Environment and Natural Resources Trust Fund (ENRTF)
M.L. 2014 Work Plan

Date of Report: January 15, 2014

Date of Next Status Update Report: January 1, 2015

Date of Work Plan Approval:

Project Completion Date: June 30, 2017

Does this submission include an amendment request? _No_

PROJECT TITLE: Identifying Causes of Exceptionally High Mercury in Fish

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Location: Northwestern (Red River of the North watershed) and northeastern (Vermilion, St. Louis, and Kettle watersheds)

Total ENRTF Project Budget:		
	ENRTF Appropriation:	**$743,000**
	Amount Spent:	**$0**
	Balance:	**$743,000**

Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 03j

Appropriation Language:
$743,000 the second year is from the trust fund to the commissioner of the Pollution Control Agency to quantify the probable causes of high mercury levels in fish within the Roseau River and two tributaries of the Red River of the North, by comparing mercury movements within watersheds to understand the drivers of mercury biomagnifications in the food web of rivers with similarly high mercury levels, and to guide further mercury reduction initiatives. This appropriation is available until June 30, 2017, by which time the project must be completed and final products delivered.

I. PROJECT TITLE: Identifying Causes of Exceptionally High Mercury in Fish

II. PROJECT STATEMENT:

Mercury is toxic to the nervous system and eating fish is the primary route of exposure to humans and wildlife. More than two-thirds of Minnesota lakes and streams evaluated by the Minnesota Pollution Control Agency (MPCA) are "impaired" because of mercury in fish. Roughly one in ten of these impaired waters have exceptionally high mercury in fish, such that they do not qualify for inclusion in Minnesota Statewide Mercury TMDL. Less than one percent of the mercury entering Minnesota's lakes and rivers comes from wastewater discharges. The primary source of mercury in Minnesota waters is the burning of coal and other compounds, which deposit on the watersheds from the atmosphere. Mercury in the environment can convert to a form that accumulates in the food chain, increasing in concentration as it moves from microscopic plants, to tiny animals, to fish, and and eventually to humans and wildlife (see graphic).

The first step in solving the problem of mercury in fish is reducing the amount of mercury entering lakes, streams and wetlands. Toward this end, the MPCA is implementing a plan to reduce the mercury released from Minnesota smokestacks by 93 percent and continue to reduce mercury from wastewater discharges. This large reduction in mercury releases in Minnesota, coupled with global reductions, will benefit all waters of the state and fully restore about 90% of Minnesota's water bodies from the effects of mercury pollution. For the remaining 10% of water bodies it is necessary to go beyond mercury source reductions, addressing the mobilization and bioavailability of mercury in the watersheds.

This proposal focuses on the ecosystem processes that control mercury into fish. These processes include mercury delivery from subwatersheds, production and destruction of methylmercury (the bioavailable form), food web feeding relationships, and the fish growth rates.Scientists understand some of the factors that cause enhanced mercury accumulation, but not well enough to know the relative importance of each factor and what actions could reduce the enhanced mercury accumulation. The goal of this project is to achieve sufficient knowledge about the causes of exceptionally high mercury levels to inform additional efforts to reduce mercury in fish.

In our original proposal, MPCA partnered with the Minnesota Department of Natural Resources (DNR) and the United States Geological Survey (USGS). Each agency committed to specific matching funds for the original proposal request. Given the LCCMR's recommendation to fund the project at one quarter of what MPCA requested, the scope has been scaled down accordingly and the commitments from the partnering agencies are no longer effective. Nevertheless, the MPCA expects the DNR and USGS will continue as partners in this research.

III. PROJECT STATUS UPDATES:

Project Status as of January 1, 2015:

Project Status as of July 1, 2015:

Project Status as of January 1, 2016:

Project Status as of July 1, 2016:

Project Status as of January 1, 2017:

Overall Project Outcomes and Results:

IV. PROJECT ACTIVITIES AND OUTCOMES:

ACTIVITY 1: Transport of Mercury and Methylmercury

Description:

Fundamental to understanding mercury availability is quantifying how much mercury and methylmercury is transported through the river. Concentrations of thirteen analytes (Table 1) will be measured 32 times over two years at the gaging station in the Roseau River and two other tributaries of the Red River of the North. Water samples will be collected as grab samples below the water surface in the main flow the stream (i.e., thalweg). Mercury and methylmercury samples will be collected using the "clean hands – dirty hands" technique (EPA Method 1669). In addition, field measurements will include pH, temperature, specific conductivity, and dissolved oxygen. Water flows are continuously measured at these sites, which are in the cooperative flow gaging network supported by the DNR and USGS (http://www.dnr.state.mn.us/waters/csg/index.html). Flow and concentration data will be used in the FLUX32 model to calculate annual mass loads at each of the sites.

Final selection of the two tributaries for comparison to the Roseau will be based on an examination of land cover and stream flow characteristics. The likely candidates are the Red Lake River, Buffalo River, and Marsh River.

All sample collection and laboratory analysis will be contractual. Sample collection will most likely be done by the USGS or DNR under contract with the MPCA. Laboratory analysis methods and costs are based on Minnesota Department of Health's Environmental Laboratory.

Table 1 Analytes for water collections

Analytes	Method	Reporting Limit	Units	Holding Time (days)
Total Organic Carbon	SM 5310C	1	mg/L	28
Dissolved Organic Carbon	SM 5310C	1	mg/L	28
Sulfate	EPA 300.1	1.00	mg/L	28
Phosphorus, Total	EPA 365.1	0.01	mg/L	28
Iron Dissolved, Low Level	EPA 200.7	14.0	ug/L	180
UV Absorbance @ 254 nm	SM 5910B	0.0050	Abs units	2
Solids, Suspended	SM 2540D	1.0	mg/L	7
Suspended Solids, Volatile	EPA 160.4	10	mg/L	7
Solids, Total Dissolved	SM 2540C	10	mg/L	7
Low Level Mercury, Total	EPA 1631	0.400	ng/L	90
Low Level Mercury, Dissolved	EPA 1631	0.400	ng/L	90
Methyl Mercury, Total	EPA 1630	0.050	ng/L	180
Methylmercury, Dissolved	EPA 1630	0.050	ng/L	180

Summary Budget Information for Activity 1:

ENRTF Budget: $ 210,000
Amount Spent: $ 0
Balance: $ 210,000

Activity Completion Date: March 30, 2017

Outcome	Completion Date	Budget
1. *Water quality sampling*	October 30, 2016	$ 132,000
2. *Laboratory Analysis*	January 1, 2017	$ 75,000
3. *Flux (mass load) calculations*	March 30, 2017	$ 3,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017:

Final Report Summary:

ACTIVITY 2: Methylmercury Production and Destruction
Description:
Mercury methylation and demethylation will be measured by the stable isotope. In situ rates of methylation activity is measured by adding inorganic mercury isotope (e.g., $^{201}Hg^{2+}$) to each sample and monitoring formation of the labelled methylmercury (e.g., $Me^{201}Hg^{+}$). Similarly, for demethylation, the same sample is spiked with another stable-isotope labelled methylmercury (e.g., $Me^{199}Hg^{+}$) and it is monitored for a decrease in concentration. The ratio of methylation rate/demethylation rate gives the net methylation rate potential. The methylation-demethylation study will be done at nine sites, with at least three samples per site visit, and each site will be visited three times to capture seasonal differences of the rates. This study will begin in the second year of this project because sites will be selected based on the first year of water quality monitoring.

Photodemethylation is considered the most important removal process of methylmercury in lakes, but it has been studied much in rivers; therefore, photodemethylation rates will be measured at the same nine sites as the methylation-demethylation rate study. The method for measuring photodemethylation of mercury is to suspend clear ("light") and opaque ("dark") bottles, in situ, with sufficient replicates to measure methylmercury concentrations before and after incubation. Ultraviolet and photosynthetically active radiation will be measured continuously during the incubations. The sites for the photodemethylation study will be downstream of the nine methylation-demethylation sites. The methylation-demethylation sites are expected to be wetlands hydrologically connected to the rivers and the photodemethylation sites will be downstream sites unobstructed by tree canopy.

The quantity and quality of dissolved organic matter (DOM) strongly influences mercury methylation and demethylation. Therefore, the DOM from the selected river sites will be quantified as total organic carbon (TOC) and dissolved organic carbon (DOC) as part of Activity 1 and the quality of the DOM will be assessed using several state-of-the-art techniques. The characterization of DOM will show if the DOM sources differ among the rivers, which could determine how they affect methylation and demethylation.

Summary Budget Information for Activity 2:

ENRTF Budget: $ 128,000
Amount Spent: $ 0
Balance: $ 128,800

Activity Completion Date: January 1, 2017

Outcome	Completion Date	Budget
1. *Methylation potential*	January 1, 2017	$ 100,000
2. *Photodemethylation*	January 1, 2017	$ 13,000
3. *DOC characterization*	January 1, 2017	$ 15,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017:

Final Report Summary:

ACTIVITY 3: Food Web Relationships
Description:
Aquatic food webs in five rivers will provide a comparison of bioaccumulation rates and possible differences in growth rates of top predator fish. Food web collections will include seston, benthic macro invertebrates, forage fish, and predator fish. Isotopic ratios of naturally-occurring stable isotopes for nitrogen (N) are carbon (C) will be measured in the biota samples to identify feeding relationships in the food webs and carbon sources. Food web collection and sample analysis will follow the procedures described in Scudder et al., 2008. This USGS publication describes the procedures for collection and processing of biota samples for mercury, methylmercury, and stable isotope analyses. Bioaccumulation of mercury in the food webs will be measured as the linear regression slope of log-transformed methylmercury concentration versus the N-isotope ratios (delta-15 N) in the biota samples. Growth rates in top predator fish will be calculated based on the aging and length data. USGS procedures include collection of otoliths from top predator fish for age determination.

Because of the natural variability in mercury and isotope levels in biota, meaningful comparisons require multiple sites and adequate samples of biota at each site. A total of 63 biota samples at each of 17 sites (1071 samples) was used to estimate the budget for the food web comparison.

Summary Budget Information for Activity 3:

ENRTF Budget: $ 331,000
Amount Spent: $ 0
Balance: $ 331,000

Activity Completion Date: March 30, 2017

Outcome	Completion Date	Budget
1. *Biota collection*	January 1, 2017	$ 114,000
2. *Fish age determination and growth analysis*	January 1, 2017	$ 7,000
3. *Lab analysis for mercury, methylmercury, & stable isotopes*	March 30, 2017	$ 210,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017:

Final Report Summary:

ACTIVITY 4: Database and Model Development
Description:

The purpose of this activity is to geo-reference all data in a single database, along with land cover summaries for each watershed. The compiled data will be statistically analyzed with as yet unspecified tests. Likely statistical tools are spatial statistics/plotting, principal components analysis, and mixed effects modeling. These statistical tools can provide a measure of the relative importance of the multiple variables and processes measured in this study. From the statistical analysis, an empirically-based conceptual model will be developed for the important drivers of mercury accumulation in the riverine food webs. This activity includes a travel budget for the project manager to visit sites, assist with sampling, and to attend in-state meetings.

Summary Budget Information for Activity 4:

ENRTF Budget: $ 74,000
Amount Spent: $ 0
Balance: $ 74,000

Activity Completion Date: June 30, 2017

Outcome	Completion Date	Budget
1. *Database development*	March 30, 2017	$ 50,000
2. *Statistical Analysis & Reporting*	March 30, 2017	$ 20,000
3. *Travel to assist field work and attend meetings*	June 30, 2017	$ 4,000

Activity Status as of January 1, 2015:

Activity Status as of July 1, 2015:

Activity Status as of January 1, 2016:

Activity Status as of July 1, 2016:

Activity Status as of January 1, 2017:

Final Report Summary:

V. DISSEMINATION:

Description:
The research findings will be initially disseminated as reports to LCCMR. From these reports, the project manager and other primary researchers in this project will prepare manuscripts for scientific peer-reviewed publications and present the results at conferences. Major results will undoubtedly be of interest to the news media, because of the public's interest in mercury and consuming fish. The results of this research should be useful for developing total maximum daily load studies for mercury in fish in these waters that do not qualify for the Statewide Mercury TMDL because of exceptionally high mercury levels. The mercury results for fish will be added to the fish contaminant database maintained by Minnesota's interagency Fish Contaminant Monitoring Program.

Status as of January 1, 2015:

Status as of July 1, 2015:

Status as of January 1, 2016:

Status as of July 1, 2016:

Status as of January 1, 2017:

VI. PROJECT BUDGET SUMMARY:

A. ENRTF Budget Overview:

Budget Category	$ Amount	Explanation
Personnel:	$ 0	Project manager salary is in-kind support and all other personnel costs included in contracts
Professional/Technical/Service Contracts: Professional/Technical (Activities 1-4) Laboratory Services (Activities 1 and 3)	 $ 454,000 $ 285,000	All field sampling, experiments, and laboratory analysis will be completed under contracts with the MPCA; Where possible, MPCA will use existing master contracts. Requests for proposals will be issued by the MPCA in the third quarter of 2014 with the intent of signed contracts by January 1, 2015.
Travel Expenses in MN:	$ 4,000	Meetings and field visits for project manager
TOTAL ENRTF BUDGET:	**$ 743,000**	

Explanation of Use of Classified Staff: N/A

Explanation of Capital Expenditures Greater Than $5,000: N/A

Number of Full-time Equivalents (FTE) Directly Funded with this ENRTF Appropriation: NONE

Number of Full-time Equivalents (FTE) Estimated to Be Funded through Contracts with this ENRTF Appropriation: TBD

B. Other Funds:

Source of Funds	$ Amount Proposed	$ Amount Spent	Use of Other Funds
Non-state			
	$	$	
State – (In-kind Support only)			
MPCA 0.5 FTE for 3 years	$ 156,000	$ 0	
TOTAL OTHER FUNDS:	**$**	**$**	

VII. PROJECT STRATEGY:

A. Project Partners: TBD (subject to revision for final work plan)

B. Project Impact and Long-term Strategy:

The long-term goal of this project is to protect public health by reducing mercury in fish. Understanding the relative importance of processes that cause high mercury levels in fish will inform future management activities. The eventual development of Total Maximum Daily Loads for these waters, funded by the Clean Water Legacy Fund, will benefit from the scientific results of this project.

C. Spending History:

Funding Source	M.L. 2008 or FY09	M.L. 2009 or FY10	M.L. 2010 or FY11	M.L. 2011 or FY12-13	M.L. 2013 or FY14

VIII. ACQUISITION/RESTORATION LIST: N/A

IX. VISUAL ELEMENT or MAP(S): See attached graphic.

X. ACQUISITION/RESTORATION REQUIREMENTS WORKSHEET: N/A

XI. RESEARCH ADDENDUM: See attached Research Addendum.

XII. REPORTING REQUIREMENTS:
Periodic work plan status update reports will be submitted no later than January 1, 2015, July 1, 2015, January 1, 2016, July 1, 2016, and January 1, 2017. A final report and associated products will be submitted between June 30 and August 15, 2017.

Environment and Natural Resources Trust Fund
M.L. 2014 Project Budget

Project Title: Identifying Causes of Exceptionally High Mercury in Fish.
Legal Citation: M.L. 2014, Chp. 226, Sec. 2, Subd. 03j
Project Manager: Bruce Monson.
Organization: *Minnesota Pollution Control Agency*.
M.L. 2014 ENRTF Appropriation: $ *743,000*
Project Length and Completion Date: *3 Years, June 30, 2017*
Date of Report: *January 15, 2014*

ENVIRONMENT AND NATURAL RESOURCES TRUST FUND BUDGET	Activity 1 Budget	Amount Spent	Activity 1 Balance	Activity 2 Budget	Amount Spent	Activity 2 Balance	Activity 3 Budget	Amount Spent	Activity 3 Balance	Activity 4 Budget	Amount Spent	Activity 4 Balance	TOTAL BUDGET	TOTAL BALANCE
BUDGET ITEM	***Transport of Mercury***			***Methylmercury Production & Destruction***			***Food Web Relationships***			***Database and Statistics***				
Professional/Technical/Service Contracts														
TBD (competitive bid): Water quality sample collection; biota collection; methylation/demethylation studies	$135,000	$0	$135,000	$128,000	$0	$128,000	$121,000	$0	$121,000	$70,000	$0	$70,000	$454,000	$454,000
TBD (competivite bid): Laboratory Services	$75,000	$0	$75,000	$0	$0	$0	$210,000	$0	$210,000	$0	$0		$285,000	$285,000
Travel expenses in Minnesota Travel expenses for meetings and field visits for project manager.										$4,000	$0	$4,000	$4,000	$4,000
COLUMN TOTAL	**$210,000**	**$0**	**$210,000**	**$128,000**	**$0**	**$128,000**	**$331,000**	**$0**	**$331,000**	**$74,000**	**$0**	**$74,000**	**$743,000**	**$743,000**

Hypothesis: variability of mercury in fish is driven by controls in the watershed.

Four major controls, which we will measure, are:

(1) Transport

(2) Transformation

(3) Degradation

(4) Food web structure and dynamics