

THE ROUGE RIVER PROJECT
A WORLD CLASS EFFORT



BRINGING OUR RIVER BACK TO LIFE

Rouge River National Wet Weather Demonstration Project

Wayne County, Michigan

TECHNICAL MEMORANDUM

Air Deposition Studies A Review of Air Deposition Literature

RPO-NPS-TM03.00

September 1994

Rouge River National Wet Weather Demonstration Project

Wayne County, Michigan

TECHNICAL MEMORANDUM

Air Deposition Studies
A Review of Air Deposition Literature

RPO-NPS-TM03.00

Author: Amarjit Sidhu

Rouge River National Wet Weather Demonstration Project

MISSION STATEMENT

The mission of the Rouge River National Wet Weather Demonstration Project is to restore the water quality in the Rouge River as necessary to:

- provide a safe and healthy environment for ourselves and future generations,
- protect downriver water resources such as the Detroit River and Lake Erie, and
- re-establish a healthy and diverse ecosystem within the Rouge River Watershed.

This will be accomplished through the development, implementation, and financial integration of a technical, social, and institutional framework leading to cost efficient, and innovative, watershed based solutions to control the wet weather problems in the Rouge River Watershed.

PREFACE

The Rouge River has historically suffered and continues to suffer from the combined stress of pollutant loadings from various sources. The vast majority of continuous point sources have been eliminated through the issuance and enforcement of National Pollutant Discharge Elimination System (NPDES) permits for municipal and industrial dischargers. Yet, as established in the Rouge River Remedial Action Plan (RAP), the river remains polluted primarily because of sources associated with wet weather flow.

The Rouge River National Wet Weather Demonstration Project (Rouge Project) is intended to evaluate each of the various sources of wet weather pollution; implement alternative remedial measures; investigate wet weather waste load allocations; establish associated pollutant load reductions; examine the financial and institutional impediments to wet weather pollution control; and recommend a plan and procedure for watershed-wide pollution control which is "implementable" in the Rouge and can be readily transferred to similar urban watersheds throughout the country.

The effort is not being conducted in isolation. The Rouge RAP provides a baseline from which Rouge Project efforts have begun. In fact, the Rouge Project can be viewed as the key component of the initial implementation of the RAP. In addition, ongoing regulatory efforts aimed at controlling Combined Sewer Overflow (CSO) discharge have also been integrated into the Rouge Project and all construction facilities will be in accordance to NPDES permits.

It is widely recognized, and reinforced by RAP recommendations, that CSO control by itself will not be sufficient to restore water quality to acceptable levels in the Rouge River and other similar urban rivers. The project has established a watershed-wide concept as its focus. Within the Rouge River Watershed, a range of pollution sources have been identified. They include: traditional urban runoff, illicit connections to drainage facilities, abandoned dumps within the river flood plain, wet fall and dry fall air deposition, and contaminated sediments within the river channel and impounded lakes.

The Rouge Project has incorporated efforts to develop analysis tools, organize existing and future data, conduct field surveys, collect and analyze water quality samples, develop and implement water quality models, design and test structural and nonstructural best management practices (BMPs), and establish loadings from nontraditional wet weather sources. Additionally, it includes components that will involve watershed residents in pollution control planning, and will study the institutional structure and financial capabilities of those entities responsible for long term implementation of the recommended watershed plan.

To efficiently manage an effort with diverse objectives, the project has been divided into ten program elements. Each of these has a specifically defined technical or operational purpose. Within each of these elements, work plans are developed to define specific activities to be performed as part of the project. These work plans define the Tasks and level of effort.

The program elements that have been established are as follows:

- Geographic Information System (GIS) and Mapping
- Data Collection and Management
- Sampling and Analytical Program
- Modeling and Decision Support System (DSS)
- Nonpoint Source Best Management Practices (BMPs)
- CSO Design, Build and Test
- Value Engineering
- Public Information and Involvement
- Financial and Institutional
- Project Management, Coordination and Reporting

This document has been generated under the Nonpoint Source Program Element and is a product of Work Plan No. 1, Task 2.2. As a part of Work Plan No. 1, an analysis of air deposition data availability, quality, and adequacy was made to identify air-related pollutant loads to the Rouge River and to support subsequent work plan efforts. This document presents a summary of the available literature relating to the topic of air deposition and makes recommendations with regard to the steps to be taken in the design and implementation of air deposition studies for the Rouge Project.

TABLE OF CONTENTS

<u>Section</u>	<u>Page</u>
1.0 INTRODUCTION	1
1.1 LITERATURE REVIEW	1
1.2 RECOMMENDATIONS FOR THE ROUGE RIVER NATIONAL WET WEATHER DEMONSTRATION PROJECT	2
2.0 LITERATURE REVIEW	4
2.1 GREAT LAKES ATMOSPHERIC DEPOSITION (GLAD) NETWORK, 1982 AND 1983: DATA ANALYSIS AND INTERPRETATION	4
2.1.1 Purpose	4
2.1.2 Sampling and Analysis Methods	4
2.1.3 Results/Conclusions	5
2.2 AN EXPERIMENTAL STUDY OF LAKE LOADING BY AEROSOL TRANSPORT AND DRY DEPOSITION IN THE SOUTHERN LAKE MICHIGAN WATERSHED	6
2.2.1 Purpose	6
2.2.2 Sampling and Analysis Methods	6
2.2.3 Results/Conclusions	6
2.3 ESTIMATING MERCURY LEVELS IN LAKES FROM MUNICIPAL SOLID WASTE COMBUSTOR STACK EMISSIONS	7
2.3.1 Purpose	7
2.3.2 Results/Conclusions	7
2.4 REPORT OF THE GREAT LAKES AIR TOXICS RESEARCH PRIORITIES WORKSHOP HELD AT NAVARRE, MINNESOTA ON MARCH 11-13, 1991	8
2.4.1 Purpose	8
2.4.2 Results/Conclusions	8
2.5 IMPLICATION OF A GRADIENT IN ACID AND ION DEPOSITION ACROSS THE NORTHERN GREAT LAKES STATES	8

TABLE OF CONTENTS (cont.)

<u>Section</u>	<u>Page</u>
2.5.1 Purpose	8
2.5.2 Sampling and Analysis Methods	9

2.5.3	Results/Conclusions	9
2.6	MICHIGAN 1991 ANNUAL AIR QUALITY REPORT	9
2.6.1	Purpose	10
2.6.2	Sampling and Analysis Methods.....	10
2.6.3	Results/Conclusions	10
2.7	ATMOSPHERIC INPUTS TO THE UPPER GREAT LAKES BY DRY DEPOSITION PROCESSES	11
2.7.1	Purpose	11
2.7.2	Model Description	12
2.7.3	Results/Conclusions	12
2.8	ATMOSPHERIC LOADINGS TO WATERS OF FOUR UPPER GREAT LAKES - A STATUS REPORT	13
2.8.1	Purpose	13
2.8.2	Sampling and Analysis Methods.....	13
2.8.3	Results/Conclusions	14
2.9	MERCURY DEPOSITION AND SOURCES FOR THE UPPER GREAT LAKES REGION	14
2.9.1	Purpose	14
2.9.2	Sampling and Analysis Methods.....	14
2.9.3	Results/Conclusions	15
2.10	THE GREAT LAKES ATMOSPHERIC DEPOSITION PROGRAM INMICHIGAN	
2.10.1	Purpose	15
2.10.2	Sampling and Analysis Methods.....	16

TABLE OF CONTENTS (cont.)

<u>Section</u>	<u>Page</u>	
2.10.3	Results/Conclusions.....	16
2.11	QUALITY ASSURANCE PROJECT PLAN FOR ASSESSING ATMOSPHERIC LEVELS AND TRANSPORT OF TOXIC CONTAMINANTS IN MICHIGAN	16
2.11.1	Purpose	16
2.11.2	Sampling and Analysis Methods.....	17
2.11.3	Results/Conclusions.....	17
2.12	ANALYSIS AND DEPOSITION OF TRACE METALS IN ONTARIO	17

2.12.1 Purpose	17	
2.12.2 Sampling and Analysis Methods	18	
2.12.3 Results/Conclusions.....	18	
2.13 ANALYSIS AND DEPOSITION OF TRACE METALS AROUND GREAT LAKES		18
2.13.1 Purpose	18	
2.13.2 Sampling and Analysis Methods.....	18	
2.13.3 Results/conclusions.....	19	
2.14A METHOD FOR THE AUTOMATED COLLECTION, PROPER HANDLING AND ACCURATE ANALYSIS OF TRACE METALS IN PRECIPITATION	19	
2.14.1 Purpose	19	
2.14.2 Sampling and Analysis Methods.....	19	
2.14.3 Results/Conclusions	19	2.15A F
2.15.1 Purpose	20	
2.15.2 Results/Conclusions	20	

TABLE OF CONTENTS (cont.)

<u>Section</u>	<u>Page</u>
3.0 RECOMMENDATIONS.....	21
APPENDIX A LIST OF ABBREVIATIONS	A-1

1.0 INTRODUCTION. With the advent of the industrial revolution man-made pollution in the environment has increased astronomically. There is no ecosystem which has not been impacted by anthropogenic (man-made) pollutants. The atmosphere plays a significant role in the dispersion of anthropogenic air pollutants into the environment. Numerous studies have been conducted to determine the effects of airborne pollutants on the environment and the role of the atmosphere in the dispersion of man-made pollutants such as metals and other toxic compounds. The National Air Deposition Program (NADP) was established to study the impacts of airborne pollutants on environmental elements such as forests and water resources. According to Gatz (1989) and Patterson and Duce (1991), atmospheric deposition represents the dominant pathway by which trace elements get into many ecosystems such as oceans and the Great Lakes.

Local weather conditions, and the type and location of emission sources may also affect the amount of air deposition in an ecosystem. Therefore, an inventory (type, size and location) of air emission sources and their emission rates are important elements of a study seeking to determine the impact of air deposition on an ecosystem.

One of the goals of the Nonpoint Source (NPS) Program Element of the Rouge Project is to review existing data developed under previous studies, refine the data as necessary and then apply the data in the development of a cost-effective watershed-wide pollution control program for the Rouge River Watershed.

There are several environmental elements that may impact the water quality within the Rouge River Watershed, of which air deposition is one of the most important. To design air deposition studies for the Rouge River Watershed, a review of available literature regarding air deposition was performed. The information collected during literature review will be used to design ambient air monitoring/sampling, analysis, and data reduction parameters for implementation in the next phase of the project.

1.1 LITERATURE REVIEW. Numerous studies have been conducted to examine the environmental factors that may impact the transportation and deposition of airborne pollutants. Numerous other studies, both wet and dry, have been conducted to examine the effects these airborne pollutants have on various environmental elements such as vegetation and water quality.

Studies conducted in the five Great Lakes regions under the Great Lakes Atmospheric Deposition (GLAD) Network (1982 and 1983) suggest strong spatial relationships in air deposition. The study included 36 monitoring stations located along the U.S. shores of the lakes. According to this study, wet deposition fluxes were 2-10 times higher in the South (S) or Southeast (SE) portion of the study area than in the North (N) or Northwest (NW). This variation was due to both an increase in average precipitation amount and an increase in

constituent concentration from N or NW to S or SE. Furthermore, annual precipitation-only loadings of lead (Pb) to the Great Lakes ranged from 125 tons (Lake Ontario) to 240 tons (Lake Michigan), whereas the annual precipitation-only loadings for cadmium (Cd) ranged from 8 (Lake Huron) to 15 (Lake Michigan) tons per lake per year. Similar results were obtained by Glass and Loucks (1986) who found that the average pH of precipitation between 1979 and 1982 declined from 5.3 to 4.3 from west to east along a cross section of sites from Minnesota to Wisconsin to Michigan. This was due to the seasonal and geographical pattern of anthropogenic acid precursor emissions and reaction products (sulfate, nitrate, hydrogen, and ammonium) that increases from west to east. Significant seasonal and geographic patterns in precipitation chemistry and deposition values were also observed.

A study conducted in Ontario, Canada, by Orr et al., (1991) revealed significant differences in the concentrations of trace metals within the study area (Province of Ontario). Higher concentrations of trace metals were found in the wet deposition that occurred in the south side of the study area than in the north side of the study area. According to this study, the strong spatial differences resulted from the location of pollutant sources which were mainly located in and to the south of the study area. Annual wet deposition of lead ranged from more than 60 g/ha/yr in the south to less than 30 g/ha/yr in the north. Manganese wet deposition rates ranged from more than 45 g/ha/yr to less than 20 g/ha/yr. For zinc the wet deposition rates ranged from more than 60 g/ha/yr to less than 20 g/ha/yr; cadmium ranged from more than 60 g/ha/yr to less than 0.5 g/ha/yr. Significant seasonal (temporal) differences in the concentration of pollutants were also observed. Similar results were reported by Klappenbach (1991). Maximum and minimum wet deposition volume weight means (VWMs) for lead, iron, zinc, copper, and sodium were found during the winter and summer months, respectively, for both rural and urban locations around the Great Lakes. Similarly, maximum VWM for potassium, magnesium, and calcium were found in spring and summer while no significant differences were found for nickel and cadmium.

A study regarding mercury deposition conducted in the upper Great Lakes region (Glass et al., 1991) suggested significant impacts of local emission sources on the wet deposition of mercury. Spatial and temporal differences in air deposition were also reported within the Great Lakes region. Rothstein, et al. (1993) summarize the findings of the Michigan Environmental Science Board which reviewed the fate and transport of mercury. One conclusion of this review was that local deposition of mercury does not occur, since soluble forms of mercury reside in the atmosphere for several days to several weeks.

1.2 RECOMMENDATIONS FOR THE ROUGE RIVER NATIONAL WET WEATHER DEMONSTRATION PROJECT. Air deposition sampling and analysis methods play an important role in the estimation of pollutant loadings. Therefore, great consideration should be given in selecting the sampling methods, sampling equipment, sample storage and

transportation, and analytical procedures and methods that must be followed. Based upon the review of available literature presented in Section 2 of this document, the National Atmospheric Deposition Program (NADP) protocols will be used to establish sampling sites for air deposition studies in the Rouge River Watershed.

AeroChem Metrics automatic sensing wet/dry precipitation collectors will be used to collect precipitation samples. HI-VOL samplers will be used to collect samples for suspended particulates, whereas PM10 samplers will be used for PM10 analysis. PM10 is the designation for particulate matter in the atmosphere that has an aerodynamic diameter of ten micrometers or less.

The following steps are recommended to reduce sample contaminations (Vermette, et al.):

- Meticulous sample handling and processing procedures. All operations involving sample manipulation (collection, acidification, partitioning, and analysis) must be performed wearing clean, powder-free polyethylene gloves.
- Use of acid-washed plasticware. Plasticware cleaning and sample analyses should be performed in a clean area and efforts should be made to minimize the exposure of the sample to airborne contamination.
- Utilization of a modified AeroChem Metrics (AC) collector having a high density polyethylene (HDPE) collection bucket.
- Use of ultra-high purity acids (nitric or hydrochloric acid) for sample acidification.
- Strict adherence to a QA/QC program.

Analytical methods are based upon the type of pollutants that will be analyzed. However, use of graphite furnace atomic absorption spectrophotometry (GFAA) and inductively-coupled plasma emission spectroscopy (ICP) are recommended for most air deposition analysis.

2.0 LITERATURE REVIEW. Brief summaries of available air deposition studies are presented below. Additional air deposition literature has also been requested from various sources such as regulatory agencies and academic institutions. These documents will be reviewed as they become available in order to determine their applicability in designing the air deposition investigations performed as part of the Rouge River National Wet Weather Demonstration Project.

2.1 Title: Great Lakes Atmospheric Deposition (GLAD) Network, 1982 and 1983: Data Analysis and Interpretation (Donald F. Gatz, Van C. Bowershox, Jack Su and Gary J. Stensland, 1988)

2.1.1 Purpose. The purpose of this study was to analyze and interpret the atmospheric wet deposition data collected by the Great Lakes Atmospheric Deposition (GLAD) network, including:

- An assessment of data quality;
- A comparison of specific pairs of GLAD and National Atmospheric Deposition Program (NADP) sites; and,
- An estimation of depositional fluxes (g/hectare) and atmospheric loadings (tons/year) of selected pollutants to the five Great Lakes.

The GLAD network was established by the Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency (EPA). Under the Great Lakes Water Quality Agreement of 1972, the United States and Canada were provided a framework for the surveillance, monitoring, research, protection and reclamation of the physical and chemical quality of the Great Lakes system. Within this framework, the monitoring of atmospheric deposition in the United States is coordinated by the GLNPO.

2.1.2 Sampling and Analysis Methods. The purpose of the GLAD network was to provide measurements of the wet-only (precipitation) atmospheric deposition measurements that may be used to estimate chemical loadings to the Great Lakes. To accomplish this task some GLAD sites were located in lakefront cities to measure deposition from industrial, transportation and residential sources in and near urban areas. To measure deposition of area-wide sources, some air samplers were located in lakeshore sites in rural areas. In addition, one site was located in central Minnesota, about 200 km west of Lake Superior, to measure regionally representative deposition from sources largely upwind of the Great Lakes.

Precipitation samples were collected in AeroChem Metrics samplers. These samplers were

designed to collect wet-only samples by uncovering a plastic bucket only during precipitation. The buckets were lined with polyethylene bags. When a bag contained a minimum of 500 mL of liquid or precipitation (or at least 1.25 inch of snow), a sample was collected and another polyethylene bag-lined bucket installed. Rain gauges were used to measure the amount of precipitation.

After collection of samples, a 20-40 mL aliquot of sample was decanted from the bag for field pH and conductance measurements. In addition, a half liter polyethylene bottle was filled and shipped to EPA analytical laboratory. In the laboratory, the samples were stored at 4°C and preserved as required by the test methods.

Calcium (Ca), magnesium (Mg) and sodium (Na) ions were measured using the inductive-coupled argon plasma (ICAP) method. Flame atomic absorption spectrophotometry (FAA) was used for potassium (K) analysis, whereas flameless FAA was used for lead (Pb) and cadmium (Cd) analyses. Automated wet chemical methods (Technicon) were used to determine ammonium (NH₄), nitrogen oxides (NO₃+NO₂), sulfates (SO₄), and chlorides (Cl).

2.1.3 Results/Conclusions. The following conclusions were drawn from this study:

- The spatial distribution of wet deposition fluxes (mass/area/year, i.e. kg/ha/yr) shows that annual values were 2-10 times higher in the South (S) or Southeast (SE) portion of the network than in the North (N) or Northwest (NW). This variation was due to both an increase in average precipitation and an increase in constituent concentrations from N or NW to S or SE.
- Annual precipitation-only loadings of lead (Pb) to the five Great Lakes ranged from 125 to 240 tons, based upon the 30-year mean annual precipitation and 1983 GLAD concentrations. Cadmium (Cd) precipitation-only loadings ranged from 8 to 15 tons per lake per year.

The loading estimates to each Great Lake for Cd and Pb are presented below (GLAD wet-only measurements, 1983):

Lead	Cadmium	
Lake	(tons/yr)	(tons/yr)
Superior	170	12
Michigan	240	15
Huron	214	8.3
Erie	142	8.7
Ontario	125	9.5

2.2 Title: An Experimental Study of Lake Loading by Aerosol Transport and Dry Deposition in the Southern Lake Michigan Watershed (Herman Sievering, Mehul Dave, Donald A. Dolske, Richard L. Hughes, and Patric McCoy, 1979)

2.2.1 Purpose. The purpose of this study was to assess the contribution to Great Lakes loading by atmospheric transport and dry deposition of aerosol (fine solid or liquid particles). The study was conducted in the southern Lake Michigan watershed during 1977 and 1978. The study involved collecting trace element and nutrient data at midlake and nearshore locations. Meteorological data were also collected for establishing a climatology for mass transfer to Lake Michigan.

2.2.2 Sampling and Analysis Methods. To compile a database for the estimation of annual dry deposition loadings of pollutants to the southern Lake Michigan watershed, meteorological data (mesoscale [large] and microscale [small]) and physical and chemical data of overlake aerosol were collected. Meteorological data were collected using portable meteorological sensors and included wind speed and direction (five meter height), temperature and relative humidity. Due to the nature of the study (dry deposition only), the occurrence of rain or fog events were not considered for any sampling episode.

Aerosol samples were collected using standard HI-VOL samplers (General Metal Works, Inc.). Samples for gravimetric analysis of total aerosol mass concentration were collected on 20 by 25 centimeter (cm) glass fiber filters; samples for chemical analysis were collected on cellulose fiber substrate and 20 by 24 cm filters.

Aerosol samples were analyzed for trace elements at EPA Central Regional Laboratory using ICP. Nutrient species phosphate, sulfate, and nitrate were determined by standard EPA automated spectrophotometric techniques.

2.2.3 Results/Conclusions. The following conclusions were drawn from this study:

- Approximately 60 percent of the total lead (Pb) input, 30 percent of the total zinc (Zn) input, and 20 percent of the total iron (Fe) input to the southern watershed of Lake Michigan was due to the dry deposition of the atmospheric aerosol. It was also found that major inputs of sulfate and nitrate occur by dry deposition.

- Dry deposition phosphorus input to the southern watershed of Lake Michigan was about equal to the precipitation input.

- The anthropogenically derived aerosol for the following trace elements were found to be: aluminum (Al), 0; calcium (Ca), 0; copper (Cu), > 90 percent; iron (Fe), > 65 percent; magnesium (Mg), 0; manganese (Mn), > 80 percent; lead (Pb), > 95 percent; titanium (Ti), 0; and zinc (Zn), 75 percent. Furthermore, more than 75 percent of these aerosols were from the Chicago/Northwest Indiana source region.

2.3 Title: Estimating Mercury Levels in Lakes from Municipal Solid Waste Combustor Stack Emissions (Bryon Clemence, Richard Rothstein, and Paul Stroller, 1992)

2.3.1 Purpose. The main objectives of this study were to review the current understanding of the behavior of mercury in the environment, characterize mercury in the waste stream and potential stack emissions, review environmental fate and transport issues, and discuss emission control technologies and regulatory policy. This study does not include detailed information regarding dry and/or wet deposition of mercury, but it does provide important information regarding source contributions to the mercury levels in lakes.

2.3.2 Results/Conclusions. Some of the conclusions of this study which may be useful for the Rouge River NPS project are presented below:

- Major sources of mercury emissions to the atmosphere include various industrial activities such as steel production, combustion of fossil fuels and solid wastes, solid waste landfills, and natural sources such as volcanoes. A significant amount of mercury emissions to the atmosphere are also attributed to land and oceans however, their contribution to the total mercury emission to the atmosphere is not known.
- Household batteries contribute approximately 87.6 percent of the total mercury in the municipal solid waste stream.
- In the atmosphere, more than 90 percent of the mercury is in gaseous elemental form. Elemental gaseous mercury is transformed into soluble form by oxidation and photolysis and can be washed out of the atmosphere by precipitation and/or dry deposition.
- Dry deposition of mercury has more pronounced effects in forested areas due to the precipitation washout of dry deposited mercury from the canopy of the forest.
- Oxidized mercury in the soil and water can be volatilized back to the atmosphere.

- The residence time of gaseous mercury in the atmosphere varies from two months up to two years. However, soluble mercury may reside several days to weeks, and therefore can be transported several thousand kilometers.
- The rate of dry deposition of mercury to water bodies is less than the deposition rate over land due to lower surface roughness characteristics. It was estimated that the dry deposition rate was approximately four times lower over lakes than over undeveloped watersheds.

2.4 Title: Report of the Great Lakes Air Toxics Research Priorities Workshop Held at Navarre, Minnesota on March 11-13, 1991 (Larry Cupitt and Jason Ching et. al., 1992)

2.4.1 Purpose. The main objectives of this workshop were to identify the research needed to address the issue of toxic pollutants in the air and their impact on the Great Lakes. Some of the research needs discussed during the workshop could be useful in the development and implementation of air deposition studies in the Rouge River Watershed.

2.4.2 Results/Conclusions. Based on the information presented in the report, the following activities should be considered for implementation during the Rouge River Wet Weather Demonstration Project:

- Establishment of a list of target chemicals. It will be very expensive and may be difficult to monitor all the chemicals that may be present in the atmosphere. Therefore, a list of chemicals that may have adverse effects on human health and the environment should be prepared for the Rouge River NPS studies.
- Characterize the local urban plumes to determine the total air toxics loading in the Rouge River Watershed.
- Collect ambient and source signature data to identify significant sources of air pollutants (criteria and non-criteria) in the watershed and to quantify their contributions.
- Study of air-soil-plant pollutant exchange processes (e.g., deposition, volatilization, resuspension) to understand its impact on the long-range transport of targeted toxic air pollutants.

2.5 Title: Implications of a Gradient in Acid and Ion Deposition across the Northern Great Lakes States (Gary E. Glass and Orle L. Loucks, 1986)

2.5.1 Purpose. The main objectives of this study were:

- To evaluate the significance of geographic patterns in the ion composition of acidic and basic reactants in the precipitation across the Great Lakes states, including the State of Michigan;
- To compare the potential significance of the snow period chemistry values with those of the rain period;
- To compare wet deposition in other regions; and
- To compare the composition of precipitation with the resulting surface water.

2.5.2 Sampling and Analysis Methods. National Atmospheric Deposition Program (NADP) protocols were used to establish precipitation sampling sites in the three western Great Lakes States of Minnesota, Wisconsin, and Michigan. In the State of Michigan, the monitoring stations were located at Douglas Lake, Wellston, and Kellogg.

Precipitation samples were collected on a weekly basis using AeroChem Metrics, Model 301 automatic sensing wet/dry precipitation collectors. National Atmospheric Deposition Program (NADP) procedures were used for field observations and measurements of environmental conditions. A portion of each sample was used to measure pH and specific conductance. The remaining portion of each sample was used for the analysis of calcium (Ca), magnesium (Mg), sodium (Na) and potassium (K) using atomic absorption spectrometer methods. Concentrations of sulfate, nitrate, chloride, and ammonium were measured colorimetrically on a Technicon Auto Analyzer II. Hydrogen ion concentration was measured with an Orion Model 811 pH meter with Beckman electrodes.

2.5.3 Results/Conclusions. The following conclusions were drawn from this study:

- The average pH of precipitation between 1979-1982 declined from west to east from 5.3 to 4.3 along a cross section of sites in Minnesota, Wisconsin, and Michigan. The decline was due to the seasonal and geographical pattern of anthropogenic acid precursor emissions and reaction products (sulfate, nitrate, hydrogen, and ammonium) that increased from west to east.
- A close relationship between strong acid anions and the sum of hydrogen and ammonium ions present in the precipitation was observed, indicating anthropogenic sources of sulfur and nitrogen oxides.
- Significant seasonal and geographic patterns in precipitation chemistry and deposition values were observed. Therefore, the impacts of local climatic

conditions, topography, land use and vegetation on the precipitation chemistry should be evaluated.

2.6 Title: Michigan 1991 Annual Air Quality Report (Division of Air Quality, Michigan Department of Natural Resources)

2.6.1 Purpose. The main objective of the Annual Air Quality Report is to track trends in the air quality of the state and to determine if the National Ambient Air Quality Standards are achieved. EPA, under the Clean Air Act, has established National Ambient Air Quality Standards for the following pollutants: suspended particulate matter, sulfur dioxide, nitrogen dioxide, carbon monoxide, ozone, volatile organic compounds, and lead. The Michigan 1991 Annual Air Quality Report presents a summary of air monitoring data collected in Michigan for 1991. The data are summarized by pollutant, county and site.

2.6.2 Sampling and Analysis Methods. The state of Michigan is divided by EPA into six Air Quality Control Regions (AQCR). There are four intrastate and two interstate regions. The Michigan Air Sampling Network (MASN) consists of over 130 monitoring sites, entailing over 250 monitoring sensors in 33 counties. Meteorological conditions are monitored continuously at 30 different locations. Air pollutants are generally monitored near ground level by a variety of accepted EPA methods.

Suspended particulate up to 100 microns in size are monitored with a high volume air sampler (HI-VOL) on an intermittent basis. The HI-VOL motor pulls ambient air through a fiberglass filter at a rate between 1.13 to 1.7 m³/minute. The sampling period is generally 24 hours with one sample generally scheduled every sixth day. A PM₁₀ monitor is used to sample particulate matter less than 10 microns. The PM₁₀ monitor operates on roughly the same sampling period as the HI-VOL. The filters are weighed before and after sampling. The total volume of air passing through the samplers is calculated and the concentration of particulate is expressed in terms of weight of particulate matter per unit volume of air. At some stations the filters are also analyzed for other pollutants such as lead, sulfates, nitrates and some metals.

A portion of the HI-VOL or PM₁₀ filter is used for determining the lead concentrations by atomic absorption. The lead samples are either a monthly composite or a quarterly average of all the individual samples obtained at a site.

Gaseous pollutants are monitored continuously. Air is drawn in by a sampler manifold through inert tubing to the vicinity of the sensing area. Filters and scrubbers are sometimes used to eliminate or minimize interference from other pollutants. The gas is then introduced into an environment where a chemical or physical reaction takes place, depending on the method. The output is converted to an electric signal whose intensity is related to the concentration of

the pollutant.

2.6.3 Results/Conclusions. The following results and conclusions were drawn for the compilation of 1991 data:

Ozone - Monitoring for ozone was performed at 35 locations. The recorded daily maximum concentrations exceeded ozone standards of 0.12 ppm at 17 sites.

Lead - The analysis for lead was performed at 56 sites, all of which met the calendar quarter lead standard of 1.5 microgram per cubic meter for 1991.

Trace Metals - Filters from 50 monitoring sites were analyzed for trace metals. A summary of the data is provided in the report.

Particulate Matter - 38 PM10 sites operated in 12 counties. The PM10 standards of 50 micrograms per cubic meter were met at all site locations. Over 60 locations continued to measure total suspended particulate concentrations in 14 counties.

Sulfur Dioxide - Sulfur dioxide is monitored at 20 locations in ten counties in Michigan. The monitoring data continues to indicate compliance with primary and secondary standards of 80 micrograms per cubic meter.

Nitrogen Dioxide - Nitrogen dioxide is monitored at 13 locations in 9 counties and continues to show compliance with annual nitrogen dioxide standards of 100 micrograms per cubic meter.

Carbon Monoxide - Monitoring for carbon monoxide was conducted at 12 locations in 7 Michigan counties. All sites met the 1-hour and the 8-hour standard of 9 ppm and 35 ppm respectively during 1991.

Non-Criteria Pollutant Monitoring - Non-criteria data from industrial monitoring sites are presented in the report. This includes data from Wayne County Act 64 facilities where samples are analyzed for the presence of volatile organic compounds.

2.7 Title: Atmospheric Inputs to the Upper Great Lakes by Dry Deposition Processes (W.J. Moroz, R.L. Kabel, M. Taheri, A.C. Miller, H.J. Hoffman, W.J. Brtko, and T. Cuscino, 1976)

2.7.1 Purpose. The main objectives of this study were to:

- Develop a numerical model that will allow for an estimation of the contamination of a water

body by airborne pollutants during dry meteorological conditions.

- Use the model to estimate the potential contribution from the atmosphere to the whole lake burden in the Upper Great Lakes (Lake Huron and Lake Superior).

The pollutants of concern were: total dissolved solids, chlorides, total nitrogen, total phosphorus, dissolved silica and pesticides.

2.7.2 Model Description. The model was formulated by use of a Gaussian plume model coupled with the Pasquill-Gifford diffusion curves. US and Canadian Air Quality Control Regions (AQCR) source-strength data was used. Each AQCR was modeled as a point source with an initial crosswind spread.

Dry deposition processes were estimated by including a deposition factor in front of the reflection term in the conventional Gaussian concentration which allowed less than 100% of the material reaching the ground to be reflected. The inclusion of the deposition factor necessitated a model of the flux of material to the surface. The flux of pollutants onto land was modeled as a function of the overall mass transfer coefficient and pollutant concentrations in the atmosphere and land. The flux of pollutants into water was modeled as a function of the liquid phase mass transfer coefficient, the solubility of the pollutant in water, the concentration of the pollutant in the atmosphere (at the interface), and the bulk concentration of the pollutant in water. The flux equation also differed depending on whether one was considering a gaseous or particulate pollutant.

Meteorological data compiled at locations over the Great Lakes watershed were used to determine an average yearly wind rose. The total yearly hours of dry weather provided an estimate of the time during which only the dry deposition processes were effective in pollutant removal. The model also compensated for seasonal variations of stability conditions over land and water surfaces.

2.7.3 Results/Conclusions. The following conclusions were drawn from this study:

- The yearly input of all the pollutants considered was larger for Lake Huron than for Lake Superior by factors ranging from 1.1 to 1.9;
- The input of pollutants into the lake in the summer was less than the input in the spring and the combined spring and summer inputs were less than the combined fall and winter inputs;
- 20 percent of the particulates emitted into the atmosphere were deposited into the Upper Great Lakes. Less than 1 percent of the nitrogen oxide (NO₂) gas and pesticides emitted were deposited into the Upper Great Lakes;

- For lakes with an inversion layer above, as the atmosphere tends toward instability, the pollutant flux to the lakes increases;
- The final pollutant input value is sensitive to the land and water deposition value;
- Atmospheric pesticide input into the Upper Great Lakes by dry deposition processes were negligible. This was attributed to the small source strengths, the large area over which the sources were spread, and the large distances of travel;
- The total nitrogen input to Lake Superior was 72 percent particulate nitrates and 28 percent gaseous nitrogen oxides (NO₂) and the total nitrogen input to Lake Huron was 60 percent particulate nitrates and 40 percent gaseous nitrogen oxides (NO₂); and,
- Chloride input into both Upper Great Lakes was 99.5 percent gaseous.

2.8 Title: Atmospheric Loadings to Waters of Four Upper Great Lakes - A Status Report (Charles T. Elly, 1980)

2.8.1 Purpose. The purpose of the study was to estimate total atmospheric loadings to waters of four upper Great Lakes for selected toxic chemicals or nutrients. Due to incompleteness of data, the report provides a summary of loadings and deficiencies of the data collection program.

The quantity of material input to waters of the Great Lakes from the atmosphere significantly impacts water quality of the Great Lakes. Studies have been conducted to measure the total loading (both wet and dry deposition), known as bulk precipitation measurements, to the lakes. Data utilized in this report were obtained using modified bulk-precipitation collectors, located within the U.S. boundary of the Great Lakes.

This report also provided data on pH, specific conductance, sulfates, chlorides and nitrates. The data can be used to supplement acid rain data sought by researchers.

2.8.2 Sampling and Analysis Methods. Modified bulk samplers were located in 30 areas selected to give representative information concerning variations in precipitation and dry particulate matter chemistry within the major agricultural, forested, and industrial/urban regions. The modified bulk samplers allowed for the analyses of pH, conductance, nitrogen, phosphorus and total metals.

Samples were collected on a monthly basis and submitted to EPA, Region V, Central Regional Laboratory (CRL) in Chicago, Illinois. In the field, the contents of the bulk sampler bags

were poured into one liter bottles. The excess volume was recorded on a data sheet and discarded. Final volumes were calculated by summing the one liter bottles plus the excess. Bulk precipitation samples were analyzed using water analysis procedures. Dry deposition matter adhering to plastic bags was leached with acid and distilled water and analyzed as water samples. All parameters were analyzed using standard EPA procedures. All metal parameters except mercury were analyzed using CRL ICP spectrometer procedure. Mercury was analyzed by CRL semi-automated method.

2.8.3 Results/Conclusions. Some conclusions of the study were as follows:

- Significant loadings for minerals, nutrients, solids and several metals were deposited in the four Upper Lakes. Higher loadings occur along the Ohio shoreline and in areas of high industrial activity.
- Higher than average loadings of aluminum, iron, zinc, titanium, and lead were deposited on Lake Superior, Bayfield, and Superior Wisconsin; and Grand Marais, Silver Bay and Two Harbors, Minnesota. The heavy loadings were attributed to an on-shore ore operation in Superior, Wisconsin.
- The pH averaged approximately 4.5 overall. The acidic precipitation appeared to be related to either the sulfate, chloride or nitrate content.
- Data were incomplete for many of the stations operated by Region V personnel.

2.9 Title: Mercury Deposition and Sources for the Upper Great Lakes Region (Gary E. Glass, John A. Sorenson, Kent W. Schmidt, George R. Rapp, Jr., David Yap, and Duncan Fraser, 1991)

2.9.1 Purpose. The objectives of this research were to determine the nature, magnitude, and seasonal variation of atmospheric mercury (Hg) inputs and to document relationships between Hg concentrations and major cations and anions present in precipitation.

Additionally, atmospheric transport from possible emission source regions, precipitation scavenging mechanisms and geographic patterns and deposition rates were investigated.

2.9.2 Sampling and Analysis Methods. Precipitation monitoring stations were established at Duluth, Marcell and Ely, MN. Each station was equipped with an automatic sensing collector with a double sensor head, movable roof and teflon lined funnel. Collected precipitation passes out the funnel through tubing into a one liter sample collection bottle containing dichromate preservative and deionized water (to reduce mercury sorption). Sample collection bottles were changed on no less than a weekly basis. Bottle overflow was captured in a graduated bucket to allow for the recording of precipitation volumes. Analysis of mercury (Hg) was performed on 150 ml aliquots.

Rain samples were also captured in four 600-ml beakers containing preservative and deionized water to assess Hg sorption from air and Hg loss from collected precipitation. Inverted Pyrex funnels were placed above two of the four beakers as rain shelters.

Precipitation samples were also collected at Marcell and Ely using AeroChem Metrics Model 301 automatic sensing precipitation collectors as part of the National Atmospheric Deposition Program (NADP). Samples were collected on a weekly basis with volume, pH and conductivity being recorded on-site. The remainder of the samples were submitted to a laboratory for additional analyses of ion concentrations.

Mercury measurement methods utilized cold vapor atomic absorption spectrometry approved by EPA with modifications for standardizing operating procedures.

Air sampling for Hg was accomplished by drawing air through 2 or 3 parallel and/or series dosimeters at flow rates typically near 1.0 liter per minute. The majority of sampling intervals were from 12 to 24 hours.

Air parcel back-trajectories were calculated for individual precipitation events where two or more subsamples were available from the Duluth monitoring site during 1988 and 1989. The trajectories were calculated by the method outlined in Yap and Kuntz (1986). This trajectory model was coupled to a meteorological data acquisition system that collects and stores raw input data supplied by Environment Canada from the North American network of weather stations.

2.9.3 Results/Conclusions. Some of the conclusions of the report are provided below:

- Wet deposition values for the Duluth, Marcell, and Ely sites were 20, 16, and 17 ug Hg per square meter (1988) and 6, 14, 42 ug Hg per square meter (1989) respectively. The increased wet deposition at Ely suggests the possibility of significant local contribution.
- Volume-weighted contributions of total mercury in precipitation averaged approximately 18 ng Hg per liter, while annual depositions averaged 15 ug per square meter. Mercury concentrations in precipitation are positively correlated with major ions, conductivity and pH, and negatively correlated with precipitation volume.
- Air parcel back-trajectories and residence time analysis indicate that possible source regions within 72-hr travel time were located primarily to the south, southeast and southwest up to a distance of 2500 km, but local sources may also be important.

2.10 Title: The Great Lakes Atmospheric Deposition Program in Michigan (Air Quality Division, Michigan Department of Natural Resources, 1993)

2.10.1 Purpose. The purpose of the study was to present the atmospheric wet deposition data collected by the Great Lakes Atmospheric Deposition (GLAD) network for sites located in Michigan. Data collected during 1981 through 1991 was presented in the report. The Michigan GLAD network includes six precipitation collector sites (Ontonagon, Beaver Island, Port Austin, Bay City, Mount Clemens, and Benton Harbor), which supplement the National Atmospheric Deposition Program.

Efforts to upgrade the Michigan Atmospheric Deposition Network commenced in January of 1981 as a cooperative agreement between the Department of Natural Resources, Air Quality Division and the United States Environmental Protection Agency (EPA). The intent of the project is to measure the impact of airborne pollution on the Great Lakes ecosystem. The Great Lakes National Programs Office does not intend to publish the results of the GLAD Program's analysis until sufficient data are available to provide clear trends.

2.10.2 Sampling and Analysis Methods. The purpose of the GLAD network was to provide measurements of the wet-only atmospheric deposition that may be used to estimate chemical loadings to the Great Lakes. To accomplish this task, the Michigan sites were chosen to reflect the ambient conditions of an area as opposed to highlighting a major area point source.

Precipitation samples were collected in AeroChem Metrics Samplers. These samplers were designed to collect wet-only samples by uncovering a plastic bucket only during precipitation. The buckets were lined with polyethylene bags. The GLAD network wet collector schedule runs from 9:00 a.m., Tuesday to 9:00 a.m. the following Tuesday. The operator changes the wet bucket, covers the sample and transports it to the field laboratory. From the bucket, a 500 ml sample is collected and submitted to Central Regional Laboratory in Chicago, Illinois. A 20 ml aliquot is set aside for analysis of pH and conductivity.

2.10.3 Results/Conclusions. No conclusions were drawn in the report, only data are presented. The data may be summarized as follows:

- The pH average for the six Michigan GLAD network sites for 1981 through 1991 are as follows: Bay City (4.4), Beaver Island (4.4), Benton Harbor (4.5), Mount Clemens (4.2), Ontonagon (4.6), and Port Austin (4.4).

The Great Lakes Atmospheric Deposition Program will continue to supply scientists with precipitation samples.

2.11 Title: Quality Assurance Project Plan for Assessing Atmospheric Levels and Transport of Toxic Contaminants in Michigan (Michigan Great Lakes Protection Fund, 1991)

2.11.1 Purpose. The purpose of the report was to provide a Quality Assurance Project Plan (QAPP) for assessing atmospheric levels and transport of toxic contaminants in Michigan. The objectives of the above referenced investigation were to:

- Determine International Joint Commission (IJC) priority pollutant concentrations in the atmosphere.
- Evaluate atmospheric transport of these species across Michigan;
- Investigate the seasonal variations of the toxic species in Michigan; and
- Estimate the contribution of each pollutant from major source regions by meteorological and hybrid modeling techniques.

The QAPP outlines procedures which will be followed during the investigation to address quality assurance and also provides detailed procedures for sampling, instrumentation and laboratory analysis.

2.11.2 Sampling and Analysis Methods. The organic compounds to be monitored in the study include total polychlorinated biphenyls (PCBs) and 90 component congeners, polynuclear aromatic hydrocarbons (PAHs), hexachlorobenzene, and dieldrin. An Anderson PS-1 polyurethane foam sampler was used to collect the samples, whereas, a XAD/PUF sandwich filter will be used to collect the vapor phase contaminants. A detailed discussion of the samplers and sampling protocol is provided in the QAPP.

Thirteen trace metal elements (barium, beryllium, cadmium, cobalt, chromium, copper, iron, lead, molybdenum, manganese, nickel, vanadium, and zinc) were collected on a Wedding PM-10 sampler. Additional details on the PM-10 is provided in the QAPP. Three samplers located at South Haven, Richmondville and Pellston were operated year around, whereas, the fourth sampler located at Ann Arbor was operated for six months. The samplers were operated every six days following the National Particulate Network (NPN) schedule for a period of six hours.

Additional information concerning quality assurance objectives, sampling procedures, sample handling and custody, sample analysis, calibration procedures, and data reduction, validation and reporting is provided in the QAPP. The QAPP also provides information on performance and system audits.

2.11.3 Results/Conclusions. The QAPP provides contaminant sampling protocols for the implementation of a project to measure and characterize concentrations of air toxics and to assess their transport across Michigan.

The Deposition and Fate of Trace Metals in Our Environment - Symposium Proceedings

The following papers were presented at a symposium held in Philadelphia, PA, on October 8, 1991.

2.12 Title: Analysis and Deposition of Trace Metals in Ontario (Daniel B. Orr, Michael J. Shaw, and Neville W. Reid)

2.12.1 Purpose. The main objectives of this study were to describe the spatial and temporal trends in selected trace metal concentrations in wet-only deposition in Ontario, Canada. Four Great Lakes namely Lake Ontario, Lake Erie, Lake Huron, and Lake Superior were selected to estimate mass loadings of pollutants.

2.12.2 Sampling and Analysis Methods. Precipitation samples were collected using AeroChem Metrics precipitation collector having a polyethylene bag insert. Each precipitation sample was preserved using 1 percent ultrapure nitric acid solution. The empty polyethylene bag used for collecting precipitation was leached for 24 hour in a 5 percent solution of ultrapure nitric acid.

Precipitation samples including leachates from the polyethylene bags were analyzed for copper (Cu), nickel (Ni), lead (Pb), manganese (Mn), zinc (Zn), cadmium (Cd), iron (Fe), aluminum (Al), vanadium (V) and arsenic (As) using graphite furnace atomic absorption spectrometry methods.

2.12.3 Results/Conclusions. The following conclusions were drawn from this study:

- Significant differences in the concentrations of trace metals were found within the study area (Province of Ontario, Canada). Higher concentrations of trace metals were found in the southern portion of the study area than in the north. Strong spatial differences were due to the location of pollutant sources which were mainly located in and to the south of the study area.

- Annual wet deposition of lead ranged from greater than 60 g/ha/yr in the south to less than 30 g/ha/yr in the north. For manganese the range was from greater than 45 g/ha/yr to less than 20 g/ha/yr. For zinc the range was from greater than 60 g/ha/yr to less than 20 g/ha/yr. For cadmium the range was from greater than 60 g/ha/yr to less than 0.5 g/ha/yr.

- Significant seasonal (temporal) differences in the concentration of pollutants were

found in the study area.

2.13 Title: Analysis and Deposition of Trace Metals Around the Great Lakes (Edward W. Klappenbach)

2.13.1 Purpose. This article includes a review of atmospheric deposition studies conducted under the Great Lakes Atmospheric Deposition (GLAD) program. Data regarding loadings for selected metals to each of the Great Lakes were discussed.

2.13.2 Sampling and Analysis Methods. Precipitation samples were collected using AeroChem Metrics precipitation collector having a polyethylene bag liners. A minimum of 500 mL precipitation sample was collected for laboratory analysis.

Each precipitation sample was analyzed for 22 metals. Atomic adsorption (AA) spectrometry method was used to analyze sodium (Na), potassium (K), arsenic (As), chromium (Cr), cadmium (Cd), lead (Pb) and nickel (Ni). Inductively coupled argon plasma (ICP) spectrophotometry method was used for the analysis of aluminum (Al), barium (Ba), beryllium (Be), boron (B), calcium (Ca), cobalt (Co), copper (Cu), iron (Fe), lithium (Li), magnesium (Mg), manganese (Mn), strontium (Sr), titanium (Ti), vanadium (V) and zinc (Zn).

2.13.3 Results/Conclusions. The following conclusions were drawn from this study:

- Maximum and minimum volume weight means (VWMs) for Pb, Fe, Zn, Cu and Na were found during the winter and summer months, respectively, for both rural and urban locations.
- Maximum VWM for K, Mg, and Ca were found in spring and summer while no significant differences were found for Ni and Cd.

2.14 Title: A Method for the Automated Collection, Proper Handling and Accurate Analysis of Trace Metals in Precipitation (J.R. Scudlark, T.M. Church, K.M. Conko, and S. M. Moore)

2.14.1 Purpose. The main objectives of this study were to develop methods and procedures to minimize contamination during precipitation sampling, handling and analysis for trace metals.

2.14.2 Sampling and Analysis Methods. To accomplish the above referenced objectives, a number of field studies were conducted to compare different methodologies that were used for the collection, handling, and analysis of precipitation samples.

2.14.3 Results/Conclusions. Based upon the procedures presented in the paper, the following steps should be taken to minimize sample contamination:

- Meticulous sample handling and processing procedures. All operations involving sample manipulation (collection, acidification, partitioning and analysis) must be performed wearing clean, powder-free, polyethylene gloves.
- Use of acid-washed plasticware. Plasticware cleaning and sample analyses should be performed in a clean area and efforts should be made to minimize the exposure of samples to airborne contamination or contaminants.
- Use of modified AeroChem Metrics collector having a HDPE collection bucket.
- Use of ultra-high purity acids (nitric or hydrochloric acid) for sample acidification.
- Use of graphite furnace atomic absorption spectrophotometry (GFAA) and inductively-coupled plasma emission spectroscopy (ICP) for sample analyses.
- Strict adherence to a QA/QC program.

2.15 Title: A Pilot Network for the Collection and Analysis of Metals in Wet Deposition (Stephen J. Vermette, Mark E. Peden, Saada Hamdy, Tim C. Willoughby, LeRoy Schroder, Steven E. Lindberg, Jim G. Owens, and Aaron D. Weiss)

2.15.1 Purpose. The main objectives of this study were to standardize sampling and analysis protocols that can be used for the determination of metals in precipitation. It included development and evaluation protocols for:

- Collection devices;
- Sample handling (field and laboratory);
- Chemical analysis; and
- Operator training.

2.15.2 Results/Conclusions. Based on the sampling and analytical results obtained during this study, the following conclusions/recommendations were made:

- The metals As, Cu, Hg, Mn, Pb, and Zn can be accurately quantified using National Atmospheric Deposition Program (NADP) protocols.
- ICP-MS can be used for the analysis of As, Cd, Cu, Mn, Pb, and Zn in precipitation and was generally better than the graphite furnace atomic absorption spectrophotometry (GFAA) method. Cold vapor atomic fluorescence

spectroscopy (CVAFS) was well suited for routine analysis of Hg in precipitation at low levels.

- Due to adsorption of Hg by Teflon bottles, pre-baked borosilicate glass bottles were better sampling containers for Hg sampling.

3.0 RECOMMENDATIONS. Based on our review of a number of air deposition studies conducted in the United States and Canada (see Section 2.0), the following steps should be taken to design and implement the proposed air deposition study under the Rouge Project:

- Prepare a list of target pollutants that have the potential to negatively impact the water quality of the Rouge River Watershed. This information may be obtained by reviewing the existing water quality data of the Rouge River Watershed.
- Review land use in the Rouge River Watershed including developed area, undeveloped area (forest), and location and size of water bodies (lakes, ponds, etc.). This information will be useful to determine the impact of local conditions on the air deposition in the area and to estimate the runoff of pollutants into the Rouge River.
- Determine the types and location of major sources of air pollutants to the Rouge River Watershed. This information is very important to determine the effects of local sources of air emissions on the water quality. It will also be useful to implement emission reduction strategies if needed.
- Select ambient air monitoring sites. Based upon the type of air-borne pollutants of concern, land use of the area, and the location of emission sources, an appropriate number of ambient air monitoring sites should be selected. Site selection and installation procedures outlined in the Instructional Manual of the National Atmospheric Deposition Program (NADP) should be followed.

The Wayne County Department of Health, Division of Air Pollution Control, maintains an extensive network of ambient air monitoring sites primarily for measuring criteria air pollutants (particulate matter, sulfur dioxide, nitrogen oxide, carbon monoxide, ozone and lead). Therefore, efforts should be made to use existing monitoring sites within the Rouge River Watershed.

- Atmospheric studies should be performed on a year-round basis and sampling should be performed at several locations to accommodate varying meteorological conditions and to obtain temporal and spatial data for air deposition. Both dry and wet deposition measurements should be performed.
- Sampling equipment should be compatible with the type of pollutants to be collected. For example, plastic buckets used in acid rain studies may not be useful for trace metal studies. Appropriate guidelines/protocols specified by NADP, EPA, or MDNR should be followed during sample collection operations.

- Appropriate EPA methods/procedures and guidelines/protocols should be followed for sample analysis.
- A QA/QC manual should be prepared for sampling, handling and analysis procedures to ensure quality control for the program.

APPENDIX A

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrophotometry
AQCR	Air Quality Control Regions
CVAFS	Cold Vapor Atomic Fluorescence Spectroscopy
EPA	U.S. Environmental Protection Agency
GFAA	Graphite Furnace Atomic Absorption
GLAD	Great Lakes Atmospheric Deposition
GLNPO	Great Lakes National Program Office
HDPE	High Density Polyethylene
HI-VOL	High Volume Sampler
ICP	Inductively Coupled Plasma
IJC	International Joint Commission
MASN	Michigan Air Sampling Network
MDNR	Michigan Department of Natural Resources
NADP	National Atmospheric Deposition Program
NPN	National Particulate Network
NPS	Nonpoint Source
PAH	Polynuclear Aromatic Hydrocarbons
PCB	Polychlorinated Biphenyls
PM10	Particulate Material, 10 micrometers or smaller
QA/QC	Quality Assurance/Quality Control
QAPP	Quality Assurance Project Plan
VWM	Volume Weight Mean