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LCMR FINAL STATUS REPORT - DETAILED RESEARCH
(Summary With Technical Reports)

I. Mitigating Mercury In Northeastern Minnesota Lakes and Streams

Program Managers: Marvin Hora (612) 296-8005
Minnesota Pollution Control Agency
520 Lafayette Road
St. Paul, Minnesota 55155-4194

A. M.L. 1991, Ch. 254, Art. 1, Sec. 14, Subd. 4(j).
Appropriation: $300,000
Balance: $0.00

Mitigating Mercury in Northeast Minnesota Lakes And Streams: This appropriation is from the Minnesota environment and natural resources trust fund to the Commissioner of the Pollution Control Agency to investigate how to mitigate the damage caused by the presence of mercury in northeast Minnesota lakes.

B. Compatible Data: During the biennium ending June 30, 1993, the data collected by projects funded under this section that have common value for natural resource planning and management must conform to information architecture as defined in guidelines and standards adopted by the Information Policy Office. In addition, the data must be provided to and integrated with the Minnesota Land Management Information Center's geographic data bases with the integration costs borne by the activity receiving funding under this section.

C. Match Requirement: $0

II. NARRATIVE

Recent studies show mercury contamination in fish from northeastern Minnesota lakes to be widespread, linked to atmospheric deposition, and increasing in fish at three to five percent per year. Mercury has contaminated over 200 lakes in Minnesota causing the Minnesota Department of Health to issue fish consumption advisories. At the current rate of increase, fish from more northern lakes will be unsafe for consumption by humans or fish-eating wildlife in the next two decades. A task force has been established at the MPCA to address point source mercury emitters within our state, but there is a concern that much of the mercury is coming to Minnesota from regional sources. These outside sources may need a long-term national and international control program. Therefore, we must rely on mitigative techniques to reduce mercury impacts on the short-term. This study will conduct mitigative experiments to decrease mercury impacts in rivers and lakes.

This project was conducted by two investigators, Dr. Gary Glass of the University of Minnesota - Duluth and Dr. Patrick Brezonik of the University of Minnesota - Twin Cities. Both have components of Objective A and of Objective B. Their reports are attached and referenced throughout the final status report. The investigation by Dr. Glass is in Phase I and still considered draft. Additional funding was obtained to complete the work in the 1994 and 1995 biennium.

III. OBJECTIVES

A. Evaluate and test various methods and means to reduce or eliminate mercury accumulation in fish and other biota.

A.1. Narrative: This objective will utilize laboratory information and field demonstrations to test and evaluate chelating compound additions, physical environment alterations, biological manipulations and chemical changes on the accumulation of mercury in fish and other biota. These techniques can be utilized where appropriate to mitigate damage done to Minnesota aquatic resources.

A.2. Procedures: Field studies will be carried out at both river and lake sites. Where field studies include the addition of stimulating and retarding agents, laboratory data and literature information will be assessed as a preliminary step. Limno-corrals appropriate for the site and test will be utilized for the field studies.

St. Louis River and Crane Lake (work by Dr. Glass)

EXPERIMENTAL DESIGN (Glass, pages 3-1 - 3-2)
The mitigative approaches that will be evaluated in this part of the study are listed in Tables I and II. These field studies will be carried out using U.S. Environmental Protection Agency (EPA) tested and approved littoral (shoreline) enclosures and the appropriate exposure design protocol described by Siefert (1989) and strengthened for use in areas of currents and wave action.

The duration of each test will be at least 21, but not greater than 30 days. After the enclosures have been prepared, each test will begin with the addition of seven-day old fathead minnows (with low mercury levels) to each enclosure. The endpoints for measurement and evaluation of test results will be based on the mercury uptake in the biota and substrates. Minnows, zooplankton, water, sediment and vegetation will be sampled after 10, 20, and 30 days and analyzed for mercury uptake. Comparisons between treated and control groups will define the effectiveness of the treatment.

METHODS AND MATERIALS (Glass, pages 3-1-3-2)
Littoral Enclosure Construction - Each six-unit littoral enclosure block (six adjacent enclosures) will be constructed by first installing seven parallel docks (10 m long) to form the superstructure of the enclosures with outer ends connected using additional dock sections. The walls of the enclosures (encompassing three sides with the fourth side being natural shoreline) will be connected to the docks after they are driven into the sediment a sufficient depth to insure a watertight seal. The walls will be constructed from a highly durable eight mil woven filament, polyolefin plastic sheeting (#888 H UV Clear Scrimweve^{R}, Sto-Cote Products, Inc., Richmond, Illinois) and wooden snowfence for skeletal reinforcement.

Table I. Mitigation Approaches for Toxic Residue Reduction-Mercury

Mitigation Approach	Reference
Category 1: Decrease exposure/bioavailability of the toxic form (mercury)	
Reduction of bioactive organic carbon content	Winfrey and Rudd (1990)
Bacterial static/demethylation stimulation	Winfrey and Rudd (1990); Lexmond et al. (1976)
Addition of sequestering agents	Gottofrey and Tjalve, 1990; Huang et al. (1990)
Covering of contaminated sediments	Glass et al. (in prep)
Limiting of sediments	Anderson and Borg (1990)
Reduction of nutrients	Rudd and Turner (1983)
Reduction of water level changes (res. effect)	Bodaly et al. (1984)
Reduction of temperature	Winfrey and Rudd (1990)
Category 2: Remove/reduce toxic chemical contributions/loadings (mercury)	
Contaminated sediment removal	Jernelov and Lann (1973); Jernelov et al. (1975)
Increase in water column flushing	Glass et al. (1990)
Reduction in plant growth (sed. to food link)	Glass et al. (in prep.)
Water column mercury degassing	Rudd and Hamilton (1978); Winfrey and Rudd (1990)
Reduction of incident mercury deposition	Sorensen et al. (1990)
Reduction of mercury from watershed runoff	Sorensen et al. (1990)

Table II. Planned Location Needed for Each Test

Test Method	St. Louis River[1] River	St. Louis River[1] Estuary	NE MN[2] Lakes	NE MN[2] Reservoirs
Category 1 approaches:				
Reduction of bioactive organic carbon	X	X	–	–
Bacterial static/demethylation stimulation	X	X	X	X
Chemical additions (sequestering agents)	–	X	X	X
Covering contaminated sediments	–	X	X	X
Category 2 approaches:				
Contaminated sediment removal	X	X	X	X
Increase in water column flushing	–	X	X	X
Water column mercury degassing	X	X	X	X

[1]Includes possible sites in Superior and St. Louis Bays, Indian Point, and Fond du Lac.
[2]Includes possible sites on Thomson Reservoir, Island, Crane, Sandpoint, and Kabetogama lakes.

Test Endpoints

The mercury concentrations in fathead minnows and indigenous zooplankton will be used as the main endpoints for measuring mercury uptake in each of the enclosures.

Mercury Measurements

Mercury measurements will be done using atomic absorption and will involve the same methods reported by us earlier (Glass et al. 1990; Sorensen et al. 1990).

Resources Involved

UMD
The north end of the Limnological Laboratory Building will be used for office space and staging for field studies.

ERL-D
This project will be conducted under the direct supervision of Dr. Gary Glass, Senior Research Chemist at ERL-D. Richard Siefert, Research Biologist/Ecologist, developer of the littoral enclosures, will be a technical consultant on this project.

The equipment and space assigned to the ERL-D mercury clean room 233 will be used.

VNP
The assistance of the Voyageurs National Park Ecologist Dr. Larry Kallemeyn and support staff will be obtained to assist in the design, implementation, and interpretation of data for the tests conducted in the Rainy River watershed area. In addition, the Park Service is considering matching funds for work done in the VNP.

Related Research Proposals
The LCMR funds ($175,000) will support the research program described above but additional funds are being solicited for an expanded program. Proposals for additional study sites have been submitted to the National Park Service ($40,000) and to the USEPA ($130,000).

References (Glass, pp. 1-4-1-5, 2-3-2-5, 3-10-3-11).

Dunnigan and/or Kjostad Lakes (work by Dr. Brezonik)

LABORATORY EXPERIMENTS ON MITIGATION MEASURES
Water, sediment and biota will be collected from an intensive-study lake in fall of 1991 and a series of microcosm-scale experiments will be set up in aquaria or carboys to evaluate potential mitigation and control strategies. The following strategies will be considered. This list is subject to modification upon further discussion with cooperators from the MPCA and upon further review of the recent scientific literature.

(1) Addition of peat and other natural materials to act as a "sponge" for mercury, absorbing it from the water column and providing a sink that competes successfully with fish for mercury;

(2) Addition of phosphorus to stimulate biological production, thus diluting the mercury being cycled into a larger biomass;

(3) Addition of non-game, bottom-feeding fish to compete with gamefish for the mercury being released from sediments; in lab experiments this would be needed to be done with small forage fish, but in mesocosm-scale experiments, larger, bottom-feeding fish could be tried.

(4) Addition of sulfate to stimulate biological sulfate reduction in the near-surface sediments;

(5) Addition of humic material (fulvic acid), which is responsible for the staining (brown color) of lakes and wetlands; and

(6) Increasing or decreasing foodchain length.

It is not practical to simulate the entire aquatic food web in lab microcosms, close attention will be given to experimental design to maintain feasibility without sacrificing realism.

Field Enclosure Experiments. Mesocosms will be constructed according to the design of landers and previous enclosure experiments at Little Rock Lake in northern Wisconsin. Following stabilization of the water and biota in the enclosures for two weeks after construction, enclosures will be manipulated according to the strategies selected from the list given above. Some treatments will be replicated, but ecosystem experimenters generally agree that complete replication of experiments at this level is impractical and inefficient. Six to eight mitigation strategies will be examined using this approach. Samples of water and biota will be collected from the enclosures and analyzed for mercury content (methyl and/or total, as appropriate).

A.3. Budget

		LCMR Funds
a.	Amount budgeted	$230,000
b.	Balance	$ 0.00

A.4. Time table for Product/Tasks:

	July 91	Jan 92	June 92	Jan 93	June 93
Detail Design	***				
Fieldwork/Sampling	**********				
Chemical Analysis	**********	**********			
Data Synthesis		**********	**********		
Final Report			**********	**********	

A.5. Status:

St. Louis River Crane Lake (work by Dr. Glass)

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

1) Tests of proven assessment methodology using littoral (shoreline) enclosure designs were successful. Minor modifications to the

original physical design were made as follows: a) commercial dock sections were used to provide a more stable and uniform perimeter for the littoral enclosures; b) wave and wind barriers were designed and tested to effectively protect the enclosures from damage; and c) the Lake Superior seiche action which causes fluctuating water levels in the St. Louis River Estuary was accommodated by creating a bellows effect in the walls of the littoral enclosures. (Glass, pages iii, 3-1-3-2.)

2) Tests of materials -- all materials used in the construction of littoral (shoreline) enclosures, repair materials and supplies, sampling equipment, and equipment used in the administration of changed conditions were tested for mercury leaching to ensure against mercury contamination. (Glass, pages iii, 3-1-3-2.)

3) Tests of appropriate exposure design and impact assessment protocols were successful. We have determined that a) full growing season tests are the most useful for uptake and growth endpoints when ambient mercury exposure levels are used; b) test endpoints should use indigenous fish from the site to be studied; and c) biweekly water sampling was appropriate for monitoring.

b. Mitigative treatment tests results -- Initial qualitative effects. Stage I enclosure tests have been completed, media and biota collected, analyses of samples are mostly completed, data synthesis is in progress, and preliminary results indicate the importance of plants in the bioaccumulation process, as an increase in bioactive carbon significantly increases mercury concentrations in fish. Treatments show a range of mercury residue reduction, with the largest and most significant residue decrease (-70%) observed due to treatment micronutrient addition. (Glass, pages v, 3-7-3-10.)

c. Additional littoral enclosure tests will be conducted in Phase II of the project.

Dunnigan and Kjostad Lakes (Brezonik report).

1) Tamarack Lake substituted for the original study lakes. This was done with MPCA approval for the following reasons: 1) Dunnigan and Kjostad lakes were too far from the Twin Cities for repeated maintenance; 2) Similar water quality characteristics; and 3) Relatively undeveloped watersheds. The enclosure work was conducted in the 1993 field season due to time needed to develop the improved total methyl mercury methodologies versus the labile methyl-mercury methodology.

2) Addition of various chemicals to 1-m dia. enclosures installed in Tamarack Lake (Pine County) did not show dramatic responses in terms of total mercury and labile methyl mercury in the water column. None of the treatments produced significant decreases in these mercury forms over the 47-day duration of the experiment, but sulfate and 2 ppb selenium resulted in elevated levels of total mercury. (Glass, pp. 31-31.)

A.6. Benefits: The testing and evaluation of mercury mitigation methods will determine which methods are effective and which are not. This will guide management decisions on the alternatives which are available in mitigating the damage done to aquatic resources by mercury. Conduct littoral enclosure studies to determine the impacts of biological manipulations.

B. Determine the distribution of total and methyl mercury burdens in water, biota of all trophic levels and surficial sediment in representative Minnesota Lakes.

B.1. Narrative: Several investigators have found that 90% of the mercury found in fish is in the toxic methyl mercury form. The atmospheric sources of mercury are predominately in the inorganic forms. Low-level methyl mercury analytical techniques recently developed at the University of Minnesota will be used to develop a data base on the dynamics of mercury transfer and cycling through aquatic food webs.

B.2. Procedures:

ROUTINE LAKE SAMPLING (work by Dr. Brezonik).

Twelve lakes of differing water chemistry and biotic structure were sampled to determine how levels of mercury change in the water column and key biotic components over the course of a year. Selection of lakes as done in consultation with scientists from the MPCA, with whom the sampling and biotic studies will be done on a cooperative basis. One lake was selected for the most intensive study and as the site of enclosure experiments in 1993. (Brezonik, page 18, figs. 7-9.)

Samples were collected of lake water and major biotic components -- phytoplankton, zooplankton, major components of the benthic communities -- at least monthly during key portions of the growth season. Biotic and water column samples will be analyzed for total methyl mercury by gas chromatography-cold vapor atomic fluorescence spectroscopy (GC-CVAFS), as described by Bloom (Canad. J. Fish. Aquat. Sci. 46:1131-1140 [1989] and developed in our laboratory under current support from the MPCA.

SOURCE IDENTIFICATION (work by Dr. Glass)
Ambient mercury concentration (total) in water and sediment from the St. Louis River and its tributaries will be measured.

B.3. Budget

		LCMR Funds
a.	Amount budgeted	$70,000
b.	Balance	$ 0.00

B.4. Time table for Product/Tasks:

	July 91	Jan 92	June 92	Jan 93	June 93
Detail Design	**********				
Fieldwork/Sampling		**********	**********		
Chemical Analysis			**********	**********	
Data Synthesis				**********	**********
Final Report					**********

B.5. Status:
ROUTINE LAKE SAMPLING (work by Dr. Brezonik)
LABORATORY STUDIES ON TRANSFER RATES
ANALYTICAL REFINEMENT

Differences between total mercury and labile methyl mercury were found in both animal and seasonal sampling (Brezonik, page 16).

Laboratory transfer rates studies were not completed at the time of this write up.

Considerable effort was expended in developing reliable methods for analysis of methyl and total mercury (Brezonik, pages 10-14).

SOURCE IDENTIFICATION (work by Dr. Glass)
St. Louis River and Crane Lakes

Water samples were analyzed for total mercury from Lake Superior to the Fond du Lac Dam (Glass, fig. 4.24) in the St. Louis River and tributaries.

Sediment core profiles were analyzed for mercury from the Thomsan, Forbay and Fond du Lac reservoirs (Glass, fig. 4.23).

Crane Lake was intensively sampled in the previous biennium.

B.6. Benefits: This objective would provide a data base on the dynamics of mercury transport and cycling through the aquatic food webs so that scientists and water quality managers can understand the key steps in the movement of mercury from its primary reservoir in lakes to gamefish. These transport and cycling processes can then be targeted for control or mitigative measures.

IV. EVALUATION:
For the FY92-93 biennium, the program can be evaluated by its ability to: 1) Determine the effectiveness of various methods to reduce mercury in fish by field demonstration and testing; 2) Increase the knowledge and understanding of the methylation process of mercury and the mechanisms which allow for bioaccumulation of methylmercury in fish.

The first year's results and activities will be peer reviewed by individuals within the Pollution Control Agency, Department of Natural Resources, University of Minnesota, and other appropriate technical experts. The list of participants in the review and all peer suggested recommendations will be submitted to the LCMR staff along with any modifications in the project due to the peer review process.

A conference on mercury research in Minnesota was held on June 23, 1993. These results were presented to approximately 50 attendees that represented academia, power generation, wastewater treatment, and several governmental agencies interests.

The implementation of mercury reduction methods evaluated by this project and subsequent mitigation of mercury damage in Minnesota lakes will determine the success of the project.

V. CONTEXT:

A. Now that atmospheric deposition has been identified as the general source of mercury, source control mitigation of existing impacts need to be conducted. This project begins to address the need to restore the already degraded aquatic resources through research, development and testing of mitigation methods.

B. To date, mercury work has been directed at determining the extent and magnitude of the problem and the sources of mercury to northeastern Minnesota. Little effort has been put forth in actual testing of methods to restore aquatic resources or mitigate the problem. This project is a logical step in a program to protect Minnesota from mercury pollution.

C. This project is the third part of the mercury program. The first part was to determine the extent and magnitude of the problem and to identify where the mercury was coming from. The second part was to determine if the atmospheric sources were from within Minnesota or were from outside the state. The third phase is this project which is to begin efforts to determine effective restoration and mitigation methods. Part III is dividied into Phase I and II. Phase I is completed with Phase II being conducted in 1994-95 biennium.

D. PCBs and Mercury In Public Waters - $500,000.

E. Biennial Budget System Program Title and Budget: Not available at this time.

VI. QUALIFICATIONS:

1. Program Manager

Marvin E. Hora
Toxics Abatement Supervisor
Section of Program Development
Minnesota Pollution Control Agency

B.S. Wildlife Biology-South Dakota State University - 1971
M.S. Aquatic Ecology-South Dakota State University - 1973

Program Manager for past two LCMR projects on mercury. Supervisor of Toxic and Ambient Monitoring Programs for MN Pollution Control Agency for the last 15 years.

2. Major Cooperators:

A. Dr. George Rapp, Jr.
Archaeometry Laboratory
College of Science and Engineering
University of Minnesota, Duluth

B.S. Geology and Mineralogy-University of Minnesota
Ph.D. Geochemistry-Pennsylvania State University.

Dr. Rapp brings to the project a varied and wide range of geological expertise. He was a major cooperator with the first two LCMR projects. Dr. Rapp was the Dean of the College of Science and Engineering at the University of Minnesota-Duluth for 14 years and is nationally recognized for his work and publications.

Dr. Gary E. Glass
Senior Research Chemist
U.S. EPA Environmental Research Laboratory

B.S. Chemistry-University of Minnesota-1962
Ph.D. Inorganic Chemistry University of Minnesota-1967
Post-Doc. Organometallic Chemistry-University of Wisconsin - 1968

Dr. Glass is currently a Senior Research Chemist with the U.S. Environmental Protection Agency in Duluth, Minnesota. Dr. Glass has a wide range of chemical knowledge and experience. He has been a major researcher in the acid rain area and has been a major cooperator in the last two LCMR projects on mercury.

Project Advisors:

Dr. Larry Kallemeyn - Ecologist - Voyageurs National Park
Richard Siefert - Ecologist - EPA Environmental Research Laboratory

B. Dr. Patrick Brezonik, Director
Water Resources Center
University of Minnesota

B.S. Chemistry/Math-Marquette University
M.S./Ph.D. Water Chemistry-University of Wisconsin

Dr. Brezonik is currently the Director of the Water Resources Center and a Professor in the Department of Civil and Mineral Engineering at the University of Minnesota. He is a member of the graduate faculty in ecology at the University of Minnesota. He was a primary researcher on the first LCMR mercury study and is involved in work for the second investigation. He brings to the project a broad range of experience and technical knowledge in limnology and toxic metals. He is a co-investigator on related mercury research in Wisconsin.

VII. REPORTING REQUIREMENTS:
Semiannual status reports will be submitted not later than January 1, 1992, July 1, 1992, January 1, 1993, and a final status report by June 30, 1993.