.10	4	-0.01	0.18
						Precipitant 2	0.14	0.10	4	-0.02	0.13
		93	0.19	0.07	9	Interior Controls[d]	0.17	0.08	3	-0.02	0.41
						Wet Deposition, 2X	0.23	0.12	6	0.04	0.29
						No Wet Deposition	0.20	0.10	6	0.01	0.83
						Mercury Complexor 2	0.22	0.08	6	0.03	0.45
						Mercury Complexor 3	0.14	0.03	6	-0.05	0.07
		94	0.07	0.03	6	Interior Controls[d]	0.06	0.03	2	-0.01	<0.01
						Organic Removal	0.32	0.24	6	0.25	0.17
						Micronutrient, 0.5 ppb	0.18	0.13	6	0.11	0.30
						Micronutrient, 1 ppb	0.17	0.09	6	0.10	0.14
						Micronutrient, 2 ppb	0.20	0.17	6	0.13	0.23
Hg in Periphyton (ng/g) [End Date and Wet Samples Only]	Sand Point L.	92	60.1	66.7	4	Micronutrient, 2 ppb	24.8	19.9	4	-35.3	0.23
						Mercury Complexor 1	25.9	23.4	4	-34.2	0.25
						Precipitant 1	21.8	8.5	4	-38.3	0.13
						Organic Additions	35.4	23.7	4	-36.7	0.39
		93	54.9	37.3	2	Micronutrient, 1 ppb	71.0	38.3	2	16.1	0.03
						Covered Sediment	18.0	0.6	2	-36.9	0.39
						Aeration, Water	11.5	3.3	2	-43.4	0.32
						Precipitant 3	28.4	6.6	2	-26.5	0.55
		94	24.3	29.0	2	Micronutrient Carryover	137.8	190.9	2	113.5	0.50
						Wet Deposition, 2X	32.9	36.6	2	8.6	0.36
						No Wet Deposition	6.2	0.0	2	-18.1	0.54
						Organic Addition	10.8	12.2	2	-13.5	0.72
	St Louis R.	92	27.9	10.0	4	Interior Controls[d]	35.5	8.2	2	7.6	0.24
						Precipitant 2	21.6	4.1	2	-6.3	0.73
		93	20.7	6.5	3	Interior Controls[d]	28.2	—	1	7.5	—
						Wet Deposition, 2X	24.1	0.2	2	3.4	0.01
						No Wet Deposition	16.1	4.3	2	-4.6	0.81
						Mercury Complexor 2	97.6	85.1	2	76.9	0.41
						Mercury Complexor 3	29.8	7.0	2	9.1	0.24
		94	15.4	3.2	3	Interior Controls[d]	17.8	—	1	2.4	—
						Organic Removal	125.4	159.0	2	110.0	0.51
						Micronutrient, 0.5 ppb	144.3	186.8	2	128.9	0.51
						Micronutrient, 1 ppb	23.7	16.8	2	8.3	0.50
						Micronutrient, 2 ppb	18.7	3.4	2	3.3	0.51

Table IVb. Continued.

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Hg in Vegetation[e] (ng/g) [Wet Leaf Samples and End Date Only]	Sand Point L.	92	66.3	28.6	2	Micronutrient, 2 ppb	64.2	15.8	2	-2.1	0.96
						Mercury Complexor 1	35.1	—	1	-31.2	—
						Precipitant 1	39.9	14.4	2	-26.4	0.23
						Organic Additions	67.1	6.6	2	0.8	0.97
		93	—	—	—	Micronutrient, 1 ppb	—	—	—	—	—
						Covered Sediment	—	—	—	—	—
						Aeration, Water	—	—	—	—	—
						Precipitant 3	—	—	—	—	—
		94	—	—	—	Micronutrient Carryover	—	—	—	—	—
						Wet Deposition, 2X	—	—	—	—	—
						No Wet Deposition	—	—	—	—	—
						Organic Addition	—	—	—	—	—
	St Louis R.	92	34.1	15.9	4	Interior Controls[d]	25.1	16.8	2	-9.0	0.11
						Precipitant 2	18.4	2.0	2	-15.7	0.25
		93	18.4	1.7	3	Interior Controls[d]	17.6	—	1	-0.8	—
						Wet Deposition, 2X	29.3	1.6	2	10.9	0.03
						No Wet Deposition	30.0	1.0	2	11.6	0.13
						Mercury Complexor 2	22.6	3.4	2	4.2	0.52
						Mercury Complexor 3	25.2	5.5	2	6.8	0.22
		94	—	—	—	Interior Controls[d]	—	—	—	—	—
						Organic Removal	—	—	—	—	—
						Micronutrient, 0.5 ppb	—	—	—	—	—
						Micronutrient, 1 ppb	—	—	—	—	—
						Micronutrient, 2 ppb	—	—	—	—	—
Hg in Plankton (ng/g)	Sand Point L.	92	294	309	14	Micronutrient, 2 ppb	195	138	14	-99	0.10
						Mercury Complexor 1	238	239	14	-56	0.57
						Precipitant 1	375	388	13	81	0.63
						Organic Additions	208	102	14	-86	0.39
		93	828	1470	14	Micronutrient, 1 ppb	448	552	14	-380	0.34
						Covered Sediment	428	334	14	-400	0.24
						Aeration, Water	343	231	10	-485	0.28
						Precipitant 3	693	1062	14	-135	0.77
		94	267	185	6	Micronutrient Carryover	231	152	6	-36	0.52
						Wet Deposition, 2X	242	175	6	-25	0.74
						No Wet Deposition	335	357	6	68	0.64
						Organic Addition	199	131	6	-68	0.40
	St Louis R.	92	165	232	36	Interior Controls[d]	219	307	18	54	0.14
						Precipitant 2	163	154	18	-2	0.19
		93	285	274	21	Interior Controls[d]	326	174	7	41	0.44
						Wet Deposition, 2X	259	190	14	26	0.94
						No Wet Deposition	338	299	14	53	0.18
						Mercury Complexor 2	205	117	14	-80	0.42
						Mercury Complexor 3	336	379	14	51	0.47
		94	167	125	12	Interior Controls[d]	205	178	4	38	0.77
						Organic Removal	173	111	8	6	0.38
						Micronutrient, 0.5 ppb	204	155	8	37	0.49
						Micronutrient, 1 ppb	117	63	8	-50	0.64
						Micronutrient, 2 ppb	217	225	8	50	0.72

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Hg in Fish (ng/g) [End Date Only]	Sand Point L.	92	65.6	12.9	15	Micronutrient, 2 ppb	20.1	2.9	7	-45.5	<0.01
						Mercury Complexor 1	50.3	15.5	10	-15.3	<0.01
						Precipitant 1	60.0	14.7	10	-5.6	0.17
						Organic Additions	100.1	27.7	10	34.5	<0.01
		93	79.6	13.6	10	Micronutrient, 1 ppb	21.7	5.3	10	-57.9	<0.01
						Covered Sediment	85.5	15.6	8	5.9	0.10
						Aeration, Water	79.2	10.9	8	-0.4	0.09
						Precipitant 3	59.9	10.4	5	-19.7	0.19
		94	59.3	29.4	5	Micronutrient Carryover	64.8	3.1	10	5.5	0.70
						Wet Deposition, 2X	89.0	25.2	10	29.7	<0.01
						No Wet Deposition	72.6	15.2	10	13.3	0.52
						Organic Addition	72.4	8.4	10	13.1	0.40
	St Louis R.	92	39.0	5.6	20	Interior Controls[d]	38.0	5.3	10	-1.0	0.36
						Precipitant 2	42.8	5.8	10	3.8	0.30
		93	57.8	5.4	13	Interior Controls[d]	59.6	4.5	5	1.8	0.49
						Wet Deposition, 2X	50.0	6.2	10	-7.8	0.12
						No Wet Deposition	60.9	11.1	15	3.1	0.54
						Mercury Complexor 2	64.0	19.7	10	6.2	0.77
						Mercury Complexor 3	68.2	14.4	15	10.4	0.02
		94	34.9	6.6	13	Interior Controls[d]	38.5	1.8	5	3.6	0.77
						Organic Removal	47.6	9.2	10	12.7	0.09
						Micronutrient, 0.5 ppb	55.5	8.1	2	20.6	<0.01
						Micronutrient, 1 ppb	28.0	3.8	8	-6.9	0.12
						Micronutrient, 2 ppb	26.5	2.0	10	-8.4	0.06
Fish Body Burden (ng Hg per Fish) [End Date Only]	Sand Point L.	92	55.3	17.3	15	Micronutrient, 2 ppb	28.6	5.1	5	-26.7	0.01
						Mercury Complexor 1	49.6	13.7	10	-5.7	0.63
						Precipitant 1	52.6	16.8	10	-2.7	0.99
						Organic Additions	119.4	48.5	10	64.1	<0.01
		93	76.9	11.8	10	Micronutrient, 1 ppb	18.5	6.6	10	-58.4	<0.01
						Covered Sediment	59.9	10.5	8	-17.0	<0.01
						Aeration, Water	62.0	18.6	8	-14.9	0.06
						Precipitant 3	62.0	16.8	5	-14.9	0.33
		94	140.1	31.8	5	Micronutrient Carryover	152.6	59.4	10	12.5	0.11
						Wet Deposition, 2X	151.0	70.0	10	10.9	0.71
						No Wet Deposition	120.0	50.6	10	-20.1	0.72
						Organic Addition	112.6	42.0	10	-27.5	0.22
	St Louis R.	92	23.0	11.8	20	Interior Controls[d]	26.6	11.9	10	3.6	0.01
						Precipitant 2	23.9	7.8	10	0.9	0.04
		93	49.3	21.5	13	Interior Controls[d]	60.8	12.9	5	11.5	0.17
						Wet Deposition, 2X	21.4	12.7	10	-27.9	0.01
						No Wet Deposition	18.1	13.4	15	-31.2	<0.01
						Mercury Complexor 2	64.4	42.8	10	15.1	0.15
						Mercury Complexor 3	27.4	14.7	15	-21.9	0.04
		94	38.6	11.5	13	Interior Controls[d]	33.5	6.3	5	-5.1	0.14
						Organic Removal	149.4	84.2	10	110.8	0.01
						Micronutrient, 0.5 ppb	44.5	8.3	2	5.9	0.21
						Micronutrient, 1 ppb	33.8	21.5	8	-4.8	0.50
						Micronutrient, 2 ppb	49.8	27.6	10	11.2	0.80

Table IVb. Continued.

Parameter (units)	Site	Year	Control[a] Mean	S.Dev.	n	Treatment Type	Mean	S.Dev.	n	Mean Diff.[b]	T-Test Prob.[c]
Hg in Sediment (ppb)	Sand Point L.	92	—	—	—	Micronutrient, 2 ppb	—	—	—	—	—
						Mercury Complexor 1	—	—	—	—	—
						Precipitant 1	—	—	—	—	—
						Organic Additions	—	—	—	—	—
		93	9.2	8.2	2	Micronutrient, 1 ppb	4.7	3.5	2	-4.5	0.68
						Covered Sediment	1.4	0.7	2	-7.8	0.38
						Aeration, Water	1.6	0.6	2	-7.6	0.39
						Precipitant 3	2.6	1.4	2	-6.6	0.40
		94	2.8	0.1	2	Micronutrient Carryover	3.9	0.1	2	1.0	0.05
						Wet Deposition, 2X	2.7	1.0	2	-1.1	0.92
						No Wet Deposition	3.2	1.1	2	0.4	0.67
						Organic Addition	6.3	0.7	2	3.5	0.10
	St. Louis R.	92	—	—	—	Interior Controls[d]	—	—	—	—	—
						Precipitant 2	—	—	—	—	—
		93	24.1	4.6	3	Interior Controls[d]	29.0	—	1	4.9	—
						Wet Deposition, 2X	20.1	3.64	2	-4.0	0.28
						No Wet Deposition	17.3	2.65	2	-6.8	0.45
						Mercury Complexor 2	18.1	5.52	2	-6.0	0.34
						Mercury Complexor 3	22.9	7.39	2	1.2	0.78
		94	21.3	2.4	3	Interior Controls[d]	24.0	—	1	2.7	—
						Organic Removal	21.0	5.57	2	-0.3	0.85
						Micronutrient, 0.5 ppb	20.5	1.11	2	-0.8	0.71
						Micronutrient, 1 ppb	23.4	0.64	2	2.1	0.02
						Micronutrient, 2 ppb	24.7	1.59	2	3.4	0.19

[a] Combined analyses of all control samples.
[b] Average of treatment minus boundary control values paired by sampling date.
[c] Probability that treatment and boundary control sample means are from the same distribution.
[d] Established interior controls to measure the difference between the total enclosure interior's condition and its boundary's condition. In 92, the interior controls were compared against its nearest boundary control. In 93 and 94, interior control was compared to each of the boundary controls separately; the results were then averaged and reported.
[e] Sand Point: aquatic grass; St. Louis River: bull rush.

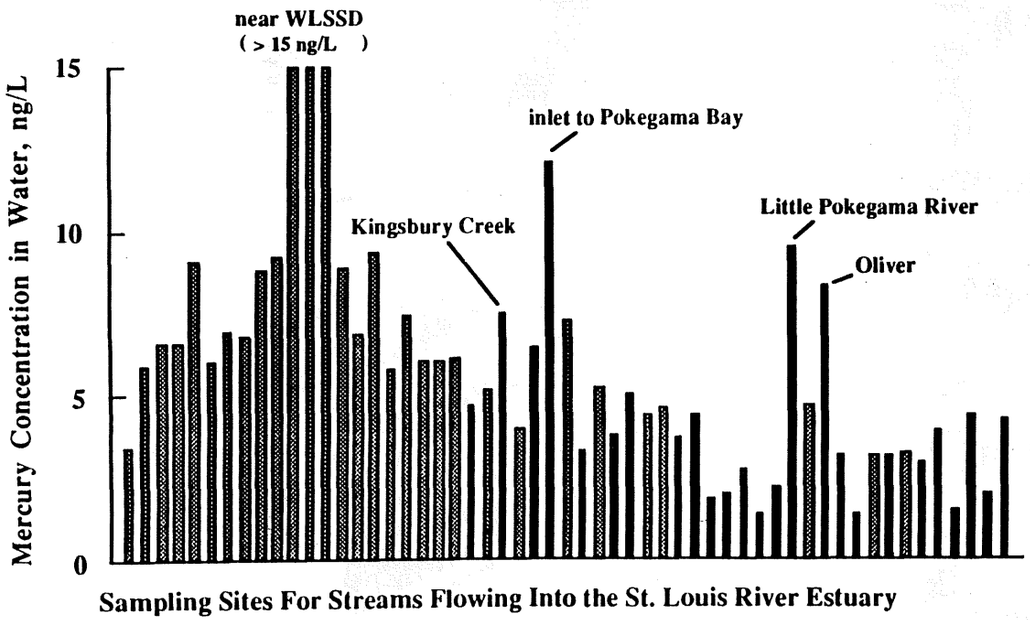


Figure 1a. Mercury concentrations in water as function of sampling sites going "up-river" from Superior Bay for the St. Louis River Estuary. Gray bars represent St. Louis River samples while black bars represent tributaries to the St. Louis River.

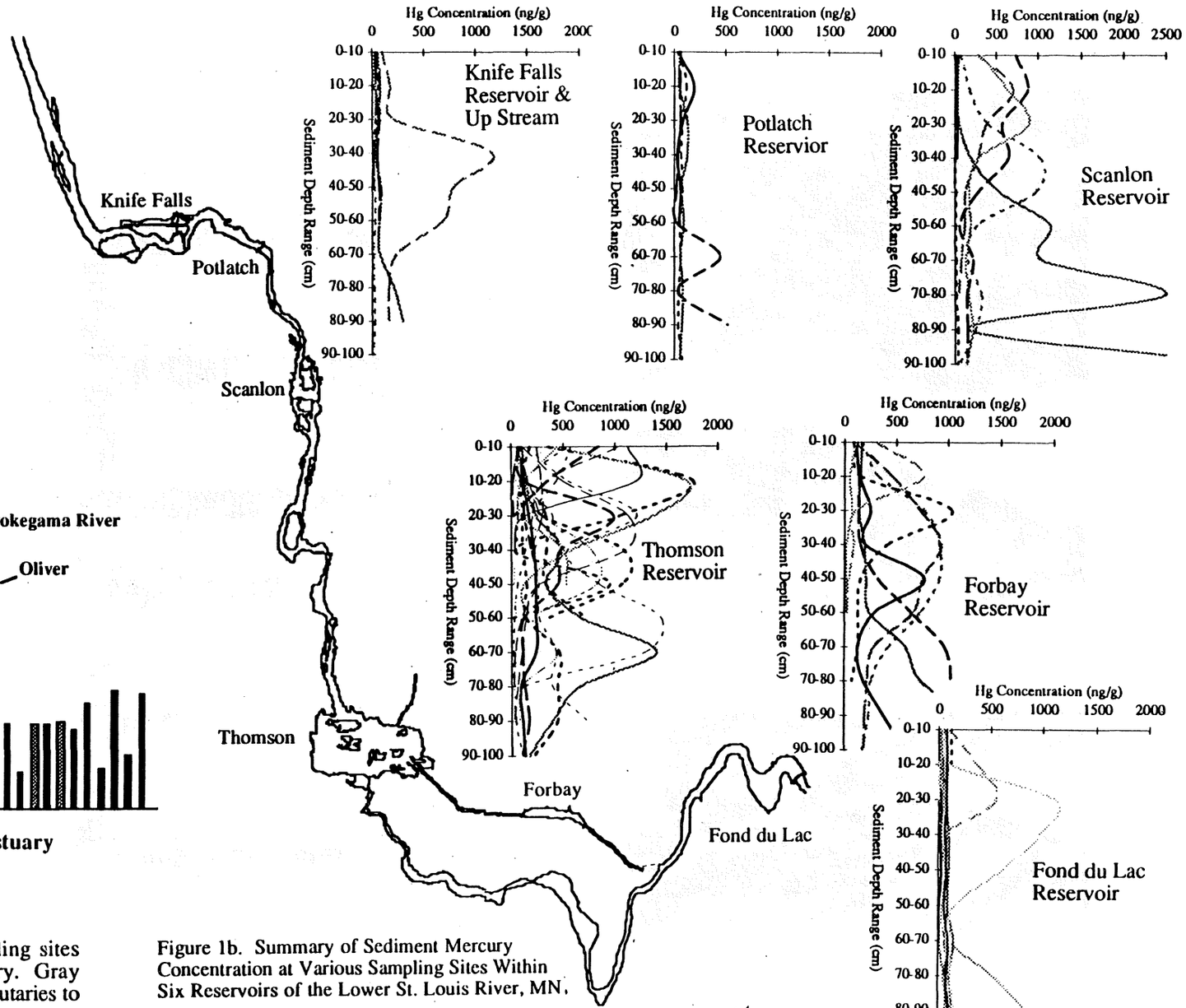


Figure 1b. Summary of Sediment Mercury Concentration at Various Sampling Sites Within Six Reservoirs of the Lower St. Louis River, MN.

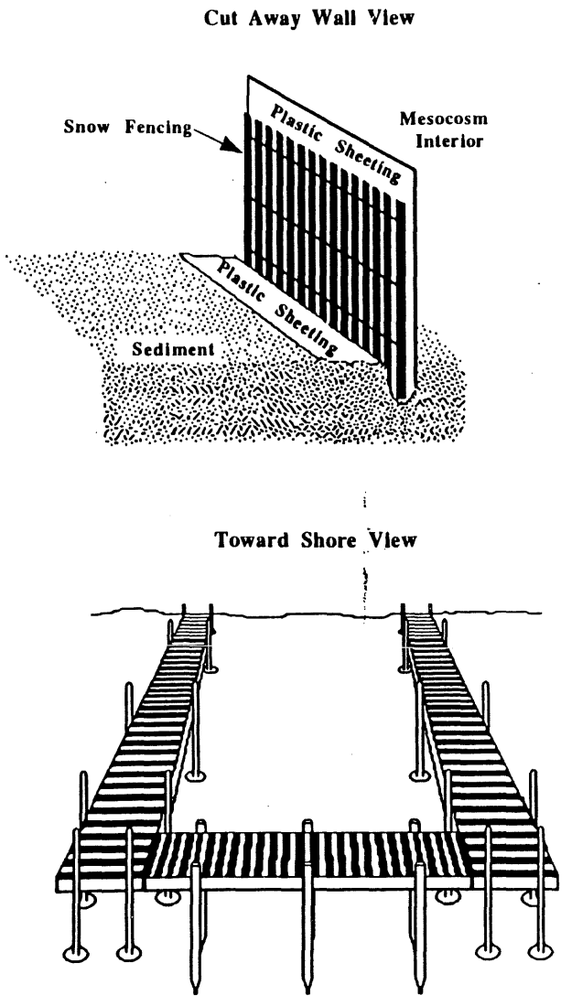


Figure 2a. Diagram of an enclosed mesocosm unit showing design features of wall and dock structures.

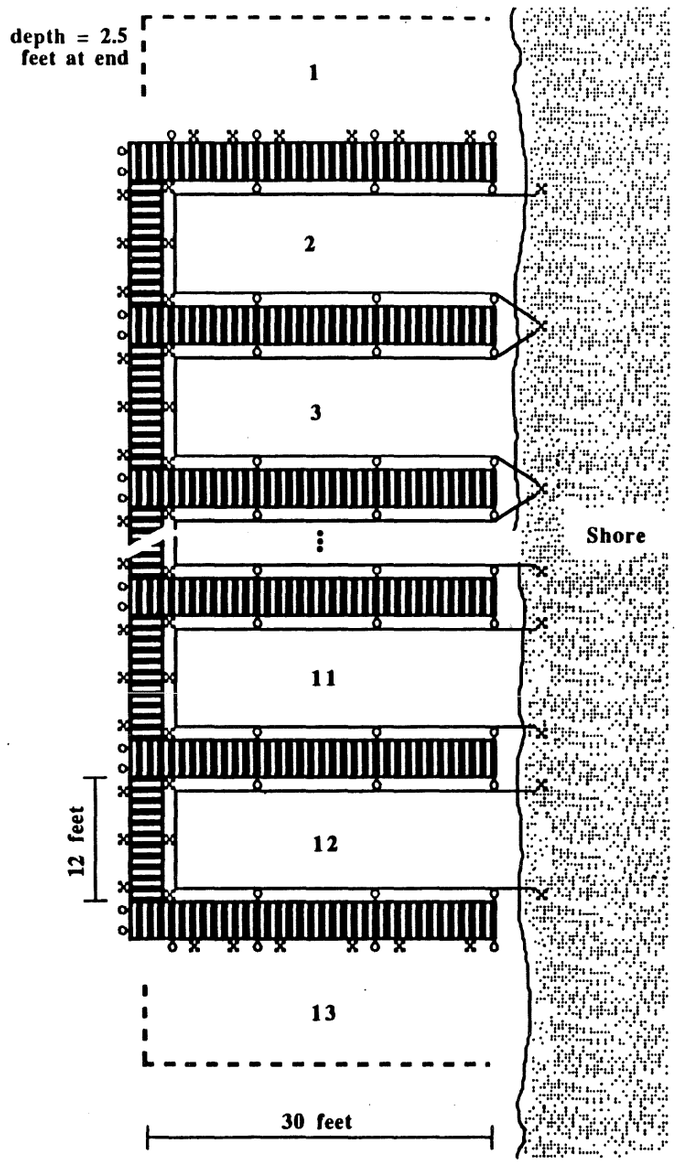


Figure 2b. Example layout for 11 enclosed mesocosms used for pilot testing mercury mitigation and cycling mechanisms.

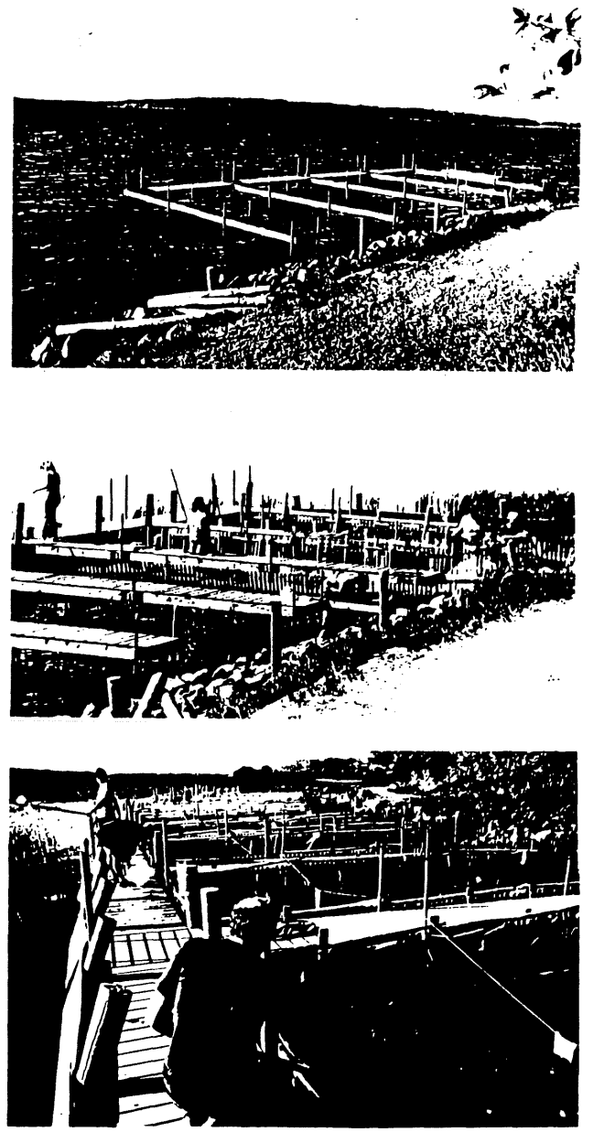


Figure 2c. Photographs of the Indian Point Study Area showing initial placement (upper), enclosure construction (middle), and final operation(s) (lower), Summer, 1994. (Photos by G.E.Glass.)

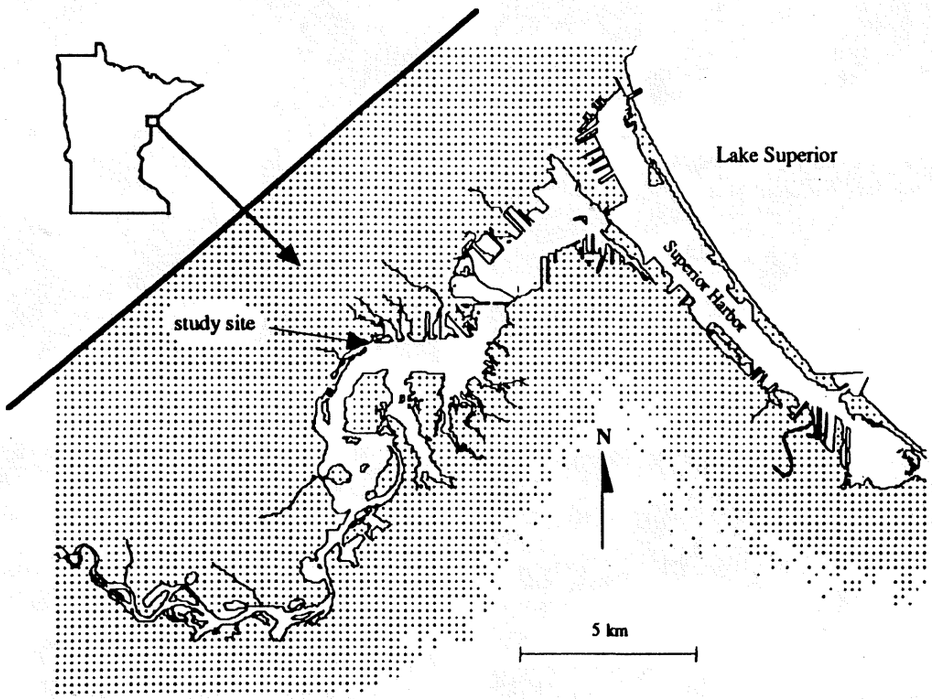


Figure 2d. Map showing the location of the Indian Point study area on the St. Louis River Estuary.

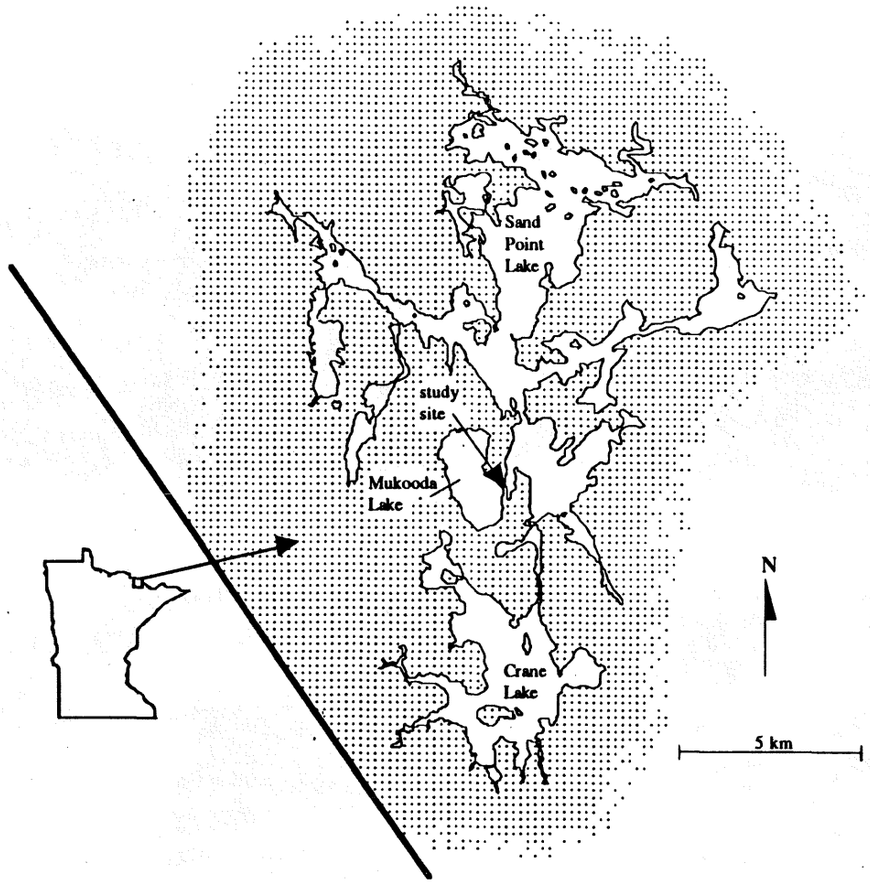
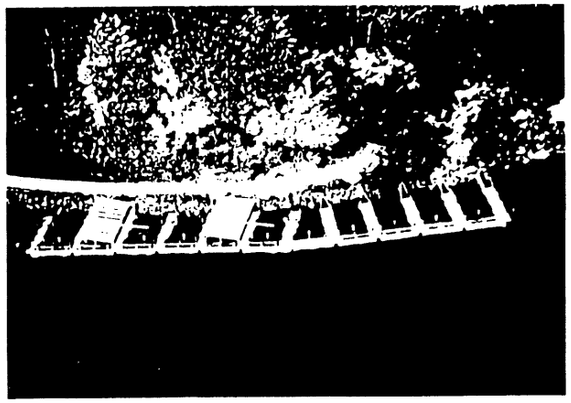
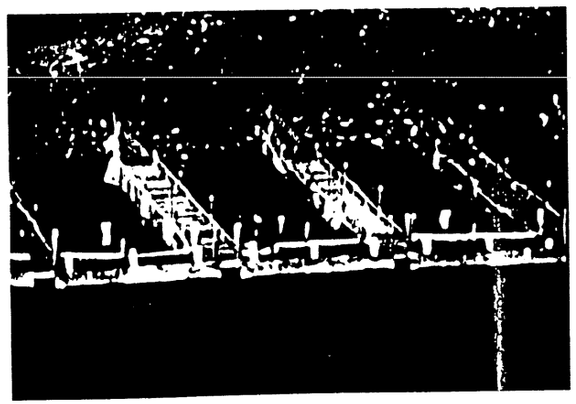


Figure 2e. Map showing the location of the Sand Point (and Crane) Lake study area in Voyageurs National Park.





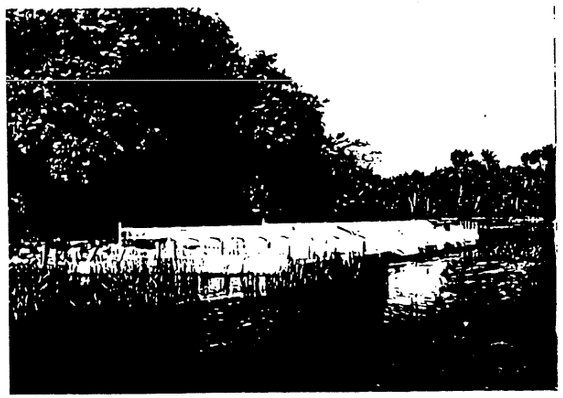
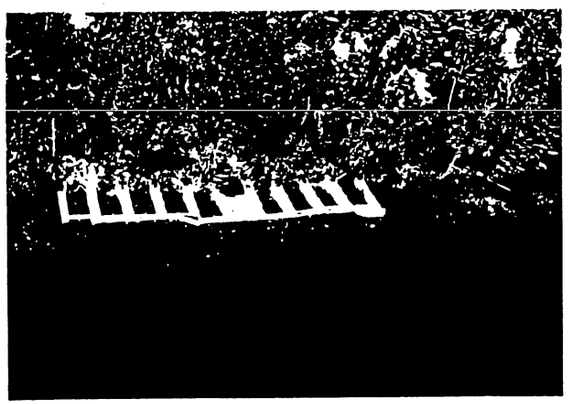


Figure 2f. Photographs of the study area showing shoreline enclosures at Indian Point, about 70th Avenue West and waterfront, Duluth, MN, Late Summer, 1993. (Photos by G.E.Glass.)



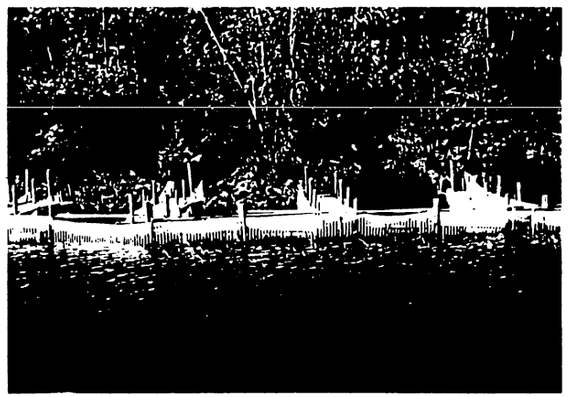


Figure 2g. Photographs of the study area at Sand Point (and Crane) Lake in Voyageurs National Park, Summer, 1993. (Photos by L.Kallemeyn.)

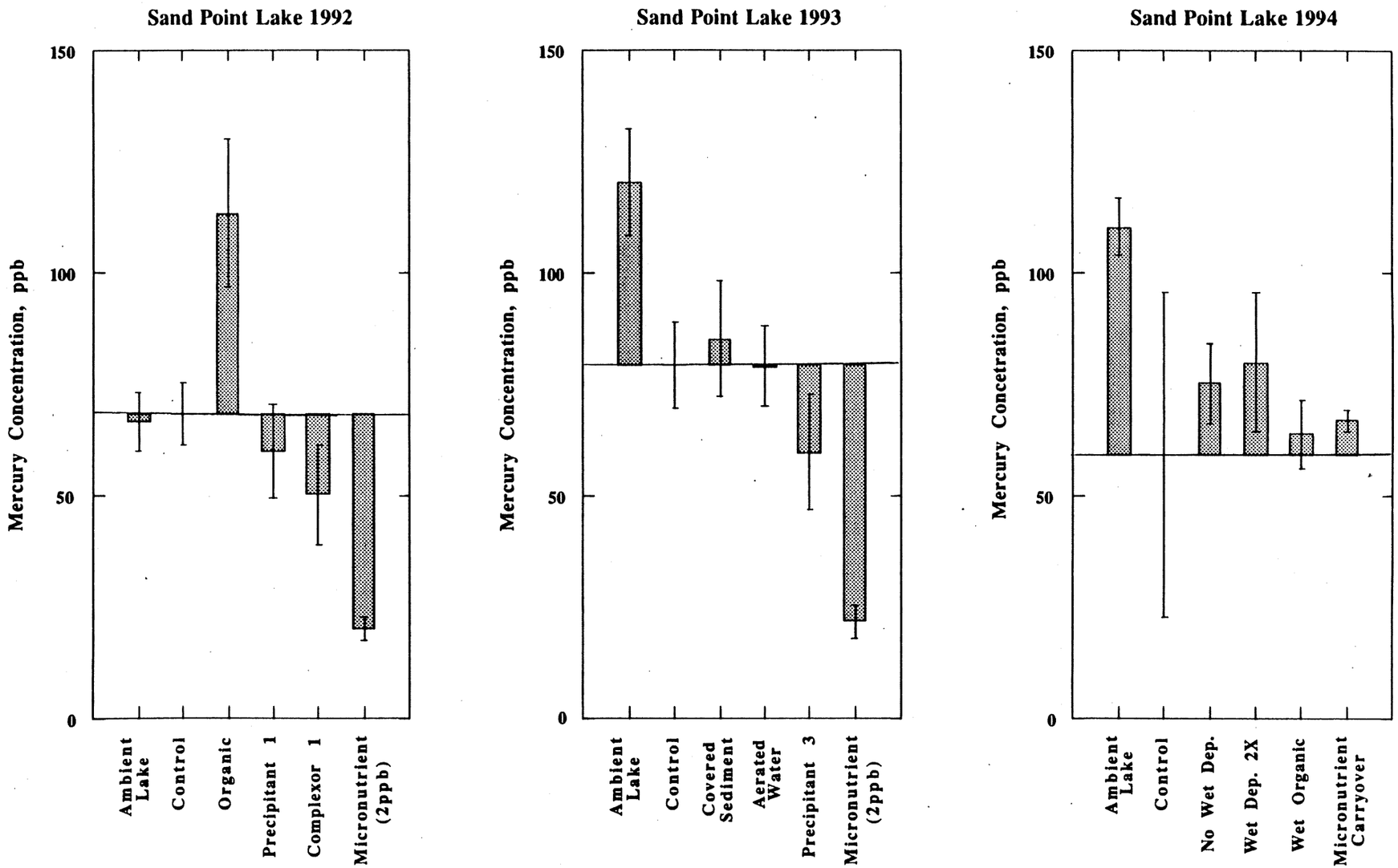


Figure 3a. Average mercury concentration results for young-of-year yellow perch studied in ambient water and in enclosed mesocosms under the indicated test conditions. Bar lengths are drawn relative to the control mesocosms. Error bars indicate a 95% confidence interval about the mean.

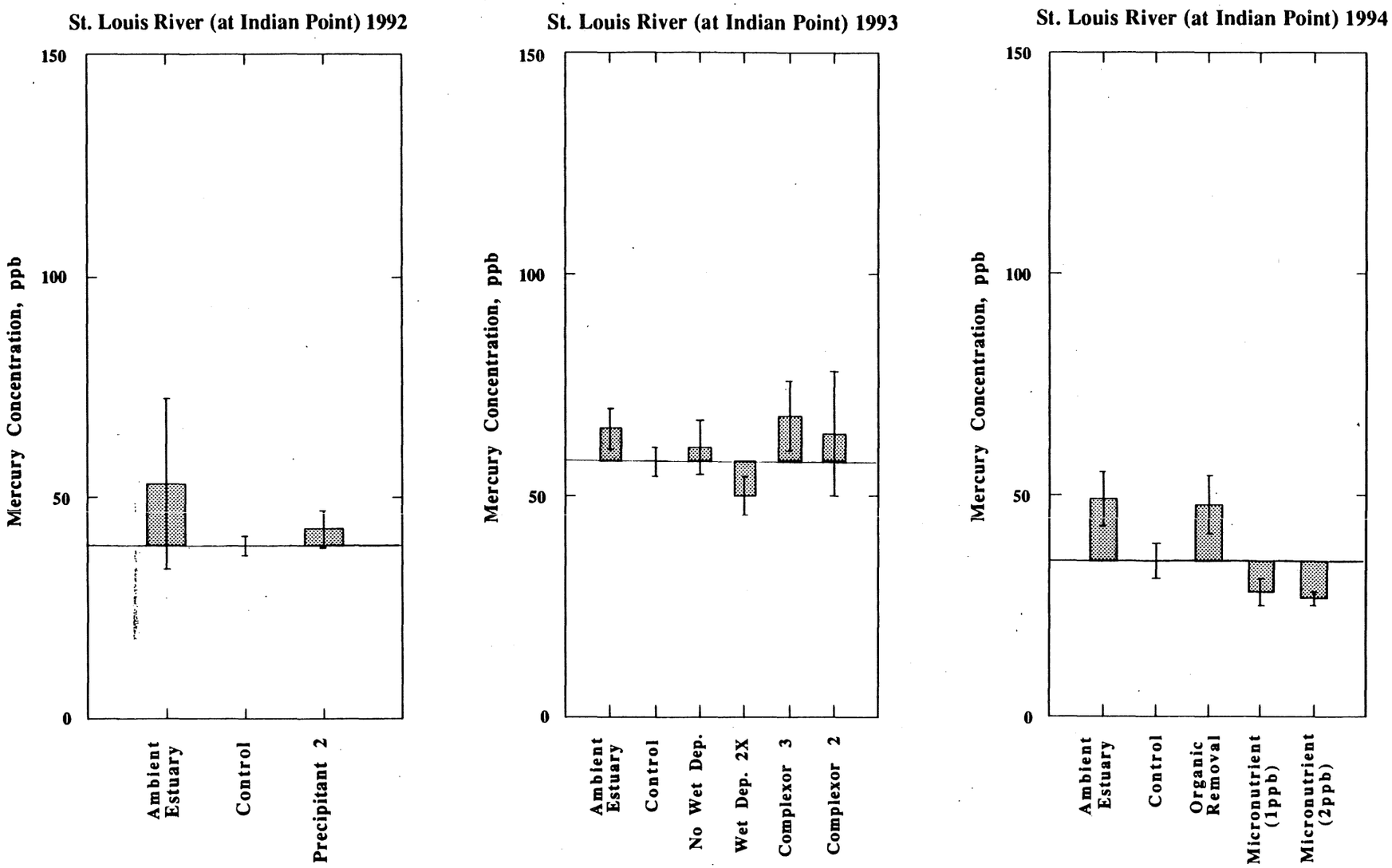


Figure 3b. Average mercury concentration results for young-of-year yellow black crappie studied in ambient water and in enclosed mesocosms under the indicated test conditions. Bar lengths are drawn relative to the control mesocosms. Error bars indicate a 95% confidence interval about the mean.