LAKE MICHIGAN URBAN AIR TOXICS STUDY
Design and Overview

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ABSTRACT

During the summer of 1991, an air toxics monitoring program was conducted in the lower Lake Michigan area. This study was designed to take advantage of the extensive meteorological and oxidant database being generated concurrently by the Lake Michigan Ozone Study (LMOS). Integrated 12-hour atmospheric samples were collected daily from July 8 through August 9, 1991 at three ground sites (two collocated with LMOS stations). Over 1,200 samples were analyzed to determine atmospheric levels of PCBs, pesticides, PAHs, VOCs, particle mass, and trace elements (including mercury). In addition, a research vessel and a small aircraft were employed on selected days to measure micro-meteorological parameters, pollutant concentrations and some fluxes at offshore locations near Chicago. The major goals of this pilot study were to evaluate methods of sample collection and analysis, quantify the atmospheric concentrations of toxic substances in the lower Lake Michigan area, compare measurements made over land and over water, attempt to differentiate the Chicago urban plume from regional background, identify categories of sources for the target pollutants, and estimate deposition to the lake.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

BACKGROUND

The presence of persistent toxic substances within the Great Lakes Basin has been a matter of interest in both the United States and Canada for many years. Of particular concern are those contaminants which tend to bioaccumulate in the food chain. These include several of the pesticides, polychlorinated biphenyls (PCBs), and some trace elements (especially mercury). Advisories have frequently been issued by local health authorities, warning against overconsumption of fish taken from the lakes. In recent years, much effort has been directed toward reducing or eliminating direct discharges of contaminants to the lakes and tributaries. In addition to these obvious sources, however, some studies have suggested that atmospheric transport and deposition processes may account for a significant portion of the overall loadings of toxic substances to the lakes. Section 112(m) of the 1990 Clean Air Act (CAA) amendments specifically requires a program to identify and assess the extent of atmospheric deposition of hazardous air pollutants to the Great Lakes, as well as to other large lakes and coastal waters.

In response to the 1990 CAA amendments and the 1987 International Water Quality Agreement between the United States and Canada, a long-term monitoring program is being jointly implemented by the two countries to assess the relative contribution from atmospheric processes to water quality degradation in the Great Lakes. This program, known as the Integrated Atmospheric Deposition Network (IADN), currently is measuring concentrations of selected toxic substances in ambient air and

precipitation at one shoreline location for each of the five lakes. Four or five monitoring sites per lake are planned for the network. The IADN siting criteria requires all monitoring sites to be located in remote areas along the shorelines, well removed from local air pollutant emission sources. A key objective of the IADN program is to detect trends in atmospheric loadings to the lakes; thus, the program focuses on the contributions from regional air masses entering the Great Lakes Basin.

INTRODUCTION

In addition to IADN, the U.S. Environmental Protection Agency (EPA) is planning to conduct a shorter, intensive study of Lake Michigan during the next few years. The Lake Michigan Mass Balance Study will employ both monitoring and modeling techniques to provide greater understanding of the sources, transport, and fate of toxic substances entering the lake. For a period of one year, measurements will be made of target contaminant concentrations in (and exchange between) lake water, tributaries, sediments, and the atmosphere. The resulting data will be used to develop whole-lake mathematical models for predicting the response of Lake Michigan and its fish to proposed regulatory actions. This project will require information on the impact of local air emission sources, as well as the contribution from regional air masses. The maximum local source density near Lake Michigan occurs along its southwestern shoreline which is dominated by the greater Chicago, Illinois and Gary, Indiana urban areas. With a population of over eight million, this is the third largest metropolitan area in the country. In addition to the usual urban air pollution sources, emissions occur from point sources such as iron and steel manufacturing in Gary, petroleum refining in southwest Chicago, and other industrial and municipal activities within the metropolitan area.

A persistent, regional air quality problem has long been expeienced in the lower Lake Michigan area with high summertime ozone levels. Multi-day ozone episodes frequently develop in the region when the predominant wind direction is from the south to southwest, temperatures are relatively high, and relative humidity is low. During such episodic periods, the National Ambient Air Quality Standard (NAAQS) for ozone is often exceeded at routine monitoring sites near the lake shore in all four states bordering Lake Michigan (i.e., Illinois, Indiana, Michigan, and Wisconsin). Typically, ozone concentration decreases rapidly with increasing distance from the lakeshore. Following several years of unsuccessful attempts to address the summer ozone problem around the lake through individual State Implementation Plans, the four states involved decided to join forces to develop a regional response. A program was undertaken, with assistance from EPA, to take intensive air quality and meteorological measurements during the summer of 1991. The resulting database will provide the basis for a photochemical reactive grid model of the lower Lake Michigan area. Once it has been fully validated and calibrated, the model will be used to assess alternative regional ozone control strategies.

The field measurement portion of the program, known as the Lake Michigan Ozone Study (LMOS), was conducted over the period from June 17 through August 9, 1991. In addition to ground-based continuous measurements, on ten selected days measurements were made of ozone, ozone precursors, and meteorological parameters aboard several vessels operating on the lake and aircraft flying transects through the study domain. Upper air soundings were also collected with balloon systems on the intensive days. In April 1991, at the request of EPA's Region 5, a decision was made by EPA's Atmospheric Research and Environmental Assessment Laboratory at Research Triangle Park, North Carolina (AREAL/RTP) to take advantage of the extensive LMOS database by conducting a concurrent air toxics monitoring study in the lower Lake Michigan area. This project was designated the Lake Michigan Urban Air Toxics Study (LMUATS) and was designed to serve as a pilot for the atmospheric measurements portion of the Lake Michigan Mass Balance Study, scheduled to begin in the spring of 1993. LMUATS participants included AREAL/RTP, NOAA's Atmospheric Turbulence and Diffusion Division (ATDD), the University of Michigan, Illinois Institute of Technology, Massachusetts Institute of Technology, ManTech Environmental, Battelle, Southwest Research Institute, and Sunset Laboratories.

OBJECTIVES

The major goals established for the LMUATS were to quantify the concentrations of selected air toxic species in the lower Lake Michigan area, identify the source categories responsible for these contaminants, attempt to differentiate the contribution of the Chicago/Gary urban plume from the regional air masses, compare measurements made over land with those made over water, estimate the rates of dry deposition to the lower lake area during the study period, and evaluate methods for the sampling and analysis of toxic substances in ambient air. This latter goal was of particular importance for measuring mercury in the vapor phase, as the AREAL/RTP has very limited experience in making such measurements.

STUDY DESIGN

Three land-based sites were selected for monitoring air toxic concentrations in the lower Lake Michigan Basin. The LMUATS sampling site locations are shown in Figure 1. Southwesterly winds are normally predominant during the summer months in the upper Midwest. The sites were located to characterize air toxic concentrations upwind, within, and downwind of the Chicago/Gary urban area. Two sites (Kankakee, IL and South Haven, MI) were collocated with the LMOS program to maximize the usefulness of the information collected. Most of the sampling equipment, set-up, and operator training for the LMUATS was provided by AREAL/RTP. Through a cooperative agreement with EPA, the University of Michigan managed the field sampling program, provided a research vessel (the R/V Laurentian) for making measurements over the lake on selected days, and performed the sampling and analytical work for vapor-phase mercury determination.

The Kankakee site was on the property of a small, private airport located just south of Kankakee and about 60 miles south-southwest of downtown Chicago. The surrounding area is agricultural, with corn being the predominant crop. The site near South Haven, MI was located in an open pasture on a farm about three miles inland from the lakeshore and 90 miles northeast of downtown Chicago. The surrounding area is rural, with fruit orchards being the major agricultural activity. The site was operated by graduate students from the University of Michigan and was used as a central staging area for the field study. Duplicates of all sampling equipment were operated at this site to provide overall method precision data. The downtown Chicago site was located on the campus of the Illinois Institute of Technology (IIT) and was operated by IIT graduate students, who also performed collocated size distribution and dry deposition measurements.

Daily samples were collected at each ground site from July 8 through August 9, 1991. The R/V Laurentian was in operation on July 11 and 12 along the eastern shore near Grand Haven, and from July 23-27 and August 5-8, 1991 at a position approximately six miles offshore from the Chicago/Gary waterfront. Samples were integrated over a 12-hour period, beginning at 8:00 a.m. CDT. Table 1 summarizes the classes of pollutants measured, the sampling and analytical techniques employed, the laboratories involved, the number of individual species and samples that were quantified. Because of the relatively high costs for mass spectrometrical analysis of semi-volatile organic compounds (pesticides, PCBs and PAHs), it was decided in advance to analyze only a subset of samples collected for these compounds. The PS-1 samples collected each day were shipped in cold packs to the appropriate laboratory. Filters and traps were combined, desorbed, and placed in cold storage. A decision regarding which samples to analyze was made after an examination of the particulate, trace element, and meteorological data.

Trace element data were obtained for both fine ($\leq 2.5\ \mu$) and coarse (2.5-10 μ) particles using a non-destructive X-ray fluorescence (XRF) technique. A subset of filters was then sent to the Massachusetts Institute of Technology Nuclear Reactor Lab for neutron activation analysis (NAA) to obtain information on mercury and other elements at very low particulate concentrations. Additionally, some filters will be examined by scanning electron microscopy to obtain element-specific size distributions for estimating dry deposition rates. Fine particle samples were analyzed by Sunset Labs

using combustion flame ionization detection (FID) to measure total elemental and volatilizable carbon content, useful for source apportionment. Samples for gaseous mercury were collected at all sites except Kankakee via amalgamation on gold-coated sand, following a pre-fired glass fiber filter. These samples, along with some filter extracts, were analyzed for mercury content at the University of Michigan using cold-vapor atomic fluorescence (CVAF). Annular denuder samplers (ADS) were operated for acid and basic aerosol measurements at the South Haven site and aboard the R/V Laurentian.

Micro-meteorological measurements were made aboard the research vessel to determine the vertical structure of the atmosphere in the layer just above the lake surface. Flux information was considered useful for making inferences about likely deposition rates of toxic substances to the lake. Rapid-response instruments were mounted off the vessel's bow to measure wind direction, wind speed, temperature, water vapor, carbon dioxide, and ozone. These measurements were taken at logarithmically spaced elevations between two and seven meters above the lake surface. In addition, on five days (July 21-25, 1991) identical and coordinated measurements were made aloft aboard a small aircraft flown at low elevations by NOAA's Atmospheric Turbulence and Diffusion Division. This information will be used, in conjunction with the LMOS database, to estimate dry deposition rates.

PRELIMINARY RESULTS

The papers that follow present preliminary results for various classes of pollutants measured in the study. As an introduction to the database, PM_{10} concentrations for three LMUATS ground sites are plotted by site and sample date in Figure 2. Particulate levels are highly correlated for all three sites, indicating that most of the ambient particulate loadings are regional in nature. The concentrations observed at the rural South Haven, MI site tended to be the lowest of the three locations. Also shown in the figure are the predominant daytime wind directions (WD). During the first week of the study, winds were from northerly and easterly directions and PM_{10} levels were relatively low at all sites. Beginning on July 15, wind direction switched first to the south and then to the southwest and remained from there for the rest of the week. Particulate concentrations rose well above the PM_{10} annual NAAQS level of 50 $\mu g/m^3$, exceeding 80 $\mu g/m^3$ at the IIT and Kankakee sites. Concurrently, a major ozone episode developed in the area on July 16 and lasted through July 20. The NAAQS for ozone was exceeded along both shorelines of Lake Michigan, with the highest concentrations occurring on July 18 and 19 along the eastern shore. The LMOS program operated in its intensive mode during this period, collecting additional measurements from boats, aircraft and balloons. On July 23, the prevailing wind direction became northwesterly and PM_{10} concentrations decreased dramatically. With winds from the north, the Kankakee site became the downwind site and the maximum concentrations were observed there. On August 1, winds once more became southwesterly for a two-day period, and PM_{10} concentrations for August 2 again approached 80 $\mu g/m^3$ at the IIT and Kankakee monitoring sites.

As previously noted, duplicate sampling instruments were operated at the South Haven base site. Results for PM_{10} concentrations (fine + coarse mass) from the pair of dichotomous samplers operated at the site are shown in Figure 3 as a linear regression of one sampler's results on the other. The slope of the regression is near 1.00, the intercept is close to zero, and the r-square value is 88 percent. This indicates very good agreement between the two instruments. In addition to collecting duplicate measurements, a field audit was conducted at each ground site during the second week of the study. Most instruments were found to be operating properly, and recalibrations were performed as necessary. For each of the pollutant classes included in the study, field blanks and audit materials were incorporated into the analysis scheme, as appropriate.

In the papers that follow, results obtained by the various analytical laboratories participating in the LMUATS are presented and discussed. Once validated and made available, the LMOS database will be combined with the LMUATS results. A final project report, including detailed analyses of the combined meteorological and pollutant databases, should be completed and published by December 1992.

Figure 1. Location of LMUATS sampling sites.

POLLUTANT CLASS	SAMPLING	ANALYSIS	LABORATORY	NO. SPECIES	NO. SAMPLES
Pesticides	PS1/PUF	GC/HRMS	SwRI	10	70
Total PCBs	PS1/PUF	GC/HRMS	SwRI	20	70
PAHs	PS1/XAD	GC/MS	Battelle	19	75
VOCs	Canister	GC/MSD	Battelle	44	120
Trace Elements	Dichot	XRF/NAA	MTE/MIT	18/14	300/120
Carbon-e/v	FPS	FID	Sunset Labs	2	150
Gaseous Hg	GFF/Au sand	CVAF	UMI	1	170
Particulate Hg	GFF	CVAF	UMI	1	80
Other Inorganics	ADS	IC	UMI	8	75

Table I. Pollutant measurements made during the LMUATS.

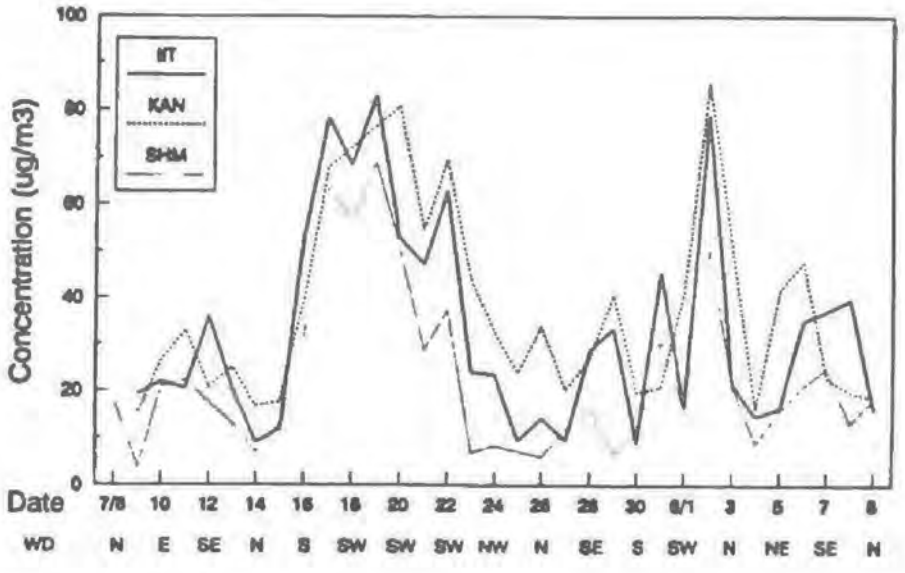

Figure 2. PM-10 concentrations observed during the LMUATS.

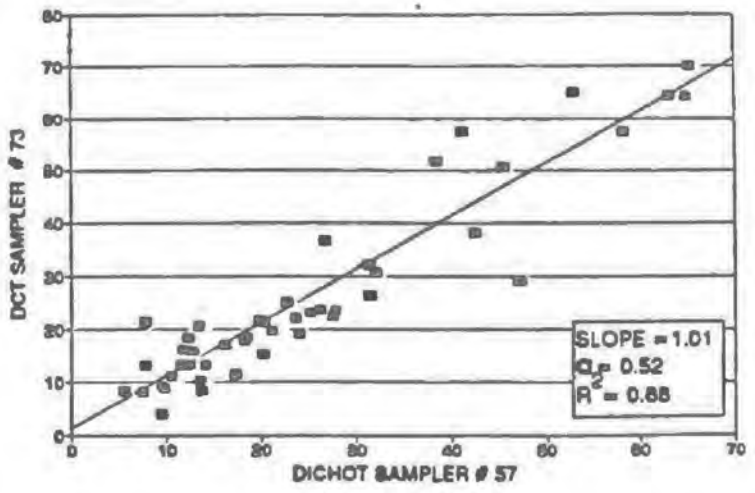

Figure 3. Duplicate PM-10 results from South Haven, MI.