Name of Organization: Oak Ridge National Laboratory

Type of Organization: Federally-funded R & D Center

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Project Title: Non-Combustion Emissions of Hg in the Great Lakes Airshed

Project Category: Pollution Prevention and Reduction - BNS

Rank by Organization (if applicable): 0

Total Funding Requested ($): 200,912 **Project Duration:** 2 Years

Abstract:

The Great Lakes receive quantifiable inputs of atmospheric mercury from many regional anthropogenic sources, and controls are now being considered. The nature of the atmospheric chemistry of mercury is such that emissions from sources outside of the local region may readily impact the Great Lakes Airshed. We propose to expand our ongoing studies of mercury emissions which may impact the Great Lakes Airshed in a collaborative study of other potentially important sources. While emissions from combustion sources are relatively well characterized (USEPA, 1998), those from various non-combustion sources are recognized, but not well quantified (Expert Panel, 1994). These sources, which include the manufacturing, recycling, and waste handling industries, are important since they may be large and may directly emit methylmercury or other organic mercury compounds (e.g. Hintelmann et. al. 1995, Carpi et. al. 1997, Lindberg and Price 1999). Our group has developed and applied a number of mercury flux measurement approaches to meet these objectives (papers cited below). The impacts of ignoring such sources in regional mercury models and data interpretation is unknown. These sources are yet uncontrolled, and the results of reducing U.S. combustion-source emissions could be less than expected because of these other sources. The overall magnitude of these sources in the Great Lakes region is unknown, but the chlor-alkali industry alone purchases over 150 tons of "makeup" mercury annually, the fate of which is unquantified.

Geographic Areas Affected by the Project

States:

- [x] Illinois
- [x] Indiana
- [x] Michigan
- [x] Minnesota
- [x] New York
- [x] Pennsylvania
- [x] Wisconsin
- [x] Ohio

Lakes:

- [ ] Superior
- [ ] Huron
- [ ] Michigan
- [ ] Erie
- [ ] Ontario
- [x] All Lakes

Geographic Initiatives:

- [ ] Greater Chicago
- [ ] NE Ohio
- [ ] NW Indiana
- [ ] SE Michigan
- [ ] Lake St. Clair

Primary Affected Area of Concern: Not Applicable

Other Affected Areas of Concern:

For Habitat Projects Only:

Primary Affected Biodiversity Investment Area:

Other Affected Biodiversity Investment Areas:

Problem Statement:

This work will address several research priorities in the GLNPO including source identification and emission inventories through application of new methods to measure the fluxes of inorganic and organic mercury compounds emitted from poorly characterized non-combustion sources within the airshed. Our research group is currently engaged in collaborative research in the Great Lakes region (see below), and the proposed research will be combined with ongoing studies for the USEPA and the Great Lakes Protection Fund to further improve our ability to address the necessary research priorities. The contribution of fugitive emissions of mercury from poorly characterized non-combustion sources has not been quantified in the Great Lakes Region, and emissions may be significant. For example, our experience in ongoing studies indicates that some industrial activities which utilize mercury are highly ventilated to reduce workplace exposure (e.g. chlorine production by the mercury-cell process). This favors external emission of volatile mercury from intermittent area sources, which are historically difficult to quantify.

Some of these sources are known to or are suspected of directly emitting organic mercury compounds to air and soils. For example, previous studies have identified direct airborne emissions of volatile methylmercury compounds from soils amended with municipal sludge which is widely applied to agricultural soils (Carpi et. al. 1997), and gases generated in Class I municipal landfills have recently been found to contain several methylated mercury compounds (Lindberg and Price 1999, Lindberg et. al. 1999). Several organo-mercury compounds, some volatile, have been identified in soils near former chemical plants in Europe (Hintelman et. al. 1995). Any existing measurements near these sources have typically been limited to total mercury, such that the important speciation characteristics may be missed. These sources include chloralkali factories, production of precision measurement instruments including mercury, electrical component manufacturers, steel mills, metal scrap yards, mercury and mercury-bearing product recyclers such as those for fluorescent lamps, and municipal and chemical waste handling and landfill facilities.

The overall objective of this study will be to assess speciated mercury emissions from non-combustion sources in the Great Lakes Airshed. This will include measurements of fugitive air emissions, release of organo-mercurials, presence of airborne reactive gaseous mercury (RGM), and determination of surface emissions from potentially contaminated on-site soils. The source(s) chosen for our study will be selected in consultation with EPA's GLNPO, and the final selection will be in support of the primary needs of State and EPA customers. We plan 2-week field measurement periods for each year during which the primary data for this study will be collected as described below. The work will include training and collaboration with State Agencies in the Region. In addition, a major portion of this study will support data analysis and preparation of journal articles based on the work performed in this and related EPA and Great Lakes projects.

Proposed Work Outcome:

We propose to characterize the primary mercury emission pathways and the speciation of the emitted mercury from the source or sources selected for study. The measurements will be performed by the PI's and their colleagues in a collaborative endeavor with the Minnesota Pollution Control Agency (MPCA) during two separate field campaigns in the Great Lakes Airshed. The measurements will be scheduled for both warm and cool periods because of the strong influence of temperature on fugitive mercury emissions (e.g. Lindberg et. al. 1995). The data collected will be subject to stringent quality assurance procedures such as those we have developed for three previous EPA projects. The data will be used with regional production and industrial land-use information to estimate overall emissions from these source types. The speciation measurements can be combined with a mercury deposition model to estimate local dry deposition fluxes (Lindberg et. al. 1992). These data will be compared to regional emission inventories to assess the potential importance of this source category.

New methodology developments now make such field measurements feasible. One recent development which we are anxious to test further involves the availability of a new sampling instrument for airborne Hg(0). This instrument has two very important advantages over more routine manual (gold traps) and new automated (Tekran) sampling devices: it is highly portable, and it provides the first ever real-time analytical capability for Hg(0) in air. This device utilizes Zeeman corrected atomic absorption spectroscopy (ZCAAS), combined with a folded 10-m path cell to produce Hg data on a 1 Hz time scale (with an LD of ~5 ng/m3). The hand-held battery operated device fills the gap very well between the highly sensitive, but less portable and slower Tekran (5-minute samples with an LD of 0.2 ng/m3) and the hand-held Jerome thin-film sensor which is often used in industrial settings (10-sec samples with an LD closer to 1000 ng/m3). In addition, the Jerome exhibits several serious interferences, from which the ZCAAS instrument is free. Our limited experience with the ZCAAS suggests it can be used very effectively to "sniff" for potential Hg sources, on a spatial scale of m's to km's, depending on source strength, and can be adapted for direct in-air flux measurements. Hence, a major portion of this study would involve continued testing and application of the ZCAAS method. ORNL has recently acquired this analyzer for testing at a Chlor-alkali plant in Georgia. Several tests are scheduled for Feb. 2000, but the ZCAAS has already proved useful as a mobile monitor to locate potential Hg sources in other studies.

Since 1990, we have published more than 30 journal papers on the development and application of laboratory, field chamber, and field micrometeorological Hg flux measurement methods to characterize emissions from both surface and area sources which address scales from 0.1 to 100,000 m2 (key references cited below). Our methods make extensive use of the Tekran automated mercury analyzer which we have utilized since 1995. ORNL currently owns and operates five Tekrans, one in Alaska, one in Nevada, and three in our laboratory. ORNL developed and published the first methods for application of the Tekran to near-real-time field mercury speciation (Lindberg et. al. in press), the first (mist chamber) method for measurement of speciated RGM in ambient air (Lindberg and Stratton 1998), and among the first methods for application of the Tekran to automated surface flux chamber measurements (Lindberg and Price 1999). We also make extensive use of standard, manual gold trap methods (e.g. Kim et. al. 1995), and now have ZCAAS capability, all of which will be available to this project.

Since 1995 we have performed several independent studies of fugitive mercury emissions from large-area sources, including a contaminated industrial site in New York, contaminated soils in Tennessee, a contaminated floodplain in Germany, a chlor-alkali plant in Georgia, and three municipal landfills in Florida (e.g. Lindberg et. al. 1995, Lindberg and Price 1999). In this latter study we collaborated with Frontier Geosciences in the first measurements of methyl- and dimethyl-mercury emissions in landfill gas (D. Wallschlager, E. Prestbo). A subcontract with Frontier brings to our project world-class expertise in the sampling and analysis of organo-mercurials. From 1975-1976 the PI's collaborated on the first field measurements of mercury emissions from chlorine waste deposits, and in 1998 we initiated a new project to measure mercury emissions from active chlor-alkali plants in a unique collaboration with the USEPA research group at Research Triangle Park. All of the methods and experience developed during these studies will be utilized in the sampling design for the proposed study once site selection has commenced.

During each 1-2-week field measurement period, we will quantify Hg concentrations in and near the selected sources, and develop a data base which will allow estimates of the overall emissions of Hg from these sources. The three primary approaches will utilize our published methods to measure vent-related fluxes, fenceline fluxes, and direct surface-area fluxes. By combining different approaches on different scales, we can better constrain overall emissions, as well as reduce the uncertainty in our estimates. All of our methods are amenable to measurement of different organic and inorganic species, although the emission of Hg(0) is expected to dominate emissions from most non-combustion sources. Our flux chamber methods can also be used to develop an understanding of the processes influencing mercury surface emissions through more detailed controlled lab studies of the waste materials of interest.

The outcomes from this project will include emission inventory data for selected non-combustion sources, estimates of emissions for selected mercury species, development and testing of specific measurement, monitoring, and speciation methods applicable to other fugitive emissions in the region, and modeling results for local-scale dry deposition of these species (dry deposition is expected to dominate the local scale inputs of the reactive species). A major part of the outcome of this work will be preparation of research papers for publication in the open literature describing the results of several ongoing EPA studies of non-combustion sources in this airshed.

Due to space limitations, the complete list of references cited in this proposal will be made available upon request, as will vitae for the PIs. For the purpose of this preproposal, these recent method papers are most relevant:

Lindberg et. al., 2000, Biogeochem., 48(2), 237-259.
Lindberg and Price, 1999, J. Air and Waste Management Assoc., 49:174-185.
Carpi and Lindberg, 1998, Atmos. Envir. 32:873-882.
Lindberg and Stratton, 1998, Envir. Sci. & Technol. 32:49-57.
Carpi et. al., 1997, J. Env. Qual. 26:1650-1655.
Carpi and Lindberg, 1997, Envir. Sci. & Technol. 31:2085-2091.
Lindberg et. al., 1995, Envir. Sci. Technol. 29:126-135.

Project Milestones:	**Dates:**
Project Start	01/2001
Prelim report of data from related proj	04/2001
Meeting to select potential sites	06/2001
Warm-weather sampling campaign	09/2001
Data report from first field study	01/2002
Cool-weather sampling campaign	03/2002
Data report from second field study	07/2002
Preparation of journal paper(s)	12/2002

☒ Project Addresses Environmental Justice

If So, Description of How:

The EPA is considering controls on combustion sources of Hg. A decision to regulate is possible in December, 2000. If combustion sources are regulated, non-combustion sources will increase in their relative importance. To consider further controls, we must locate, quantify, and inventory these non-combustion sources. Ultimately, reducing atmospheric mercury concentrations is expected to reduce methylmercury concentrations in freshwater fish, opening resources whose use is presently impaired due to fish consumption advisories. Expanding the availability of these public resources will benefit all citizens, but especially economically disadvantaged groups for whom recreational fishing provides an important source of food.

☒ Project Addresses Education/Outreach

If So, Description of How:

The primary users of the information generated in this study are regulatory staff and decision makers in Federal and state agencies responsible for permitting the atmospheric emissions of mercury from various sources. Findings of this study will be communicated to key staff at state and Federal agencies through informal networking and formally to a nationwide audience, through conference presentation and peer-reviewed journal publication. We routinely employ students and postdocs in all of our field studies, and we have formal ties with Universities in the Great Lakes Region, thereby providing for direct education outreach with these schools (e.g. the PI is an adjunct faculty member at the University of Michigan).

Project Budget:

	Federal Share Requested ($)	Applicant's Share ($)
Personnel:	110,770	12,000
Fringe:	0	2,000
Travel:	11,500	0
Equipment:	0	50,000
Supplies:	9,625	0
Contracts:	16,720	0
Construction:	0	0
Other:	0	0
Total Direct Costs:	148,615	64,000
Indirect Costs:	52,297	0
Total:	200,912	64,000
Projected Income:	0	0

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

NOTE: ORNL budgets include fringe costs in the Personnel line.

Dr Swain of the Minnesota Pollution Control Agency (MPCA) and University of Minnesota (UMn) will collaborate on the project under his own internal funding provided by MPCA/UMn (in-kind, cost-share value = $14,000). Oak Ridge National Laboratory will supply sampling and flux equipment such as Tekran and Lumex automated Hg analyzers and flux chambers valued at more than $50,000.

Description of Collaboration/Community Based Support:

The proposed work is a direct collaboration between Oak Ridge National Laboratory, the Minnesota Pollution Control Agency, and the University of Minnesota, and will thereby provide important technology transfer from this Federal Laboratory to a State Agency in the Great Lakes Region. The work will address the needs of Federal and State environmental agencies in the Great Lakes region to better quantify non-combustion point and diffuse area sources of mercury and methylmercury emissions. Through the Great Lakes National Program Office we will address three of the FY2000-2001 Great Lakes Priorities: the research results will primarily address Pollution Prevention and Reduction/binational Toxics Strategy, but the outcomes will have implications for Ecological (habitat) Protection and Restoration, and can be considered Emerging Issues. Our research group is engaged in ongoing collaborative research in the Great Lakes region (e.g. with these State Agencies: MN PCA and MI DEQ, and the universities of MI and WI). The proposed research will benefit from ongoing studies for the USEPA and the Great Lakes Protection Fund to further improve our ability to quantify Hg and methylmercury emission sources, to understand the role of non-combustion sources, and to predict the fate of atmospherically emitted mercury.