

DEC 22 1994



Project Summary

Lake Michigan Urban Air Toxics Study

Gerald J. Keeler

During the summer of 1991, an air toxics monitoring program was conducted in the lower Lake Michigan area. This study, designated the Lake Michigan Urban Air Toxics Study (LMUATS), was designed to take advantage of the intensive meteorological 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). A research vessel and a small aircraft were deployed on selected days to measure micrometeorological parameters and pollutant concentrations at offshore locations near Chicago. Over 1,200 samples were collected and analyzed to determine atmospheric levels of polychlorinated biphenyls (PCBs), pesticides, polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), particle mass, and trace elements.

In addition, Nuclear Activation Analysis and Scanning Electron Microscopy (SEM) were employed for selected subsets of the particulate samples to yield information on specific trace elements and size distribution. The LMUATS goals 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, differentiate the Chicago urban plume from regional background, identify categories of sources for the target pollut-

ants, and estimate deposition to the lake.

This Project Summary was developed by EPA's Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

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 that tend to bioaccumulate in the food chain. These include several of the pesticides, PCBs, and some trace elements (especially mercury (Hg)). 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 Amendments (CAAAAs) 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.



Printed on Recycled Paper

EPA's Atmospheric Research and Environmental Assessment Laboratory at Research Triangle Park, NC (AREAL/RTP), in consort with EPA's Region 5, decided to take advantage of the extensive meteorological database being generated by the 1991 LMOS by conducting a concurrent air toxics monitoring study in the lower Lake Michigan area. This project, the LMUATS, was designed to serve as a pilot for the atmospheric measurements portion of the 1994-1995 Lake Michigan Loadings Study. LMUATS participants included AREAL/RTP, the National Oceanic and Atmospheric Administration's (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.

Procedure

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, setup, 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, performed the sampling and analytical work for determining Hg concentrations in both the vapor and particulate phases, and managed the data analysis for the entire study.

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, MI, 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 sampling and analytical techniques employed for each class of pollutants measured. Because of the rela-

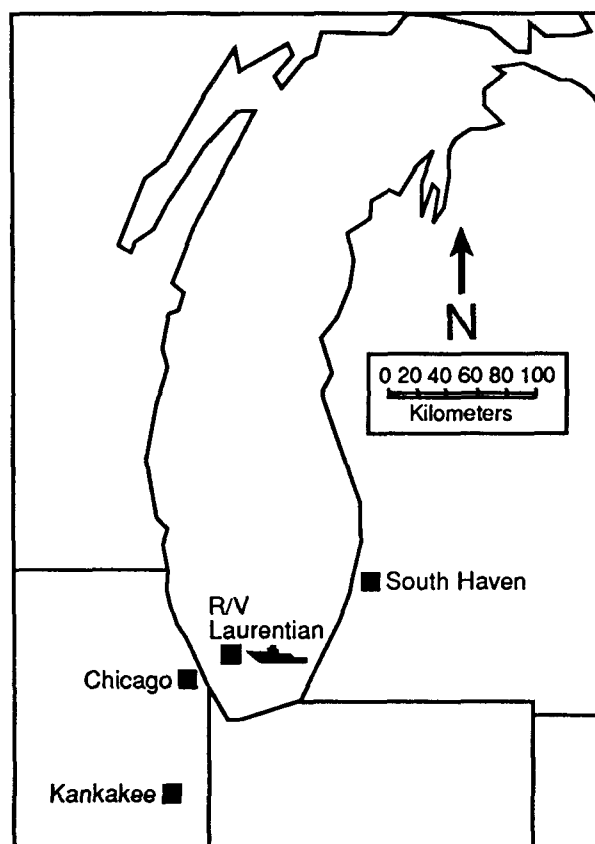


Figure 1. Lake Michigan Urban Air Toxics Study sampling locations.

Table 1. Measurements from the Lake Michigan Urban Air Toxics Study

Sampler	Samplers Per Site	Sample Duration (hours)	Sampling Media	Analysis Method
PS1-PUF Sampler	2	12	PUF/Quartz	GC/MS
FPS	1	12	Filter	Carbon
Annular Denuder/FP	1	12	47 mm Quartz	IC
DICHOT	1	12	NaCO ₃ /Teflon	XRF/INAA/SEM
VOC Canister System	1	12	37 mm Teflon	GC/MS
Hg Systems			6-L Canisters	
1. Au Sand/Filter	1	6/12		CVAFS
2. Filter w/INAA	1	12/24	Au/Quartz	INAA
3. Filter	1	12/24	47 mm Teflon	CVAFS
Micro-Orifice Impactor*	1	24	47 mm Quartz	IC
			37 mm Teflon	

* Micro-orifice impactors were only run on the *RV Laurentian* and at the South Haven site for a limited number of days.

tively high costs for mass spectrometrical analysis of semivolatile organic compounds such as pesticides, PCBs, and PAHs, it was decided in advance to analyze only a subset of samples collected for these compounds. The Particulate Sampler-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 ($< 2.5 \mu$) and coarse ($2.5\text{--}10 \mu$) particles using a nondestructive 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 to obtain information on Hg and other elements at very low particulate concentrations. Additionally, some filters were examined by SEM to obtain element-specific size distributions for estimating dry deposition rates. Fine particle samples were analyzed by Sunset Labs using combustion flame ionization detection to measure total elemental and volatilizable carbon content, useful for source apportionment. Samples for gaseous Hg 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 Hg content at the University of Michigan using cold-vapor atomic fluorescence (CVAF). Annular denuder samplers were operated for acid and basic aerosol measurements at the South Haven site and aboard the *R/V Laurentian*.

Micrometeorological 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 ATDD. This information was used, in conjunction with the LMOS database, to estimate dry deposition rates.

Results and Discussion

During the course of the month-long investigation, two periods were encountered in which the prevailing wind flow was from the south-southwest and pollutant levels were elevated on a regional scale. This provided an opportunity to observe the behavior of the many classes of compounds as they were advected from source regions in Illinois (and further south) across the lake to South Haven. The concentrations of particulates and vapor phase Hg decreased as they were advected from the urban source region. From the shift in size distribution, it was evident that the coarse matter was being depleted by dry deposition as the aging air mass was advected from Chicago over the water to the downwind monitoring site in South Haven. As a result of both dispersion and deposition, the concentrations of most compounds decreased rapidly to the regional or "background" levels within a short distance from the urban/industrial areas.

Generally, the monitoring site in urban Chicago (IIT) had the highest concentrations of the toxic pollutants and trace elements measured. The trace element concentrations in Kankakee, however, were often comparable to Chicago. This is in contrast to the other two sites, over-water and South Haven, where levels of most trace elements were at least a factor of two less than at IIT. Specifically for Hg, the median concentration of vapor phase Hg was four times higher at IIT when compared to over-water and South Haven measurements, while the maximum concentration was more than 15 times higher. Particulate Hg levels were also 5 to 15 times higher at IIT than at South Haven or on the *R/V Laurentian*, suggesting that local sources are primarily responsible for the Hg levels observed at the IIT site.

During periods of air flow from the north and northwest, pollutant concentrations measured at Chicago, South Haven, and aboard the *R/V Laurentian* were typically quite low. Levels of some of the fine fraction metals such as Pb, Fe, Mn, and Zn measured in Kankakee during these periods were elevated above the levels observed at IIT. Since the IIT site in Chicago is only 1.6 km from the lake, this suggests an impact due to source(s) between the two sites (e.g., in the southeast Chicago/Gary area).

Concentrations of the more reactive compounds, such as many PAHs, were uniformly and significantly (order of magnitude) higher at IIT than at the other three monitoring sites. It is interesting to note that most of the measured PAHs

were found in higher concentrations over the water than at the South Haven site for several days and on average. Concentrations of naphthalene, acenaphthylene, and retene exhibited somewhat uniform concentrations among sites, suggesting a more regional source distribution.

A review of the total PCB measurements during the period for which the prevailing flow was from the southwest indicates that total PCBs were not transported from the Chicago urban area downwind to South Haven. This implies a strong concentration gradient of PCBs around Chicago, with rapid dispersion of the already low levels of these compounds similar to the pattern observed for Hg. However, the low levels of these compounds do not imply that they are unimportant with regard to deposition. On the contrary, the deposition of relatively small amounts of pollutants such as Hg and PCBs, which biomagnify in the food chain, are currently believed to account for a substantial portion of these toxins entering the Great Lakes.

The majority of the pesticides/herbicides quantified during the LMUATS were highest in concentration at Kankakee. Notable exceptions were aldrin and simazine, which were found in higher concentrations at IIT than at the other three sites, and DDT and its derivatives, which were highly elevated at the South Haven site. The ratio of DDT to DDE at South Haven (0.3) strongly suggests that these levels were due to re-emission of a much earlier DDT application. Average concentrations for many currently used pesticides/herbicides (e.g., atrazine) were two to three times higher on average at Kankakee than at IIT. Significant concentrations of many pesticides were observed at over-water sites, both in the eastern portion of the lake (at the 100 m station off Muskegon) as well as offshore of Chicago.

The influence of the iron-steel industry on the composition of the aerosol measured during the LMUATS was clearly observed. The Fe concentrations in both fractions of PM_{10} were elevated at all three sites and exceeded the contribution expected from windblown dust. Analysis of the fine fraction trace element data from IIT using principal component analysis yielded four dominant source categories: iron and steel manufacturing, metals processing, soil-derived components, and a regional coal combustion source dominated by sulfur. A secondary Al smelter located in the St. Louis area may be the source of several metals, including Al, measured at relatively high concentrations at the land-based sites on several occasions.

The chemical mass balance approach to source apportionment was applied to the IIT measurement data using source categories based on the EPA database SPECIATE in conjunction with published source profiles. For days with predominant flow from the southwest, this model was able to explain up to 69% of the observed coarse mass with significant contributions from crustally derived material, lime dust, and fugitive steelyard and incinerator emissions. Due to the complexity of the airshed and lack of appropriate source profiles, the model was not able to effectively explain the fine mass measured at IIT.

To verify the results of statistical source apportionment, scanning electron microscopy was applied to a subset of particulate samples collected at IIT. This analysis provides a description of morphology and elemental composition on an individual particle basis. The SEM results lend strong evidence to support many of the suspected source categories including iron and steel, coal combustion, incineration, Al production, diesel emissions, and resuspended soil. The complexity of the particulate matter collected is evident in the photomicrographs generated by the SEM process. The long-chain Fe spheres, proliferation of sulfate aerosols, soot conglomerates, and intricately patterned salts and other crustal matter illustrate the diverse particulate mixture abundant in the Chicago urban atmosphere.

The measurements documented in this study provide evidence to support the hypothesis that near-shore urban areas can be significant contributors to atmospheric levels and, therefore, to deposition of toxic pollutants to adjacent water bodies. The 1990 CAAA require that the sources and rates of atmospheric deposition of hazardous air pollutants to water bodies be investigated and determined. Critical to this determination is a characterization of the impact of local urban plumes on the total toxic burden to the Great Lakes and other "Great Waters."

The dry deposition fluxes to Lake Michigan for selected trace metals associated with both fine and coarse particles were estimated using a novel hybrid receptor-deposition modeling approach. This model included parameters that take into account the variability in

deposition flux over the lake as a function of meteorological variables, particle size distributions, the physics of water waves, and the type and location of sampling sites. Significant temporal and spatial variations in deposition velocities were obtained for trajectories traversing Lake Michigan from one day to the next, demonstrating the unreliability of calculating deposition flux using deposition velocities assumed to be constant in time or space over the entire area of the water body.

The results of the dry deposition modeling indicate that Si had the highest deposition flux during the LMUATS (360 tons) for trace elements measured, followed by Ca (254 tons), Fe (160 tons), Al (150 tons), K (58.3 tons), S (55 tons), Zn (4 tons), Mn (2.35 tons), Cu (2.2 tons), Cd (1.07 tons), Pb (1.07 tons), Se (0.93 tons), Ni (0.8 tons), Cr (0.53 tons), As (0.44 tons), Br (0.38 tons), and total Hg (0.035 tons). The dry deposition flux to Lake Michigan for specific pollutants contributed by sources in the Chicago/Gary urban area is estimated to be two to ten times greater than that from regional sources.

Conclusions and Recommendations

The following conclusions are based on the measurements made during the LMUATS and the subsequent analysis of those and related data:

1. The median concentration of vapor phase Hg was four times higher at IIT than over water or downwind (South Haven), while the maximum concentration was over 15 times higher. Particulate Hg levels were also 5 to 15 times higher in Chicago (IIT) than at South Haven or on the research vessel, suggesting that local sources are primarily responsible for the Hg levels observed in Chicago.
2. Median PAH concentrations were generally 10 times higher at the urban site (IIT) than at the rural monitoring locations. Some PAH (e.g., naphthalene, retene, acenaphthylene) exhibited regional patterns, indicating long-range transport.
3. PCB levels were about three times higher at IIT than at the other sites and were generally found to be

higher over the lake than at the downwind or upwind sites.

4. Most currently used pesticides were observed at their highest concentrations at the background site (Kankakee), no doubt due to local agricultural usage patterns. However, DDT and its derivatives were found primarily at the Michigan site in patterns suggesting historical rather than current usage.
5. Source apportionment models clearly indicated the influence of the iron and steel industry on trace element concentrations, particularly at the IIT site. SEM analysis of a subset of particulate filters confirmed those results.
6. A dry deposition flux model was developed to use observed contaminant concentrations and meteorological data to estimate deposition by integrating over both time and lake surface area.
7. Using this hybrid receptor-deposition model, estimates were obtained for summer dry deposition fluxes ranging from 360 tons Si to 0.035 tons total Hg.

Some recommendations for further "Great Waters" research developed from the experience gained in the LMUATS are as follows:

1. Develop accurate emission inventories for the highest priority pollutants.
2. Obtain better source profiles for modeling through stack and other source sampling.
3. Perform research of depositional processes for use in deterministic and hybrid models.
4. Characterize large particle contribution to deposition for near-shore urban areas.
5. Evaluate the importance of over-water vs. inland vs. shoreline monitoring locations.
6. Investigate gas-particulate partitioning processes for semivolatile compounds.
7. Determine re-emission rates for Hg, PCBs, and pesticides that have been discontinued.