LAKE MICHIGAN URBAN AIR TOXICS STUDY

by

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lower Lake Michigan area. This study was designed to take advantage of the intensive meteorological and oxidant data base being generated concurrently by the Lake Michigan Ozone Study (LMOS stations). Over 1,200 samples were collected and analyzed to determine atmospheric levels of PCBs, pesticides, PAHs, VOCs, particle mass, and trace elements. In addition, a research vessel and a small aircraft were employed on selected days to measure micro-meteorological parameters and pollutant concentrations at offshore locations near Chicago. The goals of this Great Waters 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.

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Dedication

This report is gratefully dedicated to Mr. Terry Clark. Terry generously invested a great deal of his time, over the last few months, constructively critiquing this report. His insightful comments on the meteorological and modeling facets of the report were extremely helpful in finalizing this document. Terry's dedication to his work which he embraced with enthusiasm is highly respected by those of us who benefited from his generosity. Terry will be deeply missed by those who have had the opportunity to work with him.

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Abstract

During the summer of 1991, a study of the dynamics of toxic pollutant transport and deposition into southern Lake Michigan was performed. This initial effort was aimed at establishing the feasibility of providing accurate and representative air samples and gradient measurements of toxic contaminants and nutrients over Lake Michigan. 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 Loading Study. The sampling conducted allowed for the quantification of most of the 14 Critical Pollutants on the International Joint Commission (IJC) list. A comprehensive suite of atmospheric measurements was performed for polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), selected pesticides, volatile organic compounds (VOCs), particulate matter, trace elements (including mercury), and fine carbon (organic and elemental). Three land-based sites were operated during the study to provide one upwind sampling point, one urban site, and one downwind site on the eastern shore of Lake Michigan. Two sites were also Lake Michigan Ozone Study (LMOS) sites which provided a complete suite of meteorological and some ancillary air quality data (ozone and nitrogen oxides). The University of Michigan Research Vessel (*R/VLaurentian*) was utilized as a collection platform for three different sampling periods during the one-month study.

The data collected during the LMUATS revealed large gradients and temporal changes in the concentrations of most compounds measured. Concentrations for most pollutants, especially the regionally distributed species, were elevated for a one-week period from 16-23 July which was associated with air mass transport from the southwest. This period enabled an initial assessment of over-water pollutant transport. The concentrations of total PCBs and most of the PAH compounds measured were greatest, by 1-2 orders of magnitude at the urban site in Chicago. Ambient concentrations of trace metals were generally two to three times higher in Chicago than at the rural sites. Atmospheric mercury concentrations were four to five times higher in Chicago. Dry deposition fluxes of trace elements associated with fine ($\leq 2.5 \,\mu$ m) and coarse (2.5-10 μ m) particles over Lake Michigan were estimated using a combined dispersiondeposition modeling approach. The effects of micrometeorological parameters, particle size distributions, wave dynamics, and type and location of sampling sites on the dry deposition flux estimates are discussed. This report was submitted in fulfillment of T901758 by the University of Michigan under the sponsorship of the United States Environmental Protection Agency. The report covers a period from June, 1991 to May, 1993 and work was completed as of May, 1994.

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Chapter 1

Introduction

The presence of persistent toxic chemicals within the Great Lakes Basin has been a matter of public and scientific 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. This list includes several pesticides, polychlorinated biphenyls (PCBs), and heavy metals (especially mercury). Advisories are frequently issued by local health authorities, warning residents against over consumption of fish taken from the lakes. In recent years, much effort has been directed toward reducing or eliminating direct discharges of contaminants to the Great Lakes and their major tributaries. However, contaminated fish are often found in remote lakes where direct water discharges can be ruled out as possible sources. These findings confirm that the atmosphere represents a significant source or pathway to the Great Lakes and the surrounding drainage basin for some of the contaminants of most concern.

The Clean Air Act Amendments (CAAA) of 1990 legislated that a wide range of environmental research and regulatory activity be undertaken by the U.S. Environmental Protection Agency (EPA) and other agencies to improve the quality of the nation's environment. Hazardous air pollutants (HAPs) are addressed in Title III of the CAAA. In regard to the Great Lakes, Section 112(m) states that the EPA Administrator, in conjunction with NOAA, "shall conduct a program to identify and assess the extent of atmospheric deposition of HAPs to the Great Lakes, the Chesapeake Bay, Lake Champlain, and coastal waters. As part of such a program the Administrator shall ... investigate the sources and rates of atmospheric deposition of air pollutants."

In March 1991, three months after the signing of the CAAA, an international workshop of environmental scientists was convened at the Gray Freshwater Biological Institute in Navarre, Minnesota. Participants included representatives from EPA, the National Oceanic and Atmospheric Administration (NOAA), Environment Canada, the Ontario Ministry of the Environment, the Canadian Centre for Inland Waters, the Canadian

Department of Fisheries and Oceans, and several states and universities. This group was assembled to assess the state of science and identify critical research needs to answer questions about the sources, concentrations, and fluxes of air toxics to the Great Lakes, as well as the other waters listed in Section 112(m) of the CAAA. Among the highest priority research needs identified during the workshop were: (1) measuring onshore and offshore deposition rates simultaneously to determine whether or not onshore measurements represent deposition to the bulk of the lake surface, and (2) characterizing the impact of local urban plumes on the total toxic burden to the Great Lakes. Both of these research issues are critical to the design of long-term monitoring networks to determine rates of atmospheric deposition to the lakes.

In response to the 1990 CAAA and the 1987 Annex to the Great Lakes 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. Eventually, five monitoring sites per lake are planned for the network. A key objective of the IADN program is to detect trends over time in atmospheric loadings to the lakes.

In addition to IADN, the U.S. Environmental Protection Agency (EPA) is planning to conduct a shorter, intensive study of Lake Michigan over the next few years. The Lake Michigan Loading 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, and the atmosphere. The resulting dat² will be used to develop models for predicting the response of Lake Michigan and its fish to proposed regulatory actions. This project will serve as a template for future studies and 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 East Chicago and Gary; petroleum refining in northwest Indiana and northeast Illinois; and other industrial and municipal activities within the metropolitan area.

A persistent, regional air quality problem has long been experienced in the 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 high. 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 concentrations decrease with increasing distance from the lake shore.

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 large-scale program was undertaken, with assistance from EPA, to take intensive air quality and meteorological measurements over and around Lake Michigan 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 17 June through 9 August 1991. Not only were ground-based continuous measurements taken, but also selected 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 rawinsonde balloon systems on the intensive days and radar profilers.

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 Loading Study, scheduled to begin in 1993. The LMUATS was performed by the University of Michigan Air Quality Laboratory and the EPA AREAL/RTP. Other participants providing

site operations, air craft measurements, or analytical services included the Illinois Institute of Technology, Massachusetts Institute of Technology, NOAA's Atmospheric Turbulence and Diffusion Division (ATDD), ManTech Environmental, Battelle-Columbus, Southwest Research Institute, and Sunset Laboratories.

1.1. Objectives

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

It is unknown how much of the toxics in the air over the lakes originates from sources near (within 20 km) the lake shoreline versus those sources farther upwind. This project was the first step in the study of the dynamics of toxic pollutant transport over and deposition into large lakes. This initial effort was aimed at establishing the feasibility of providing accurate and representative air samples and gradient measurements of toxic contaminants and nutrients over Lake Michigan. The primary tasks for the project were:

- 1) Measurements of the horizontal gradients in concentrations of selected toxic contaminants across Lake Michigan;
- 2) Interpretation of the measured concentrations to ascertain the probable source areas and pathways for the contaminants;
- An initial assessment of the importance of over-water deposition monitoring for specific toxic contaminants; and
- 4) An initial assessment of the relative importance of the urban input to the total loadings of toxic contaminants to Lake Michigan.

1.2. Technical Approach

The primary objective of this Cooperative Research Project was to assess the atmospheric deposition of toxic contaminants to the Great Lakes using actual near-shore and over-water measurements of the critical pollutants and relevant meteorological parameters for a one-month period concurrent with the Lake Michigan Ozone Study. The States of Michigan, Indiana, Illinois, and Wisconsin formulated a coordinated research program entitled the Lake Michigan Ozone Study to investigate the formation and transport of pollutants from the Chicago/Milwaukee metropolitan areas across Lake Michigan and to quantify the atmospheric source-receptor relationships in the area surrounding Lake Michigan. Α comprehensive suite of surface and upper-air meteorological and air quality measurements were collected. These measurements included airborne measurements with tethered balloons around the lake and on the ships, and by several research aircraft. Figure 1-1 shows the location and density of the surface sampling sites utilized for the LMOS. By performing meteorological and standard air quality measurements aboard two research vessels strategically positioned on Lake Michigan; the University of Michigan was an integral part of the 1990 LMOS Pilot Study. The experience gained in taking the over-water measurements during the summer of 1990 formed the basis for a proposal submitted to the Great Lakes National Program Office in the Fall of 1990. The proposed concept was eventually adopted by AREAL/RTP and ultimately became the basis for the LMUATS.

Observations made during the 1990 Pilot Study suggested that the study objectives would best be served by positioning a vessel along the western shore of Lake Michigan at a distance offshore from Chicago. Positioning the research vessel offshore of the major urban/industrial centers allowed for the direct measurement of the transported urban toxic contaminants. The influence of the various urban centers can be directly measured by tracking the urban plumes out over the Lake, using meteorological and chemical tracer techniques, and comparing the concentrations measured on the research vessels. Measurements of varying sampling duration were performed from 12 to 24 hours in duration to allow the complex meteorological and chemical transformations to be observed and investigated. The measurements provide some essential data to investigate the "urban hot spot" concept that a large fraction of the atmospheric deposition into Lake Michigan may occur at relatively short distances from shore. In addition, the atmospheric contaminant and nutrient data coupled with the meteorological and tracer measurements should provide the needed information for a preliminary assessment of the relative importance of the urban centers in the total loading of toxic contaminants to Lake Michigan.

Figure 1-1. The Location of the Surface Air Quality and Meteorological Sampling Sites for the Lake Michigan Ozone Study.



These data can potentially be merged with climatological data to investigate deposition trends or patterns to the lake. In addition, the study design may provide the necessary data to allow a detailed source apportionment of the measured toxic contaminants. The local and regional scale receptor modeling utilizes the VOC and trace element measurements taken during the month-long investigation. This project was unique in its attempts to couple actual over-water measurements of critical toxic species with intensive meteorological and tracer measurements to begin to quantify the actual atmospheric deposition of these contaminants while determining the potential sources of the measured species. A direct, but limited comparison of the over-water and land-based measurements was carried out. This comparison provided an initial assessment of the need for actual over-water measurements but can not be extrapolated to other large lakes or to other time periods for Lake Michigan. A hybrid receptor-deposition modeling framework was developed concurrently with this project to provide a more comprehensive framework for assessment of atmospheric deposition to large bodies of water. This framework can be utilized for the Lake Michigan Loading study and for other investigations dealing with the Great Waters.

Chapter 2

Summary and Conclusions

The Lake Michigan Urban Air Toxics Study was a pilot investigation aimed at assessing the impact of the urban plume on the deposition of air toxic pollutants into Lake Michigan. Several conclusions can be drawn from this study which can be used in planning for future investigations on the other Great Lakes and for the Great Waters including Lake Champlain, Chesapeake Bay, and coastal estuaries.

The major objectives of the study were: 1) to quantify the horizontal gradients in concentrations of selected toxic contaminants across Lake Michigan; 2) to identify the source categories and most probable pathways for these contaminants; 3) to provide an initial assessment of the relative importance of the urban input to the total loadings of toxic contaminants to Lake Michigan, including the differentiation of the contribution of the Chicago/Gary urban plume from the regional air mass; and 4) to assess the importance of over-water versus over-land deposition monitoring for specific toxic contaminants.

In order to accomplish these objectives, a comprehensive suite of atmospheric measurements was performed during a month long study. The approach used in this study was to quantify the levels of a large number of HAPs at three land-based locations (upwind, central, and downwind of Chicago) often linked by air mass transport and at an additional over-water platform along the path between the urban and the downwind site. Kankakee, IL was identified as the site upwind of Chicago. IIT, approximately 1.6 km from the shore of Lake Michigan, was chosen as the central Chicago site. The downwind site was located across Lake Michigan in South Haven, MI. The University of Michigan R/V *Laurentian* was deployed offshore of Chicago for over-water measurements of HAPs.

2.1 Concentration Gradients of Pollutants in the Southern Lake Michigan Basin

Generally, the monitoring site in urban Chicago (IIT) had the highest concentrations of HAPs and trace elements (Si, K, Ca, Ti, V, Mn, Fe, Cu, Zn and Pb). However, there were notable exceptions. The trace elements concentrations in Kankakee 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 2 less than IIT. Specifically for Hg, the median concentration of vapor phase Hg was four times higher at IIT site when compared to over-water and South Haven, while the maximum concentration was more than 15 times. Particulate Hg levels were also 5 to 15 times higher in Chicago (IIT) than at South Haven or on the R/V *Laurentian*, suggesting that local sources of Hg are likely to be responsible for the Hg observed at the Chicago (IIT) site.

During the course of the 30-day investigation, two periods in which the prevailing wind flow was from the south-southwest were encountered. This provided an opportunity to observe the behavior of the many different classes of compounds as they were advected from source regions in Illinois across the water to South Haven. The concentrations of particulates and several vapor phase Hg compounds decreased as they were advected from the urban source region. From the shift in the size distribution of the particulate matter between Chicago (IIT) and South Haven, it was evident that the coarse particulate matter was being depleted (by dry deposition) as the aging air mass was advected over the lake to the downwind monitoring site in South Haven. As a result of both dispersion and deposition, the concentration of some compounds, such as vapor and particulate mercury, decreased rapidly to the regional 'background' levels within a short distance from the urban/industrial source areas.

During periods of flow from the north and northwest (14, 15, 24-27 July 1991), pollutant concentrations measured at Chicago, South Haven, and on 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 IIT in Chicago is only 1.6 km from the lake, the higher levels observed at Kankakee suggest an impact due to source(s) between the two sites (e.g. in southeast Chicago/Gary area).

Concentrations of the more reactive compounds, such as many of the PAHs, were uniformly higher concentration at IIT when compared to the other three monitoring sites. Also, concentrations of carcinogenic compounds such as benzo(a)pyrene and indeno(1,2,3-c,d)pyrene were approximately 10 times higher than the other sites. Dispersion, deposition, and transformation of the compounds are responsible for these lower concentrations. 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. At Kankakee, there is an apparent impact due to combustion processes, as evidenced by elevated levels of naphthalene and the peak concentration of benzo(a)pyrene measured at Kankakee on 17 July 1991. Concentrations of several compounds, such as naphthalene, acenaphthylene and retene exhibited somewhat similar concentrations between sites, which indicates a more regional source distribution. Since these compounds are predominantly found in the vapor phase in the atmosphere, their lifetimes may be appreciably shorter than that of the larger molecular weight compounds associated primarily with the particulate phase.

The ambient concentrations of most of the PCBs measured at IIT were at least a factor of 3 greater than at the other measurement locations. Also, total PCB concentrations at IIT were slightly higher than many of the reported PCB measurements in the Great Lakes region during the last 5-years (Table 5-13). There were two exceptions to this. First, the concentrations of low molecular weight PCBs (2-PCB and Total mono-PCB) measured on the R/V *Laurentian* and in South Haven were 4 times greater than the concentrations observed at IIT when flow was out of the east from Michigan. This is an interesting finding, especially since quantification of these low molecular weight PCBs is most likely an underestimate due to their high volatility and inherent difficulty to be captured quantitatively. Second, the concentration of PCBs measured over the lake were greater than measurements taken in Kankakee and South Haven.

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 urban Chicago area downwind to South Haven. This implies a strong concentration gradient of PCBs around Chicago with rapid dispersion of the already relatively low levels of these compounds. A similar trend was observed for mercury. Dispersion alone results in concentrations of these compounds at levels too low to detect with adequate precision within a short distance from the source(s). However, the low levels of these compounds does not imply that they are not important with regard to the

problem of deposition. On the contrary, the deposition of picogram and nanogram quantities of pollutants such as mercury and PCBs which bioaccumulate in the food chain are currently believed to be responsible for a substantial portion of these toxins entering the Great Lakes (Strachan and Eisenreich, 1992).

The majority of the pesticides/herbicides quantified during the LMUATS were highest on average at Kankakee. Notable exceptions were Aldrin and Simizine, which were found in higher concentrations at IIT than at the other 3 sites; and DDT (and its derivatives) which were greatly elevated primarily at the South Haven site. Chlorpyrifos had similar concentrations at Kankakee and South Haven and Mirex had similar concetrations at IIT and Kankakee. The elevated mean determined for several pesticides at Kankakee is largely due to samples collected on 29 July, and 2, 5, and 6 August 1991 which were highly elevated in a-HCH, y-HCH, hexachlorobenzene, Mirex, y-chlordane, and Dieldrin. Under certain meteorological conditions (e.g. strong southwesterly flow), it is possible that elevated concentrations of some pesticides in the Kankakee region are serving as an important source of these compounds to the lakes. Average concentrations for many currently used pesticides/herbicides (e.g. atrazine) are 2 to 3 times higher on average at Kankakee than at IIT. Current pesticide use in areas along the Michigan coast, especially in the case of aircraft application, may contribute substantially to the total burden of these compounds to the Great Lakes. Significant concentrations of many of the pesticides were observed over-water both in the northcentral portion of the lake (at the 100m station off Muskegon) as well as offshore of Chicago. For most of the pesticides, concentrations varied dramatically by location and magnitude on the basis of regional crop distribution, pesticide use patterns, and application requirements. Emissions from these source areas will depend on the properties of the pesticide and evaporation, which are largely controlled by precipitation and temperature.

Some pollutants had higher concentrations at the upwind (Kankakee) site and the downwind (South Haven) site as a result of local emissions (present and historical) in these locations. Kankakee experienced the highest mean concentration of fine mass as well as several of the lighter elements such as AI, Si, S and CI in the fine fraction. In addition, the mean fine Se concentration was highest at Kankakee, indicating that the regional coal combustion influence has a dominant impact on this site. Observations of particulate matter measured during the study indicate that locations such as Kankakee are highly susceptible to frequently elevated pollutant levels as a result of transport from several large point sources as well as strong regional source areas. The findings indicating the apparent importance of few large point sources was somewhat unexpected with the cement producing facilities in Oglesby, IL 40 km west-northwest of Kankakee, and the many coal-fired power plants distributed in the southern Illinois region. These sources make selection of a non-polluted 'upwind' site for Chicago measurements very problematic.

One of the most unexpected and important findings of the LMUATS was the discovery of significantly elevated ambient concentrations of DDT, DDD and DDE in South Haven, MI. The concentrations of the parent 4,4--DDT compound in samples collected at South Haven are significantly elevated above other reported values. The levels of the daughter compound, p,p'-DDE, are an order of magnitude greater in concentration than previously reported total DDT levels. These high levels have been confirmed by further studies at this site during 1992-1993 (Keeler, unpublished data). The average DDT DDE concentration ratio measured in South Haven is 0.3. Since the concentration of the DDT breakdown product is three times that of the parent compound; this provides sufficient evidence that levels observed are probably due to release of previously applied DDT. The time for degradation of DDT to DDE is slow enough to implicate re-emission of a much earlier DDT application as the source of this compound. While the levels of DDT, DDD, and DDE, were interestingly high during the LMUATS only at South Haven it should be noted that the levels continue to be elevated at this southwestern Michigan site today. Samples analyzed for Semivolatile Organochlorine (SOCs) compounds, including DDT, as part of a Michigan Great Lakes Protection Fund sponsored project, confirm that the elevated levels during the 1-month study in 1991 were not anomalous in nature or due to a one-time application of the banned pesticide (Keeler, Monosmith, and Hermanson, unpublished data). The elevated levels of DDT seen in South Haven are not observed at the other Michigan sites located across the state (Ann Arbor, Pellston, or Deckerville).

The atmospheric chemistry of the pollutants as they are advected over the water from source regions including the Chicago/Gary urban area is extremely complex. Measurements made during LMUATS suggest that when transport is from the southwest, over-water measurements of aerosol acidity (H⁺), and the H⁺ to SO_4^{2-} ratios indicate that the sulfate transported from upwind sources remained largely unneutralized (ratio close to 1 on the R/V Laurentian), and not totally neutralized in South Haven (average ratio of 0.4). The aerosol acidity has been hypothesized to have a large impact on the composition, solubility, and biological availability of toxic species as they are deposited from an air mass advected from a source region out over the lakes. Cadmium samples

taken using Hi-volume samplers taken during the LMUATS were analyzed to determine the water soluble and acids soluble fractions of this toxic metal (Hashim, J., 1993). The water soluble fraction of the Cd was found to increase with increasing aerosol acidity measured concurrently. The highly acidic air masses are also accompanied by highly oxidative conditions caused by increased concentrations of ozone found in the air masses as they impact the downwind shore. Air masses that arrived in South Haven after transport from the southwest were often found to contain the chemical reactants involved in complex oxidations involving both inorganic and organic compounds. Ozone levels in South Haven exceeded the NAAQS on several days, reaching 158 ppb during the period from 16-22 July which resulted from southwest transport.

2.2 Source Categories Responsible for Pollutants Measured

2.2.1. Sources of Particulate Mass and Trace Elements

Sources and source categories for a subset of the HAPs measured were assigned based on specific source tracer species and emission profiles determined from previous studies. This information was then used to interpret the results from principal component analysis, chemical mass balance modeling, and other approaches such as ratios of specific tracer compounds and elements, and individual particle analysis by scanning electron microscopy.

Through careful review of extensive work performed by Sweet and Vermette (1992, 1993) and through discussions with emissions and permit specialists at the State of Illinois and other County Agencies, the major pollutant sources in Illinois, and the major urban/industrial areas in the southern Lake Michigan Basin including Chicago, can be inventoried. Among the major hazardous pollutant sources in the region are iron and steel manufacturing, petroleum refining, municipal waster incineration, coal-fired power plants, plating industry, and non-ferrous metal industry.

The influence of the iron-steel industry on the composition of the measured aerosol during was clearly observed. The Fe concentrations in both fractions of the PM10, were elevated, at all 3 sites and are above the contribution that would be expected from windblown dust. Analysis of the IIT fine fraction trace element data using principal component analysis yielded four dominant source categories: iron and steel manufacture, soil derived components, metals industry, and a regional coal-combustion source dominated by sulfur. A secondary Al smelter located in the St. Louis area may be the

source of elevated concentrations of several metals, in addition to Al, measured at the land-based sites on several occasions.

At Kankakee the factor analysis results were less clear identifying a soil-derived component, mixed metals source component, and the dominant regional sulfate component. The factor analysis results at South Haven included a three factor model with iron and steel emissions, resuspended soil and the regional sulfate as the dominant contributors to the fine mass measured at South Haven.

The chemical mass balance approach applied to the IIT measurement data used source categories based on the U.S. EPA data base SPECIATE in conjunction with source profiles published by Vermette *et al* (1990). For the days during which the predominant flow was from the southwest, this model was able to explain 41-69% of the coarse mass with the largest contribution from crustally derived material, 12-19% was due to limedust, 3-5% was due to fugitive steelyard emissions and 1-2% was due to incinerator emissions. However, due to the complexity of the airshed and the lack of appropriate source profiles for many of the previously defined major source categories, the model could not effectively explain the fine mass measured at IIT.

The episode of elevated PM10 observed from 16-22 July is also seen in the time series plots of fine Fe, Mn, and Zn, which are marker elements for iron-steel combustion. The levels of these elements are higher both at IIT and South Haven during the period 16-20 July. This would suggest that the steel plants in the Gary/southeast Chicago area are the most important contributor to the levels of these metals measured in South Haven. On 21 July the concentrations of Fine Fe are elevated at both Kankakee and IIT in Chicago but not at South Haven. This is due to a stationary front sitting between South Haven and Chicago which meteorologically cut South Haven off from the dominant southerly flow to the sites south of the front. The levels observed at the 3 land-based sites on 22 July for the iron-steel related elements are all elevated. The highest concentrations are first observed in Kankakee. This is consistent with the mixed layer trajectories for this day which meteorologically "connect" Kankakee with Chicago and South Haven. The elevated concentrations of iron-steel plant marker elements were again seen on 5-8 August.

In order to determine the relative impact of combustion sources for some trace elements measured at the sites versus the crustal components, the ratios of Al/Si, K/Fe, and Fe/Si were calculated. The Kankakee site appears to be impacted by a combustion source emitting Al in the PM10 range. The fine Al/Si concentration ratio for South Haven is also elevated above the crustal average at 0.80. This average is strongly influenced by the extremely elevated Al concentration measured on 2 August which comprised more than half of the mean. If this one sample were removed, the fine Al/Si ratio would drop to 0.4, which is closer to the IIT ratio and the crustal average. In addition, the ratios suggest that a source or combination of sources of fine Fe is also contributing to the Fe observed at all of the sites. Except for the coarse Al/Si ratio at Kankakee the remaining concentration ratios are similar to the crustal average, suggesting that the coarse-fraction aerosols are primarily of soil or crustal origin. This allows for the utilization of the crustal ratios for these elements in investigating the origin of other elements which are of a mixed soil and anthropogenic origin.

Sources of vapor phase Hg measured at IIT were described using a 4-component model. The majority of vapor phase Hg was explained by the factor which indicated iron and steel sources. A smaller amount of the variability in the data was accounted for by the regional sulfate and soil components. Two important findings of this study are that coarse particle Hg can be measured in both urban and rural locations; and that the form, and perhaps the reactivity, of the particulate Hg seems to vary depending upon the source and meteorological conditions. Since the study on Lake Michigan, data indicate that the particulate Hg is not *always* submicron in aerodynamic size but can be found with super-mircon particulate matter. As a result, some dry deposition estimates have probably underestimated the dry deposition of this toxic compound.

In order to verify the statistical conclusions of source type, scanning electron microscopy was utilized on a subset of samples collected at IIT to describe individual particles in terms of the morphology and their elemental composition. This analysis, although carried out for only 6 samples, lends strong evidence to support many of the suspected source types including iron and steel, coal combustion, incineration, Al production, diesel emissions, and resuspended soil or urban and dust. The use of SEM points to areas for future study and has implications for attempts to model the deposition and chemical characterization of the aerosols under study. The complexity of the particulate matter is evident in the photomicrographs generated by SEM. The long chain Fe spheres, proliferation of sulfate aerosols, soot conglomerates and intricately patterned salts and other crustal elements illustrate the complex nature of the mixture that must be sorted out in trying to understand the urban atmosphere.

2.2.2. Sources of Organic Compounds

Recent studies of Vermette *et al* (1992) and Sweet and Vermette (1992) indicate that sources for organic compounds in the region of Illinois encompassing the Kankakee site include rubber reclaiming, petroleum refining, chemical manufacture and hazardous waste incineration.

Sources of the specific PAHs quantified in this study, include a multitude of stationary and mobile combustion sources. Most of the source apportionment techniques used in the past to delineate sources of trace elements are difficult, or at best problematic, to apply to PAHs. An attempt was made in this report to compare results of ratios of several of the more stable particulate PAHs to those ratios observed by other investigators in order to determine source signatures for gasoline exhaust and diesel exhaust. Although some generalizations can be made, however, much more extensive work is required before conclusive statements can be postulated concerning the origin of the PAH aerosols and gases quantified in an urban air mass.

In general, the concentration ratios indicate that PAHs measured in Chicago at the IIT site (benzo(g,h,i)perlyene, coronene, benzo(g,h,i)pereylene, indeno(1,2,3-c,d)pyrene, benzofluoranthenes, crysene, benzo(e)pyrene, benzo(a)anthracene and benzo(a)pyrene) have a substantial contribution from mobile sources including diesel and gasoline exhaust. The ratios of PAHs calculated using the Kankakee, R/V *Laurentian* and South Haven concentration data, were less similar to those found by Li and Kamen or Tong and Karasek indicating that at those sites, sources for the higher molecular weight PAHs are likely due to transport from distant sources or other local emissions, rather than predominantly a result of local mobile emissions.

Sources for pescicides measured at Kankakee and South Haven are due to current or historical application to local crops. Both Kankakee and South Haven are intensively farmed for a variety of crops, mainly corn, beans and wheat in the Kankakee area and fruit and table vegetables in the South Haven area. Historical use and subsequent re-emission of DDT appears to continue to be a major source of this compound to the atmosphere at South Haven.

In the extremely complex airshed encompassed in the LMUATS study, any one of the techniques may not independently yield all of the necessary information regarding sources. Using additional hybrid modeling techniques such as Quantitative Transport Bias Analysis should yield important interpretation to the data collected during LMUATS.

2.3 Urban Input of Hazardous Air Pollutants

The measurements of hazardous air pollutants documented in this study provide evidence to support the hypothesis that urban areas are significant contributors to atmospheric levels and, therefore, significant contributors to deposition of HAPs to adjacent water bodies. The data also indicate that for some pollutants such as Hg and PAHs, elevated concentrations and strong horizontal concentration gradient exists downwind of a large urban/industrial area.

The near field input of potentially toxic pollutants to the Great Lakes from onshore urban/industrialized areas is likely elevated above levels found in the midlake regions as well as those off-shore from rural, non-industrialized areas. The Clean Air Act Amendments required that the sources and rates of atmospheric deposition of hazardous air pollutants be investigated and determined. Critical to determining the rate of deposition of atmospheric compounds is characterizing the impact of local urban plumes on the total toxic burden to the Great Lakes.

2.3.1. Differentiating the Contribution of Toxic Pollutants To Lake Michigan From Chicago/Gary versus the Contribution From Upwind Locations

During the LMUATS, it was discovered that the concentrations of many hazardous trace compounds at the "upwind" site at Kankakee were elevated on occasion above those concentrations measured in Chicago (IIT). Therefore, it was hypothesized that pollutant sources upwind of Chicago/Gary must be contributing to the total loading of atmospheric pollutants to Lake Michigan. In order to separate the source contribution of the regional component from the Chicago/Gary urban input to the lake, tracer species (or a source fingerprint of some type) would be needed by which the upwind contribution could be distinguished, allowing it to be identified after mixing with the urban aerosol. This is a difficult and complex task and has been accomplished only in part by the techniques utilized in this study. There is a pronounced episode of elevated PM-10 concentrations from 16-22 July where the levels exceeded 80 μ g/m³ at both Kankakee and Chicago (IIT), and exceeded 60 μ g/m³ at South Haven. Mixed layer trajectories reveal that the stagnant air masses were transported from the southwest during this period. The maximum PM-10 concentrations were observed on 19 July with air mass transport from the St. Louis area to each site. The PM-10 concentrations at each site peaked again on 2 August when winds again were light and from the southwest.

Perhaps more interesting then the elevated PM-10 levels during the study is the change in the aerosol size distribution after transport from Kankakee to IIT to South Haven as reflected by the fine fraction of the PM-10. One objective of the LMUATS was to capture an episode where air mass transport "linked" the upwind site (Kankakee) with the urban site (IIT) and the over-water transport site (R/V Laurentian) and the downwind site (South Haven). The episode from 16-23 July provided the perfect opportunity for linkage between 3 of the 4 sites with the research vessel which was, unfortunately, not on station during this period. However, at the beginning of the episode on 16 July, about 78% of the PM-10 observed at Kankakee was in the fine fraction which is typical of a regionally transported aerosol. The PM-10 level and the percentage of coarse particulate matter at Kankakee rose from 18-22 July as a result of transport from sources upwind of Kankakee such as the St. Louis and East St. Louis urban/industrial area. As the air mass moved into Chicago the concentration of the fine particulate mass dropped due to dispersion. The addition of coarse mass occurred from the activities in the urban/industrial area. The PM-10 levels observed at IIT were only slightly lower than those measured in Kankakee but about 40% of the PM-10 was now in the fine fraction. As the air masses continued across Lake Michigan, without additional sources en route to South Haven, the fine fraction reasserted itself as the dominant portion of the PM-10. This is what one typically observes at a site influence_ primarily by long range transport. The PM-10 levels in South Haven during the episode were about 20 μ g/m³ less on the average than the levels observed concurrently at Chicago (IIT). This decrease can be largely explained by The change in the particle size distribution, however, cannot simply be dispersion. explained by dispersion en route. It appears that larger particles observed in IIT do not make it to South Haven and are probably lost by deposition. Therefore, the PM-10 is primarily made up of fine particles in South Haven after over-water transport. This loss of large particles probably would have been accentuated if the particles greater than 10 μ m in size had been sampled (Holsen et al., 1993).

For some species, such as elemental carbon, differentiation of the urban plume from upwind sources is simplified. During the transport period 16-22 July, the elemental carbon levels observed in Kankakee do not indicate an impact from upwind sites and are much lower than those levels at Chicago. This suggests that local combustion sources in Chicago are responsible for the elevated levels measured there as well as at the downwind site in South Haven.

More extensive source profiles for a variety of industrial types in both St. Louis and Chicago would be needed to quantitatively differentiate the regional source contributions from the urban aerosol. In lieu of this deficiency, routine monitoring data from the States of Illinois, Indiana, Wisconsin, and Michigan were obtained to provide better spatial coverage for measurements of particulate matter. The more comprehensive set of PM10 and TSP measurements made in Illinois during the LMUATS period reveal that there are more substantial sources of fine and coarse particulate matter in the vicinity of the Kankakee site.

2.3.1. Relative Importance of the Urban Input of Toxic Compounds to the Total Atmospheric Contaminant Loading to Lake Michigan

It is unknown how much of the toxics in the air over the lakes originated from sources near (< 20 km) the lake shoreline versus those originating from sources further upwind. Evidence suggests that during periods of southwest transport sources upwind of Chicago were impacting this site, thus entering the air mass being advected over the lake. An important goal of the LMUATS was to supply data that would provide an opportunity to compare model results with measurements of deposition in order to ascertain the degree of agreement between them. This study provides insufficient over-water HAPs measurements, due to poor meteorological conditions, to adequately evaluate deposition models. The data do provide critical information regarding whether the model results are reasonable.

The relative contribution of the coarse and fine fractions to the overall particle loadings from the urban sources is a very complex and difficult problem to address. The extremely uniform PM10 and particulate sulfate concentrations measured from southern Illinois across the lake into Michigan suggest that the fine fraction material is not the result of the Chicago/Gary urban emissions. The course fraction of the PM10 and coarse particles greater than 10 μ m may be the dominant fraction to understand in relation to urban deposition. One study of particulate mass distributions and dry deposition flux in Chicago and over-water during the LMUATS concluded that the majority of the particle loading to the lake is the result of particles greater than 6.5 μ m (Holsen *et al.*, 1993). These conclusions are supported by measurements of the size distribution of the aerosol system in Chicago.

The dry deposition fluxes to Lake Michigan for selected trace metals associated with 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 the deposition flux over the lake as a function of meteorological parameters, particle size distribution, parameters controlling the physics of water waves, and the type and location of sampling sites. Significant temporal and spatial variations in the deposition velocities were obtained for trajectories traversing lake Michigan from one day to the next. The results of the dry deposition modeling indicate that one must not assume that the deposition flux, calculated using dry deposition velocities, to be constant in time or space for the total area of the lake. A large uncertainty in the deposition flux is associated with assuming constant deposition velocities.

Holsen et al. (1993) estimated that fine particles are responsible for about 2% of Pb and 0.6% of Ca in the total deposition flux at the Chicago (IIT) site. The Pb and Ca deposition flux associated with coarse particles with an aerodynamic diameters in the range of 2.5 to 10 µm accounted for about 11.5% and 8% of the total fluxes of Pb and Ca, respectively. Based on these estimates, the dry deposition flux to Lake Michigan during the LMUATS by the fine and coarse fraction of the PM10 calculated by Holsen et al. (1993) and by this study are shown in Table 7-3. The higher ratios for the coarse fraction may be due to (a) particle growth in a humidity gradient (not considered in this study) when the air parcel crosses the lake leaving submicron particles in the inertial deposition range, yielding higher deposition fluxes; (b) position of the sampling station in the plume; (c) statistical uncertainty related to deposition measurements; (d) small representativeness of measured fluxes in one point for the whole lake area; (e) the obvious limitation of annual estimates discussed by Holsen et al. (1993) in which deposition fluxes measured during the summertime are assumed valid throughout 1991; and (f) different deposition flux distributions for particle size obtained in Chicago (IIT) (used in this comparison) might be obtained by sampling directly on Lake Michigan.

To estimate the urban contribution of the deposition loading to Lake Michigan and to evaluate the choice of sampling site (i.e., rural, urban/industrial) and its location in the basin on the deposition estimates, the ratio between the calculated Chicago (IIT) and
South Haven dry deposition loads for trace metals associated with fine and coarse particles was calculated. The ratios for most trace metals in the fine fraction are in the range of 0.6 to 3 with the exception of total Hg which has a ratio of 16. The high ratio for total Hg is probably due to strong local sources in the Chicago area since ambient Hg concentrations measured in Chicago (IIT) are about 10 times higher than those measured at South Haven.

Using the hybrid modeling approach to estimate dry deposition fluxes, it was determined that Si had the highest deposition flux during the LMUATS (360 tons) for trace metals primarily of soil or crustal origin, followed by Ca (254 tons), Fe (160 tons) and K (58.3 tons). The deposition flux of Al (150 tons) was the highest loading followed by 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 for specific compounds to Lake Michigan contributed by sources in the urban area of Chicago/Gary is estimated to be 2 to 10 times greater than that from regional sources. A factor of 10 increase in the deposition flux of many of the SOCs attributed to the Chicago urban/industrial was also determined.

2.4 Comparison of Simultaneous Measurements Over-Land and Over-Water

The question of whether it is reasonable to utilize shoreline or inland monitoring locations to represent over-lake deposition is critical to our ability to accurately assess the atmospheric deposition component of the toxics loading to the Great Lakes. This question can only be answered by a systematic study of the complex meteorological conditions which are necessary to parameterize the deposition process. This project is only the first step in the development of a program to study the dynamics of toxic pollutant transport over and deposition into large lakes. Since historical data collected in the Great Lakes utilized land-based monitoring locations, this study also provides an initial comparison of the validity of land-based measurements with those made over-water. Due to the expense of ship time, the number of days of concurrent over-water and over-land measurements were limited. The ship was on-station approximately 20 miles west of Muskegon, MI for an initial 'shake-down' cruise and the ship was on-station 5-10 miles off-shore from Chicago/Gary for two periods later in the 30 day intensive. The mixed-layer trajectories associated with these sampling days were given in Figure 5-6.

2.4.1. Individual Cruise Descriptions

2.4.1.1. On-Station Off-Shore from Muskegon, MI 10-11 July 1991

During the sampling period off-shore from Muskegon, MI predominant easterly flow advected pollutants from several sources in the Muskegon and Grand Rapids, MI area to the lake. Elevated concentrations of Se, Zn and low molecular weight PCBs were measured, in addition to one highly elevated sample with As. The concentrations of SO_4^{2-} , NH₃ and HNO₃ were comparable on the R/V *Laurentian* and at South Haven. The concentration of retene observed on the R/V *Laurentian* during this cruise was elevated above the level observed simultaneously at South Haven, potentially indicating impact from a combustion source utilizing wood or other vegetative material upwind. Levels of coronene observed over-water during this period were similar to the observed measurements in South Haven, indicating similar impact due to motor vehicle emissions or other sources.

Average concentrations of several pesticides measured during this cruise were similar on the R/V *Laurentian* and at South Haven (α -HCH, trans-nonachlor, Mirex, Chlordane, Aldrin, Metolachlor, γ -Chlordane and α -Chlordane), with a notable elevation in *Laurentian* levels observed on 12 July. Concentrations of DDT and its breakdown products as well as Dieldrin and Chlorpyrifos were highly elevated in South Haven. Atrazine was the only pesticide measured which was elevated in concentration on the *Laurentian* (11 July 93). Low molecular weight PCBs (total mono-PCB and 2-PCB) were also measured in elevated levels on the *Laurentian* on 11 July as well as in South Haven.

Analysis of samples collected for organic compounds were not analyzed from Chicago (IIT) or Kankakee during the first cruise since funds available for this very expensive analysis were limited. The prevailing transport pattern during the period indicated that this data would be of less value than for different time periods during the study.

2.4.1.2. On-Station Off-Shore from Chicago/Gary, 23-27 July 1991

For the first sampling period off-shore from Chicago/Gary, levels of the trace elements measured aboard the R/V *Laurentian* were similar to or slightly lower than those levels monitored at Chicago (IIT), largely due to the prevailing northerly flow that the vessel received while on station. Since there are no large sources in the lake and the

upwind fetch from the sampling point in southern Lake Michigan is 100s of kilometers of open water, the levels of most pollutants would not be expected to be very high. Exceptions to this were levels of vapor phase and particulate mercury as well as coronene and naphthalene which were greatly elevated at Chicago (IIT) in comparison to those concentrations observed on the R/V *Laurentian*. As a result of westerly winds from the greater Chicago are, the daytime sample on 24 July aboard the R/V *Laurentian* revealed elevated Pb levels, both fine and coarse, as well as elevated Zn.

Concentrations of acidic sulfate aerosols and were comparable at South Haven and on the R/V *Laurentian* during this period. Gaseous NH_3 concentrations were elevated on the R/V *Laurentian* above the levels observed in South Haven especially on 24 July when mixed layer flow was out of the west-southwest to the ship. Concentrations of NH_3 and other species associated with urban activities were higher during one twelve hour sampling period.

2.4.1.3. On-Station Off-Shore from Chicago/Gary, 5-7 August 1991

During the second of the two cruises on which the R/V *Laurentian* was located off-shore from Chicago/Gary, prevailing flow was from the east-southeast. These conditions provided direct measurements of the transport of toxic compounds to the lake. Increased levels of fine Fe and Mn, impacted by the plume from the Gary steel industry were evident.

The PAH concentrations appear to mimic the behavior of atmospheric Hg, being about three to ten times higher at Chicago (IIT) than over-water. The mean pesticide concentrations measured at Chicago (IIT) and aboard the R/V *Laurentian* are within a factor of 2 of each other with some being higher at Chicago (IIT) and others being greater on the R/V *Laurentian*. Atrazine and Simazine were both found in greater concentrations over the water than at IIT. The concentrations of pesticides observed in South Haven and in Kankakee are generally much higher than those observed at either Chicago (IIT) or over the lake. This is not surprising as both sites are in the middle of large agricultural and fruit growing areas. Local application of pesticides strongly influences the levels seen at a site and therefore, prevent a single land-based site from being used to estimate the overwater levels with any certainty. However, on selected occasions, the concentration of some pesticides measured on the R/V *Laurentian* were determined to be greater than the concentration measured simultaneously at any of the land sites. This occurred on 5 August for the pesticide Atrazine and on 7 August for γ -HCH. This finding may be the

result of special meteorological conditions that allow for the advection of concentrated pesticide-laden air masses over the water.

Also of interest is a second observation of elevated levels of low molecular weight PCBs on board the R/V *Laurentian*, with high concentrations of 2-PCB and total mono-PCB measured on the 5 and 7 August.

2.4.2. General Conclusions Regarding Over-Water Measurements

For the two periods when the R/V *Laurentian* was on-station, average fine mass levels measured at the Chicago site and over-water were comparable. These measurements suggests that estimates of deposition for many compounds would have been fairly accurate using data collected at Chicago (IIT). The fairly close agreement in measured values for most species may appear to indicate that the land-based site would function as an adequate surrogate for over-water measurements of trace elements.

The major flaw with this assumption is that while the ship was on-station off Chicago/Gary, two different and fairly uncommon summertime meteorological patterns were observed: prevailing wind flow was strong and from the northwest during the first cruise (providing a relatively non-polluted air mass to both the R/V *Laurentian* and Chicago (IIT)) and transport to the ship was from the east southeast during the second cruise (providing a relatively polluted air mass to the R/V *Laurentian*). The average of these two events causes the over-water and Chicago based site to appear to experience quite similar pollutant levels. In order to adequately assess the validity of utilizing land-based monitors instead of over-water sites a representative sampling of several meteorological conditions that reflect the complex dynamics of Lake-meteorology would have to be obtained.

For example, in July 1990 during the preliminary study for the Lake Michigan Ozone Study, a pollutant plume was observed as it traveled up the shoreline of Michigan controlled in a tight, relatively non-dispersed plume. The role of these meteorological phenomena (and others like it which provide for capture of a pollutant plume near the lake surface as it is advected away from the source) in the deposition of toxic compounds to the Lake may be highly significant. It is often the case that a few isolated instances with a particular set of meteorological and source influence characteristics can be responsible for major pollutant episodes.

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Important exceptions to the general finding of comparable levels of fine mass are the striking differences in measured concentrations of Hg, several PAHs and pesticides and noticeable differences in coarse mass which could greatly affect calculations of total loading to the lake.

Generalizations regarding over-water measurements cannot be made from the limited data collected in this initial study. The data indicate that over-water measurements involve a very special set of circumstances that can, on occasion, play an important role in the deposition of toxic compounds to the water. Further work in this area will help to determine if taking into account seasonal differences in dominant meteorology and atmospheric chemistry and transport to land based sites can be used as an adequate surrogate for over-water deposition calculations on a yearly average basis. If the uncertainty measured for such estimates turns out to be quite large, the air sampling community may have to accept the burden of collecting this critical data in the most accurate manner possible: taking representative samples over-water for limited portions of each season, or potentially setting up unmanned monitoring stations for some of the critical pollutants that would at least allow extrapolation to other compounds and would provide accurate measure for a few of the species of interest.

Chapter 3

Recommendations

This project was a first step in the study of the dynamics of toxic pollutant transport over and deposition into large lakes. Our initial effort was aimed at establishing the feasibility of providing accurate and representative air samples and gradient measurements of toxic contaminants and nutrients over Lake Michigan. Among the highest priority research needs identified are: (1) measuring onshore and offshore deposition rates simultaneously to determine whether or not on-shore measurements represent deposition to the bulk of the lake surface, and (2) characterizing the impact of local urban plumes on the total toxic burden to the Great Lakes. Both of these research issues are critical to the design of long-term monitoring networks to determine rates of atmospheric deposition to the lakes.

This investigation provided preliminary information to assess these questions. Because of the complexity of the meteorology in the lake shore environment and the multitude of sources coupled with the limited number of days of over-water measurements, the ability of this study to adequately compare over-land versus over-water measurements was limited. Some changes in the design and implementation of this study are proposed in attempt to optimize similar research attempts made in the future. In addition, future research needed to answer the original study goals is outlined. During the course of this investigation, additional objectives were identified and are described below.

3.1. Proposed Changes in the Study Design

Changes in the present study which would enable a more complete description of the airshed investigated include an improved location for an upwind location, improvements in analysis, and most importantly, additional and flexible periods aboard the research vessel.

In light of the observation that Kankakee was often subjected to several, varied sources in the Illinois area, an alternative 'upwind' control site should be selected in the region.

Alternatively, if the source characterization for the Illinois/Indiana region is better described, specific source influences on the upwind sites may be subtracted from the 'background' input to the urban measurements.

In order to obtain accurate and reliable measurements of all species being measured, sampler deployment, cleaning, analysis should be pre-tested and field blanks collected to confirm the ability to obtain accurate quantification of the levels required. In addition, the first samples collected at each site should be analyzed and results reported immediately to the project officer and principal investigator in order to confirm that samples are being collected and analyzed properly. Implementation of this procedure could have potentially avoided the loss of the majority of the VOC data collected for this study.

Additional and more flexible time aboard the research vessel is imperative for optimizing the sampling performed over-water during selected meteorological conditions. This flexibility is essential to our ability to assess the question of over-water versus over-land measurements.

Additional measurements such as analysis of both particulate and vapor phase SOCs including pesticides, PCBs and PAHs, as well as other urban tracers, e.g. CO, at each of the sampling sites would have helped in the modeling portion of this project. An additional site on the west-side of Lake Michigan and additional measurement sites between IIT and Gary, IN would allow for a better estimation of the total deposition to the southern portion of the basin.

3.2. Future Research Needed to Meet the Original Objectives

The data also indicate that for some pollutants a high concentration and strong gradient exist over the water downwind of an urban area, which points out the importance of future investigations to include urban site monitoring in all proposed studies of the transport and deposition of hazardous air pollutants to the lakes.

In order to accurately quantify the urban input of toxic contaminants to Lake Michigan at least one additional monitoring location in Chicago/Gary region is necessary. This site is critical to accurately estimating the loading to the lake during periods of south and southeast flow. A measurement site closer to the industrial sources would allow us to better characterize the size range of particulate matter emitted from the iron-steel coke ovens, oil refining and other sources in the vicinity. If, as it is suspected, the large particle mass is an

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extremely important contribution to deposition in the southern portion of Lake Michigan, a monitoring location in the heart of the industrial processes would greatly improve estimates of loading to the lake.

To improve calculations of deposition and attempts at deposition modeling, both theoretical and experimental research is needed to improve direct measurements to the water as well as improvement of computational techniques to determine the impact of dry deposition of atmospheric contaminants to water bodies. It is intrinsically difficult to compare the estimated deposition fluxes from this work with those obtained by others based upon measurements made with surrogate surfaces, or with estimates obtained using limited point measurements at a few land-based sites, which may not represent the real physical situation at the air-water interface during the transfer of particles from the atmosphere to the water surface and vice versa.

3.3. Future Research Needed to Meet Additional Objectives

Additional Objectives

1. Developing an accurate emissions inventory for the compounds of highest priority.

2. Obtain a better source emissions library for modeling by performing stack testing and source sampling of current sources including motor vehicles.

The urgent need for accurate information regarding source emission profiles for each of the major source types in the Great Lakes Basin cannot be overemphasized. In the absence of such information, models of transport, chemistry and deposition provide only crude approximations of the total load and potential impact of the release of hazardous atmospheric pollutants. In addition, the ability of legislators to formulate and implement appropriate control regulations is highly dependent on identification of specific sources and the impact of these emissions.

3. Perform research to improve parameterizations of the depositional processes that can be utilized in both determinisitic models and hybrid receptor-deposition models as described in this report.

This study was designed to serve as an intensive initial investigation of the importance of atmospheric transport and deposition of hazardous air pollutants to Lake Michigan. The data generated provides a unique resource for the design of future work in the Great Lakes.

- 4. Characterize the large particle (> $10 \ \mu m$) contribution to toxic deposition, particulary in and near urban source areas.
- 5. Further evaluate the importance of over-water vs inland vs shoreline monitoring locations.
- 6. Develop re-emission estimates for Hg, PCBs, and pesticides that have been banned or discontinued in the U.S.
- 7. Need to better understand the gas-particle partitioning of semi-volatile compounds between the source and the receptor site.

Chapter 4

Methods

4.1. Meteorological Measurements

4.1.1. Tower Platform

Meteorological measurements were taken from a tower located 10 feet off the bow of the ship. Figure 4.1 shows the design of the bow tower used in the study. The tower assembly consisted of two main components: a retractable arm and a five-meter aluminum tower. The retractable arm was designed to allow the tower to be pulled back onto the ship's deck when instrument maintenance was necessary. The arm was attached to the tower via a hinge, which allowed the tower to be tipped back before being slid back onto the ship's deck.

The tower itself was triangular in shape, with each side approximately 6 inches in length. When deployed, the tower base was two meters above the lake surface (during relatively calm conditions). The tower was guyed to the ship using three steel cables. Two cables were attached to the top of the tower, and each was attached to a side of the ship. The third guy-wire ran from the bottom of the tower to the ship's bow. Once in place, the guy-wires successfully kept the position of the tower fixed with respect to the ship, so there was not any significant twisting of the tower about either the vertical or horizontal axis. However, given that the tower was rigidly attached to the ship, significant rolling of the tower was noted due to the movement of the ship's motion, however the sensors were not available at the time of the study. As a result, other techniques were used to remove the effect of the ship's motion from the data. These methods will be discussed in the following section. The instruments that were placed on the tower are described in detail below.

4.1.2. Slow-Response Wind Measurements

Three R.M. Young wind vanes (Model 05701) were used in combination with a sonic anemometer to measure the wind field over the lake surface. The wind vanes have a specified working range of 0 to 40 meters/sec, a propeller threshold of 0.2 meter/sec and a distance constant of 1.0 meter. The wind vane has a distance constant of 1.2 meters. These instruments are widely used in many air quality measurement programs. As indicated in Figure 4-1, the vanes were placed on the bottom half of the bow tower. The vanes were spaced logarithmically (in combination with the sonic anemometer) so as to test the validity of the "log wind profile" law in the atmospheric surface layer over the lake. The lowest vane was placed such that its average height above the lake surface was 2.5 meters. The other wind vanes were then placed 3.0 and 4.0 meters above the lake surface, respectively. Wind data from these instruments were sampled at 1 Hz.

4.1.3. Fast-Response Wind Measurements

Fast-response wind measurements were made using an Applied Technologies' SWS-311/3K three-axis sonic anemometer. The ATI sonic has a horizontal measurement range of \pm 20 meters/sec and a vertical measurement range of \pm 5 meters/sec. The instrument has a specified accuracy of \pm 0.05 m/sec for wind speed and \pm 0.1 degree for wind direction. The sonic anemometer was placed on the tower so that it had an average height of 5.5 meters above the lake surface. This instrument was sampled at a frequency of 10 Hz and was recorded at this same frequency using LabTech Notebook software.

4.1.4. Temperature and Humidity Measurements

Temperature and humidity measurements were made using two Rotronic Instrument Corporation MP-100F Temperature/Relative Humidity probes. Each probe was housed in a radiation shield provided by the same manufacturer. The instrument ranges for temperature and relative humidity are -30 to + 70 °C and 0 to 100%, respectively. The specified accuracies are ± 0.2 °C and ± 2.0 %, respectively. The time constant for both sensors is listed as 10 seconds. One Temp./RH probe was placed at the base of the tower (2 meters above the lake surface), while the second probe was placed at the top of the tower (7 meters above the lake surface). The purpose of this placement was to allow for a crude measurement of the atmospheric surface layer temperature gradient.

R/V Laurentian Bow Tower Assembly



4.1.5. Carbon Dioxide and Water Vapor Measurements

The carbon dioxide and water vapor measurements were acquired using an instrument borrowed from the National Oceanic and Atmospheric Administration's Atmospheric Turbulence and Diffusion Division (NOAA-ATDD), Oak Ridge, TN. Since wave-induced vertical motion rendered the vertical wind data from the ATI Sonic unusable, we did not have such measurements to correlate with measured fluctuations in the carbon dioxide and water vapor. For this reason, the results from the measurement of these two variables are not presented.

4.1.6. Data Collection

4.1.6.1. Slow-Response Instruments

A Campbell Scientific 21X Datalogger was used to collect the data from the "slow response" instruments (temperature/relative humidity probes and wind vanes). Data were sampled at a frequency of 1 Hz, then stored as one-minute averages. The information stored includes:

- temperature and relative humidity at the 2.0 and 7.0 meter levels, and
- wind speed, wind direction and sigma-theta (standard deviation of the wind direction) at the 2.0, 2.5 and 3.5 meter levels.

This information was later converted to one-hour averages, and can be found in the Appendix.

4.1.6.2. Fast-Response Instruments

The data from the "fast response" instruments (ATI sonic anemoreter and the NOAA-ATDD's CO_2/H_2O vapor sensor) were collected using a personal computer and a commercial data acquisition software package (LabTech Notebook). Data were sampled and at a frequency of 10 Hz. Data smoothing or filtering was performed during post-processing.

4.2. Chemical Measurements

Table 4-1 summarizes the pollutants measured, sampling methods and number of species of each pollutant quantified. Because of the relatively high costs for mass analysis

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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 extracted together for each sample and were placed in cold storage. A decision regarding which samples to analyze was made after an examination of the particulate, trace element, and meteorological data.

POLLUTANT CLASS	SAMPLER	NO. SPECIES
Pesticides	PS1/PUF	10
Total PCBs	PS1/PUF	20
PAHs	PS1/XAD	19
VOCs	Canister	44
Trace Elements	Dichot	18
Carbon	FPS	2
Gaseous Hg	Au Sand	1
Particulate Hg	GFF	1
Other Inorganics	ADS	8

Table 4-1. Pollutant Measurements Made during the LMUATS.

4.3. Sampling Schedule and Operations

The EPA AREAL labs provided the majority of equipment utilized in this investigation. In addition, support staff from EPA AREAL set up sampling equipment at each of the sites, trained operators and performed field audits.

4.3.1. Schedule

The field-sampling portion of the study commenced on July 8 at all of the landbased sites and continued until 9 August 1991. Integrated samplers were operated each day from 8 AM CDT to 8 PM CDT at each site. Nighttime samples were also routinely taken at the South Haven site from 8PM - 8AM throughout the study. Mercury sampling and annular denuder samplers were operated more intensely during the 12 days that the R/V *Laurentian* was on-station off-shore of Chicago. Two six-hour samples were taken during the 12-hour daytime period from 8AM - 8PM CDT. A more intensive Hg sampling campaign was conducted at the IIT site while the annular denuders were only operated aboard the R/V *Laurentian* and in South Haven.

4.3.2. Sampling Procedures

The sampling methods utilized in this study are detailed in the Sampling and Quality Assurance Project Plan as well as in the Final Report submitted by Battelle entitled "Analytical Support for Lake Michigan Urban Air Toxics Study". These documents should be referred to for specific details of the sampling and analysis portions of this study.

4.3.3. Sampling Locations

The sampling locations utilized in the study are shown in Figure 4-2. These sites were selected after careful consideration of the data collected during the 1990 LMOS Pilot Study in which the University of Michigan participated. The limited data from the Pilot Study suggested that three sites strategically placed on-shore and at least one sampling platform off-shore would allow an initial investigation of the importance of the urban areas on deposition to Lake Michigan.

4.3.3.1. Over-water Measurement of Atmospheric Contaminants

The University of Michigan Research Vessel (R/V) *Laurentian* was operated for the LMUATS for three different sampling periods during the one-month study. The ship was positioned in two areas during the study. The sampling inlets were roughly 5 feet above the deck but off the side of the bow of the ship (which stood an additional 20 feet above the surface of the water). Sample collection took place only when the vessel was anchored which kept the bow pointing into the prevailing wind at all times.

The first cruise was a test period to make sure that all of the sampling equipment could be deployed safely from the vessel. This cruise was a two-day voyage that brought the research vessel approximately 20 miles off-shore of Muskegon, MI. The second cruise was a five-day sampling campaign that started in Grand Haven, MI with sampling at locations from 4-6 km off-shore of the Chicago/Gary area. The cruise down to Chicago took 9.5 hours on the R/V *Laurentian* and sampling occurred from 23-27 July. The last cruise occurred from 5-8 August and the sampling occurred in the same general location



Figure 4-2. Sampling Locations for the Lake Michigan Urban Air Toxics Study.

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as during the previous cruise. Extremely violent weather on 8 August forced the research vessel back into port.

4.3.3.2. Land-Based Sampling Locations

Three land-based sites were operated from 8 July through 9 August 1991. The sites were chosen to provide one upwind sampling point, one urban site, and one site downwind on the eastern shore of Lake Michigan. The upwind site chosen for the study was located at the Kankakee Regional Airport in rural Illinois (Figure 4-2). This site was chosen as the "upwind site" to provide the levels of atmospheric contaminants transported into the Chicago/Gary Urban areas with southerly or southwesterly transport. The Kankakee Regional Airport is in an agricultural area and during the period under study, the site was primarily surrounded by corn crops. The urban site was located on the campus of the Illinois Institute of Technology (IIT). This site had been utilized previously for air pollution studies and provided a central Chicago location only 1.6 km from the lake shore. The IIT site was atop a campus building which was the same height or higher than buildings in the adjacent vicinity. The downwind site was located in South Haven, MI, which was one of the LMOS Pilot Study Sites. The South Haven site was located in a rural area approximately 5 miles from the lake. The South Haven area is largely agricultural with fruit trees and vegetable produce dominating the local terrain. This site was ideal for the intensive land-based operations that were necessary for the study. The South Haven Site was the largest of the sites and duplicate sampling for all species was performed there. The inlet to the samplers was approximately 7 feet above the ground in an open field. Kankakee and South Haven were also LMOS sites which provided a complete suite of meteorological and some auxiliary air quality data to be used. Auxiliary data were also available at the IIT site. Continuous monitoring equipment were operated at the sitep providing hourly ozone (O_3) , NOx, and meteorological data.

4.3.4. Samplers

The air monitoring instrumentation employed for this project was well-tested sampling equipment that provided the high-quality data necessary to meet the project objectives. The EPA AREAL labs provided all the necessary instrumentation with the exception of mercury sampling supplies which were provided by the University of Michigan. The sampling equipment employed allowed for the quantification of most of the 14 Critical Pollutants on the IJC list, including Hg. In addition, various airborne nutrients, additional trace elements by Neutron Activation Analysis (INAA), a complete set of size-distribution particulate data for selected species over the lake, and sizedistribution measurements using scanning electron microscopy (SEM) on specially collected substrates were also collected. A list of the samplers that were employed at each location are given in Table 4-2. A duplicate sampler of each type was run at the Michigan land site for the period of the study. The particle size information obtained from the micro-orifice impactors and the SEM analysis, as well as the Hg determinations were obtained for a subset of the sampling days on the R/V *Laurentian* and one shore line site.

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/M	
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	

 Table 4-2.
 Samplers Deployed for the LMUATS.

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

4.4. Sample Analysis

Battelle Laboratory in Columbus, Ohio and Southwest Research Institute in San Antonio, TX were responsible for the analyses of the organic compounds including VOCs, PCBs, PAHs, and pesticides. Sunset Laboratory in Portland, OR performed all sample preparation and analyses for organic and elemental carbon. EPA AREAL performed the trace element determinations by X-Ray Florescence (XRF). Pollutant species measured are given in Table 4-3.

Inorganic	РАН	Pesticides	VOCs
Species		and PCBs	
Al	naphthalene	monochlorobiphenvis	trichlorofluoromethane (Freon-11)
As	acenapthvlene	α -hexachlorocyclohexane	dichlorodifluoromethane (Freon-12)
Br	acenapthene	dichlorobiphenvls	1,1,2-trichloro-1,2,2-trifluorethane
Ca	fluorene	hexachlorobenzene	(Freon-113)
Cl	phenanthrene	atrazine	1.2-dichloro-1,1,2,2-tetrafluorethane
Cr	anthracene	τ-hexachlorocyclohexane	(Freon-114)
Cu	fluorenone	trichlorobiphenvls	methyl chloride
Fe	retene	tetrachlorobiphenvls	vinyl chloride
Hg	fluoranthene	alachlor	methyl bromide
ĸ	pyrene	mirex	ethyl chloride
La	cyclopenta[c,d]pyrene	aldrin	1,1-dichloroethene
Mg	benz[a]anthracene	metolachlor	dichloromethane
Mn	chrysene	trans-Nonachlor	3-chloropropene
Мо	benzofluoranthenes	pentachlorobiphenyls	1,1-dichloroethane
Na	benzo[e]pyrene	dieldrin	cis-1,2-dichloroethene
Ni	benzo[a]pyrene	hexachlorobiphenyls	trichloromethane
Pb	indeno[1,2,3-c,d]pyrene	heptachlorobiphenyls	1,2-dichloroethane
S	benzo[g,h, 1]pervlene	4,4'-DDT	1,1,1-trichloroethane
Sb	coronene	octachlorobiphenyls	benzene
Se		nonachlorobiphenyls	carbon tetrachloride
Si		decachlorobiphenyls	1,2-dichloropropane
Sm			trichloroethene
Ti			cis-1,3-dichloropropene
V			trans-1,3-dichloropropene
Zn			1,1,2-trichloroethane
SO ₄ 2-			toluene
NO_3^-			1,2-dibromoethanc
NU ₂			tetrachloroethene
NH ⁴ '			chlorobenzene
H ¹			ethylbenzene
SO_2			mæp-xylene
			styrene
			1,1,2,2-letrachioroethane
Nn ₃			4 sthul toluono
			4-ethyl toluene
			1,3,3-trimethylbenzene
			henzyl chloride
			m-dichlorobenzene
			n-dichlorobenzene
			o-dichlorobenzene
			1 2 4-trichlorobenzene
			hexachlorobutadiene

Table 4-3.	Pollutant	Species	Measured	during	the	LMUATS.

The inorganic analyses and mercury analyses were primarily performed at the University of Michigan with the assistance of Brooks Rand Ltd. in Seattle, WA. Ultraclean room facilities operated at the University of Michigan were utilized for preparation and analyses of all mercury samples. The University of Michigan Ultra-Clean room facility is a Class 100 laboratory designed to minimize any possible trace element contamination.

In addition, Neutron Activation Analysis was performed on a subset of the dichotomous sampler filters. The INAA provided better sensitivity for many of the important elements needed for receptor modeling. By providing more accurate and sensitive determination for some critical elemental species, INAA was also performed on a subset of filters for total particulate Hg determinations. The INAA was performed under the direction of Dr. Ilhan Olmez at the MIT Nuclear Reactor Laboratory.

4.4.1. PAH Sampling and Analysis

The PS-1 samplers (General Metal Works, Cleves, OH) located at each sampling site were used to collect both particle-bound and vapor-phase PAH onto a quartz fiber filter (104 mm QAST, Pallflex, Putnam, CT) and XAD-2 (Supelco, Bellefonte, PA), respectively. The clean filters and XAD-2 traps were prepared at Battelle and sent to each sampling site. A standard operating procedure for loading, operation, and unloading of PS-1 samplers was prepared for the field sampling teams by Battelle lab. In addition, at the beginning of the field sampling campaign, an experienced Battelle technician went to the South Haven site and demonstrated the proper sample handling procedure to minimize any possible field contamination and to ensure the integrity of the collected samples.

PAHs were collected at a nominal flow rate of 4 cfm and the collected samples were stored in the dark at 0°C before they were sent back to Battelle for analysis. Sample tracking forms containing all sample collection information were filled out by the field operators for each set of filter and XAD-2 samples and sent to Battelle with each sample.

The filter and corresponding XAD-2 trap were combined and extracted with dichloromethane (DCM). The DCM extract was concentrated by Kuderna-Danish (K-D) evaporation and analyzed by GC/MS in electron impact (EI) mode to determine target PAHs. A Finnigan TSQ-45 GC/MS/MX operated in GC/MS mode was employed. Data acquisition and processing were controlled by an INCOS 2300 data system. The MS was operated in the selected ion monitoring (SIM) mode. Peaks monitored were the molecular ions and characteristic fragment ions of the target analytes. The GC column was a DB5

fused silica capillary column (30 m x 0.25 mm; 0.25 μ m film thickness, Supelco). The GC temperature was held at 70°C for 2 minutes, and then programmed to 290°C at 8°C/min. Identification of target analytes was based on correct molecular ions, correct fragmentation ions, and their GC retention times relative to that of the corresponding internal standards (phenanthrene-d₁₀ and/or 9-phenylanthracene). Quantification of target analytes was based on the comparison of the respective integrated ion current responses of target ions to that of the corresponding internal standard, with average response factors generated from analyses of standard solutions. Target PAHs quantified are listed in Table 4-3.

4.4.2. Pesticide and PCB Sampling and Analysis

Polyurethane foam and quartz fiber filters for collection of gaseous and particulate PCB's and pesticides were prepared by Southwest Research Institute and shipped to the South Haven site for distribution to the other sampling locations. Combined PUF and filter samples were received from the sampling sites and were analyzed by Southwest Research Institute by GC/MS. Upon receipt, samples were Soxhlet extracted (PUF plug with the corresponding quartz filter) with DCM. Analysis of the extract was performed on a Fisons VG Autospec high-resolution mass spectrometer equipped with a Hewlett-Packard 5890 gas chromatograph and CTC-A auto sampler. Since a mixture of heat-sensitive pesticides were analyzed in conjunction with high-boiling PCBs, injector temperature, inertness, and injection technique were optimized to result in the least amount of thermal degradation of the target pesticides.

Target pesticides and PCBs quantified are listed in Table 4-3. Target compounds were quantified using internal standards and a five point calibration curve. In order to provide an indication of extraction efficiency, 3,3',4,4'-tetrachlorobiphenyl- ${}^{13}C_{12}$ was introduced into each sample prior to extraction.

4.4.3. Elemental and Organic Carbon Sampling and Analysis

Quartz fiber filters, treated prior to sampling to remove all organic and elemental carbon traces, were shipped in two batches to the South Haven site from which they were distributed to the other sites. After sampling, filters were returned to aluminum foil-lined petri dishes which were sealed with Teflon tape. At the conclusion of the study, all samples and blanks were shipped to Sunset Labs for analysis. Fine particle samples were analyzed using combustion flame ionization detection (FID) to measure total elemental and volatilizable carbon content. This information is useful for determining source apportionment.

4.4.4. VOC Sampling and Analysis

VOC sampling canisters were cleaned by U.S. EPA and sent to the field for sampling. A total of 129 canister samples were collected in the field and sent to Battelle for analysis of VOC. Standards were analyzed for each of the target compounds of interest in the LMUATS. The compounds analyzed are listed in Table 4-3.

Samples were analyzed using an automated GC system equipped with a Supelco two-phase adsorbent trap which utilized a bed of Carbopack B and Carbosieve S-III adsorbent. The system incorporates a Hewlett-Packard 5880 gas chromatograph and parallel flame ionization and mass spectrometric detectors. Target compounds were chromatographically resolved using a 50m-by-0.32mm internal diameter, OV-1 fused silica column. The column exit flow was split to direct one third of the flow to the mass spectrometric detector with the remaining flow passing through the flame ionization detector. The mass spectrometer was operating in the selective ion monitoring (SIM) mode. In this mode, the mass spectrometer monitored the characteristic ions of each target VOC, rather than scanning all masses continuously between two mass limits. The advantage of monitoring only pre-selected ions was increased sensitivity and improved quantitative analysis. A detection limit of 0.10 ppbv was obtained in this mode.

4.4.5. Atmospheric Acidity Measurements

A primary goal of the study was to quantify the levels of toxic air pollutants in the southern Lake Michigan Basin in order to determine how much of the airborne pollutants are being deposited to aquatic and terrestrial ecosystems. Measurements of atmospheric acidity, gaseous and aerosol strong acidity (H^+) were performed to characterize the chemical composition of the atmosphere and to investigate the behavior of the regional and urban plumes advecting across Lake Michigan. The acidity of the aerosols was hypothesized to be related to the form of the toxic trace elements present on aerosols that are transported long distances.

Annular denuder/filter pack systems (ADS) were operated at two of the four sites during the LMUATS including South Haven, MI and aboard the University of Michigan's research vessel (R/V) *Laurentian*.

Acidic aerosol and gas measurements were taken 2 to 3 times a day at South Haven throughout the duration of the study while the size fractionated samples were collected on selected days. While the R/V *Laurentian* was docked, two 12-hour samples were collected in South Haven from 8AM-8PM and 8PM-8AM CDT. While the ship was on station, 3 samples were taken daily at South Haven and on the R/V *Laurentian*: 8AM-2PM, 2PM-8PM, 8PM-8AM CDT. All size fractionated samples collected at South Haven and on the R/V *Laurentian* were 24-hours in duration starting at 8AM CDT. ADS samples were also collected in Ann Arbor as part of an ongoing study of atmospheric acidity in Michigan.

The annular denuder sampling system was used for collection of acidic aerosols and gases and has been described previously (Koutrakis, *et al.* 1988, Keeler *et al.*, 1990a). The ADS was utilized to quantify gaseous SO₂, HNO₃, HONO, NH₃, and fine fraction (<2.5 μ m) particulate species SO₄²⁻, NO₃⁻, NH₄⁺, and aerosol strong acidity (H⁺). Additionally, the system removes the gaseous ammonia and protects the collected particulate matter from possible neutralization.

Size-fractionated samples were collected at South Haven and aboard the R/V *Laurentian* using a six-stage micro-orifice type impactor (Keeler *et al.*, 1990a). The six stages have been characterized to separate atmospheric aerosols into the following size ranges when operated at 30 LPM: $\#1: > 5 \ \mu\text{m}$; $\#2: 5-2.5 \ \mu\text{m}$; $\#3: 2.5-1 \ \mu\text{m}$; $\#4:1-0.6 \ \mu\text{m}$; $\#5: 0.6-0.18 \ \mu\text{m}$ and; $\#6: <0.18 \ \mu\text{m}$ (Marple and Rubow, 1984). The system is designed to operate with a minimal pressure drop so that vaporization of water and subsequent alteration of the aerodynamic diameter of the particles being collected is avoided (Biswas *et al.*, 1987). The impactors were placed in a stand which forced incoming air to pass through 8-citric acid-coated honeycomb-style aluminum denuders to remove ambient ammonia (Koutrakis *et al.*, 1988). The aerosol rulaterial was collected onto Teflon filters (Teflo) and analyzed identically to the Teflon filters from the ADS.

Sulfate collected on ADS, MOI and on dichotomous filters (analyzed by XRF) were compared to assess the precision of the three techniques. Regression analysis of XRF S against ADS SO_4^{2-} shows quite good results with a slope of 0.33 ng/m³ and a correlation coefficient of 0.994. Likewise, the regression of ADS SO_4^{2-} versus MOI SO_4^{2-} (fine fraction, stages 3, 4, 5 and 6) displays a slope of 0.93 and a correlation coefficient of 0.986. These results indicate that the collection and analytical techniques utilized were comparable and precise.

4.4.6. Scanning Electron Microscopy Analysis of Individual Particles

Six aerosol samples collected at the IIT were analyzed by Scanning Electron Microscopy and Energy-Dispersive X-ray spectroscopy (SEM/EDX). The objective of the SEM/EDX analyses was to characterize a representative number of individual aerosol particles for each sample in order to provide additional information about particulate sources impacting the IIT site. SEM/EDX analyses revealed significant differences in aerosol composition among the six samples. These differences indicated that various sources may have impacted the IIT site simultaneously. The observed differences are also supported by results obtained using X-ray fluorescence (XRF) and receptor modeling applied to the same sample set.

The six samples selected for SEM analysis were collected on 18 July, 19 July, 21 July, 2 August, 6 August, and 8 August 1991. The "bulk" elemental composition (elements heavier than Mg) of these samples had previously been measured by XRF. All samples were coarse fraction samples (2.5-10 μ m aerodynamic dynameter) collected on Teflon filters using a dichotomous sampler with an upper size cutoff of 10 μ m. A feature of this sampling device is that about 10% of all fine particles (< 2.5 μ m) also deposit on the coarse filter, thus enabling both size fractions to be analyzed on the same filter. An effort was made in the present study to characterize a minimum of 100 particles in each size fraction for each sample. This is considered the minimum number required in order to distinguish real differences in aerosol composition among the samples.

Each sample was analyzed using the following procedure: (1) after scanning the sample at low magnification to confirm uniformity of loading and to avoid regions of anomalous loadings, several fields of view were randomly selected for analysis; (2) for a coarse or fine fraction particle analysis, all particles within a field with geometric diameter $\geq 2.5 \ \mu m$ or $\leq 1.5 \ \mu m$, respectively are characterized; (3) for each particle the size, morphology, elemental content and category are recorded in a data book. Elemental composition is qualitatively determined by collecting an X-ray spectrum of the particle, while the category is determined by the microscopist based on the particle's morphology and composition; (4) micrographs are recorded for particles of special interest; (5) at the conclusion of the analysis, particles of a given size fraction are sorted into a size/category matrix as shown in the particle data tables included in Appendix A. It should be noted that the EDX system is only capable of detecting major and minor elements in a particle, i.e. elemental mass exceeding a few tenths of a percent of the total particle mass.

For all of the samples analyzed, sulfate particles account for nearly all of the particles in the fine fraction and are typically 0.3 μ m to 0.4 μ m in diameter. These particles were not included in the 100 particles analyzed in the fine fraction. Instead, an estimate of the sulfate concentration in each sample was made by obtaining an average sulfate particle count from several micrographs of the sample at high magnification. However, XRF analyses provided a better estimate of sulfate concentration.

4.5. Mercury Sampling and Analysis Methods

4.5.1. Vapor Phase Collection

A total of 147 vapor phase samples were taken at three sites during the period from 8 July - 9 August 1991. Samples were only collected at the Barden Farm near South Haven, Michigan (SHA), on the Research Vessel *Laurentian* (LAU) and at the Illinois Institute of Technology (IIT) in Chicago, Illinois. Atmospheric vapor-phase mercury was captured on gold-coated sand traps with pre-fired glass fiber pre-filters in Teflon filter packs to exclude particles. Gold-coated sand traps supplied by Brooks Rand, Ltd. contain approximately 0.6 cm³ of sand which has a coating of gold 1-2 atoms thick. The goldcoated sand is supplied in a quartz tube 10 cm in length held in place by a quartz frit on one end and quartz wool on the other end. Gold sand traps were connected to sampling equipment by Teflon friction fit connectors. Clean techniques necessary for accurate determination of low levels of mercury were employed in all procedures of sample handling and custody.

Vacuum pumps at SHA and LAU utilized mass flow controlling units (Tylan Co.), and at IIT flow was controlled by a needle valve and diaphragm pumping system set to maintain flow below 0.3 LPM (0.27 at IIT, 0.29 at LAU and 0.28 at SHA). A minimum of one blank was taken for every six samples. Thirty eight twelve-hour (8AM-8PM, CDT) samples and nine blanks were collected at SHA (Table 4-4). For each day the LAU was on-station, two daily six-hour samples (8AM-2PM, 2PM-8PM) and one overnight 12 sample (8PM-8AM) were collected for a total of twenty five samples and six blanks. At IIT, 58 samples and 10 blanks were collected on a more intensive schedule than other sites. Two daily six-hour and one overnight 12-hour sample (8PM-8AM) were taken when the LAU was on-station and one daily 12-hour sample was collected while the LAU was in port.

Type of Sample	IIT	R/V Laurentian	South Haven
Daytime Samples	46	18	38
Nighttime Samples	12	7	1
Blanks	10	6	9

 Table 4-4. Vapor Phase Mercury Samples Collected during the LMUATS.

4.5.2. Vapor Phase Analytical Procedure

After collection, samples were stored with end-plugs Teflon-taped inside individual polyethylene tubes and then triple bagged in polyethylene zip-lock bags. Samples were stored outdoors in waterproof containers and shipped at least every five days to Brooks Rand, Ltd. for analysis. Elemental mercury levels were determined by thermal desorption (at 400°C) using the dual amalgamation technique described by Bloom and Fitzgerald (1988) followed by cold vapor atomic fluorescence spectrometry (CVAFS). Peak area was used to quantify the amount of mercury detected. Standards were analyzed prior to sample analysis and controls were analyzed in-between sample analyses. Results were reported in nanograms Hg/trap and subsequently converted to ng Hg/m³. Values reported are at ambient conditions and have not been converted to standard temperature and pressure.

Analytical precision for replicate mercury standards analyzed before, during, and after analysis of vapor phase mercury samples at Brooks Rand, Ltd. varied from 0.07-17% with an avorage precision of 6% (Table 4-5). A total of 50 standards were analyzed during analysis of the 147 samples collected during LMUATS. These standards were produced by purging a known amount of mercury from solution after reduction with stannous chloride. Typically 1 and 2 ng standards were analyzed. However, on one occasion standards of 0.5 to 10 ng Hg were analyzed.

The reproducibility of purged standards is strongly influenced by technician handling and analytical set-up. Consequently, the 6% precision is likely to be more an assessment of the ability to reproduce standards than a measure of analytical precision of vapor phase samples. There are fewer places for error during analysis of a vapor phase

sample than there are in the preparation of purged standards. The precision with which the analyzer can reproduce response based on the same Hg input is much better than 6%.

Number of Standards	50
Average % Precision for Standards	6
Median % Precision	7
Std Dev. of % Precision	7
Min. % Precision	0.07
Max. % Precision	17

 Table 4-5. Precision between Replicate Hg Standards.

The detection limit for CVAFS at an instrument gain setting of 90 is less than 1 picogram. During the course of this study the operational detection limit was 45.7 pg. The operational detection limit was defined as 3 x the standard deviation of all field blanks collected at the three sampling sites. Average field blank values by site are given in Table 4-6. The average field blank at IIT is strikingly lower than that at the other sites. This is most likely due to operator error in following the protocol for field blanks. Field blanks at SHA and on the LAU were prepared by removing the end plugs from the gold sand trap, placing a pre-filter on the trap and putting the filter and gold trap in the sampling box for 2 minutes. At IIT it is likely that end plugs on the traps were not removed; consequently, these would not be true field blanks. Because of this, vapor phase mercury measurements reported here are not corrected for field blank values. In addition, the blank values are below the level reported for ambient measurements (i.e. blanks are hundred^{+hs} of a ng/m³).

Site	n	Average Blank (pg)	Std Dev. of Blanks (pg)	Detection Limit (3 σ)
IIT	10	4.3	3.3	9.9 pg
LAU	6	17.7	19.0	57.0 pg
SHA	9	25.6	23.4	70.2 pg
Overall	25	15.9	15.2	45.6

 Table 4-6. Results of Field Blanks for Vapor Phase Mercury by Site.

4.5.4. Particulate-Phase Collection.

Particulate sample collection was carried out through filtration of moderately sized air samples (approx. 20-40 m³) onto one of a variety of filter media. The media examined during the sampling and development period included glass-fiber, quartz-fiber and Teflon. Historically, these different media have been used for different applications because of a variety of properties which they possess. These properties include inertness, pore size, cost, Hg background, and applicability for other uses. The evaluation described below focused on the last two factors, and sought to determine if filters which were to be used for INAA (Teflon) might be usable for wet extraction and the amount of Hg background each media might contribute.

4.5.4.1. Glass-Fiber

Millipore Corporation, Bedford, MA. 47mm, AP40 style. These filters are made of borosilicate glass c...d formed into a mat of microfibers. They do not contain any additional binders and may be heated to quite elevated temperatures to remove volatile impurities, such as Hg. The listed pore size is $0.8 \,\mu\text{m}$.

Gelman Sciences, Inc., Ann Arbor, MI. 47mm, A/E style. These filters are also made of borosilicate glass. The listed "aerosol retention" is .3 μ m at 32 LPM and >99.98% efficiency.

4.5.4.2. Quartz-Fiber

Pallflex Products Corp., Putnam, CN. 47 mm, 2500QAT-UP type. This material is ultra-pure binderless quartz which is washed with soft water during production. Filter efficiency is 99.99% at 0.3-0.05 μ m. As with the glass, these filters may be baked to reduce background Hg.

4.5.4.3. Teflon

Gelman Sciences Inc. 47 mm, Teflo with ring style. Teflon is an inherently clean and inert medium, which is the industry standard for PM10 measurements using Dichotomous samplers and non-destructive analytical techniques (e.g. INAA, XRF and PIXE). The pore size is $2 \mu m$. This media cannot be heated to lower the Hg background.

Investigations of the background concentrations of Hg on these filters indicate that after firing at 500 °C for 3 hours, the glass and quartz-fiber materials are roughly comparable in mercury content (40-200 pg Hg/filter). However, the glass appears to have a slightly lower mercury content. The Teflon filters need not be treated before use and have similar background levels (200 pg Hg/filter).

Filters were placed in acid-cleaned Teflon filter packs. Total suspended particulate (TSP) samples were collected using an open-faced filter pack (Savillex Corp., Minnetonka, MN) while fine fraction ($d_a < 2.5 \mu m$) particles were collected using a Teflon filter pack connected to a Teflon-coated aluminum cyclone inlet system (University Research Glassware, Carrboro, NC).

Air was pulled through these sampling systems using two different methods. Diaphragm-type pumps (Gast Co., Benton Harbor, MI) were used for the moderate-tohigher flow rate applications (10-30 LPM) often with a needle valve (Hoke) to control flow. The flow rate during sampling was measured using a spirometer-calibrated rotameter (Matheson), with the flowmeter on the inlet of a flow-test filter pack connected to the sample pump. The use of a flow test filter pack was used to avoid contamination of the true sample. The second approach employed was moderate-and high-flow-rate sampling using mass-flow-controlled pump units. These units contained a variety of Tylan mass flow control units and custom electronic panels which enabled careful flow rate adjustment. These devices were also used for low flow (<1 LPM) applications related to gas-phase Hg measurements. In most applications, total sample volume was measured with spirometer-calibrated dry test meters (Schlumberger). All of the particulate mercury [Hg(p)] samples reported here were collected for a nominal duration of 24 hours. While some samples were considerably shorter in duration, most samples were found to have Hg levels significantly elevated above the detection limit. As discussed below, adequately detectable samples may be expected from samples as short as 6 hours under typical ambient conditions.

All sample handling was carried out using cleanroom (particle-free) vinyl gloves. This included the loading and unloading of the filter packs as well as any handling of the filter packs (i.e., during flow measurements). The loading and unloading of filters was conducted out-of-doors to take advantage of the low Hg levels in ambient air.

Filters were loaded into the filter packs using acid-cleaned Teflon-coated forceps just prior to sampling. Immediately after sampling, the filters were removed from the filter packs and carefully placed into clean storage containers. Acid-cleaned polyethylene petri dishes (Gelman Sciences, Inc.) or Teflon vials (Savillex) were the primary storage containers used in all of the studies. After placing or folding the filters carefully into the containers using the forceps, the container lids were sealed with Teflon tape to help prevent diffusion of Hg vapor into the containers. Samples were kept in acid cleaned Teflon jars which were taped and double-bagged in polyethylene "ziplock"-type bags and stored at -40 °C in the dark until the time of analysis.

4.5.5. Particulate Phase Analytical Procedure

Two different analysis techniques were used to analyze the Hg(p) samples. They are neutron activation analysis and dual-amalgamation cold vapor atomic fluorescence spectrometry.

4.5.5.1. Neutron Activation Analysis

Neutron Activation Analysis is a non-destructive, radiation-based analytical (Radiochemical) technique. Its usefulness stems from its high level of sensitivity combined with the capability to simultaneously determine of many elements in a wide range of sample media. The ability to quantitatively determine the elemental composition of samples is particularly useful for source profiling and source/receptor modeling.

Briefly, INAA involves the activation of elemental constituents in a sample by bombarding them with thermally excited neutrons which collide with the atomic nuclei and convert some of the material present into radioactive isotopes of the original elements

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(radionuclides). The neutrons are frequently generated by the radioactive discharge of a nuclear reactor. Following activation, the elements that are present and their abundance are determined by gamma-ray spectrometry which identifies elements by the characteristic energy of their gamma-ray discharge and their concentrations by the intensity of their decay product emissions. Calibration of the results is achieved through comparison of the detector response in the samples to the response from established Standard Reference Materials (SRMs).

All of the INAA results which are presented here were obtained through the efforts of Dr. Ilhan Olmez at the Massachusetts Institute of Technology Nuclear Reactor Laboratory. This particular laboratory is unique in that the irradiation process takes place near room temperature, whereas most reactors used for this technique expose samples to elevated temperatures. For a highly volatile species such as mercury, this is critically important in obtaining accurate and reliable data (Olmez, 1992, personal communication).

4.5.5.2. Cold Vapor Atomic Fluorescence Spectrometry

CVAFS is a member of the emission spectrometry family of analytical techniques. In these methods, an aliquot of analyte material is temporarily suspended in the path of an electromagnetic radiation source (usually ultraviolet or visible light) and excited by the light. A photomultiplier tube (PMT) then detects transmitted light of the same frequency or emitted light of the same or different frequency from the excited analyte. In atomic fluorescence, the incident energy is long-wave UV (254 nm) supplied by a Hg vapor lamp. This UV light excites Hg atoms suspended in a stream of carrier gas (He or Ar) and a PMT situated perpendicular to the incident light beam detects the 254 nm photons released during the fluorescent relaxation of the Hg atoms to their ground state energy. Because of the geometry of the system and the inherently narrow bandwidth of the fluorescent emissions, additional monochromators or filters are not necessary. Thus the CVAFS method has a high energy throughput which results in excellent specificity and sensitivity.

The "dual amalgamation" pre-concentration technique (Fitzgerald and Gill, 1979) coupled with CVAFS (DACVAFS) aids in the analysis of minute amounts of mercury in environmental samples from a variety of media. In this procedure, Hg° amalgamates to gold-coated sand on a "sample" trap which contains approximately one gram of gold-coated sand. While passing an inert gas (He or Ar) through the trap, the Hg is desorbed by heating the trap to 400°C onto a second, "analytical" trap, from which it is desorbed

into the spectrometer. This approach is effective in removing water, the primary positive interference, from the system before quantification of Hg. This further increases the sensitivity, specificity and applicability of the CVAFS method.

To use this analytical method for the determination of Hg(p), the Hg present in various chemical forms in the particle phase (and for most other media as well) must be captured as Hg^o vapor on a gold-coated sand trap. This process involved the extraction and volatilization of the Hg present on a collection filter. The Hg(p), presumably present in a variety of chemical forms, was first separated from the particle mass matrix collected on the filter material through an acid digestion process accompanied by sonication. The sample filter was folded and placed into a 33-ml acid-cleaned Teflon vial. A 20-ml aliquot of a 10% solution of 70% nitric, 30% sulfuric acid was then added as the primary solubilizing agent in the extraction. The acids used for the extraction solution were purged of Hg by bubbling with a Hg-free stream of pure nitrogen through the liquid for an extended period of time (12-18 hours). The sample was then sonicated for 30 minutes to break up the particle matrix without heating. Previous experiments indicated this to be a more effective technique for extraction than heating the filter in the extraction solution. This is possibly due to the lower temperature (estimated at 40-60 °C) of the technique and less loss through volatilization. Following extraction, all of the solubilized forms present were converted to Hg²⁺ through a 1-hour oxidation using 0.5 ml of BrCl solution. Also, this step may aid in the extraction of Hg from the matrix. Next, the BrCl is reduced by the addition of 0.1 ml of NH₂OH solution to a 5-ml aliquot of the extract. This was necessary to remove the halogens from solution which may damage the gilded surface of the goldsand traps. Finally, 0.5 ml of SnCl, solution is added to the aliquot in a bubbler/impinger setup which reduces the Hg²⁻ to Hg^o. The volatile Hg^o was bubbled out of solution with Hg-free N₂, and the Hg vapor recaptured on the "sample" gold-sand trap. The analysis is completed through detection as described above. Thus, the DACVAFS approach yields a value for Hg(p) which represents total "acid-extractable" Hg, and cannot distinguish the chemical forms that were present at the time of sampling. The technique is precise (<15% variability) and sensitive (detection limit ~250 pg/filter or 5 pg/m³ for a 24-hour sample collected at 30 LPM).

It was essential, especially when performing Hg(p) analysis using this technique, to carry out the extraction/volatilization/quantification procedures under ultra-clean conditions (Class 100) (Boutron, 1990). For most of the data presented here, a simple cleanroom was constructed from a plastic frame draped with clear vinyl to isolate it from room air. A high efficiency particle filter (HEPA) and motor assembly supplied the cleanroom with class 100 quality air, and particle-free gloves, suits and boots allowed analysts to handle sample extraction and analysis in the cleanest possible conditions. Ultra-clean conditions also demand extremely pure reagents, and many of the chemicals which were used during analysis had to be further purified or purged of Hg before they could be used. The simple cleanroom, in use for a part of this investigation, has been replaced by a state-of-the-art ultra-trace element analysis facility at the University of Michigan Air Quality Laboratory. The laboratory is constructed of all plastic and wood with no exposed metal in the room. Vapor mercury levels are approximately 1 ng/m³.

4.6. Quality Assurance

Several steps were taken to assure the reliability and replicability of data collected during the LMUATS. Site audits were performed at each of the four LMUATS sites during the course of the study. Results of these audits determined that air samplers were performed within the criteria set forth in the quality assurance project plan. The final report of these performance and systems audits, prepared by Jack A. Bowen of the EPA QATSD and Mike Pleasant of METI, are found in the Appendix.

Audit samples were prepared by EPA for analysis of VOCs, pesticides and PCBs on PUF, and PAHs in solution. Results of these analyses are reported in the Appendix. In addition, collocated samples were analyzed for elemental and organic carbon, PCBs, pesticides, and a comparison between XRF and INAA analysis of 12 elements from identical Teflon filters was conducted.

Collocated elemental and organic carbon analyses reveal excellent agreement between samples (Figure 4-3). Mean elemental carbon values from the 26 collocated pairs were 0.36 and 0.35 with standard deviations of 0.41 and 0.37, respectively; and $r^2=0.92$. Mean organic carbon values (n=26) were 3.72 and 3.55 (standard deviation 2.62 and 2.74, respectively), with an $r^2=0.94$.

Fine fraction elements (Al, Cl, K, Ti, V, Cr, Mn, Fe, Zn, As, Se and Br) were analyzed on the same filter by both XRF and INAA for 25-31 samples from IIT (Table 4-7). Results of this comparison indicate good agreement between the two analytical methods for these elements.

Figure 4-3. Collocated Elemental and Organic Carbon Samples at South Haven.

Comparison of two samplers at South Haven

Elemental Carbon



Date

Elements	n	XRF	XRF INAA		r ²	p value
		Mean <u>+</u> Std Dev. (ng/m ³)	Mean <u>+</u> Std Dev. (ng/m ³)			
Mn	32	6.18 <u>+</u> 10.72	5.81 <u>+</u> 8.55	0.99	0.98	0.0001
Zn	32	38.8 <u>+</u> 59.18	32.45 <u>+</u> 53.35	0.99	0.98	0.0001
Fe	32	124.78 <u>+</u> 122.82	154.38 <u>+</u> 159.21	0.89	0.79	0.0001
Se	32	0.99 <u>+</u> 1.03	1.05 <u>+</u> 0.79	0.88	0.77	0.0001
К	26	62.47 <u>+</u> 40.91	63.31 <u>+</u> 37.4	0.77	0.59	0.0001
Al	31	77.59 <u>+</u> 94.64	103.58 <u>+</u> 80.28	0.76	0.58	0.0001
Ti	25	4.88 <u>+</u> 7.67	9.3 <u>+</u> 6.08	0.75	0.56	0.0001
Cr	32	0.61 <u>+</u> 0.79	1.26 <u>+</u> 0.77	0.60	0.36	0.0003
Cl	32	8.71 <u>+</u> 12.87	9.18 <u>+</u> 3.38	0.58	0.34	0.0004
As	32	0.21 <u>+</u> 0.93	0.51 <u>+</u> 0.43	0.56	0.31	0.0009
Br	32	2.81 ±1.02	0. 83 <u>+</u> 0.94	0.47	0.22	0.0070
V	32	0.68 <u>+</u> 1.82	0.73 <u>+</u> 0.66	0.45	0.20	0.0100

Table 4-7. XRF vs. INAA Comparison at IIT.

PCB and pesticide replicate analyses are reported in Table 4-8. In general, there was good agreement between several PCB isomers and congener groups and several pesticides.

In addition, 46 collocated samples were collected at South Haven for fine and coarse elements using the Dichot sampler. Results of XRF analysis of the paired filters are presented in Tables 4.9 and 4.10. Fine elements and total fine mass were highly correlated between the collocated samples for the majority of elements (Table 4-9).

Comparison of collocated filters for coarse particle mass (Table 4-10) indicates that, in general, replicate samples could be reliably collected and analyzed for the majority of coarse fraction elements.

		Sampler		Sam	pler		
a .		<u>No. 93</u>	3411	<u>No. 93</u>	3413		_
Compound	n	Mean	Std Dev.	Mean	Std Dev.	r	r ²
		(pg/m ³)		(pg/m ²)			
p,p'-DDD	5	6.6	9	7.6	6	0.99	0.9 8
Dieldrin	5	109.7	100.3	163.6	84	0.9 8	0.95
gamma-Chlordane	5	28.2	21.1	32.4	19.2	0.91	0.83
trans-Nonachlor	5	17.3	19.3	22.2	17.2	0.88	0. 78
Mirex	5	6.2	4	9.8	4.4	0.88	0.78
2,2',4,4',5,6' - PCB	5	0.1	0.1	0.2	0.3	0.88	0.78
alpha-Chlordane	5	24.5	19.5	30.6	15.2	0.85	0.72
Atrazine	5	246.3	402.4	333.8	335.3	0.84	0.71
TOT.mono-PCB	5	191.7	101.9	240.6	118.2	0.82	0.67
TOT.hexa-PCB	5	46.4	35.4	52.9	17.5	0.81	0,66
2,2',3,4,5'-PCB	5	7.6	6.9	12.7	5.5	0. 79	0.62
TOTAL PCBs	5	721.4	378.7	843.8	266.9	0.78	0.61
4,4'-DDT	5	224.5	175.2	252.9	74.5	0.78	0.61
2,3-PCB	5	20.6	10.7	24.5	5.5	0.77	0.60
TOT.pen-PCB	5	251.1	124.9	281.1	88.7	0.74	0.55
hexachlorobenzene	5	42.1	17.2	58.7	5.8	0.71	0.50
TOT.tri-PCB	5	54	33.8	68.4	28.6	0.70	0.48
TOT.tet-PCB	5	68.7	46.1	82	42	0.68	0.47
Metolachlor	5	87.9	130.2	44.9	61.9	0.49	0.24
p,p'-DDE	5	948.9	515.8	1271.6	334.1	0.40	0.16
Chlorpyrifos	5	146.5	116.4	222.8	185.3	0.37	0.14
TOT.di-PCB	5	104.4	61. 8	113.6	28 .9	0.27	0,07
alpha-HCH	5	84.9	42.6	125.9	22.9	0.27	0.07
TOT.hep-PCB	5	4.9	3.8	4.4	2.9	-0.16	0.03
Aldrin	5	0.3	0.4	0.4	0.4	J.15	0.02
TOT.octa-PCB	5	0.2	0.2	0.2	0.3	-0.10	0.01
gamma-HCH	5	49.9	29.8	75.7	21.9	0.11	0.01
TOT nona-PCB	5	0	0	0.1	0.2	-	-
Simazine	5	0	0.1	0	0	-	-
deca-PCB	5	0	0	0.5	1.1	-	-
Alachlor	5	0	0	33.4	74.7	-	-
2-PCB	5	0	0	3.4	5.1	-	-
2,4,5-PCB	5	0	0	0	0	-	-
2,2'3,4',5,6,6'-PCB	5	0	0	0.1	0.2	-	-
2,2',4,6-PCB	5	0.1	0.2	0	0	-	-
2,2',3,3',4,5',6,6'-PCB	5	0	0	0.1	0.2	-	-

Table 4-8.	Comparison	of PCBs	and	Pesticides	in	Collocated	Samples	at
		Soi	ith H	laven.				
Variable	n	Sampler 1 Mean <u>+</u> Std Dev. (ng/m ³)	Sampler 2 Mean <u>+</u> Std Dev. (ng/m ³)	r	r ²	p value		
----------	----	---	---	--------------	----------------	---------		
S	46	2218 + 2640	2100 + 2501	0 08	0.96	0 0001		
Mass	40	16710 ± 14270	2190 + 2391	0.96	0.00	0.0001		
IVIA55	40	10/10 <u>+</u> 142/9	10072 ± 13337	0.90	0.92	0.0001		
Fe	46	90.37 ± 93.98	68.5 ± 65.02	0.96	0.92	0.0001		
Pb	46	6.92 ± 5.86	6.47 <u>+</u> 5.17	0.94	0.88	0.0001		
К	46	54.08 <u>+</u> 37.01	50.23 <u>+</u> 31.13	0.92	0.85	0.0001		
Zn	46	16.47 <u>+</u> 14.2	15.98 <u>+</u> 13.92	0.91	0.83	0.0001		
Mn	46	3.45 <u>+</u> 3.39	3.25 <u>+</u> 2.65	0.86	0.74	0.0001		
Ca	46	61.5 <u>+</u> 53.23	46.13 <u>+</u> 31.59	0. 78	0.61	0.0001		
Br	46	2.07 <u>+</u> 1.05	1.99 <u>+</u> 1.03	0.74	0.55	0.0001		
Se	46	1.08 ± 0.82	1.04 <u>+</u> 0.91	0.72	0.52	0.0001		
Ti	46	4.37 ± 4.21	3.11 <u>+</u> 3.46	0.61	0.37	0.0001		
Si	46	157.85 <u>+</u> 137.53	122.5 <u>+</u> 100.57	0.59	0.35	0.0001		
Cu	46	3.22 <u>+</u> 2.17	4.1 <u>+</u> 3.22	0.38	0.14	0.0090		
Cl	46	3.75 ± 4.71	7.14 <u>+</u> 5.44	0.37	0.14	0.0100		
Sc	46	0.22 <u>+</u> 1.67	0.29 <u>+</u> 1.65	0.36	0.13	0.0100		
Te	46	1.29 <u>+</u> 6.78	-0.31 ± 6.63	0.35	0.12	0.0200		
Ni	46	0.01 <u>+</u> 0.7	0.05 <u>+</u> 0.74	0.34	0.12	0.0200		
Ba	46	11.62 ± 13.76	12.29 <u>+</u> 12.19	0.32	0.10	0.0300		

Table 4-9. Comparison of Collocated XRF Fine Particle Data at SouthHaven.

Variable n		Sampler 1 Mean <u>+</u> Std Dev. (ng/m ³)	Sampler 2 Mean <u>+</u> Std Dev. (ng/m ³)	r	r ²	p value	
G	16		105 50 + 100 1	0.97	0.74	0.0001	
5	46	136.81 <u>+</u> 119.73	125.52 ± 120.1	0.80	0.74	0.0001	
Ca	46	307.34 <u>+</u> 279.17	408.32 <u>+</u> 359.66	0.76	0.58	0.0001	
Fe	46	186.07 ± 166.56	236.4 <u>+</u> 213.39	0.75	0.56	0.0001	
Si	46	854 <u>+</u> 713	1121 <u>+</u> 834	0.74	0.55	0.0001	
Mn	46	6.11 ± 5.28	7.97 <u>+</u> 6.68	0.73	0.53	0.0001	
Al	46	194.18 <u>+</u> 186.14	258.41 <u>+</u> 207.62	0.69	0.48	0.0001	
Pb	46	2.49 ± 3.26	2.13 ± 3.13	0.69	0.48	0.0001	
Ti	46	15.46 <u>+</u> 12.4	20.13 ± 15.06	0.67	0.45	0.0001	
К	46	94.58 <u>+</u> 56.27	108.99 <u>+</u> 59.83	0.60	0.36	0.0001	
Ni	46	0.39 ± 0.98	0.15 <u>+</u> 1.45	0.60	0.36	0.0001	
Mass	46	8071 <u>+</u> 4782	9288 <u>+</u> 5003	0.47	0.22	0.0009	
Р	46	19.06 ± 17.3	24.25 ± 17.03	0.45	0.20	0.0020	
Sr	46	1 <u>+</u> 0.96	1.04 <u>+</u> 1.09	0.40	0.16	0.0060	
Cr	46	0.74 <u>+</u> 0.97	0.5 ± 1.02	0.34	0.12	0.0200	
Y	46	0.77 ± 4.02	0.92 <u>+</u> 4.9	0.32	0.10	0.0300	

Table 4-10. Comparison of Collocated Coarse Particle XRF Data atSouth Haven.

4.7. Data Processing

All data processing and analysis was completed using strict quality control and quality assurance measures. Finalized data sets received from laboratories at which the samples had been analyzed were checked for consistency with master files of sampling dates and identification numbers. Figure 4-4 describes the data acquisition stream for each measurement made as part of the LMUATS and the analytical method and reporting organization responsible for the data.

Figure 4-5 outlines the processing stream used to generate a complete, checked data file for use in statistical analyses. Data from original files received from analysis laboratories were used to prepare input files for SAS (Statistical Analysis Software, Cary, NC) using a consistent format including site, date, time of sample collection, sample identification number, pollutant concentration and note codes so that each row of data described one unique sample. These files were saved as ASCII files with the filename specifying site and group of compounds contained in the data set.

SAS programs were run to create SAS data sets for each group of compounds for each site. SAS program and SAS data set names corresponded to site and group of compounds, for example KAIPCB.SAS is a SAS program which reads in original PCB data for Kankakee and generates a SAS data set named KAIPCB.SSD. Once SAS data sets were created on personal computers, the data files were converted to XPO files and transferred to a UNIX based system which could handle the manipulations of such a large data set with much greater speed. Compound-specific data were merged to create four summary data sets by site. A final data set was created by merging these four data sets into one main data set.

4.8. Mixed-Layer Trajectories

Surface and upper air meteorological observations were obtained from the National Weather Service (NWS) with additional soundings from the Lake Michigan Ozone Study measurements. On-site meteorological measurements of temperature, pressure, dew point and wind speed and direction were also utilized to estimate the time of frontal passages. Mixed-layer 72-h back trajectories were calculated for air masses arriving at the site at 0200, 0800, 1400, and 2000 EDT daily (Heffter, 1980). The backward trajectories were calculated starting at monitoring sites moving backwards in time in 3-h time steps. The trajectories represent the most probable path of an air parcel advected with the mixed-layer-averaged winds. Trajectory calculations are *not* exact and have associated uncertainties which generally increase with the time or distance upwind of the receptor location (Kahl and Samson, 1986;Draxler, 1987).



Figure 4-4. LMUATS Data Aquisition Stream.





Chapter 5

Composition of the Atmospheric Aerosol System

This section of the report presents the results of the elemental and chemical analysis of the samples collected during the study. The comprehensive characterization of the atmospheric aerosol system (gases and particles) includes both inorganic and organic chemical analysis, and in many cases in two or more size fractions. The extensive suite of the measured chemical compounds provides critical information on the composition and the sources of the potentially toxic air pollutants found in the lower Lake Michigan Basin.

The concentrations of several classes of compounds were determined at four locations during the study period. The classes were PAHs, pesticides, PCBs, and metals which included Hg, elemental and organic carbon, and inorganic species. The data presented here are perhaps the most extensive attempt to completely characterize the chemical composition of the atmosphere at multiple sites simultaneously. The data will be discussed by compound class with attention focused on the inter-site differences for specific compounds rather than day to day fluctuations in the concentrations of each compound.

5.1. **PM10** and Ionic Composition

Figure 5-1 shows the PM-10 concentrations measured between 8 July and 9 August, 1991. The fine fraction mass (< 2.5 μ m) is shown in black on the bottom of each bar. There is a pronounced episode of elevated PM-10 concentrations from 16-22 July where the levels exceeded 80 μ g/m³ at both Kankakee and IIT and exceeded 60 μ g/m³ in South Haven. Mixed layer trajectories reveal that the stagnant air masses were transported from the southwest during this period. The maximum PM-10 concentrations were observed on 19 July with air mass transport from the St. Louis area to each site (Figure 5-2). The PM-10 concentrations also peaked on 2 August when winds were light and from the southwest at each site.



Figure 5-1. Variations in Measured PM10 Concentrations at Four Measurement Sites.

Figure 5-2. Mixed Layer Trajectories Ending at the Three Land-Based Sites on 19 July, 1991. (Squares indicate position of the air mass in 3-hour time increments moving backward from the site.)



Perhaps more interesting than the elevated PM-10 levels during the study is the change in the aerosol size distribution after transport from Kankakee to IIT to South Haven as reflected by the fine fraction of the PM-10 shown in Figure 5-3. One objective of the LMUATS was to capture an episode where air mass transport "linked" the upwind site (Kankakee) with the urban site (IIT) and the over water transport site (R/V Laurentian) and the downwind site (South Haven). The episode from 16-23 July provided the perfect opportunity for linkage between 3 of the 4 sites with the research vessel. Unfortunately, the vessel was not on station during this period. However, Figure 5-3 shows that at the beginning of the episode on 16 July about 78% of the PM-10 observed at Kankakee was in the fine fraction which is typical of a regional transported aerosol. From 18-22 July, the PM10 level at Kankakee rose as did the percentage of coarse particulate matter due to transport from sources upwind of Kankakee such as the St. Louis urban/industrial area. As the air mass moved into Chicago the concentration of the fine particulate mass dropped due to dispersion. The addition of coarse mass occurred from the activities in the urban/industrial area. The PM-10 levels observed at IIT were only slightly lower than those measured in Kankakee but about 40% of the PM-10 was now in the fine fraction. As the air masses continued across Lake Michigan, without additional sources en route to South Haven, the fine fraction again reasserted itself as the dominant portion of the PM-10. This again is what one typically observes at a site influenced primarily by long range transport. The PM-10 levels in South Haven during the episode were about 20 μ g/m³ less on the average than the levels observed concurrently at IIT. This decrease can be largely explained by dispersion. The change in the particle size distribution, however, cannot simply be explained by en route dispersion. It appears that larger particles observed in Chicago do not make it to South Haven and are probably lost by deposition. Therefore, the PM-10 is primarily made up of fine particles in South Haven after overwater transport. This loss of large particles probably would have been accentuated if the particles greater than 10 µm in size had been sampled (Holsen et al., 1993).

Figure 5-4 shows the fine S concentrations determined by XRF at the four locations during the study. Sulfur, in the form of sulfate, is the largest contributor to the fine mass at each site. The pattern in the fine S concentrations is very similar from site to site with the maximum concentrations measured in Kankakee. Annular denuder systems (ADS) were operated during the study at two of the four sites during LMUATS. There were a total of 74 ADS samples collected in South Haven, and 22 on the R/V *Laurentian* of 6 and 12 hours in duration. Figure 5-5 shows the time series for fine particulate SO_4^{2-}



Figure 5-3. Variations in Measured Fine Fraction PM10 Concentrations.



Figure 5-4. Variations in Measured Fine Particle S Concentrations.

Figure 5-5. Variations in Measured Fine Particle SO₄²⁻ Concentrations.



South Haven



measured during the study at the two locations. The 6-hour samples were averaged into 12-hour data for statistical analysis so that the data would be comparable to the 12-hour integrated elemental and organic composition data. It should be noted that the XRF fine S data agreed quite well with the ADS fine particulate SO_4^{2-} determined by ion chromatography (r=0.99).

The average composition of the fine particles collected is given in Table 5-1. The concentrations measured in Ann Arbor, MI during the same period are also shown in the table for comparison. Levels measured on the R/V *Laurentian* were typically very similar to those measured concurrently in South Haven. It should be noted that the levels observed while the R/V *Laurentian* was on station are, in general, quite low as would be

· · · · · · · · · · · · · · · · · · ·	Laurentian			South Haven	Ann Arbor		
	n	Mean Std Dev.	n	Mean Std Dev.	n	Mean Std Dev.	
NH ₃ (ppb)	14	1.7 <u>+</u> 1.4	63	1.2 ± 0.9	22	3.1 ± 0.8	
Maximum		5.2		5.8		4.4	
HONO (ppb)	14	0.3 ± 0.3	64	0.3 ± 0.2	22	0.4 ± 0.3	
Maximum		1.0		1.1		1.5	
HNO ₃ (ppb)	14	1.3 <u>+</u> 0.9	64	0.8 ± 0.9	22	0.8 ± 0.7	
Maximum		3.4		3.9		2.6	
SO ₂ (ppb)	14	3.4 <u>+</u> 4.4	64	1.9 ± 2.1	22	2.8 <u>+</u> 2.0	
Maximum		15.8		8.9		8.7	
SO_4^{2-} (nmole/m ³)	14	34 <u>+</u> 33	64	52 <u>+</u> 66	22	79 <u>+</u> 102	
Maximum		115		281		329	
H^+ (nmole/m ³)	14	14 <u>+</u> 11	64	25 <u>+</u> 43	22	24 <u>+</u> 41	
Maximum		34		241		130	
NH_4^+ (nmole/m ³)	14	53 <u>+</u> 64	64	82 <u>+</u> 98	22	131 <u>+</u> 171	
Maximum		204		398		544	

Table 5-1. Summary of ADS Concentration Data Collected from8 July - 9 August, 1991.

Figure 5-6. Mixed Layer Trajectories to the R/V Laurentian while On-Station Off-Shore of Chicago 23-27 July and 5-8 August 1991.





expected with the strong north-northwesterly or east-northeasterly flow to the vessel when it was on-station near Chicago (Figure 5-6).

The concentrations measured in South Haven are typical of summertime values previously measured in the midwestern U.S. (Pierson et al., 1989). The average levels observed are also very similar to those measured during September 1989 in Green Bay, Wisconsin (Mamane et al., 1993). Mean SO_4^{2-} concentrations in South Haven and aboard the R/V Laurentian were 52 and 34 nmole/m³ (5.0 and 3.3 µg/m³), respectively. The mean SO_4^{2-} concentration at Chicago over a 1-year period was 5.55 µg/m³ (Lee et al., 1993). The interesting difference in the sulfate observed during the LMUATS and those previously observed in Chicago is the acidity of the sulfate. The mean and maximum H⁺ concentrations measured in Chicago were 8 and 78 nmole/m³ compared to 14 and 34 on the R/V Laurentian and 25 and 241 nmole/m³ in South Haven. The fact that the maximum H⁺ level observed in Chicago was one-third that measured in South Haven suggests that SO₂ to H₂SO₄ conversion is occurring over the lake en route to South Haven. Figure 5-7 displays the H⁺ concentrations measured at the two sites during the study. The figure clearly indicates that acidic SO_4^{2-} was observed in South Haven during the transport episode 16-22 July. It is also clear that the SO_4^{2-} measured over the lake was not neutralized to a great extent. However, as seen in Figure 5-8, NH_4^+ is the dominant cation even during the transport episode. Considerable neutralization had already occurred when the air mass reached South Haven during the 5-day period. Fine particle nitrate concentrations shown in Figure 5-9 were typically very low during the study and near detection limits during the transport episode previously discussed.

Changes can be observed in the chemical profile of fine fraction aerosols measured during the LMUATS. The H⁺ to SO_4^{2-} ratios at different sites were 0.78, 0.44, and 0.16, on the R/V *Laurentian*, South Haven, and Ann Arbor, respectively. This ir dicates that the acidic SO_4^{2-} aerosol measured over the lake is to a large extent unneutralized. However, as the aerosol is transported inland (even a short distance as at South Haven) an additional 25% of the acidity is neutralized. This is most likely due to rapid fumigation of the air mass after reaching the shoreline where relatively high levels of ammonia react rapidly with the acidic SO_4^{2-} . However, compared to the average inland values measured in Ann Arbor during the study, both the over-lake and South Haven areas appear to be exposed to relatively unneutralized sulfate.

Measurements of the gaseous compounds were limited to those species quantified by the ADS or those measured as part of the LMOS. Figure 5-10 shows the gaseous NH_3

















R/V Laurentian





Date





R/V Laurentian





Date





ррв

South Haven



Date

РРВ

concentrations measured at the two sites using the ADS. The NH₃ concentrations on the R/V *Laurentian* were elevated when the flow to the vessel was directly from shore. This occurred both on the 11-12 July and on the 24 July when the vessel experienced a period of transport from Chicago to the ship. SO₂ concentrations measured at the two sites were generally quite low with a few exceptions. The SO₂ levels observed in South Haven increased 4-5 fold during the period of southwesterly flow from 16-22 July. Southwest flow also resulted in elevated concentrations on 2 August. The SO₂ concentrations measured on the R/V *Laurentian* 6-7 August reached 16 and 10 ppb respectively as seen in Figure 5-11. The 12-hour average values were elevated due to direct plume impact from the Fe-steel industry in Gary. The plume from the plant was in contact with the vessel for about 2 hours during the 12-hours of sampling, thus, the concentrations in the plume were substantially higher that the levels displayed.

The levels of photochemically derived pollutants HNO_3 and O_3 are shown in Figures 5-12 and 5-13. Ozone levels exceeded the NAAQS on several days in South Haven during the transport period from 16-22 July. HNO_3 concentrations also were elevated during this period at South Haven reaching 4.0 ppb on 18 July corresponding to the highest O_3 observed during the study of 153 ppb. In fact, the correlation between the maximum hourly O_3 and the 12-hour integrated HNO_3 concentration was 0.92. This is similar to the relationship observed in other areas with elevated photochemical pollutant levels (Keeler *et al.*, 1990a). The elevated oxidant concentrations measured in South Haven after over-water transport is clearly seen. While the levels of all of the particulate species are not elevated during this period, most of the combustion or secondary species, such as sulfate, are elevated.

5.1.1. Carbon Measurements

The fine fraction carbon measurement data are shown in Table 5-2. The C_v refers to organic carbon species in the fine particulate matter that could be volatilized. The C_e is the elemental carbon or black carbon in the fine particulate matter often associated with diesel exhaust. At the IIT site the mean elemental carbon concentration is only about 12% of the organic carbon concentration. A ratio of C_e/C_v of 1/8 is similar to that reported in the Green Bay study for the fine fraction carbon. However, the ratios of C_e/C_v at the other sites are smaller with ratios of 1/12, 1/10, and 1/10 at the more rural Kankakee, R/V *Laurentian*, and South Haven sampling locations.



Figure 5-11. Variations in Measured Gaseous SO₂ Concentrations.

South Haven



Date

Figure 5-12. Variations in Measured Gaseous HNO₃ Concentration.



2











Figure 5-13. Variations in Measured Maximum Hourly O₃ Concentrations.

		Kankakee		IIT		R/V Laurentian		South Haven	
	Mean S		Std Dev	Mean	Std Dev	Mean	Std Dev	Mean	Std Dev
C _v		4.4 ± 1.8		6.7 <u>+</u> 3.5		3.2 ± 1.7		3.7 <u>+</u> 2.6	
	Max	7.9		26		6.1	l	10.1	
C _e		0.3	<u>+</u> 0.3	1.21	<u>+</u> 1.0	0.3	3 <u>+</u> 0.4	0.35	<u>+</u> 0.4
	Max	1.0		4.6		1.1	l	1.4	

Table 5-2. Average and Maximum Concentrations for Fine Fraction Carbon (Units are $\mu g/m^3$).

While the proportion of the carbon in the elemental and organic forms is similar to that observed in Green Bay, the concentration levels observed in this study are on the average, about two times greater with the mean at IIT being four times greater for both elemental and organic carbon.

Figures 5-14 and 5-15 show the temporal variation observed in the carbon levels measured during LMUATS. Both C_v (organic) and C_e (elemental) carbon levels are elevated during the transport episode from 16-22 July at IIT and South Haven. The elemental carbon levels observed in Kankakee are much lower during this period suggesting that local combustion sources in Chicago are responsible for the elevated levels there as well as at the downwind site in South Haven. Elemental carbon concentrations on the lake were typically very low as would be expected from the previous discussion.

5.1.2. Micro Orifice Impactor Results

Results of the analysis of filters from the Micro Orifice Impactor (MOI) were used to observe the size distribution of chemical species at the two sampling sites. $SO_4^{2^-}$, NH_4^+ and H^+ consistently appeared on stages 4, 5 and 6 (primarily 4 and 5). The observation of these species in <1 µm diameter particles is typical of other similar measurements (Pierson *et al.*, 1989). The mass mean diameters (MMD) of H^+ , $SO_4^{2^-}$ and NO_3^- were calculated from data from all 6 stages by determining the nominal diameter at which 50% of the mass resided. H^+ and $SO_4^{2^-}$ were on very small particles with a mass mean diameter approximately 0.35 µm while NO_3^- appeared to reside on slightly larger sizes (1.5 µm).



Figure 5-14. Variations in Measured Elemental Carbon Concentrations.



2

Figure 5-15. Variations in Measured Organic Carbon Concentrations.

5.2. Average Trace Element Concentrations

Trace element determinations were made on Teflon filters collected using dichotomous samplers as described earlier. X-Ray Fluorescence (XRF) analysis was performed on each pair (fine and coarse) of samples collected at the 3 land-based sites and on the R/V *Laurentian*. Tables 5-3 and 5-4 provide a statistical summary of the concentrations of the 16 elements and the particulate mass in the fine and coarse fraction of the PM10. The Kankakee site was found to have the highest mean concentrations for fine mass as well as several of the lighter elements such as Al, Br, S, and Cl in the fine fraction. The fine fraction Se concentration was on average the highest, suggesting the regional coal combustion influence is dominant at Kankakee. The highest concentrations for the remainder of the elements, most of which are anthropogenic in origin, were observed at the IIT site.

Sulfur, almost entirely in the form of sulfate, is the largest elemental contributor to the fine particulate mass at each site. As discussed earlier, the measured sulfate is often very acidic and is found in various states of neutralization. The next most abundant elemental species was Si (with the exception of the Kankakee site, where Si composed an average of about 10% of the total PM10). The soil-derived elements Al, K, Ca, and Fe were the next most abundant in terms of mass, together contributing about 5% to the PM10 measured.

The average Al concentration measured at the Kankakee site, both fine and coarse, is elevated above the levels observed at the other sites. Table 5-5 gives a comparison of the ratios of Al/Si, K/Si, Ca/Si, and Fe/Si at the sites to the average crustal abundance given by Mason (1966) to investigate if other source impacts are found in addition to soil. It is clear that the Kankakee site is being impacted by a combustion source emitting Al in the PM10 range. The fine Al/Si concentration ratio for South Haven is 0.80 which is also elevated above the crustal average. This average is strongly influenced by the extremely elevated Al concentration measured on 2 August which comprised more than half of the mean. If this one sample were removed, the fine Al/Si ratio would drop to 0.4, which is closer to the IIT ratio and the crustal average. The table also suggests that a source or combination of sources of fine Fe and Ca are also contributing to the Fe and Ca observed at all of the sites. Except for the coarse Al/Si ratio at Kankakee, the remaining concentration ratios are similar to the crustal average, suggesting that the coarse-fraction aerosols are primarily of soil or crustal origin.

		Kankakee	ПТ	R/V Laurentian*	South Haven
Mass *	Avg	20.1 ± 14.1	17.9 ± 11.9	9. 8 <u>+</u> 6.8	13.6 ± 12.6
	Max	54.7 (7/18)	45.4 (7/19)	28.6 (8/7)	50.1 (7/17)
Al	Avg	550.9 <u>+</u> 905.3	77.6 <u>+</u> 94.6	8.7 <u>+</u> 44.0	101.1 <u>+</u> 356.6
	Max	4529.9 (7/22)	429.9 (7/22)	79.9 (8/7)	2756.4 (8/2)
Si	Avg	154.3 <u>+</u> 204.1	169.4 <u>+</u> 178.8	71.9 <u>+</u> 53.7	126.1 <u>+</u> 138.4
	Max	1044.8 (7/22)	858.2 (8/2)	162.3 (7/11)	911.7 (7/22)
S	Avg	2921.6 <u>+</u> 2718 .0	2437.3 <u>+</u> 2153.7	1229.8 <u>+</u> 1217.6	1811.3 <u>+</u> 2339.1
	Max	10355.3 (7/17)	7566.3 (7/17)	4708.2 (8/7)	8994.3 (7/17)
Cl	Avg	12.1 ± 8.9	8.7 <u>+</u> 12.9	8 .7 ± 7.0	6.3 ± 5.3
	Max	46.9 (8/2)	74.1 (8/8)	19.4 (7/12)	24.7 (7/11)
K	Avg	50.7 <u>+</u> 24.9	62.5 <u>+</u> 40.9	54.9 <u>+</u> 49.9	46.5 ± 31.8
	Max	124.0 (7/18)	175.4 (7/21)	169.2 (8/7)	145.0 (7/22)
Ca	Avg	69.0 <u>+</u> 52.9	78.6 ± 57.0	44.7 <u>+</u> 24.2	44.2 <u>+</u> 33.1
	Max	254.4 (7/25)	230.8 (7/22)	86.7 (7/24)	143.9 (7/22)
Ti	Avg	4.8 <u>+</u> 6.7	4.9 <u>+</u> 7.7	3.5 <u>+</u> 2.7	3.7 <u>+</u> 5.1
	Max	32.0 (7/22)	33.9 (7/22)	9.6 (7/24)	34.7 (7/22)
V	Avg	0.5 <u>+</u> 1.2	0.7 <u>+</u> 1.8	0.5 <u>+</u> 1.4	0.4 <u>+</u> 1.7
	Max	2.7 (7/20)	3.6 (7/22)	2.5 (8/5)	3.5 (7/22)
Mn	Avg	3.2 <u>+</u>	6.2 <u>+</u> 10.7	4.1 <u>+</u> 4.9	2.9 <u>+</u> 2.5
	Max	10.1 (8/1)	59.3 (7/22)	19.4 (8/6)	11.7 (11/17)
Fe	Avg	74.3 <u>+</u> 67.6	124.8 <u>+</u> 122.8	78.5 <u>+</u> 102.6	63.7 <u>+</u> 67.5
	Max	291.5 (7/22)	558.1 (8/8)	401.1 (8/6)	316.6 (11/22)
Ni	Avg	0.5 ± 0.9	0.2 <u>+</u> 0.7	0.1 ± 0.7	0.0 <u>+</u> 0.7
	Max	2.7 (7/29)	1.5 (7/14)	1.2 (8/5)	1.6 (8/2)
Cu	Avg	6.2 <u>+</u> 4.0	10.0 ± 5.2	5.6 <u>+</u> 5.2	3.7 <u>+</u> 2.9
	Max	20.2 (8/2)	22.3 (7/21)	23.2 (7/23)	15.4 (8/8)
Zn	Avg	22.3 <u>+</u> 15.5	38.8 <u>+</u> 59.2	21.2 <u>+</u> 20.1	13.8 <u>+</u> 12.8
	Max	78.8 (7/11)	294.1 (8/8)	63.9 (8/6)	63.9 (7/17)
Se	Avg	1.5 <u>+</u> 1.7	1.0 <u>+</u> 1.0	1.1 <u>+</u> 1.4	0.9 <u>+</u> 0.8
	Max	9.4 (8/6)	4.1 (8/8)	4.5 (8/7)	3.0 (7/18)
Br	Avg	3.6 <u>+</u> 1.7	2.8 ± 1.0	2.4 <u>+</u> 1.3	1.8 <u>+</u> 1.0
	Max	7.4 (8/6)	4.9 (8/8)	4.3 (7/12)	4.8 (7/17)
РЬ	Avg	13.2 ± 7.1	14.3 <u>+</u> 14.9	8.5 <u>+</u> 9.8	5.7 <u>+</u> 4.9
	Max	32.4 (7/12)	62.1 (8/8)	36.3 (8/6)	27.5 (7/24)

Table 5-3. Average and Maximum Concentrations for Fine Fraction TraceElements Determined by XRF (ng/m³).

◆µg/m³ (mass, only)

* Sampling Dates R/V on-station 7/11-7/12, 7/25-7/27, 8/5-8/8, reflect periods of predominantly northerly flow

		Kankakee	IIT	R/V Laurentian	South Haven
Mass	Avg	18511 <u>+</u> 13470	15135 <u>+</u> 12386	6281 <u>+</u> 3636	8271 <u>+</u> 4969
	Max	54991 (8/2)	48282 (8/2)	14631 (7/24)	22697 (7/19)
Al	Avg	4736.2 <u>+</u> 5251.1	615.6 <u>+</u> 582.7	165.9 <u>+</u> 188.2	232.1 <u>+</u> 210.2
	Max	19772.2 (8/2)	2472.9 (8/2)	533.5 (7/24)	757.6 (7/19)
Si	Avg	1066.5 <u>+</u> 722.1	2000.2 <u>+</u> 1995.9	713.3 <u>+</u> 509.9	1010.9 <u>+</u> 785.1
	Max	2859.4 (7/20)	8368.1 (8/2)	1862.5 (7/24)	3285.3 (7/19)
S	Avg	193.8 <u>+</u> 115.2	141.5 <u>+</u> 130.4	78.5 <u>+</u> 65.0	107.1 <u>+</u> 113.2
	Max	591.5 (8/6)	510.3 (8/6)	257.9 (8/6)	448.9 (7/18)
Cl	Avg	32.1 <u>+</u> 19.5	47.7 <u>+</u> 41.1	32.5 <u>+</u> 47.3	24.9 <u>+</u> 27.1
	Max	72.4 (7/26)	174.9 (8/6)	210.5 (8/6)	155.9 (7/19)
К	Avg	112.8 ± 46.8	192.7 <u>+</u> 183.4	78.2 <u>+</u> 45.7	98.5 <u>+</u> 58.5
	Max	216.1 (8/2)	776.8 (8/2)	181.6 (7/24)	263.1 (7/19)
Ca	Avg	676.2 <u>+</u> 388.1	1150.7 <u>+</u> 1036.7	381.1 <u>+</u> 289.9	355.9 <u>+</u> 335.0
	Max	1505.3 (7/17)	4082.5 (8/2)	1123.4 (7/24)	1276.0 (7/18)
Ti	Avg	23.3 <u>+</u> 15.4	44.8 <u>+</u> 41.4	16.6 <u>+</u> 11.1	18.0 ± 14.8
	Max	64.9 (7/22)	166.6 (8/2)	49.8 (7/24)	57.5 (7/19)
v	Avg	1.0 ± 2.3	1.9 <u>+</u> 2.2	0.7 ± 1.1	0.7 ± 2.5
	Max	3.7 (7/20)	7.7 (7/19)	2.5 (7/12)	3.6 (7/11)
Mn	Avg	7.9 <u>+</u> 5.2	15.6 <u>+</u> 14.6	7.6 <u>+</u> 7.3	6.9 <u>+</u> 6.3
	Max	23.1 (7/26)	64.2 (8/6)	29.5 (8/6)	23.3 (7/19)
Fe	Avg	233.5 ± 132.5	589.2 <u>+</u> 472.8	247.9 ± 283.4	207.0 <u>+</u> 199.7
	Max	609.8 (7/26)	1894.4 (8/2)	1153.2 (8/6)	742.5 (7/18)
Ni	Avg	1.3 ± 1.5	0.5 ± 1.2	0.1 ± 0.8	0.1 ± 1.3
	Max	4.4 (8/2)	5.4 (7/19)	1.6 (7/12)	7.7 (7/17)
Cu	Avg	13.4 ± 12.0	9.9 <u>+</u> 15.8	3.1 ± 3.1	3.7 <u>+</u> 6.1
	Max	40.1 (7/19)	93.0 (7/19)	11.7 (8/6)	30.1 (8/5)
Zn	Avg	14.9 <u>+</u> 10.4	21.9 <u>+</u> 17.6	8.2 ± 8.3	6.4 <u>+</u> 6.7
	Max	42.2 (8/5)	67.4 (8/8)	31.2 (7/24)	37.1 (7/17)
Se	Avg	0.0 + 0.4	0.0 + 0.3	0.0 + 0.4	0.0 + 0.4
	Max	1.1 (7/26)	0.8 (7/21)	0.6 (8/6)	1.0 (7/20)
Br	Avg	0.5 + 0.6	0.6 + 0.6	0.7 + 1.1	0.5 + 0.6
	Max	1.7 (7/9)	1.8 (7/22)	3.9 (8/6)	2.0 (7/16)
Pb	Avg	3.3 + 2.2	10.6 + 14.9	2.9 + 2.9	1.8 + 2.8
	Max	7.8 (7/19)	80.6 (7/9)	11.1 (8/6)	18.4 (7/17)

Table 5-4. Average and Maximum Concentrations for Coarse Fraction Trace Elements Determined by XRF (ng/m³).

•ug/m³ (mass, only)
* Sampling Dates R/V on-station 7/11-7/12, 7/25-7/27, 8/5-8/8, reflect periods of predominantly northerly flow.

Site	Al/Si		K/Si		Ca/Si		Fe/Si	
	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Kankakee	3.60	4.40	0.33	0.11	0.45	0.63	0.48	0.22
IIT	0.46	0.31	0.36	0.10	0.46	0.58	0.74	0.29
R/V Laurentian	0.12	0.23	0.76	0.11	0.62	0.53	1.1	0,35
South Haven	0. 80	0.23	0.37	0.10	0.35	0.35	0.50	0.20
Green Bay (Aerosol Study)	1.4	0. 78	0.9	0.13	0.66	0.61	0.96	0.20
Crustal Average (Mason)	0	20	0.	.10	0	.13	0	18

Table 5-5. Average Compositional Ratios for Selected Elements.

The levels of many elements measured during the LMUATS are similar from one site to the other. While it was expected that Kankakee would have lower levels due to its rural location with little local industrial activity, this was not the case. Kankakee observed higher average levels of trace elements, in both size fractions, than the "downwind" rural site in South Haven. For example, Figure 5-16 shows the fine Pb concentrations measured at the four measurement sites. The range in Pb levels observed in Kankakee are greater than what was observed in South Haven. Interestingly, the maximums observed aboard the R/V *Laurentian* (nearly 40 ng/m³) are higher than those measured in Kankakee. Both of the peaks observed on the R/V *Laurentian* were observed on days when, for at least a portion of the sampling period, the vessel was downwind of the Chicago or Gary urban/industrial areas.

The urban site in Chicago (IIT) observed comparable or slightly higher levels of most trace elements found in the fine fraction. The concentrations of fine Mn, Fe, Cu, and Zn were only two times higher than those measured in Kankakee and about three times greater, on the average, than those measured in South Haven. The concentration of coarse fraction elements was also about two to three times greater in Chicago than at the other sites. Figure 5-17 displays the coarse Pb concentrations measured at the four sites. The levels of coarse Pb are much higher at IIT than at any of the other sites.











While Pb was typically sub-micron in size when leaded gasoline was still used prior to the late 1980s, the industrial Pb emission is more bi-modal in size suggesting that fugitive emissions may be comparable in importance to the current combustion emissions.

The levels of the trace elements measured aboard the R/V *Laurentian* were lower, on the average, than those measured at the shoreline sites. This is largely because of the prevailing northerly flow that the vessel received while on station. Since there are no large sources in the lake and the upwind fetch from the sampling point in southern Lake Michigan is hundreds of kilometers of open water, the levels of most pollutants would not be expected to be very high. However, the first cruise on 11-12 July positioned the R/V *Laurentian* 20 miles offshore from Muskegon and easterly flow resulted in elevated levels of many elements including Se and Zn. There were also westerly winds from the Greater Chicago area for the daytime sample on the 24 July which brought elevated Pb levels, both fine and coarse, as well as elevated Zn. The last cruise was also successful in being influenced by the industry in Gary, IN.

The influence of the iron-steel industry on the composition of the measured aerosol is observed clearly in Figures 5-18 through 5-20. The fine Fe concentrations are seen in Figure 5-18. Elevated Fe levels are seen at all three sites, and as suggested earlier, above what would be expected from windblown dust. The peaks in the fine Fe are seen in Chicago and aboard the R/V *Laurentian* during the last few days of the study. These days were characterized by southeast winds bringing emissions from southeast Chicago and Gary to both measurement sites. Concurrent peaks in the fine Mn concentration are seen in Figure 5-19. The PM10 episode observed from 16-22 July is also obvious in these plots of fine Fe, Mn, and Zn. The plots clearly show that the levels of these marker elements for iron-steel combustion are higher both at IIT and South Haven during the period 16-20 July. This would suggest that the cleel plants in the Gary/southeast Chicago area are the most important contributor to the levels of these metals measured in South Haven. On July 21, the concentrations of fine Fe are elevated at both Kankakee and IIT but not at South Haven. This is because a stationary front sitting between South Haven and Chicago cut this site off from the southerly flow hitting the sites south of the front. The levels observed at the three land-based sites on 22 July are all elevated except that the highest concentrations are observed first in Kankakee. This is consistent with the mixed layer trajectories for this day which connect Kankakee with Chicago and South Haven. The elevated concentrations of iron-steel plant marker elements is also seen on 5-8 August.







Figure 5-19. Variations in Measured Fine Particle Mn Concentrations.




This period was one in which the R/V *Laurentian* was on station off Chicago and was impacted by the plume from the Gary steel industry. The winds were out of the southeast during this period at both the IIT site and the R/V *Laurentian*.

The concentrations of fine Si are shown in Figure 5-21. Aerosol Si is typically a good marker element for windblown soil but elevated concentrations of fine Si suggest another source contributing to the levels observed. Peaks in the fine Si concentration are observed at each site, but not always on the same day. It has been suggested that fine particle Si is a product of the reduction of the original oxide in coal (SiO₂) during combustion, causing volatilization of SiO followed by re-oxidation to form SiO₂. While this explanation is possible, it is hard to see a clear relationship between the fine Si and the fine Se (marker for coal combustion) shown in Figure 5-22.

5.3. Atmospheric Mercury Levels

5.3.1. Measured Vapor-Phase Levels

The concentration of atmospheric Hg varied greatly from site to site and from day to day during the study. At IIT the vapor-phase Hg concentrations measured from 10 July - 9 August, 1991 ranged from 1.8 - 62.7 ng/m³, with an average of 8.7 ng/m³ (Table 5-6). The peak concentration was measured from a 6 hour sample in the afternoon on 8 August. The subset of samples collected at IIT and at South Haven for 6 hour periods were averaged to generate a 12 hour mean for purposes of comparison among sites (Figure 5-23). Twenty-five vapor-phase Hg samples were collected on the R/V *Laurentian*, during the three separate cruises. The average vapor-phase Hg concentration measured on the R/V *Laurentian* was 2.3 ng/m³. The mean vapor-phase Hg concentration observed in South Haven was quite typical of previous measurements in the Great Lakes basin, 2.0 ng/m³. (Schroeder, 1982 Glass *et al.*, 1990 and Fitzgerald *et al.*, 1991). A total of four duplicate samples were collected at South Haven. The average precision for the vaporphase sampling was better than 15%.





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Figure 5-22. Variations in Measured Fine Particle Se Concentrations.



Figure 5-23. Variations in Measured Vapor-Phase Hg Concentrations.

Date

5.3.1.1. Diurnal Variation of Vapor-Phase Mercury

Samples were collected more intensively at the IIT site with 18 samples collected between 8AM-2PM (designated as AM), 17 samples collected between 2PM-8PM (PM), 11 daytime 12-hour samples collected between 8AM-8PM (DAY) and 12 nighttime samples were collected from 8PM-8AM (NIGHT). This frequency of sampling allowed us to investigate the diurnal behavior of vapor-phase Hg. The average concentration (ng/m³) for the AM samples was 3.3 times larger than that for the NIGHT samples. The average concentration for the PM samples was 2.1 times larger than NIGHT samples (Figure 5-24). The mean vapor-phase Hg concentration for AM and PM samples was 10.1 ng/m³, while for the DAY samples it was 9.9 ng/m³.

SITE	n	MEDIAN	MEAN	STD DEV	MIN	MAX
IIT	58	4.5	8.7	12.0	1.8	62.7
LAU*	25	2.2	2.3	0.7	1.3	4.9
SHA	38	1.8	2.0	0.6	1.8	4.3

Table 5-6. Vapor-phase Hg Measurements in Chicago (IIT), on the R/V Laurentian (LAU) and in South Haven (SHA) (ng/m³).

*DATES: R/V on-station 7/11-7/12, 7/25-7/27, 8/5-8/8

5.3.1.2. Spatial Variation in Vapor-phase Hg

Vapor-phase Hg concentrations were significantly lower at sites distant from Chicago. The concentrations of vapor-phase Ho measured in South Haven and aboard the R/V *Laurentian* were on average half those concentrations measured at IIT. Two episodes were evident during the study, marked by predominant flows from the southwest, carrying pollutants such as sulfate and particulate matter from upwind sites to downwind sites on the RV and in South Haven. During the first episode, 19-23 July, a slight increase in Hg^o at the IIT site was observed; a corresponding increase in Hg^o at the South Haven site was not detected.



Figure 5-24. Variations in Measured Vapor-Phase Hg in Chicago.

5.3.2. Measured Particulate-Phase Levels

At two of the land sites, the Illinois Institute of Technology in Chicago (south side) and South Haven, MI, and on the research vessel R/V *Laurentian*, vapor- and particle-phase Hg samples were collected. The particle-phase samples [Hg(p)] were collected on glass-fiber filters for 24 hours (8AM - 8AM CDT) at 30 LPM in open-faced filter packs and at 10 LPM in cyclone-inlet filter packs. In some instances, additional open-faced filter packs were taken with glass-fiber and Teflon filters. The glass-fiber TSP samples were analyzed by CVAFS while the fine mass and TSP samples collected on Teflon were analyzed by INAA at MIT. The results from these samples are summarized in Figure 5-25.

The Hg(p) results from the different analytical techniques together with values for vapor-phase Hg, aerosol mass, aerosol elemental content, and meteorological parameters begin to define some potential trends in the atmospheric chemistry for Hg(p). The Hg(p)detected using CVAFS was in almost all instances significantly lower than that measured by INAA. Values for both techniques yielded higher concentrations for the Chicago site (IIT) and less for the R/V Laurentian and in South Haven. However, the differences between the radiochemical and wet extraction techniques were much smaller in Chicago than in South Haven. Size-segregated samples (fine and total suspended mass) from South Haven analyzed by INAA indicate significant amounts of Hg(p) in the coarse fraction. The CVAFS and INAA results on fine fraction samples were very similar. This apparent chemical- and/or size-dependent distinction strongly indicates a natural source for Hg found in the coarse fraction at the South Haven site. In the coarse fraction, particulate Hg which is strongly bound to particulate matter appears to be unavailable for extraction using strong acids and is only quantified by radiochemical techniques. In contrast, fine fraction particulate Hg appears to be equally recovered by acid digestion and neutron activation analysis.

Other data collected during this study support this explanation for the difference between results from the acid digestion versus neutron activation analysis of particulate Hg. The Hg(p) value for TSP as determined by INAA correlates significantly ($r^2=0.72$ P<.0001) with the coarse-to-fine-mass ratio (Figure 5-26). The values for fine Hg(p) by INAA (no corroborative data for CVAFS) display peak values during the primary air quality "episode" from 16-22 July.





Figure 5-26. Correlation of Hg(p) by INAA Measured at South Haven with the Coarse-to-Fine-Mass Ratio.



During the 16-22 July episode, air flow was predominantly from the SW and was accompanied by elevated ozone, sulfate, acidity and marker elements for various metallurgical industries. Unfortunately, TSP mass concentrations at South Haven were not measured. Information on typical soil concentrations of Hg given by Fergusson (1991) suggests that soil Hg ranges from 0.01 - 0.5 ppm (pg Hg/µg soil) globally. In order to observe the concentrations of Hg(p) found in South Haven by INAA (200 pg/m³), coarse fraction particle mass (in the size range 2.5 - 10 µm and >10µm) would have to range between 4 - 200 µg/m³.

The observed coarse mass in the size range $2.5 - 10 \ \mu\text{m}$ at South Haven ranged between $2 - 22 \ \mu\text{g/m}^3$, which is not enough to account for all of the Hg(p) measured. This finding indicates that particles greater than $10\mu\text{m}$ are likely to be a contributing factor to the particulate Hg measured, since particles of size $10 - 30 \ \mu\text{m}$ are collected as part of particulate Hg sampling. The Hg content of the soil in South Haven was measured by the University of Michigan Air Quality Laboratory to be 0.99 ppm, about twice the unperturbed background level given above. Therefore, resuspended soil particles in the size range $10 - 30 \ \mu\text{m}$ could be responsible for a significant portion of the Hg observed in the coarse fraction. The local soil in South Haven may have been previously contaminated through deposition of Hg or the application of mercury-containing compounds (pesticides).

The behavior outlined above (between INAA and CVAFS) was not observed in Chicago. At IIT, the INAA and CVAFS results more closely approximate each other in most instances. The difference in behavior observed between South Haven and Chicago can be explained by first assuming that anthropogenically emitted Hg(p) can exist in both the fine and coarse fractions. This assumption has been initially confirmed from a brief sampling program carried out in Ann Arbor with the collection of TSP and fine mass quartz-fiber illters side-by-side followed by analysis with CVAFS. Figure 5-27 and Table 5-7 summarize these results. It is clear from these samples that Hg(p) which is acid-extractable by our technique may be found in both the coarse and fine fractions, but that on some occasions, it resides primarily in the fine fraction. In Chicago, a similar profile may exist, but during transport across Lake Michigan, the larger coarse fraction material is lost from the urban plume more rapidly than the fine material by settling. Thus, the profile of the urban plume will change during transport, becoming devoid of anthropogenic, "acid-extractable" Hg in the coarse fraction when it reaches South Haven.

Figure 5-27. Results of Size Segregated Particulate Hg Sampling in Ann Arbor.



The findings just presented were further explored during a two-week sampling campaign at the Ann Arbor NDDN site outside of Dexter. The same sampling and analytical schemes were utilized in the more recent study. The findings from that longer experiment corroborated the results presented here: Aerosol Hg(p) can be found in both the fine and coarse fraction, and that the total particulate Hg is, on occasion, equal to the fine. At this point we cannot state what controls the size distribution of the atmospheric particulate Hg we have measured. The findings presented here *may be the first to substantiate the existence of a coarse particle Hg* in the Great Lakes Basin. Ongoing research at the UMAQL will continue to shed new light on this important topic.

Day	PM 2.5	TSP	% in Fine
1	182	187	97
2	56	112	50
3	43	72	60
4	10	27	37
5	85	158	54

Table 5-7. Results From TSP v. FM CVAFS Analysis of Hg (pg/m³).

5.4. Average VOC Concentrations

The concentrations of volatile organic compounds (VOC) were measured using summa canisters as discussed previously in Section 3. A summary of the arithmetic mean, standard deviation, and maximum concentrations determined by Battelle Columbus is given in Table 5-8. Also shown is the date that the maximum occurred to help assist us in determining the cause of the elevated concentrations measured at each site. This also helps to identify concurrent maximums between sites, and to facilitate the cross correlation of maximum days with other maximums found for the other compounds.

The VOC data were not utilized extensively for this report. The data were thought to be somewhat suspect since the levels are significantly lower than typical ambient concentrations. The poor data quality was explained by a contaminant problem in the majority of canister samples. Analytical contamination was ruled out by routine processing of standard reference materials. A subset of samples collected at Kankakee were collocated with 2 hour VOC collections as part of the LMOS study. For the three collocated samples, only benzene concentrations agreed well. Concentrations of toluene, ethyl benzene, and p+p-xylene were significantly lower in LMUATS measurements as compared to LMOS study measurements. Potential reasons for the low values may include poorly cleaned canisters, poor vacuum seal or preparation, inadequacies in sample collection or handling or improper extraction procedures. This problem may have been avoided if proper blanks had been collected and analyzed before shipment of canisters to collection sites and immediate analysis of the first subset of samples from each of the sites to ensure that valid data was being collected. The research teams should have been notified immediately when a problem was discovered.

As a result of the inadequate data, the VOC data will not be useful in receptor modeling as it has in other studies. This is a disappointment as the EPA-AREAL has successfully utilized this type of data in the past in CMB-type analyses.

5.5. Average PAH Concentrations

The average and maximum of atmospheric concentrations of total (vapor + particle) PAHs at four sites are summarized in Table 5-9. The concentrations at IIT were the highest among four sites and the concentrations at South Haven were the lowest while the concentrations on R/V *Laurentian* were slightly higher than those at Kankakee. Except retene, which showed a more regional distribution largely due to its natural vegetative source (Figure 5-28), the concentrations of volatile PAHs in Chicago (IIT) were about ten to fifty times greater than the concentrations observed at South Haven. The concentrations of the higher molecular weight PAHs were about ten times higher in Chicago. The steady concentration profile for coronene, a marker compound for motor vehicles is shown in Figure 5-29. The elevated levels of coronene observed in Chicago are expected due to the density of motor vehicle traffic in the large urban area. The 10-fold decrease in the coronene concentrations observed both in South Haven and in Kankakee is an indication of both the dearth of local traffic at those sites and dispersion that is taking place between the source and the sites.



Figure 5-28. Variations in Measured Retene Concentrations.



Figure 5-29. Variations in Measured Coronene Concentrations.

		Kankakee	IIT	Laurentian	South Haven
1) dichlorodifluoromethane	Avg	0.52 ± 0.21	0.68 ± 0.20	0.54 ± 0.20	0.48 ± 0.08
	Max	1.1 (7/17)	1.22 (7/24)	1.05 (7/26)	0.67 (7/17)
2) methyl chloride	Avg	0.49 ± 0.20	0.57 ± 0.17	0.51 ± 0.21	0.54
	Max	0.72 (7/19)	0.89 (7/15)	0.75 (7/26)	0.54 (7/22)
8) trichlorofluoromethane	Avg	2.27 + 2.92	1.94 ± 1.99	0.78 ± 0.21	0.73 ± 0.13
	Max	9.34 (7/21)	8.76 (7/21)	1.33 (7/27)	1.08 (7/21)
10) 1,1-dichloroethene	Avg	< 0.1	0.38 ± 0.13	< 0.1	< 0.1
	Max		0.47 (7/19)	-	-
11) dichloromethane	Avg	0.29	0.63 ± 0.38	0.31 ± 0.03	0.28 ± 0.07
	Max	0.29 (7/30)	1.40 (7/31)	0.33 (7/24)	0.40 (8/6)
12) 3-chloropropene	Avg	< 0.1	0.37 ± 0.11	< 0.1	0.97 <u>+</u> 1.20
· · ·	Max		0.45(7/21)	-	1.82 (7/25)
13) 1,1,2-trichloro-1,2,2-trifluoroethane	Avg	3.11 ± 3.60	1.76 + 2.15	0.18 ± 0.06	1.14 ± 0.96
	Max	15.31 (7/19)	6.32 (7/23)	0.35 (7/24)	3.47 (7/20)
17) 1,2-dichloroethane	Avg	0.16 + 0.06	< 0.1	0.24	< 0.1
	Max	0.24 (7/29)	-	0.24 (8/6)	-
18) 1,1,1-trichloroethane	Avg	0.20 ± 0.08	0.29 + 0.13	0.24 ± 0.08	0.22 ± 0.11
	Max	0.46 (7/25)	0.76 (7/24)	0.41 (7/24)	0.52 (7/12)
19) benzene	Avg	0.41 ± 0.15	0.85 ± 0.68	0.33 ± 0.14	0.34 ± 0.45
	Max	0.83 (7/19)	4.11 (8/2)	0.61(8/7)	2.34 (7/21)
20) carbon tetrachloride	Avg	0.12 ± 0.04	0.12 ± 0.05	0.12 ± 0.04	0.11 ± 0.01
	Max	0.22 (7/25)	0.25(7/24)	0.23(7/27)	0.11 (8/6)
22) trichloroethene	Avg	< 0.1	0.14 + 0.06	0.23	0.20
	Max		0.23(7/24)	0.23 (7/24)	0.20 (7/12)
27) toluene	Avg	0.38 ± 0.27	2.33 + 2.72	0.67 + 0.67	0.97 + 1.86
	Max	1.06 (7/19)	15.08 (8/2)	2.39(7/11)	8.26 (7/21)
29) tetrachloroethene	Avg	0.69 + 0.67	0.33 + 0.36	0.23	0.13
	Max	1.16 (7/19)	1.44 (7/9)	0.23 (7/24)	0.13 (7/18)
30) chlorobenzene	Avg	0.39 + 0.22	< 0.1	< 0.1	< 0.1
· · · · · · · · · · · · · · · · · · ·	Max	1.01 (7/22)	-	-	-
31) ethvl benzene	Avg	0.12 + 0.02	0.28 ± 0.38	0.28 ± 0.12	0.44 + 0.48
· · ·	Max	0.13 (7/25)	1.96 (8/2)	0.47 (7/11)	0.99 (7/21)
32) m+p-xvlene	Avg	$C.20 \pm 0.08$	0.73 ± 1.19	0.72 ± 0.62	0.69 ± 1.31
	Max	0.28 (7/25)	6.87 (8/2)	2.10(7/11)	3.90 (7/21)
33) styrene	Avg	< 0.1	< 0.1	0.18 ± 0.06	0.59 ± 0.81
	Max	-	-	0.27(7/11)	2.22 (7/12)
35) o-xylene	Avg	0.11	0.29 ± 0.47	0.33 ± 0.21	0.50 ± 0.65
	Max	0.11 (7/25)	2.52 (8/2)	0.72(7/11)	1.46 (7/21)
36) 4-ethvl toluene	Avg	< 0.1	0.24 + 0.25	< 0.1	0.44
· •	Max	-	0.79 (8/2)	-	0.44 (7/21)
37) 1,3,5-trimethylbenzene	Avg	< 0.1	0.18 ± 0.16	< 0.1	0.29
· · · ·	Max	-	0.55 (8/2)	-	0.29 (7/21)
38) 1,2,4-trimethylbenzene	Avg	< 0.1	0.30 ± 0.39	< 0.1	0.63 <u>+</u> 0.56
	Max	-	1.95 (8/2)	-	1.02 (7/21)

Table 5-8. Average and Maximum Concentrations of VOC (ppbv).

		Kankakee	ШТ	Laurentian	South Haven
Naphthalene	Avg	287.59 + 342.48	507.25 + 179.84	119.38 ± 125.36	66.32 <u>+</u> 66.06
-	Max	963.14 (7/16)	805.66 (7/16)	421.42 (8/7)	230.04 (7/17)
Acenaphthylene	Avg	2.61 ± 2.18	4.79 <u>+</u> 2.82	1.41 <u>+</u> 0.98	0.49 ± 0.24
	Max	6.72 (7/29)	14.21 (8/8)	3.81 (8/7)	1.00 (8/6)
Acenaphthene	Avg	1.82 <u>+</u> 0.93	55.91 <u>+</u> 39.68	2.28 ± 2.11	1.10 ± 0.37
	Max	3.42 (8/6)	133.38 (7/16)	8.10 (7/23)	1.78 (8/2)
Fluorene	Avg	3.69 <u>+</u> 1.81	53.67 <u>+</u> 33.55	7.17 <u>+</u> 4.50	3.45 ± 1.90
	Max	6.51 (8/6)	132.29 (7/16)	15.69 (8/7)	7.79 (7/17)
Phenanthrene	Avg	7.97 <u>+</u> 3.89	167.92 <u>+</u> 125.07	10.78 <u>+</u> 9.11	4.81 <u>+</u> 2.05
	Max	14.16 (8/6)	427.53 (7/22)	31.13 (7/23)	8.94 (7/18)
Anthracene	Avg	0.30 ± 0.34	7.59 <u>+</u> 5.87	0.27 <u>+</u> 0.25	0.13 <u>+</u> 0.06
	Max	1.40 (7/17)	17.60 (7/16)	0.78 (7/23)	0.23 (8/5)
Fluorenone	Avg	1.02 ± 0.43	12.08 <u>+</u> 7.30	1.11 ± 0.63	0.86 ± 0.46
	Max	2.00 (8/6)	23.42 (7/31)	2.39 (7/24)	1.99 (7/18)
Retene	Avg	0.27 ± 0.15	0.58 ± 0.25	0.57 <u>+</u> 0.31	0.45 ± 0.22
	Max	0.53 (7/16)	0.92 (7/18)	1.30 (7/11)	0.76 (7/18)
Fluoranthene	Avg	2.09 ± 1.63	46.58 <u>+</u> 29.26	3.22 <u>+</u> 2.87	1.50 <u>+</u> 0.91
	Max	7.13 (7/17)	109.70 (7/22)	8.80 (8/6)	3.72 (7/17)
Pyrene	Avg	1.11 ± 1.17	23.58 ± 14.37	1.60 ± 1.52	0.77 ± 0.42
	Max	5.19 (7/17)	55.30 (7/22)	5.18 (8/6)	1.75 (7/17)
Benz(a)anthracene	Avg	0.25 ± 0.66	3.02 ± 2.78	0.26 ± 0.39	0.14 ± 0.15
	Max	2.70 (7/17)	8.88 (7/22)	1.25 (8/6)	0.57 (7/17)
Chrysene	Avg	0.33 ± 0.66	5.17 <u>+</u> 3.82	0.62 <u>+</u> 0.86	0.31 <u>+</u> 0.36
	Max	2.77 (7/17)	12.96 (7/22)	2.50 (8/6)	1.32 (7/17)
Cyclopenta(c,d)pyrene	Avg	0.03 ± 0.03	0.22 <u>+</u> 0.16	0.09 ± 0.15	0.05 ± 0.05
	Max	0.11 (8/6)	0.63 (8/2)	0.52 (8/6)	0.18 (7/17)
Benzofluoranthenes	Avg	0.58 ± 1.21	10.16 ± 9.55	0.91 ± 1.24	0.57 ± 0.71
	Max	5.09 (7/17)	32.89 (7/31)	3.74 (8/6)	2.59 (7/17)
Benzo(e)pyrene	Avg	0.17 ± 0.32	2.81 ± 2.61	0.25 <u>+</u> 0.32	0.17 ± 0.20
	Max	1.35 (7/17)	9.09 (7/31)	1.03 (8/6)	0.74 (7/17)
Benzo(a)pyrene	Avg	0.26 <u>+</u> 0.60	3.04 ± 3.88	0.25 <u>+</u> 0.31	0.14 <u>+</u> 0.16
	Max	2.49 (7/17)	15.31 (7/31)	0.80 (8/7)	0.69 (7/17)
Indeno(1,2,3-c,d)pyrene	Avg	0.30 <u>+</u> 0.53	3.90 <u>+</u> 3.17	0.41 ± 0.52	0.26 <u>+</u> 0.33
	Max	2.26 (7/17)	10.21 (7/22)	1.63 (8/6)	1.32 (7/17)
Dibenzo(a,h)anthracene	Avg	0.19 <u>+</u> 0.16	1.39 <u>+</u> 0.89	0.21 <u>+</u> 0.16	0.16 <u>+</u> 0.13
	Max	0.76 (7/17)	3.24 (7/22)	0.58 (8/6)	0.60 (7/17)
Benzo(g,h,i)perylene	Avg	0.23 ± 0.39	3.32 <u>+</u> 2.35	0.33 ± 0.43	0.21 <u>+</u> 0.26
	Max	1.68 (7/17)	7.99 (7/22)	1.39 (8/6)	1.02 (7/17)
Coronene	Avg	0.13 ± 0.10	1.39 <u>+</u> 0.97	0.16 <u>+</u> 0.15	0.09 <u>+</u> 0.07
	Max	0.34 (7/17)	3.90 (8/8)	0.43 (8/7)	0.31 (7/17)

Table 5-9. Average and Maximum Concentrations of PAHs (ng/m³).

Naphthalene was the most abundant PAH at all four sites and cyclopenta(c,d)pyrene was the least abundant. Results from studies of PAH concentrations in Boston and Houston, reported by Kelly *et al.* (1992), were from equivalent sampling and analytical protocols as those employed for LMUATS, allowing direct comparison between these sites. The concentrations of 2- to 3- ring PAHs at IIT were comparable to the levels measured in Boston during the Summer 1991 (Kelly *et al.*, 1992), while the concentration of the larger molecule PAHs was about five times higher at IIT than at Boston (Table 5-10). In general, the concentration of PAHs in Chicago appears to be significantly higher than those measured in Boston or Houston.

	IIT	Boston	Houston
Author Time	<i>This Study</i> Summer 91	Kelly <i>et al.</i> Summer 91	Kelly <i>et al.</i> Summer 91
Naphthalene	507	606	515
Acenaphthene	56	24.1	22.8
Fluorene	54	36.2	24.2
Phenanthrene	168	101	50.1
Anthracene	8	3	1.4
Fluorenone	12	10.2	5.4
Fluoranthene	47	16.7	10.2
Pyrene	24	8.4	7.9
Benz(a)anthracene	3	0.9	0.6
Chrysene	5	1	0.6
Cyclopenta(c,d)pyrene	0.22	0.3	0.2
Benzofluoranthenes	10	1.1	0.5
Benzo(e)pyrene	2.8	0.4	0.2
Benzo(a)pyrene	3.0	0.4	0.2
Indeno(1,2,3-c,d)pyrene	3.9	0.5	0.2
Dibenzo(a,h)anthracene	1.4	0.3	0.2
Benzo(g,h,i)perylene	3.3	0.6	0.3
Coronene	1.4	0.3	0.2

Table 5-10. Comparison of Urban Polynuclear Aromatic Hydrocarbons Concentrations Measured in Three Cities (ng/m³).

Figure 5-30 shows the naphthalene concentrations measured at the four sites. The maximum concentrations observed in Kankakee were associated with local stagnation and with weak transport to the south of the site. Maximum concentrations were also reported at IIT on the same days but they were lower in magnitude. The concentrations of benzo(a)pyrene measured during the month are shown in Figure 5-31. The concentrations are about an order of magnitude higher in Chicago than at any of the other sites.

The concentrations for five volatile PAHs measured on the R/V Laurentian were comparable to the daytime average concentrations at Glendora, CA, approximately 20 km northeast of Los Angeles and generally downwind of downtown Los Angeles. The average concentrations observed on the R/V Laurentian were about five times higher than the concentrations on Chesapeake Bay (Baker *et al.*, 1992) except for benzofluoranthenes and dibenzo(a,h)anthracene. Compared to the ambient concentrations measured on Lake Superior as reported by Baker and Eisenreich (cited in Eisenreich and Strachan, 1992), Table 5-11 shows the concentrations measured on Lake Michigan aboard the R/V Laurentian were about five to fifty times higher, except for dibenzo(a,h)- anthracene, which was about 500 times higher.









	Lake Michigan	South Haven	Lake Superior	Lake Superior	Chesapeake Bay
Author/Source Period of Study	This Study Summer '91	This Study Summer '91	Baker, 1992 1986	Hites, 1992 1981	Baker, 1992 1990
Naphthalene	119	66			
Acenaphthylene	1.4	0.49			
Acenaphthene	2.3	1.1			
Fluorene	7.2	3.5	0.5		0.7
Phenanthrene	10.8	4.8	2.7	2.1	2.1
Anthracene	0.27	0.13		0.004	0.06
Fluorenone	1.1	0.86			
Retene	0.6	0.5			
Fluoranthene	3.2	1.5			0.5
Pyrene	1.60	0.8	0.3	0.2	0.5
Benz(a)anthracene	0.26	0.14	0.03	0.008	0.05
Chrysene	0.62	0.31	0.06	0.2	0.1
Cyclopenta(c,d)pyrene	0.09	0.05			
Benzofluoranthenes	0.91	0.57	0.05		0.2
Benzo(e)pyrene	0.25	0.17	0.006	0.009	0.08
Benzo(a)pyrene	0.25	0.14	0.004	0.003	0.04
Indeno(1,2,3-c,d)pyrene	0.41	0.26	0.01	0.007	0.07
Dibenzo(a,h)anthracene	0.21	0.16	0.0004		0.01
Benzo(g,h,i)perylene	0.33	0.21	0.02	0.005	0.08
Coronene	0.16	0.09			

Table 5-11. Comparison of PAH Concentrations Measured On or Near the GreatWaters (Units are ng/m³).

5.6. Average PCB Concentrations

Atmospheric concentrations of total PCBs measured at IIT were 2.6-3.3 times higher than the total PCBs measured at the other 3 LMUATS sites (Table 5-12). In addition, total PCB concentrations measured at IIT were slightly higher than many of the other PCB measurements made in the Great Lakes region during the last five years (Table 5-13). Other investigations in the Great Lakes Basin in which elevated total PCBs were measured include a study by Hermanson in northern Michigan (reported in Eisenreich and Strachan, 1992) in which levels of total PCBs ranged from 31-1,860 pg/m³ and an investigation by Hornbuckle *et al.* (1992) in Green Bay, WI where total PCBs measured over the water ranged from 160-2200 pg/m³.

Average concentrations of total PCBs measured during LMUATS were slightly greater over Lake Michigan on the R/V *Laurentian* than the two rural land-based sites (Kankakee and South Haven). This same observation was reported by Hornbuckle *et al.* (1992) for Green Bay, WI. However, in their study, even larger differences in over-water vs. land-based concentrations were observed. The day-to-day variations in the total PCB concentrations measured are seen in Figure 5-32. Total PCB levels observed at Kankakee, on the R/V *Laurentian* and in South Haven ranged from 639 to 808 pg/m³. Other reported values for measurements made in Michigan and in other Great Lakes states are similar to, or lower than, the concentrations observed in this study.

Analysis of atmospheric samples for PCBs has historically suffered from poor source profile information, poor analytical and inter laboratory analytical comparisons and marked differences in PCB profiles between source and receptor locations. Individual PCB congeners exhibit widely varying physical and chemical properties, which determine their preferential phase partitioning. As a result of this lack of information, sourcereceptc. relationships for PCB congeners are very poorly understood. Further complicating the ability to interpret source-receptor relationships, is the lack of standardization of PCB congeners quantified and reported.

In the LMUATS PCB samples, 8 congeners were quantified: IUPAC Nos: 1, 5, 29, 50, 87, 154, 188 and 201 (Table 5-12). Since the numbers and the types of PCB congeners measured are different between studies, few data are available for comparison. In a study by Hoff *et al.* (1992) in Egbert, Ontario, PCB 87 levels measured were much lower than those quantified at the 4 LMUATS sites. However, Hoff reports levels of PCB 201 of 0.92 pg/m^3 from Egbert, which is almost identical to the concentration of this congener measured at IIT.

		Kankakee	IIT	Laurentian	South Haven
2-PCB	Avg	1 <u>+</u> 2	6 <u>+</u> 21	25 <u>+</u> 66	13 <u>+</u> 52
	Max	5 (8/7)	85 (7/19)	233 (8/7)	234 (8/7)
TOT. mono-PCB	Avg	60 <u>+</u> 49	77 <u>+</u> 68	164 <u>+</u> 113	101 <u>+</u> 105
	Max	138 (7/16)	267 (7/16)	356 (7/11)	428 (7/10)
2,3-PCB	Avg	12 <u>+</u> 18	94 <u>+</u> 57	30 <u>+</u> 42	28 <u>+</u> 36
	Max	51 (7/16)	189 (7/19)	160 (7/24)	171 (7/18)
TOT. di-PCB	Avg	83 <u>+</u> 106	186 <u>+</u> 124	107 <u>+</u> 73	82 <u>+</u> 60
	Max	267 (7/19)	425 (7/18)	252 (7/24)	191 (7/19)
2,4,5-PCB	Avg	0.03 <u>+</u> 0.13	0.05±0.19	0.02 <u>+</u> 0.09	0.00 <u>+</u> 0.00
	Max	0.51 (7/23)	0.74 (8/6)	0.32 (8/6)	0.00 (8/8)
TOT.tri-PCB	Avg	115 <u>+</u> 59	422 <u>+</u> 255	89 <u>+</u> 47	84 <u>+</u> 67
	Max	254 (8/5)	779 (7/20)	199 (7/24)	338 (8/8)
2,2',4,6-PCB	Avg	0.7 <u>+</u> 2.2	0.2 ± 0.4	0.4 <u>+</u> 0.6	0.9 <u>+</u> 2.6
	Max	8.4 (8/2)	1.2 (7/24)	1.7 (8/7)	11.5 (8/8)
TOT.tet-PCB	Avg	92 <u>+</u> 56	463 <u>+</u> 262	101 <u>+</u> 36	86 <u>+</u> 57
	Max	253 (7/18)	855 (7/23)	174 (7/24)	285 (8/8)
2,2',3,4,5'-PCB	Avg	11 <u>+</u> 24	47 <u>+</u> 37	16 <u>+</u> 7	9 <u>+</u> 7
	Max	95 (7/18)	134 (7/19)	30 (7/24)	25 (7/17)
TOT.pen-PCB	Avg	212 <u>+</u> 306	707 <u>+</u> 479	290 <u>+</u> 163	263 <u>+</u> 127
	Max	1296 (7/18)	1744 (7/19)	606 (7/24)	519 (7/17)
2,2',4,4',5,6'-PCB	Avg	0.2 ± 0.3	0.3 ± 0.4	0.1 ± 0.2	0.1 <u>+</u> 0.2
	Max	0.9 (7/23)	1.1 (7/16)	0.5 (7/24)	0.6 (7/15)
TOT.hexa-PCB	Avg	68 <u>+</u> 145	230 <u>+</u> 171	50 <u>+</u> 28	50 <u>+</u> 32
	Max	589 (7/18)	660 (7/19)	101 (7/11)	137 (7/17)
2,2'3,4',5,6,6'-PCB	Avg	0.1 <u>+</u> 0.3	0.00 <u>+</u> 0.00	0.00 <u>+</u> 0.01	0.1 ± 0.1
	Max	1.3 (7/23)	0.00 (8/8)	0.04 (7/11)	0.5 (7/17)
TOT.hep-PCB	Avg	6.7 <u>+</u> 9.8	42 <u>+</u> 33	7 <u>+</u> 5	5 <u>+</u> 4
	Max	41 (7/18)	108 (8/2)	16 (8/6)	13 (7/17)
2,2',3,3',4,5',6,6'-PCB	Avg	0.3 <u>+</u> 0.9	0.9 <u>+</u> 0.7	0.01 <u>+</u> 0.03	0.1 <u>+</u> 0.2
	Max	3.4 (7/23)	2.2 (8/2)	0.1 (7/11)	0.8 (7/17)
TOT.octa-PCB	Avg	0.4 <u>+</u> 0.5	10 <u>+</u> 9	0.6 <u>+</u> 0.7	0.3 ± 0.5
	Max	1.6 (7/18)	27 (8/2)	2.2 (7/24)	2.2 (7/17)
TOT.nona-PCB	Avg	0.6 <u>+</u> 1.6	1.9 <u>+</u> 3.3	0.3 <u>+</u> 0.5	1.2 <u>+</u> 3.2
	Max	6.2 (7/23)	11 (7/24)	1.6 (8/7)	11.9 (8/8)
deca-PCB	Avg	0.9 <u>+</u> 3.3	0.2 <u>+</u> 0.9	0.00 <u>+</u> 0.00	0.1 <u>+</u> 0.6
	Max	12.6 (7/23)	3.8 (7/24)	0.00 (8/7)	2.5 (7/12)
Total PCBs	Avg	639 <u>+</u> 602	2139 <u>+</u> 1214	808 <u>+</u> 357	672 <u>+</u> 279
	Max	2669 (7/18)	3999 (7/19)	1594 (7/24)	1216 (7/17)

Table 5-12. Ambient PCB Concentrations (pg/m^3) .

Author, period of study	Location	ΣΡCΒ
LMUATS, 1991	Kankakee, IL	639
	Chicago, IL	2139
	R/V Laurentian	808
	South Haven, MI	672
Keeler et al. (1993), 1993	Pellston, Michigan	24-860
(Unpublished data)	South Haven, Michigan	60 - 620
	Deckerville, Michigan	91-399
	Ann Arbor/Dexter, Michigan	83-640
Hermanson (1992), 1990-1991	Michigan	31 - 1,860
Holsen et al., 1991	IIT	940
Sweet (1992), 1989-1990	Michigan	120
Hornbuckle et al. (1992), 1991	N. Green Bay	100-300
Hornbuckle and Eisenreich (1992), 1991	Michigan	160 - 1,900
McConnell (1992), 1990	Huron	180
Hornbuckle and Eisenreich (1992), 1991	Huron	120 - 200
McConnell (1992), 1990	St. Clair, Erie	410, 520
Hornbuckle (1992), 1991	St. Clair, Erie	570, 470
Sweet (1992), 1990-1991	Pt. Petre	310
Hornbuckle (1992), 1991	Ontario	440 - 600
Hoff, Muir, Grift (1992) 1988 - 1989	Great Lakes	380 - 470
Hoff, Bidleman (1992), 1988 - 1989	Great Lakes	78 - 290
McConnell (1992), 1988 - 1989	Great Lakes	80 - 170
Murphy (1992), 1985	Chicago (1980-1981 n=4)	5,500 +/-2000
Manchester-Neesvig and Andren (1989),	Northern Wisconsin	135 winter to
1989		1,820 summer

Table 5-13. Polychlorinated Biphenyls Measured in the Great Lakes Basin(Units are pg/m³).





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During LMUATS, the concentration of congener 201 was three times lower in Kankakee than IIT and was even lower at South Haven and not detected on the R/V *Laurentian*. Schwackhamer *et al.* (1988) report levels of particulate 201 of 0.33 pg/m³, similar to the total 201 measured at Kankakee. The particulate 201 measurements by Schwackhamer *et al.* were made during the summer at Siskewit Lake on Isle Royal, a remote island in Lake Superior. In the same investigation, the authors report summertime levels of total PCBs that are almost 5 times higher than winter levels (2.9 vs. 0.62 ng/m³), with the summer values exceeding those measured in Chicago during the LMUATS.

At IIT the di- to hexa-PCBs were the dominant forms present, however, high concentrations of larger PCBs (hepta- and octa-PCB) were observed. Murphy *et al.* (1985) measured predominantly tri- to hexa-PCB from incinerator stack (sewage sludge and municipal incinerator) emissions in the Midwest.

Holsen *et al.* (1991) report data from samples collected at IIT in Chicago, peaks of tri- and hexa-PCB homologues independent of season. In Summer, penta-PCBs also were high in the Holsen study (and during Spring hepta-PCBs were high). At IIT in LMUATS, PCB 5 and 87 were highly elevated. The most-elevated homologues quantified in samples during the LMUATS were the di-, tetra- and penta-PCBs. Penta-PCB concentrations at IIT were almost 2 times higher than other homologue groups.

In the Manchester-Neefig and Andren (1989) report, congeners 28+31 were highest in concentration, followed by 52, 153+105+132, then 118. During LMUATS, these congeners were not measured, however, the dominant fraction of congeners that were measured were the mono-PCBs at South Haven and on the R/V *Laurentian*. The mono-PCBs were in high concentration at IIT and Kankakee as well, but also with a strong influence of a source of penta-PCB (87), which is observed at much lower levels in South Haven and on the R/V *Laurentian*.

5.7. Average Pesticide Concentrations

Pesticide concentrations and isomer ratios measured during LMUATS may be valuable tools in discerning urban vs. rural inputs in the transport of these and other toxic compounds. Concentrations of the individual pesticides quantified in LMUATS samples are listed by site in Table 5-14 with the maximum value for each sample recorded by site and the date the maximum value occurred. Several studies have demonstrated the temperature/seasonal dependence of atmospheric pesticide levels (Table 5-15). Since LMUATS sampling occurred during the summer, the levels of the more volatile pesticides as well as those still in use may be elevated above levels reported for yearly averages for areas of the Great Lakes Basin.

Summertime α -HCH values measured at LMUATS sites were similar to or slightly lower than the consensus average of 300 pg/m³ reported by Eisenreich and Strachan (1992) for the Great Lakes Basin. The highest average value for this compound occurred at Kankakee (268 pg/m³), the site at which a peak value of 1,243 pg/m³ was observed on July 29, 1991 (Figure 5-33).

Average concentrations of γ -HCH measured over the water and at South Haven (103 and 90 pg/m³, respectively) were very similar to the average summertime value of 100 pg/m³ reported for other rural Great Lakes locations. However, at IIT γ -HCH concentrations were almost one half the value at the other sites (58 pg/m³) and at Kankakee, the average level (180 pg/m³) measured was more than 1.5 times higher than the average values of over-water and South Haven measurements. Figure 5-34 shows that peak values of γ -HCH on the R/V *Laurentian* were 3 times and 5 times the average summertime concentrations for the Great Lakes region, while at IIT, the peak value of γ -HCH measured only slightly exceeded the 'consensus' average (Eisenreich and Strachan, 1992). At Kankakee, the peak value of γ -HCH measured during LMUATS was 936 pg/m³, strongly suggesting a large local source component.

		Kankakee	IIT	Laurentian	South Haven
α-HCH	Avg	268 <u>+</u> 60	111.86 <u>+</u> 39	169.20 <u>+</u> 205	128.14 <u>+</u> 27
	Max	1243 (7/29)	169 (7/23)	821 (8/5)	214 (7/24)
Hexachlorobenzene	Avg	139 <u>+</u> 204	68 <u>+</u> 40	104 <u>+</u> 154	54.90 <u>+</u> 23
	Max	692 (7/29)	195 (7/19)	606 (8/5)	111 (7/29)
Atrazine	Avg	373 <u>+</u> 461	183 <u>+</u> 153	286 <u>+</u> 272	223.12 <u>+</u> 189
	Max	1504 (7/22)	418 (7/31)	806 (8/5)	805 (7/15)
γ-HCH(lindane)	Avg	180 <u>+</u> 251	58 <u>+</u> 36	103 <u>+</u> 100	90 <u>+</u> 104
	Max	936 (8/6)	131 (7/21)	299 (7/12)	522 (7/29)
Alachlor	Avg	549 <u>+</u> 1186	76 <u>+</u> 208	57 <u>+</u> 205	26 <u>+</u> 65
	Max	4713 (8/6)	610 (7/29)	739 (7/23)	190 (7/19)
Mirex	Avg	43 <u>+</u> 37	44 <u>+</u> 26	9 <u>+</u> 7	11 <u>+</u> 7
	Max	151 (8/6)	114 (7/21)	24 (7/12)	33 (8/8)
Aldrin	Avg	1.0 <u>+</u> 1.3	6 <u>+</u> 5	0.3 <u>+</u> 0.4	0.4 <u>+</u> 0.6
	Max	3.9 (8/8)	15 (8/8)	1 (7/11)	2 (8/7)
Metolachlor	Avg	184 <u>+</u> 182	8 <u>+</u> 27	10 <u>+</u> 29	42 <u>+</u> 65
	Max	551 (7/29)	110 (7/29)	104 (7/12)	251 (7/23)
trans-nonachlor	Avg	65 <u>+</u> 40	55 <u>+</u> 29	12 <u>+</u> 7	31.2 <u>+</u> 21
	Max	153 (8/6)	100 (7/18)	27 (7/12)	77 (7/17)
Dieldrin	Avg	371 <u>+</u> 302	159 <u>+</u> 76	46 <u>+</u> 25	169 <u>+</u> 90
	Max	1176 (8/6)	271 (8/8)	111 (8/6)	402 (7/21)
Simazine	Avg	90 <u>+</u> 112	103 <u>+</u> 198	85 <u>+</u> 116	54 <u>+</u> 141
	Max	319 (7/24)	637 (8/2)	345 (7/24)	587 (8/2)
Chlorpyrifos	Avg	83 <u>+</u> 75	44 <u>+</u> 26	12 <u>+</u> 10	88 <u>+</u> 122
	Max	258 (7/19)	113 (7/21)	32 (8/6)	514 (7/13)
γ-Chlordane	Avg	113 <u>+</u> 69	83 <u>+</u> 49	27 <u>+</u> 14	4 5 <u>+</u> 23
	Max	288 (8/6)	182 (7/18)	49 (8/7)	90 (7/21)
α -Chlordane	Avg	88 <u>+</u> 54	7/6 <u>+</u> 39	22 <u>+</u> 9	42 <u>+</u> 22
	Max	226 (8/6)	166 (7/8)	40 (7/23)	85 (7/20)
4,4'-DDT	Avg	10 <u>+</u> 16	183 <u>+</u> 133	33 <u>+</u> 34	339 <u>+</u> 167
	Max	54 (8/8)	530 (8/2)	121 (8/6)	574 (7/20)
P,P'-DDE	Avg	36 <u>+</u> 26	119 <u>+</u> 99	57 <u>+</u> 63	1331 <u>+</u> 351
	Max	95 (8/6)	395 (8/8)	244 (7/24)	1944 (8/2)
P,P'-DDD	Avg	3 <u>+</u> 6	4 <u>+</u> 6	3 <u>+</u> 5	12 <u>+</u> 7
	Max	19 (8/6)	21 (7/31)	20 (8/7)	27 (8/7)

Table 5-14. Ambient Pesticides Concentrations (pg/m³).

Compound, Season	Average (pg/m ³)
α-HCH, Summer	300
α-HCH, Fall & Spring	200
α-HCH, Winter	100
γ-HCH, Summer	100
γ-HCH, Fall & Spring	40
γ-HCH, Winter	40
HCB, Winter	100
HCB, Other	150
Σ-Chlordane, Summer	80
Σ -Chlordane, Fall	30
Σ -Chlordane, Winter	20
Σ -Chlordane, Spring	40
Σ-DDT, (mainly DDE), Summer - Superior. Michigan, Huron	50
Σ -DDT, (mainly DDE), Summer - Erie, Ontario	100
Σ -DDT, (mainly DDE), Other - all lakes	20
Dieldrin, Winter	20
Dieldrin, Other	80
Atrazine, May & June	5,000
Atrazine, Other	10

Table 5-15. Concentrations of Pesticides in Rural Locations in the Great LakesRegion (Consensus Values from Eisenreich and Strachan, 1992).



Figure 5-33. Variations in Measured α - HCH Concentrations.



Figure 5-34. Variations in Measured y- HCH Concentrations.

In general, previous investigations in the northern Hemisphere report higher concentrations of α -HCH than γ -HCH (Table 5-16). Typically, the α -/ γ -HCH ratios in the northern Hemisphere are greater than 5 (Tatsukawa *et al.*, 1990). Samples analyzed for HCH during the LMUATS investigation revealed α -/ γ -HCH ratios of 8.3 at Kankakee, 8.8 at IIT, 8.6 on Lake Michigan, and 7.1 in South Haven. The lower ratio at South Haven may reflect the use of Lindane in the vicinity (Lindane contains predominantly γ -HCH) versus the more commonly used technical HCB (which contains a higher percentage of α -HCH than γ -HCH). This theory is also supported by the ratio of peak α -/ γ -HCH at South Haven of 0.4 (peak α -HCH occurred on 24 July and peak γ -HCH occurred on 29 July).

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Author, period of study	Location	α-HCH Average	γ-HCH Average
		Average	Average
LMUATS, 1991	Kankakee, IL	268	180
	Chicago, IL	112	58
	R/V Laurentian	169	103
	South Haven, MI	128	90
Reid (1992), 1989-1990	Lake Superior, Turkey Lake	0-20	0-50
Hornbuckle and Eisenreich	Lake Michigan, Green Bay	40-460	24-240
(1992), 1989			
Reid (1992), 1989-1990	Lake Huron	0-270	0-130
Reid (1992), 1989-1990	Inland (Dorset)	0-500	0-500
Reid (1992), 1989-1990	Lake Erie	0-400	0-130
Reid (1992), 1989-1990	Ontario (Pt. Petre)	0-560	0-200
Lane, Hoff, Bidleman	Great Lakes, Summer	220-430	40-130
(1992), 1985-1990			
Lane, Hoff, Bidleman	Great Lakes, Autumn	170-230	28-38
(1992), 1985-1990			
Lane, Hoff, Bidleman	Great Lakes, Winter	70-190	13-40
(1992), 1985-1990			
Lane, Hoff, Bidleman	Great Lakes, Spring	110-290	75-130
(1992), 1985-1990			

Table 5-16. Atmospheric Concentrations of α - and γ - Hexachlorocyclohexanes in the Great Lakes Basin (Units are pg/m³).

The average level of hexachlorobenzene (HCB) at Kankakee (139 pg/m³) is also elevated above the average concentration measured at the other three sites. The value reported here is also at the top end of the ranges of HCB reported from other investigations in the Great Lakes Basin (Table 5-17). The maximum value of HCB measured at Kankakee (642 pg/m³) during LMUATS occurred on 29 July and is one of the highest concentrations of this compound reported for a rural location in the Great Lakes Basin. The maximum value of 606 pg HCB/m³ was measured over Lake Michigan on 5 August, 1991. The mixed-layer trajectories for this day revealed flow reaching the vessel initially from the east and then to the north traversing southwestern Michigan.

Average HCB concentrations measured at IIT and SHA (68 and 55 pg/m^3) were significantly lower than levels at Kankakee and on the R/V *Laurentian*. However, on the R/V *Laurentian* the mean is heavily weighted by the maximum HCB value.

Chlordane has been distributed widely in the U.S. as a potent pesticide, one of its uses being primarily termite control (Bidleman *et al.*, 1990). The concentrations of α -chlordane measured during LMUATS are quite similar (by site) to the concentrations of γ -chlordane. Mean and maximum α - and γ -chlordane concentrations at Kankakee are slightly elevated above those concentrations measured at IIT. Concentrations of the two isomers at IIT and Kankakee are elevated above total chlordane levels reported in the Great Lakes Basin (Table 5-18). At IIT this may be due, in part, to the extensive use of chlordane in the control of indoor insects, primarily termites.

Measurements of chlordane in South Haven and over Lake Michigan on the R/V *Laurentian* are similar to other levels reported in the region. Since chlordane has been banned in the U.S. for several years, the presence of this compound in the atmosphere represents revolatilization of soil-bound chlordane, loss from stockpiled/stored sources, or long distance transport.

The ratio of γ (trans)- to α (cis)-chlordane yields information concerning the nature and age of the air mass and source of the chlordane measured. A γ/α ratio greater than 1 indicates a regional source or local emission of chlordane, whereas a γ/α ratio of less than 1 indicates a transported and more-aged air mass. Ratios of the average concentrations of each of these isomers measured during LMUATS were greater than one at all four sites (1.3 at Kankakee, 1.1 at IIT, 1.2 on the R/V *Laurentian* and 1.1 in South Haven).

Author, period of study	Location	Average HCB
LMUATS, 1991	Kankakee, IL	139
	Chicago, IL	68
	R/V Laurentian	104
	South Haven, MI	55
Kelly, et al. (1991)	Lake Erie, Summer	50
Reid (1992), 1989-1990	Lake Superior, Turkey Lake	0-220
Hornbuckle and Eisenreich (1992), 1989	Lake Michigan. Green Bay	10-80
Bidleman (1992), 1989	Michigan, Green Bay	160
Reid (1992), 1989-1990	Lake Huron	0-100
Reid (1992), 1989-1990	Inland (Dorset)	0-130
Reid (1992), 1989-1990	Lake Erie	0-180
Reid (1992), 1989-1990	Ontario (Pt. Petre)	0-230
Lane, Hoff, Bidleman (1992), 1985- 1990	Great Lakes, Summer	40-130
Lane, Hoff, Bidleman (1992), 1985- 1990	Great Lakes, Autumn	28-38
Lane, Hoff, Bidleman (1992), 1985- 1990	Great Lakes, Winter	13-40
Lane, Hoff, Bidleman (1992), 1985- 1990	Great Lakes, Spring	75-130

 Table 5-17. Atmospheric Concentrations of HCB in the Great Lakes Basin

		3
(Units	are	pg/m ²).

Author, period of study	Location	Average (pg/m ³⁾
LMUATS, 1991	Kankakee, IL	201
	Chicago, IL	159
	R/V Laurentian	49
	South Haven, MI	87
Reid (1992), 1989-1990	Lake Superior	0-42
Bidleman (1992), 1989	Green Bay, WI	9
Bidleman (1992), 1990	Green Bay, WI	42
Reid (1992), 1989-1990	Lake Huron	0-50
Reid (1992), 1989-1990	Dorset	0-105
Hoff (1992), 1988-1989	Egbert, Ontario, Summer	76
Hoff (1992), 1988-1989	Egbert, Ontario, Autumn	26
Hoff (1992), 1988-1989	Egbert, Ontario, Winter	15
Hoff (1992), 1988-1989	Egbert, Ontario, Spring	41
Reid (1992), 1989-1990	Lake Erie	0-182
Reid (1992), 1989-1990	Ontario, Pt. Petre	0-110
Bidleman (1992), 1990	Great Lakes, Summer	187

Table 5-18. Atmospheric Concentrations of Total Chlordane in the Great Lakes Basin (Units are pg/m^3).
Three chlordane-related and derivative pesticides were quantified in LMUATS samples. These include trans-nonachlor, alachlor and metalachlor. Average transnonachlor concentrations were lowest over Lake Michigan (12 pg/m^3) and were similar at Kankakee and IIT and were slightly lower in South Haven (65, 55 and 31 pg/m³). Peak values for this compound were twice that observed in South Haven and 1.5 times the peak value observed at IIT.

Alachlor and metalachlor have been listed as the two most heavily used pesticides by weight in the Great Lakes Basin for 1986 (Baker and Richards, 1990). These chlorinated compounds were used as herbicides in large agricultural areas. The levels of Alachlor varied greatly at each of the LMUATS sites, by as much as an order of magnitude. The highest concentrations of this herbicide were recorded from samples collected at Kankakee where the average concentration was 549 pg/m³ and the peak value for the study period was 4,713 pg/m³. The Alachlor concentration was lower at IIT by almost an order of magnitude and even lower in over-water measurements. The lowest values for alachlor were recorded at South Haven. While the concentration of this compound decreased away from Kankakee at the measurements sites in this study, there were occasions of highly elevated alachlor concentrations recorded at both IIT and over Lake Michigan. These peak events occurred on 29 July and 23 July and represented atmospheric concentrations of 610 and 739 pg/m³, respectively.

Similar behavior, was observed for levels of Metalachlor, but the concentrations in South Haven were also elevated. Average Metalachlor levels at Kankakee were higher than those at the other sites by a factor of 2 to 25. Maximum concentrations of this herbicide were recorded in Kankakee and IIT on the same sampling date (29 July) However, the concentration observed at IIT on this day was 110 pg/m^3 and the concentration recorded at Kankakee was 551 pg/m^3 . Maximum values recorded on Lake Michigan and in South Haven (on 12 July and 23 July, respectively) suggest a local source (or sources) in the South Haven area.

Figure 5-35 displays the time variation in the 4,4--DDT levels measured during the month of study. DDT levels measured during the LMUATS study reveal alarming information. Table 5-19 shows that the concentrations of the parent 4,4--DDT compound in samples collected at South Haven are significantly elevated above other reported values. The levels of the daughter compound, p,p'-DDE, shown in Figure 5-36, are an order of magnitude greater in concentration than previously reported total DDT levels. These high levels have been confirmed by further studies at this site during 1992-1993 (Keeler,

unpublished data). The average DDT:DDE concentration ratio measured in South Haven is 0.3, providing sufficient evidence that levels observed are due to release of previously applied DDT since the concentration of the DDT breakdown product is three times that of the parent compound. The time for degradation of DDT to DDE is slow enough to implicate re-emission of a much earlier DDT application as the source of this compound.

At IIT, DDT and DDE levels measured were elevated (183 and 119 pg/m³, respectively). Few reports document total DDT levels similar to those observed at IIT. Concentrations of the DDT metabolite, DDD, shown in Figure 5-37 was significantly lower than 4,4'-DDT and p,p'-DDE at all the LMUATS sites, and represents a small fraction of the Σ DDT reported in other studies.

At IIT, the ratio of the average DDT:DDE concentration is 1.5, indicating that a source of new DDT is present. The transport of new DDT is partially evident in the overwater measurements since on the R/V *Laurentian* the average DDT:DDE concentration is 0.6. At Kankakee, the DDT:DDE ratio is 0.3 indicating a previously applied source of this toxin. Current DDT:DDE ratios in air from the Great Lakes region are typically less than 1. Nevertheless, there are some situations in which DDT:DDE is greater than 1 in North America. McConnell *et al.* (1992) gives ratios of DDT:DDE for samples collected in 1989-1990 in the Great Lakes region. One sample taken in Green Bay during June, 1989 showed a DDT:DDE ratio of 1.8. This sample was also enriched in toxaphene and chlordane, and was associated with airflow from the S-SW. Another air sample from Lake St. Clair in August 1990 contained unusually high levels of DDT with a DDT:DDE ratio of 2.4. Although preliminary, these observations suggest that pulses of "new" DDT are being superimposed on a North American background of atmospheric residues that are largely DDE.

In a separate study, Rapaport *et al.* (1985) hypothesized that since the DDT in peat core samples from the Great Lakes region and eastern Canada was largely p,p'-DDT and o,p'-DDT, it was freshly deposited and most likely the result of transport from current use in Mexico and Central America. However, the recent finding of elevated DDT levels in only two of the four sites in LMUATS (IIT and South Haven) indicates a local source. Furthermore, the elevated DDT levels in Michigan seem to be isolated to the southwestern corner of the state, based on this study and recent measurements made at four sites in lower Michigan (Keeler, unpublished data). It is difficult to conceive of a Mexican or Central American source that selectively impacts only one corner of the state.



Figure 5-35. Variations in Measured DDT Concentrations.

Author, period of study	Location	Average	
		(particulate + vapor)	
		Σ DDT (pg/m ³)	
LMUATS, 1991	Kankakee, IL	10	
	Chicago, IL	183	
	R/V Laurentian	33	
	South Haven, MI	339	
Kelly et al.(1991)	Lake Erie, Summer	140	
Kelly et al.(1991)	Lake Erie, Winter	30	
Reid (1992), 1989-1990	Lake Superior, Turkey Lake	0-70	
Bidleman (1992), 1989	Lake Michigan, Green Bay	24	
Hornbuckle and Eisenreich (1992), 1989	Lake Michigan, Green Bay	20-70	
Reid (1992), 1989-1990	Lake Huron	0-50	
Reid (1992), 1989-1990	Inland (Dorset)	0-30	
Hoff (1992), 1988-1989	Inland (Egbert), Summer	180	
Hoff (1992), 1988-1989	Inland (Egbert), Autumn	80	
Hoff (1992), 1988-1989	Inland (Egbert), Winter	20	
Hoff (1992), 1988-1989	Inland (Egbert), Spring	100	
Reid (1992), 1989-1990	Erie	130-270	
Reid (1992), 1989-1990	Ontario, Pt. Petre	0-120	
Bidleman (1992), 1990	Great Lakes, Summer	120	

Table 5-19. Atmospheric Concentrations of DDT in the Great Lakes Basin.







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Figure 5-37. Variations in Measured DDD Concentrations.

Dieldrin, a highly toxic pesticide, was quantified in LMUATS samples. Typical concentrations for this pesticide measured in other samples collected in the Great Lakes Basin range from 20 pg/m³ in winter to 80 pg/m³ in samples collected during other times of the year (Table 5-20). In one set of samples collected from Egbert, Ontario, Hoff (cited in Eisenreich and Strachan, 1992) reports Dieldrin levels from 23 - 620 pg/m³. This range is closer to those values obtained during LMUATS sampling. The Dieldrin concentration averaged 371 pg/m³ in Kankakee with a maximum of 1176 (on 6 August). Dieldrin concentrations at IIT, over Lake Michigan and in South Haven were all lower than in Kankakee, with levels at IIT and South Haven being roughly equivalent (159 and 169 pg/m³, respectively). The concentration of Dieldrin in samples collected over Lake Michigan averaged 46 pg/m³ with a peak value of 110 pg/m³. These later levels closely reflect rural concentrations reported by other investigators and indicate that Dieldrin is not effectively transported from potential source locations.

Author, period of study	Location	Average (pg/m3)	
LMUATS. 1991	Kankakee, IL	371	
	Chicago, IL	159	
	R /V Laurentian	46	
	South Haven, MI	169	
Kelly et al. (1991)	Lake Erie, Summer	10	
Sweet (1992), 1989-1990	Green Bay, WI	20	
Hornbuckle and Eisenreich (1992), 1989	Green Bay, WI	3-130	
Hoff (1992), 1988-1989	Egbert, Ontario, Summer	70-100	
Hoff (1992), 1988-1989	Egbert, Ontario, Autumn	24 -7 0	
Hoff (1992), 1988-1989	Egbert, Ontario. Winter	7-24	
Hoff (1992), 1988-1989	Egbert, Ontario, Spring	23-620	

 Table 5-20. Atmospheric Concentrations of Dieldrin Measured in the Great

 Lakes Basin.

For several of the compounds measured in LMUATS, a consensus on the Great Lakes regional atmospheric concentration does not exist. Among those compounds are aldrin, mirex, simazine, chlorpyrifos, alcohol and metalachlor. Aldrin is used as an insecticide and in modeling work completed by Stiver and Mackay (1990), it is predicted that for steady-state soil emission, the atmospheric concentration of this compound would be approximately 1 pg/m³. During the LMUATS this is, in fact, the concentration of Aldrin found at Kankakee (0.95 pg/m³) and exceeds the concentration found over the water (0.26 pg/m³) and in South Haven (0.35 pg/m³). However, Aldrin concentrations in Chicago at IIT were six times higher than levels measured at any of the other sites, indicating a local source for this compound. Interestingly, the peak value for Aldrin measured in Kankakee and IIT was on 8 August and in South Haven on 7 August, days with easterly flow to each of the sites.

Mirex is a highly chlorinated insecticide. The average and maximum concentrations of Mirex in the atmosphere in both Kankakee and IIT were strikingly similar as were the average levels and maximum values reported for R/V *Laurentian* and South Haven measurements. One value reported by Hoff for Mirex collected in Egbert, Ontario in the Great Lakes region was 22 pg/m^3 (Eisenreich and Strachan, 1992). Levels observed at LMUATS sites fall on both sides of this range and do not show wide variability in concentrations, indicating that for this compound, the sources may be diffuse and constant.

Additional compounds, to those mentioned above. which rank in the top twenty of the pesticides for quantity used in the Great Lakes Basin in 1986, are Atrazine (ranked 3rd), Chlorpyrifos (ranked 16th) and Simazine (ranked 20th). Among the three, Atrazine and Simazine are currently used heavily. Atrazine is a common herbicide applied to corn crops as well as other vegetation. Ambient concentrations of Atrazine demonstrated marked seasonal changes linked to the time of application. Eisenreich and Strachan (1992) report consensus levels of Atrazine measured in the months of May and June averaging 5,000 pg/m³, while levels averaged from samples collected during other months of the year indicate atmospheric concentrations of 10 pg/m³. In a springtime investigation by Sweet (1992) in the Lake Michigan Watershed, Atrazine levels were reported to be 100,000 pg/m³. These reported values are significantly greater than average Atrazine levels measured during LMUATS which varied from 183 pg/m³ at IIT to 372 pg/m³ at Kankakee. The maximum value observed was at Kankakee (1504 pg/m³ on 22 July). This may have reflected the high percentage of corn crop land in the area and thus the use of large amounts of Atrazine. The peak Atrazine concentrations observed over Lake

Michigan and in South Haven were half the peak level measured at Kankakee. At IIT, peak Atrazine was half the level measured over Lake Michigan and in South Haven.

Chlorpyrifos is a potent insecticide. In the LMUAT study, the average atmospheric Chlorpyrifos concentration was similar in Kankakee and in South Haven (83 and 88 pg/m^3) but underwent very wide fluctuation (maximum values at these sites were 560 and 514 pg/m^3 with a standard deviation of 75 and 122 pg/m^3 , respectively). The day to day pattern for this insecticide is clearly very different than seen for the other pesticides (Figure 5-38). Mean levels of this compound were significantly lower at IIT (44 pg/m^3) and over Lake Michigan (12 pg/m^3).

Simazine is in widespread use as a herbicide and is applied heavily by Michigan fruit growers. This application is most likely responsible for the peak in Simazine concentration measured at South Haven on 2 August 1991. The peak concentration at IIT was observed on the same date and is greater than the level observed in South Haven (637 pg/m³). Average concentrations of Simazine measured during LMUATS do not demonstrate a marked difference between sites. The average concentration of Simazine at KAN was 90 pg/m³, 103 pg/m³ at IIT, 85 pg/m³ over Lake Michigan and 54 pg/m³ in South Haven.

5.8. Over-Water versus Land-Based Measurements

The question of whether it is reasonable to utilize shoreline or inland monitoring locations to represent over-lake deposition is critical to our ability to accurately assess the atmospheric deposition component of the toxics loading to the Great Lakes. This question can only be answered by a systematic study of the complex meteorological conditions which are necessary to parameterize the deposition process. This project is the first step in the development of a program to study the dynamics of toxic pollutant transport over and deposition into large lakes. Since data collected historically in the Great Lakes utilized land-based monitoring locations, this study also provides an initial comparison of the validity of land-based measurements with those made over-water. Due to the expense of ship time, the number of days of concurrent over-water and over-land measurements was limited. The ship was on-station approximately 20 miles west of Muskegon, MI for an initial pilot cruise and for two periods later in the 30-day intensive, the ship was on-station 5-10 miles off-shore from Chicago/Gary. The mixed-layer trajectories associated with these sampling days are given in Figure 5-6.





5.8.1. Individual Cruise Descriptions

5.8.1.1. On-Station Off-Shore from Muskegon, MI 10-11 July 1991

During the sampling period off-shore from Muskegon, MI predominant easterly flow advected pollutants from several sources in the Muskegon and Grand Rapids, MI area over the lake. Elevated concentrations of Se, Zn and low molecular weight PCBs were measured, in addition to one sample with high As levels. The concentrations of SO_4^{2-} , NH₃ and HNO₃ were comparable on the R/V *Laurentian* and at the South Haven site. The concentration of retene observed on the *Laurentian* during this cruise was elevated above levels observed simultaneously at South Haven, potentially indicating impact from a combustion source utilizing wood or other vegetative material upwind. The elevated retene levels at the location farther to the north may also reflect the different species and tree density north of Muskegon. Levels of coronene observed over-water during this period were similar to the observed measurements in South Haven, indicating similar impact due to motor vehicle emissions or other sources.

Average concentrations of several pesticides measured during this cruise were similar on the *Laurentian* and in South Haven (α -HCH, trans-nonachlor, Mirex, Chlordane, Aldrin, Metalachlor, γ -Chlordane and α -Chlordane) with a notable elevation in *Laurentian* levels observed on 12 July. Concentrations of DDT and its breakdown products as well as Dieldrin and Chlorpyrifos were highly elevated in South Haven. Atrazine was the only pesticide measured which was found in elevated concentration on the *Laurentian* (11 July). Low molecular weight PCBs (total mono-PCB and 2-PCB) were also measured in elevated levels on the *Laurentian* on 11 July as well as in South Haven.

Analysis of samples collected for organic compounds were not analyzed at IIT or Kankakee during the first cruise. The funds available for this expensive analysis were limited and the prevailing transport pattern during the period indicated that this data would be of less value than for different time periods during the study.

5.8.1.2. On-Station Off-Shore from Chicago/Gary, 23-27 July 1991.

For the first sampling period off-shore from Chicago/Gary, levels of the trace elements measured aboard the R/V *Laurentian* were similar to or slightly lower than those levels monitored at IIT, largely due to the prevailing northerly flow that the vessel

received while on station. Since there are no large sources in the lake and the upwind fetch from the sampling point in southern Lake Michigan is hundreds of kilometers of open water, the levels of most pollutants would not be expected to be very high. The exceptions to this observations were levels of vapor-phase and particulate mercury as well as coronene and naphthalene which were greatly elevated at IIT in comparison to those concentrations observed on the Laurentian. Also, the daytime sample on 24 July aboard the Laurentian revealed elevated Pb levels, both fine and coarse, as well as elevated Zn as a result of westerly winds from the greater Chicago area.

Concentrations of most acidic aerosols were comparable at the South Haven and Laurentian sites during this period, with the exception of NH₃ which was elevated above the levels observed in South Haven.

5.8.1.3. On-Station Off-Shore from Chicago/Gary, 5-7 August 1991

During the second of the two cruises for which the Laurentian was located offshore from Chicago/Gary, prevailing flow was from the east-southeast. These conditions provided direct measurements of the transport of toxic compounds to the lake. Levels of fine Fe and Mn, impacted by the plume from the Gary steel industry were evident.

The PAH concentrations appear to mimic the behavior of atmospheric Hg, about a factor of three to ten times higher at IIT than was measured over-water. The mean pesticide concentrations measured at IIT and aboard the R/V Laurentian are within a factor of 2 of each other with some being higher at IIT and others being greater on the Laurentian. Atrazine and Simazine were both found in greater concentrations over the water than at IIT. The concentrations of pesticides observed in South Haven and in Kankakee are generally much higher than those observed at either IIT or over the lake. This is not surprising as both sites are in the middle of large agricultural and fruit growing areas. Local application of pesticides strongly influences the levels seen at one site and, therefore, prevent a single land-based site from being used to estimate the over-water levels with any certainty. However, on selected occasions the concentration of some pesticides measured on the Laurentian were determined to be greater than the concentration measured simultaneously at any of the land sites. This occurred on 5 August for the pesticide Atrazine and on 7 August for γ -HCH. This finding may be the result of special meteorological conditions that allow for the advection of concentrated pesticide-laden air masses over the water.

Also of interest is a second observation of elevated levels of low molecular weight PCBs on board the Laurentian, with high concentrations of 2-PCB and total mono-PCB measured during 5 and 7 August.

5.8.2. General Conclusions Regarding Over-Water Measurements

For the two periods when the R/V *Laurentian* was on-station, average fine mass levels measured at the Chicago site and over the water were comparable. These measurements suggest that estimates of deposition for many compounds would have been fairly accurate using data collected at the Chicago site. The fairly close agreement in measured values for most species appear to indicate that the land-based site would function as an adequate surrogate for over-water measurements of trace elements.

The major flaw with this assumption is that while the ship was on-station off Chicago/Gary, two different and fairly uncommon summertime meteorological patterns were observed. For instance, the prevailing wind flow was strong and from the northwest during the first cruise. This provided a relatively non-polluted air mass to both the *Laurentian* and the Chicago site. During the second cruise, transport to the ship was from the east-southeast which provided a relatively polluted air mass to the *Laurentian* coming from the Chicago/Gary area. Both of these events produced similar levels of pollutants measured over water and at the Chicago land based site. In order to adequately assess the validity of utilizing land-based monitors instead of over-water sites, a representative sampling of several meteorological conditions that reflect the complex dynamics of lake meteorology would have to be obtained.

For example, during the preliminary study for the Lake Michigan Ozone Study in July 1990 a tight, relatively non-dispersed pollutant plume was observed as it traveled North along the shoreline of Michigan. The role of these meteorological phenomena in the deposition of toxic compounds to the Lake may be highly significant because they may provide capture of a pollutant plume near the lake surface as it is advected away from the source. It is often the case that a few isolated instances with a particular set of meteorological and source influence characteristics can be responsible for major pollutant episodes.

Important exceptions to the general finding of comparable levels of fine mass are the striking differences in measured concentrations of mercury, several PAHs and pesticides and noticeable differences in coarse mass which could greatly affect calculations of total loading to the lake.

Generalizations regarding over-water measurements cannot be made from the limited data collected in this initial study. The data indicate that over-water measurements involve a very special set of circumstances that can, on occasion, play an important role in the deposition of toxic compounds to the water. Further work in this area will help to determine if considering seasonal differences in dominant meteorology, atmospheric chemistry, and transport to land based sites can be used as an adequate surrogate for overwater deposition calculations on a yearly average basis. If the uncertainty measured for such estimates turns out to be quite large, then the air sampling community may have to accept the burden of collecting this critical data in the most accurate manner possible. For example, representative samples taken over-water for limited portions of each season or using unmanned monitoring stations for some of the critical pollutants may be necessary to extrapolate to other compounds. This could provide an accurate measurement for a few of the species of interest.

The values given in Table 5-21 suggest that for the brief LMUATS period when the R/V *Laurentian* was off-shore of Chicago, the levels observed at IIT are quite similar to those measured over the water. In fact, the averages are indistinguishable from each other. The exception to this is Hg which was much higher at IIT, in both the vapor and particulate phases, than that measured aboard the *Laurentian*. The levels of fine mass and most trace metals, PAHs and several of the pesticides observed at Kankakee and in South Haven are quite different and would not agree well with the *Laurentian* values. The levels of fine fraction elements measured at South Haven are approximately one-half of those measured aboard the *Laurentian* for this period. Again, the Hg levels observed at South Haven were more similar to those measured concurrently aboard the *Laurentian* than those measured at IIT.

Table 5-22 shows that the average PAH concentrations measured at the four locations during the period when the R/V *Laurentian* was on station near Chicago. The PAH concentrations appear to mimic the behavior of atmospheric Hg and are about a factor of three to ten times higher, on average, at IIT than measured over-water. For example, naphthalene concentrations averaged 397 ng/m³ at IIT and were 151 ng/m³ on the *Laurentian*. Anthracene was found to be 3 ng/m³ on average at IIT and only 0.3 ng/m³ 6 miles offshore.

Table 5-23 lists the average concentrations of pesticides measured at the 4 LMUATS monitoring sites. The mean pesticide concentrations measured at IIT and aboard the R/V Laurentian are within a factor of 2 of each other with some being higher at IIT and others being greater on the *Laurentian*. Atrazine was 5 times greater over the water than at IIT (258 vs. 51 pg/m³). Simazine was also much higher on the Laurentian than at IIT with an average concentration of 103 pg/m^3 compared to 6 pg/m^3 . The concentrations of pesticides observed in South Haven and in Kankakee are generally much higher than those observed at either IIT or over the lake. This is not surprising as both sites are in the middle of large agricultural and fruit growing areas. Local application of pesticides strongly influences the levels seen at one site and therefore, prevent a single land-based site from being used to estimate the over-water levels with any certainty. However, on selected occasions, the concentration of some pesticides measured on the Laurentian were determined to be greater than the concentration measured simultaneously at any of the land sites. This occurred on 5 August for the pesticide Atrazine and on 7 August for γ -HCH. This finding may be the result of special meteorological conditions that allow for the advection of concentrated pesticide-laden air masses over the water.

	Kankakee	IIT	R/V Laurentian	South Haven
Mass	1410 <u>+</u> 1030	1070 <u>+</u> 810	920 <u>+</u> 870	580 <u>+</u> 360
Al	293 <u>+</u> 306	74 <u>+</u> 109	26 <u>+</u> 41	24 <u>+</u> 59
Si	76 <u>+</u> 32	63 <u>+</u> 32	59 <u>+</u> 54	67 <u>+</u> 138
S	1700 <u>+</u> 1718	1183 <u>+</u> 1442	1171 <u>+</u> 1293	553 <u>+</u> 395
Cl	13 <u>+</u> 7	6 <u>+</u> 6	7 <u>+</u> 7	5 <u>+</u> 5
K	51 <u>+</u> 24	46 <u>+</u> 42	54 <u>+</u> 50	27 <u>+</u> 32
Ca	77 <u>+</u> 76	43 <u>+</u> 28	42 <u>+</u> 24	31 <u>+</u> 33
Mn	4 <u>+</u> 3	4 <u>+</u> 4	4 <u>+</u> 5	2 <u>+</u> 3
Fe	69 <u>+</u> 54	98 <u>+</u> 132	83 <u>+</u> 103	32 <u>+</u> 68
Cu	4 ± 1	9 <u>+</u> 7	6 <u>+</u> 5	3.4 ± 3
Zn	25 <u>+</u> 15	16 <u>+</u> 17	20 ± 20	8.4 <u>+</u> 13
Se	2 ± 3	0.85 ± 1.1	1 ± 1	1 ± 1
Br	4 <u>+</u> 2	2.6 ± 1.0	2 ± 1	2 ± 1
Pb	15 <u>+</u> 7	9 <u>+</u> 10	9 <u>+</u> 10	3 <u>+</u> 5

Table 5-21. 12-hour Average Concentrations for Fine Fraction Trace Elements Determined by XRF When R/V Laurentian on Station Near Chicago (ng/m³).

	Kankakee	IIT	R/V Laurentian	South Haven
	Avg	Avg	Avg	Avg
Naphthalene	162.32 <u>+</u> 270.66	396.64 +156.38	151.28 <u>+</u> 130.47	25.85 <u>+</u> 23.84
Acenaphthylene	1.45 <u>+</u> 0.95	3.82 ±1.56	1.60 <u>+</u> 1.06	0.52 <u>+</u> 0.33
Acenaphthene	1.96 ±1.36	20.04 <u>+</u> 12.50	2.57 <u>+</u> 2.38	0. 85 <u>+</u> 0.36
Fluorene	3.99 <u>+</u> 2.76	23.42 <u>+</u> 10.58	8 .00 <u>+</u> 4.97	2.06 <u>+</u> 0.73
Phenanthrene	8.52 <u>+</u> 4.71	51.56 <u>+</u> 22.53	12.94 +9.51	3.90 <u>+</u> 0.73
Anthracene	0.24 <u>+</u> 0.15	3.07 <u>+</u> 1.89	0.31 <u>+</u> 0.27	0.16 <u>+</u> 0.07
Fluorenone	1.32 <u>+</u> 0.52	4.69 <u>+</u> 2.55	1.23 <u>+</u> 0.60	0.60 <u>+</u> 0.30
Retene	0.21 <u>+</u> 0.17	0.38 <u>+</u> 0.22	0.52 <u>+</u> 0.23	0.28 <u>+</u> 0.14
Fluoranthene	1.72 <u>+</u> 1.05	18.8 <u>+</u> 9.10	4.05 <u>+</u> 2.86	1.08 <u>+</u> 0.39
Pyrene	0.79 <u>+</u> 0.48	9.18 <u>+</u> 4.00	2.01 <u>+</u> 1.55	0.53 <u>+</u> 0.22
Benz(a)anthracene	0.10 <u>+</u> 0.08	1.14 <u>+</u> 0.78	0.34 ±0.42	0.05 <u>+</u> 0.02
Chrysene	0.20 <u>+</u> 0.12	2.09 <u>+</u> 1.28	0. 8 0 <u>+</u> 0.93	0.11 <u>+</u> 0.03
Cyclopenta(c.d)pyrene	0.04 <u>+</u> 0.04	0.20 <u>+</u> 0.19	0.12 ±0.17	0.03 <u>+</u> 0.03
Benzofluoranthenes	0.32 <u>+</u> 0.15	3.88 <u>+2</u> .70	1.17 ±1.35	0.12 <u>+</u> 0.04
Benzo(e)pyrene	0.11 <u>+</u> 0.05	1.04 <u>+</u> 0.69	0.32 <u>+</u> 0.35	0.05 <u>+</u> 0.01
Benzo(a)pyrene	0.14 <u>+</u> 0.05	1.64 <u>+</u> 1.26	0.31 <u>+</u> 0.34	0.05 <u>+</u> 0.03
Indeno(1,2,3-c.d)pyrene	0.19 <u>+</u> 0.09	1.84 <u>+</u> 1.22	0.52 <u>+</u> 0.57	0.09 <u>+</u> 0.05
Dibenzo(a,h)anthracenc	0.17 <u>+</u> 0.07	0.76 <u>+</u> 0.41	0.23 ±0.17	0.11 <u>+</u> 0.04
Benzo(g,h,i)perylene	0.15 <u>+</u> 0.07	1.65 <u>+</u> 0.89	0.42 <u>+</u> 0.47	0.07 <u>+</u> 0.04
Coronene	0.12 <u>+</u> 0.06	0.74 <u>+</u> 0.27	0.18 <u>+</u> 0.16	0.06 +0.03

Table 5-22. Average Concentrations of PAHs when the R/V Laurentian was onStation Near Chicago (ng/m³).

	Kankakee	IIT	R/V Laurentian	South Haven
	Avg	Avg	Avg	Avg
alpha-HCH	204 <u>+</u> 124	135+40	192 <u>+</u> 232	152 <u>+</u> 37
Hexachlorobenzene	172±277	71 <u>+</u> 16	121 <u>+</u> 174	69 <u>+</u> 13
Atrazine	254 <u>+</u> 123	51 <u>+</u> 70	258 <u>+</u> 254	220 <u>+</u> 123
gamma-HCH(lindane)	299 <u>+</u> 399	43 <u>+</u> 25	90 <u>+</u> 93	59 <u>+</u> 12
Alachlor	1096 <u>+</u> 2045	0 <u>+</u> 0	74 <u>+</u> 234	0 <u>+</u> 0
Mirex	48 <u>+</u> 59	26 <u>+</u> 21	8 <u>+</u> 6	8 <u>+</u> 6
Aldrin	1 <u>+</u> 2	3 <u>+</u> 2	0.2 <u>+</u> 0.4	0.9 <u>+</u> 1.1
Metalachlor	97 <u>+</u> 96	0 <u>+</u> 0	3 <u>+</u> 8	66 <u>+</u> 109
trans-nonachlor	55 <u>+</u> 55	29 <u>+</u> 18	11 <u>+</u> 6	17 <u>+</u> 7
Dieldrin	492 <u>+</u> 423	83 <u>+</u> 44	48 <u>+</u> 28	95 <u>+</u> 70
Simazine	199 <u>+</u> 147	6 <u>+</u> 13	103 <u>+</u> 121	18 <u>+</u> 40
Chlorpyrifos	38 <u>+</u> 25	29 <u>+</u> 20	11 <u>+</u> 10	18 <u>+</u> 15
gamma-Chlordane	128 <u>+</u> 110	45 <u>+</u> 23	29 <u>+</u> 14	31 <u>+</u> 6
alpha-Chlordane	98 <u>+</u> 88	38 <u>+</u> 20	23 <u>+</u> 9	27 <u>+</u> 13
4,4'-DDT	12 <u>+</u> 16	104 <u>+</u> 72	38 <u>+</u> 37	267 <u>+</u> 145
P.P'-DDE	60 <u>+</u> 26	71 <u>+</u> 32	63 <u>+</u> 71	1127 <u>+</u> 371
P.P'-DDD	<u>8+</u> 8	3 <u>+</u> 2	4 <u>+</u> 6	13 <u>+</u> 9

Table 5-23. Ambient Pesticides Concentrations when the R/V Laurentian was onStation Near Chicago (pg/m³).

Chapter 6

Meteorological Analysis

6.1. Synoptic Overview for LMUATS

The overall weather pattern during the first half of the Lake Michigan Urban Air Toxics Study period (8 July - 9 August 1991) was rather non-dynamic. Throughout the first two weeks of the study, the jet stream set up in a zonal (west to east) flow pattern, lying mainly across the U.S.-Canadian border. The result of this pattern was a series of alternating high and low pressure systems that passed directly over the Great Lakes region. With the jet stream to the north of the Great Lakes, the various weather systems tended to move north of the study area. Under these conditions, the southern Lake Michigan Basin experienced prolonged periods of northerly winds. As areas of high pressure moved across the Great Lakes, the winds were initially northwesterly (i.e., from the northwest), gradually becoming northeasterly and then easterly. As areas of low pressure moved across the Great Lakes, winds became southerly for a short period, before returning to the northwest with the storm's passage.

The final week of July proved to be the most meteorologically dynamic of the LMUATS period. Early in the week, an upper-level low developed over the Hudson Bay and essentially remained in place during the entire week. The upper-level low produced a series of fronts that moved across the study area during this week. This system eventually weakened and moved eastward during the weekend of 27-28 July 91. As a result, no sustained flow patterns were able to form over the region during this period.

The final week of the study saw the return to a zonal upper-level flow pattern across the northern United States. A split in the jet stream left the Great Lakes under the influence of the weak, southern branch of the jet. As a result, a slowly moving, broad area of high pressure dominated the weather during the final week.

6.1.1. Week of 8-13 July 91

Monday, 8 July 91, was the first day of the LMUATS period. On this day, a cold front moved through the study area during the early morning hours. The passage of the front brought scattered showers and a switch from warm, southerly winds to much cooler, northwesterly winds. Behind the front, an area of high pressure was located across the northern Great Plains. As the high moved toward the Great Lakes, it helped to maintain the north to northwest winds for the remainder of the day. Despite clearing skies, temperatures were considerably cooler behind the front. Temperatures across the southern Great Lakes were in the 90s during the previous day, but only warmed into the mid 70s Monday. The high continued to move toward the Great Lakes during the night, with winds becoming more northerly across the study area.

On Tuesday morning, the high pressure area that had been in the Great Plains the previous day was now located near Houghton Lake, MI. As a result, the winds across the southern Great Lakes were from the east at 5-10 mph. Skies across the study area were partly sunny, while temperatures remained cool. Afternoon temperatures only warmed into the upper 70s. Without much upper-level support, the high pressure area weakened over the Great Lakes Tuesday night. As a result, the overnight winds across the study area were light and variable.

The high pressure area stalled across the state on Wednesday, maintaining a rather diffuse wind field across the entire Great Lakes region. The predominant wind direction across the study area was from the east during this period. Skies were sunny across the region on Wednesday, with afternoon temperatures rebounding into the low to mid 80s. The exception was along the Wisconsin/Illinois shorelines, where temperatures were cooler due to weak onshore flow.

An upper-level ridge strengthened over the Great Lakes on Thursday, causing a strong high to develop. The wind field across the study area therefore became more organized, with east to northeast winds dominating during the morning hours. As can be seen in Figure 6-1, the difference in the wind field on opposite sides of the lake appears to have been caused by a very weak trough of low pressure. However, this feature did not persist through the remainder of the day, and winds across the entire study area gradually became easterly.



Figure 6-1. Plot of Surface Station Data for 11 July 1991.

The high began to drift eastward on Friday, allowing winds across the study area to become southeasterly ahead of an approaching low pressure center. The low pressure center was located over Madison, WI around sunrise. As the low moved through the southern Great Lakes, clouds increased over the region. Scattered light precipitation was reported in the study area, with rainfall totals generally less than 0.1 inch. With the passage of the system across southern Lake Michigan Friday night, winds were variable across the southern Lake Michigan Basin.

On Saturday morning, most of the precipitation ended as the low pressure system worked its way eastward. Skies were variably cloudy during the remainder of the day, with a few isolated afternoon showers developing. Behind the departing low, the winds became northerly, with speeds ranging from 10-15 mph. As the low pressure area continued to pull away from the Great Lakes, wind speeds across the study area diminished to 8-10 mph. Despite the northerly winds that had developed during the day, afternoon highs warmed into the mid to upper 70s.

6.1.2. Week of 14-20 July 91

The second week of the study was much like the first, with a slow-moving area of high pressure dominating the weather in the Great Lakes for several days. On Sunday, a large area of high pressure was located over the northwestern Great Lakes. Cool, northerly winds were reported statewide with weak land breeze characteristics evident in the light wind pattern during the morning. In the afternoon, onshore winds kept temperatures cool near the southern lake shore, while sunny skies helped to warm the inland areas into the lower 80s. Late in the day, the center of the high pressure area moved over western Michigan. As a result, the overnight winds became light and variable.

Monday saw the high pressure center pass across the central Lower Peninsula of Michigan. Winds remained light and variable through the day. The high pressure kept skies sunny across the entire Great Lakes area. Temperatures warmed into the low 80s in most areas, but were cooler along the southern Lake Michigan shoreline. As the high continued to drift eastward overnight, some light southerly winds developed across the eastern Great Lakes. However, the winds across the study area remained light and variable through the night.

By Tuesday morning, the center of the high pressure area had shifted eastward into Pennsylvania. The morning winds around the Chicago area were offshore, while all other shoreline locations reported calm winds. As the day progressed the winds became more organized. South to southwesterly winds were reported across the study area by late afternoon, with temperatures rising to near 90 across the entire southern Lake Michigan Basin. Winds remained southwesterly through the night.

A weak trough worked into the northern Great Lakes Wednesday morning, but had little effect on conditions in the study area. High pressure across the eastern U.S. helped to produce a weak, but very warm south to southwesterly flow across the region. Afternoon highs again climbed to 90°F. With the East Coast high stalling just off the Carolina coast, conditions remained constant from Wednesday through Saturday. Skies remained generally sunny, though haze was reported across the southern Lake Michigan Basin each day. Temperatures soared during the period, with readings in the 90s reported through Saturday. Temperatures in Chicago, IL reached the 100-degree mark on Friday and Saturday. On Saturday, a cold front approached the Great Lakes from the northwest and stalled across central Michigan during the early part of the day. The front remained stationary for the remainder of the weekend, producing a strong south to southwesterly flow across the entire study area.

6.1.3. Week of 21-27 July 91

As noted in the above section, a stationary front continued to hold across the central Great Lakes on Sunday. The front stretched from just north of Milwaukee, WI to near Port Huron, MI. Scattered showers and thundershowers persisted near the front during the day Sunday, with generally light amounts reported across the study area (0.1 to 0.3 inches). The flow across the study area remained from the south-southwest, with speeds reported around 10 mph. With the front to the north of the study area, afternoon temp_ratures warmed into the mid 80s on Sunday.

On Monday, a strong upper-level low started to move out of the Canadian Rockies. A surface cold front associated with this upper-level feature began to move out of the Central Plains states. In response to the approaching cold front, winds across the study area increased from the southwest to around 10-15 mph. The strengthening southwesterly winds helped to push the stationary front northward, allowing very warm air to move into the study area. Temperatures climbed into the upper 90s to near 100 on Monday, with Chicago, IL reporting a high of 102°F.

On Tuesday morning, a cold front from the Central Plains moved across the study area. The winds behind the front were from the northwest, with speeds ranging from 10-20 mph. Scattered precipitation accompanied the front, with all precipitation ending by 12Z (8AM EDT). As the day progressed, the winds remained strong from the northwest. This northwest flow pattern resulted in significantly cooler temperatures on Tuesday, with afternoon highs remaining in the upper 70s. On this day the R/V *Laurentian* made its first trip to the southern Lake Michigan sampling station.

A weak trough of low pressure moved through the study area early Wednesday morning. As a result, the winds across the southern part of Lake Michigan were from the southwest (Figure 6-2). However, the winds quickly returned to the west-northwest with the passage of the trough. Despite the northwesterly winds reported on the ship, emissions from the Gary, Indiana industrial area were observed moving to the northeast (i.e., over the lake) for several hours. Figure 6-2 shows that Gary did have winds from the southwest during this period. Further analysis determined these southwesterly flows were likely caused by the deceleration of the weak trough. It is likely that the wind-shift line remained between the R/V *Laurentian* and Gary for several hours before moving to the southeast. A second weak trough moved through the study area that night.

The trough that moved into the study area Wednesday night was located just to the south of Lake Michigan on Thursday morning. When the Canadian upper-level low started to pull to the northeast, an area of surface high pressure was able to move in behind the trough. Winds across the study area were generally from the north. Along the Wisconsin shoreline, the wind appeared to be most affected by the surface high and the resulting flow was from the northwest. Along the Michigan shoreline, the winds were affected by the departing trough and the flow was from the northeast throughout the day. The R/V *Laurentian* similarly reported northeasterly winds on Thursday.

Early Friday morning, the area of high pressure was located over northern Wisconsin. The high gradually drifted eastward through the day and consequently, the winds remained from the northeast across the study area. Skies remained sunny across the Great Lakes, with afternoon highs only warming into the lower 70s. Little change was noted on Saturday, as the high continued to slowly make its way toward the East Coast.

Figure 6-2. Plot of Surface Station Data for 24 July 1991.



6.1.4. Week of 28 July-3 August 91

The high pressure system that dominated the weather on 26 July and 27 July slowly moved to the northeast on Sunday. A weak low-pressure system moved out of eastern Nebraska and introduced clouds into the Great Lakes. The winds were generally from the east on Sunday due to the continued influence of the Canadian high pressure area. The combination of cloudy skies and easterly winds resulted in relatively cool temperatures with afternoon highs in the 70s. As the night progressed, scattered showers associated with the approaching low moved into the Great Lakes.

Monday began with scattered showers across the southern Lake Michigan Basin. The surface low producing the showers was located just east of Rockford, IL at sunrise. As a result, early morning winds were from the southeast across the study area. As the storm center passed over the south-central part of Lake Michigan, winds across the area became variable for a short time. Once the storm had passed, rain showers tapered off and winds across the study area remained light and northwesterly. Generally light rainfall totals were reported with most areas receiving less than 0.1 inch of rain. However, just to the north of the study area heavier rains were reported, with Muskegon, MI reporting 1.70 inches.

By Tuesday morning, the low pressure system had moved into southern Ontario. A weak area of high pressure then moved into the Great Lakes that afternoon. Winds were light and generally from the north during the day, though the wind field was light enough to be altered by land breeze mechanisms during the morning hours. As a result, the morning winds across the Lake Michigan shoreline contained a lakeward component. As the day progressed, the weak surface high continued to drift eastward. In response, winds across the southern Great Lakes became light and southerly late in the day. Cool temperatures prevailed over the area on Tuesday, with afternoon highs remaining in the 70s under sunny skies.

On Wednesday, the weak high pressure system moved into the Ohio Valley. Consequently, the winds across the study area were mild and southerly. With skies remaining sunny through the day, temperatures warmed well into the 80s across the region. Afternoon highs rose to near 90°F in both Milwaukee, WI and Chicago, IL. As the day progressed, winds increased in speed as a cold front began moving into the Midwest from the Northern Plains. Winds remained from the south for most of the night.

The approaching cold front moved through the Chicago area early Thursday morning. The southerly winds across the study area became west to northwest with the front's passage. The cold front was relatively weak with some clouds developing but no precipitation reported. A weak high pressure area quickly moved in behind the front, producing generally sunny skies. The temperature remained virtually unchanged from the day before, with the exception of the southern shores of Lake Michigan. The Thursday afternoon temperatures there were only in the 70s due to the onshore flow ahead of the high. The surface high pressure center weakened during the day on Thursday. As a result, the weak cold front that had passed through the study area Thursday morning was not pushed far to the south. A developing low pressure system in Nebraska produced a southerly flow to the south of the front, which caused it to move northward Thursday night, eventually stalling across the study area.

As can been seen in Figure 6-3, the front stretched from the Wisconsin/Illinois border to Flint, MI Friday morning. Winds to the north of the front were easterly, while south of the front the winds were from the south. The arrival of the front brought variably cloudy skies to the southern Great Lakes during the morning hours Friday. As the day progressed, two low pressure areas developed along the front and headed to the east, toward the Great Lakes. The first low pressure system moved across the study area Saturday morning. Rainfall totals from the storm's passage ranged from .02 inches in Chicago, IL to .57 inches in Muskegon, MI. As the first storm center moved east of the study area, winds across the southern Lake Michigan Basin became northerly. The front, as well as the second storm system, moved southeastward Saturday afternoon. A large area of high pressure then moved in from Manitoba, Canada, bringing clearing skies and brisk northerly winds. Cooler air associated with this system moved in, resulting in Saturday afternoon temperatures in the low to mid 70s.

6.1.5. Week of 4 August - 10 August 1991

On Sunday, 4 August, high pressure continued to push toward the Great Lakes. While the center of the high pressure was located along the North Dakota-Manitoba, Canada border, it was still able to influence the winds across the Great Lakes. The winds across the region were from a northerly direction. Early in the day, a weak trough was responsible for variable wind directions across the study area. At 12Z (8AM EDT), the trough ran from just south of Lansing, MI to near the South Haven, MI sampling site. The winds to the north of the trough were due north at the time of observation, while

Figure 6-3. Plot of Surface Station Data for 2 August 1991.



south of the trough, the winds were northwesterly across southern Michigan. At that time, the winds across northern Illinois were all from the northeast. There is some evidence of a second weak trough in this area, which would explain the variation in the wind directions across the lake. The wind speed generally increased throughout the day. The strong winds (10-20 mph) were blowing straight down the north/south axis of the lake for approximately 24 hours. As a result, the waves on Lake Michigan swelled to 3-6 feet. Sunday was to be the first day of the second sampling intensive aboard the R/V *Laurentian*. However, due to the rough lake conditions, the ship was docked in Benton Harbor for the night. During the night, the high pressure area continued its push toward the Great Lakes. As the high moved closer, the winds diminished, allowing the R/V *Laurentian* to reach its sampling position off the shore of Chicago.

By Monday morning, the center of the high was located over the western Upper Peninsula of Michigan. The high was still close enough to produce sunny skies across the southern part of Lake Michigan, though a cloud line was located near Chicago. From the R/V *Laurentian*, skies south of Chicago appeared quite dark and capable of producing rain. Indeed, records show that rain did fall just to the south of the lake, while skies over the ship's location remained partly sunny throughout the day. With the approach of the area of high pressure, the winds across the study area become northeasterly and eventually easterly during the day.

By sunrise Tuesday, the winds had become slightly south of east. The center of the high was now located near Saulte Ste. Marie, MI. As can be seen in Figure 6-4, a weak trough of low pressure extended from eastern Iowa to southern Lake Michigan. As a result, the flow over the study area was from a southeasterly direction. Conversely, the remainder of the Great Lakes experienced easterly winds. The wind speeds over the lake ranged from 5-10 mph. That evening, the trough began to shift to a more west-east orientation, and the winds observed from the ship's location shifted to a northeasterly direction (SE -> NE in 30 minutes). It was decided that movement of the ship farther to the south would place it in a more favorable wind flow pattern for sampling. For this reason, the ship was moved southward that evening. In the ship's new location, the winds were from the southeast once again, and remained that way throughout the night. It is believed that the difference in the wind directions at the two locations was a result of the trough moving slightly to the south of the ship's earlier location.

On Wednesday, the high pressure area was still the dominant feature across the Great Lakes. The storm system that was developing in the Central Plains continued to



Figure 6-4. Plot of Surface Station Data for 6 August 1991.

move slowly toward the Great Lakes. These two synoptic features helped to maintain southeasterly winds across the study area for much of the day, with winds becoming easterly during the early evening. The winds remained from the east for several hours. During the early morning hours, the winds shifted to the southeast once again. The change in wind direction was in response to the approaching low pressure system from the Central Plains. The storm system arrived in the study area shortly after midnight, with light rain beginning at the R/V *Laurentian* at 1:15AM.

By 7AM Thursday morning, the storm center was located in eastern Iowa. Showers and thunderstorms continued across the area throughout the day. The winds over the lake increased significantly from the southeast as the storm system approached. At that time, the winds over the lake shore areas were from the east. Two factors are believed to be responsible for the observed divergent wind conditions. First, at 12Z a weak trough ran from Milwaukee, WI to Muskegon, MI. The orientation of the pressure field was conducive to a localized southeasterly flow over the southern half of the lake. In addition, for the given pressure pattern, less friction across the lake surface (as compared to the land surface) would also be conducive to a flow more parallel to the isobars (lines of constant pressure). Winds reached 20-25 mph from the southeast, and large waves developed on the lake. Sampling activities were suspended and the ship returned to shore to avoid unsafe conditions.

As the day progressed elsewhere across the region, the winds across the southern Great Lakes continued from an easterly direction. The storm center passed through the southern Great Lakes during the afternoon and evening hours of Thursday, causing the winds to become northerly behind the surface low. By morning, the storm center was located over western Pennsylvania. Thursday precipitation totals across the area ranged from 0.5-2.0 inches. With the storm now off to the east nigh pressure began moving in from the Northern Plains on Friday morning. The skies across the area began to clear somewhat, with variably cloudy skies reported through the day. Despite the sunshine, temperatures remained cool due to the northerly winds that had developed ahead of the advancing high. Afternoon temperatures only warmed into the mid 70s across the study area.

6.2. Micrometeorological Measurements

One of the goals of the Lake Michigan Urban Air Toxics Study (LMUATS) was to investigate the possible relationship between the concentration of toxics in the ambient air

over Lake Michigan and their corresponding concentrations in the lake surface water below. If such a correlation were found to exist, further information would be needed to understand the potential exchange processes occurring at the air-lake interface. For this purpose, a series of meteorological measurements were taken aboard the R/V *Laurentian* during two ship borne measurement periods: 23-27 July 91 and 5-8 August 91. These measurements were used to characterize the micrometeorological environment that existed in the atmospheric surface layer above Lake Michigan during these intensives. These data were also used to compute surface layer fluxes of heat, momentum and moisture. These fluxes were then used to gain insight into the aforementioned exchange processes occurring at the air-lake surface interface.

6.2.1. Analysis of Micrometeorological Data

As noted earlier in this report, one of the goals of the ship borne intensives during the Lake Michigan Urban Air Toxics Study was to investigate the possible relationship between the concentration of toxic pollutants in the air over Lake Michigan and their corresponding concentrations in the lake surface water below. In order to accomplish this task, it was necessary to characterize the state of the atmospheric surface layer over the lake during the measurement periods. The state of the surface layer will greatly influence the various processes by which pollutants are transported through the atmosphere and to the surface. To make this characterization, a set of micrometeorological measurements was conducted off the bow of the ship. Once collected, the data were disseminated in two unique ways to determine the likelihood of the deposition of the airborne toxics. One method of analysis involves simply looking at the stability of the atmosphere. The second more qualitative method used meteorological data to determine the actual deposition velocity of the pollutants. In the sections that follow, the methods by which pollutants can be deposited to a surface are discussed as well as the aforementioned methods of determining if there was a likelihood of deposition during this study period.

6.2.2. Deposition Processes

Once emitted into the atmosphere, pollutants are transported by the prevailing winds. Heavier particles will usually fall out of the atmosphere quickly, mainly due to the effects of gravity. Smaller, lighter particles and gases are less likely to fall out of the atmosphere due to this gravitational settling. As a result, the lighter particles are more likely to be transported over longer distances. Since the lighter particles will not settle out

of the atmosphere on their own, they must rely on turbulent motions in the atmosphere to assist in their deposition to the Earth's surface (in the absence of precipitation). These turbulent motions can be generated via mechanical and/or via thermal effects (Figure 6-5).

Mechanical turbulence is caused by wind shear (a change in the wind speed/direction with height). The particles or gases become caught up in the turbulent motions or eddies, which in turn help to transport them toward the surface. In much the same way, particles can be transported toward the surface via thermally induced turbulence. In this case, if the air above a surface is cooler than the surface itself, the layer of air immediately above the surface is warmed. This warmer air will rise, causing the development of buoyant, turbulent eddies. Once again, the eddies will aid in the transport of the lighter particles or gases toward the surface.

To a large degree, the intensity of turbulence in the atmosphere depends on the stability of the atmosphere. Some of the micrometeorological measurements made aboard the R/V *Laurentian* were done specifically to determine the stability of the atmosphere over the lake. In the next section, the role that stability plays in the control of turbulence intensity will be addressed. In addition, measurement results, conclusions regarding the stability of the atmospheric surface layer during the intensives, and how this may have affected pollutant deposition will be discussed.

6.2.3. Stability of the Atmospheric Surface Layer

Regardless of how turbulence is produced, the stability of a layer in the atmosphere will determine if this turbulence is damped or allowed to grow in that layer. A stable atmosphere will act to suppress turbulence, while an unstable atmosphere will allow for the generation and/or growth of turbulence. During the ship borne intensive measurement periods, continuous measurements were made of the wind and temperature fields in the lowest 7 meters of the atmospheric surface layer above the lake. In addition, temperature measurements were taken from the lake surface layer. These parameters were used to determine the stability of the atmospheric surface layer.

A layer is considered statically stable if the potential temperature in that layer increases with increasing height. The potential temperature of a layer is the temperature that the layer of air would have if it were adiabatically lowered to the surface. Since the potential temperature of any parcel (or layer) of dry air does not change when moved

Figure 6-5. Schematic of the Micrometeorological Effects on Pollutant Deposition.



Mechanically Induced Turbulence



Thermally Induced Turbulence



vertically, vertical movement in a stable layer will result in the parcel being colder and denser than its surroundings. Therefore the parcel will want to sink back to its original position. In a statically unstable atmosphere, the same parcel would be warmer than its surroundings when lifted, and the parcel would want to continue to rise. In these ways, turbulence is either damped or enhanced by the thermal structure (and thus stability) of a particular layer.

For this study, it was the stability of the atmospheric surface layer above Lake Michigan that was of interest. The hypothesis stated that if the layer was stable, turbulence would be suppressed. In the absence of turbulence, the lighter particulates and gases would not have a significant deposition mechanism. If the layer was unstable, enhanced turbulence would be expected, resulting in enhanced deposition of pollutants. While numerical results will not be presented at this time, the following can be said regarding the stability of the surface layer during the intensive periods.

6.2.3.1. 24 July 1991

On 24 July 1991, weak high pressure initially prevailed across the southern Lake Michigan Basin, producing sunny skies and warm temperatures. Afternoon high temperatures along the Lake Michigan shoreline ranged from 80-85° F. As a cold front approached from the northwest during the afternoon, the winds became southeasterly with speeds ranging from 8-12 mph. Under these conditions, mild air was carried across the southern portion of Lake Michigan and across the area in which the R/V *Laurentian* was anchored. During the afternoon, measurements aboard the R/V *Laurentian* indicated that the temperature was constant through the atmospheric surface layer, with an average temperature of approximately 77°F. During this same period, measurements were taken of the temperature of the lake surface water. These readings indicated a surface temperature of approximately 75°F. A cold front moved across the area that evening (9PM-12AM). With the passage of the front, winds became northwesterly at 12-16 mph, and significantly cooler air moved in behind the front.

The above information suggests the following about the atmospheric surface layer stability for that day. The surface temperature of the lake was significantly cooler than the temperature of the airmass as it left the Lake Michigan shoreline. The afternoon temperature readings taken aboard the R/V *Laurentian* indicate that the airmass cooled as it traveled to the ship's position. This cooling of the airmass' lower layer would have

produced a thermally neutral-to-stable atmospheric surface layer during the afternoon and evening periods. The net effect would be to stabilize the surface layer.

A Reynolds number was also calculated for this period. The Reynolds number is a measure of atmospheric stability which considers both thermal and mechanical effects. During the afternoon and evening hours, the Reynolds number indicated neutral to slightly unstable conditions. Values of the Reynolds number ranged from 0.0 to -0.1.

When the two sets of information are both considered, the following can be deduced about the stability conditions over Lake Michigan that day. Wind data show adequate surface wind shear to produce some mechanical turbulence. The apparent stability of the surface layer suggests that in all likelihood this turbulence would have been damped. As a result, long-range transport of pollutants from the Lake Michigan urban region across the lake was probable. The highest probability for pollutant deposition to the lake's surface would have been during and after the passage of the frontal systems.

6.2.3.2. 25 July 1991

As noted in the discussion of 24 July, the passage of a cold front on Tuesday evening caused a shift in surface wind directions. While the winds initially became northwesterly after the front's passage, the direction became north to northeast during the early morning of 25 July. Wind speeds ranged from 12-16 mph during the early morning hours, before diminishing somewhat to 10-14 mph for the remainder of the day. The passage of the front brought a new, cooler airmass across the southern Lake Michigan Basin. The intrusion of the cooler airmass was somewhat masked by the typical diurnal fall in temperatures. However, its effects became apparent during the daylight hours of 25 July. While the afternoon highs on 24 July were in the range of 80-85°F, the daytime highs cross the region on 25 July ranged from 70-73°F. Skies remained sunny as a new area of high pressure moved into the Great Lakes region.

As previously observed, the surface water temperature was approximately 74-75°F during this period. Unlike conditions of 24 July, the airmass that flowed off the land and over the water was now colder than the lake surface. Rather than cooling the lower part of the atmospheric surface layer, the lake now served to warm the lower portion of the surface layer. The temperature at the lake surface was as much as 0.5°F warmer than the temperature 7 meters above the lake surface. This trend began to develop during the early morning hours, when the air temperature dropped below the temperature of the lake

surface. This situation is termed statically unstable, as the potential temperature was decreasing with height. These conditions persisted throughout the day. Now, rather than suppressing turbulence, the thermal structure was such that it should have enhanced any existing turbulence.

As before, Reynolds number values were estimated. The calculated values ranged from -0.1 to -0.3, and were indicative of unstable conditions. This information, together with the thermal evidence discussed above, strongly suggests that the conditions present throughout 25 July were increasingly conducive to turbulence and enhanced pollution deposition to the lake surface.

The prediction of increased turbulence on 25 July is further supported in the next section of this report. In this section, a second method of analysis for investigating pollutant deposition will be discussed. The concept of deposition velocity will be reviewed. Although it is not practical to measure the deposition velocity directly, it can be calculated by measuring the degree of turbulence in the surface layer. This turbulence can be inferred through the measurement of a quantity called momentum flux.

6.2.4. Deposition Velocity

A second method of investigating the deposition of pollutants to any surface is through consideration of a quantity called deposition velocity. This parameter describes the average velocity at which a particular pollutant is deposited under a given set of circumstances. Calculations of the deposition velocity consider stability, the chemical nature of the pollutant and the characteristics of the surface to which deposition is occurring. There are two types of deposition velocities which are usually considered: wet deposition and dry deposition. Wet deposition involves the removal of pollutants from the atmosphere via various precipitation processes. For the days being considered (24 and 25 July), no precipitation occurred. Therefore, only dry deposition will be discussed in this section.

When considering the dry deposition of pollutants to any surface, it is often useful to think in terms of an electrical resistance analogy. In a series circuit, the amount of current flowing through the circuit is inversely proportional to the amount of resistance in that circuit. Similarly, the velocity at which a pollutant is deposited to a surface is inversely proportional to the resistance to deposition offered by a variety of factors. The expression for the deposition velocity is as follows:
$$V_d = 1 / [R_a + R_s + R_t]$$
 (1)

where V_d is the deposition velocity, R_a is the aerodynamic resistance, R_s is the surface layer resistance and R_t is the transfer resistance (Seinfeld, 1986).

The aerodynamic resistance accounts for the turbulent diffusion of material from the free atmosphere to the surface laminar sub layer (immediately next to the surface). This aerodynamic resistance is a function of typical meteorological parameters, such as wind speed, surface roughness and atmospheric stability. The surface layer resistance depends on parameters characterizing diffusion across the laminar sub layer (directly next to the surface in question). This resistance is dependent on molecular, rather than turbulent, properties. Finally, the transfer resistance depends on the physical-chemical interaction between the pollutant and the surface.

For most species where the deposition under consideration is to a water surface, the limiting (or dominant) term in equation (1) is the aerodynamic term. For this reason, the other two terms will not be discussed at this time. Further information on these terms can be found in the previously mentioned reference.

6.2.5. Aerodynamic Resistance

As noted above, the aerodynamic resistance is a function of wind speed, atmospheric stability and surface roughness. It is independent of the species being deposited. Seinfeld states that this resistance can be viewed as being characteristic of the resistance of momentum transfer to the surface. He offers the following relationship:

$$V_{M}(z_{1},z_{0}) = U_{*}^{2} / U(z_{1})$$
 (2)

where $V_M(z_1,z_0)$ is the momentum transfer velocity, z_1 is the height above the surface, z_0 is the roughness length, U_*^2 is the momentum flux and $U(z_1)$ is the average wind speed at height, z_1 . Seinfeld goes on to state that if the aerodynamic resistance is the only (or dominant) resistance to dry deposition, then $V_d = V_M$. Simply, what equation (2) tells us is that the velocity with which a pollutant is deposited to a surface is proportional to the momentum flux above that surface. While it is not currently possible to measure the deposition velocity directly, it is possible to measure the momentum flux. Therefore, our goal was to measure the flux of momentum to Lake Michigan, then infer the deposition velocity of pollutants over the lake from these measurements.

6.2.6. Momentum Flux Calculations

The flux of any quantity can be described as the transfer of that quantity through a unit area per unit time. There are four standard techniques that are generally used for calculating fluxes of various parameters. In order of preference, these techniques are:

- 1. eddy correlation (or direct correlation),
- 2. inertial subrange energy dissipation,
- 3. flux/gradient (or profile), and
- 4. bulk aerodynamic methods.

During the LMUATS, the fluxes of momentum, heat, moisture, CO_2 and ozone were of primary interest. While planning the measurement strategy before the intensives, it was decided that the eddy correlation technique to estimate the fluxes of interest would be used. This is the most direct procedure for measuring turbulent fluxes and is thus the most accepted method. Unfortunately, considerable problems were encountered during the intensives. Significant wave action was encountered on Lake Michigan during both ship borne measurement periods. This caused many problems when trying to compute the momentum flux from the measurements. As a result, several methods were used to compute the momentum flux, in an attempt to remove wave motion from the data. Methods 1, 2 and 4 were chosen for the analysis. Of the 3 techniques, only method 4 proved successful.

The following is a discussion of the three methods utilized in the analysis. The discussions of methods 1 and 2 include explanations as to why these methods were deemed unsuccessful. The discussion of method 4, the bulk aerodynamic method, includes interpretations of the final results. Finally, this section concludes with suggestions on how to carry out such measurements in the future.

6.2.7. Eddy correlation

The eddy correlation technique is the most direct method available for determining the atmospheric flux of various quantities caused by the turbulent (or eddy) motions in the atmosphere. In essence, the method tries to correlate fluctuations in the wind with fluctuations in the quantity of concern. The ultimate goal was to estimate the relative magnitude of **vertical** transport of pollutants to the lake surface. Therefore, the main concern was with making a correlation between fluctuations in the **vertical** component of the wind and fluctuations in the species (or meteorological variable) in question. To calculate the momentum flux described above, it was necessary to correlate fluctuations in the **vertical** component of the wind with fluctuations in the **horizontal** component of the wind.

At any instant in time, the vertical velocity may be broken into two parts: the average velocity and some perturbation about that average. This is mathematically stated as:

$$W = \overline{W} + W' \tag{3}$$

where \overline{W} is the average value of W and W' is the perturbation about the mean. Likewise, for the horizontal component of the wind:

$$U = \overline{U} + U' \tag{4}$$

In lieu of a lengthy, mathematical discussion, it can simply be stated that the time averaged value of the correlation between the U- and W-components of the wind can be written as:

$$\overline{UW} = \overline{UW} + \overline{U'W'}$$
(5)

where \overline{UW} is the product of the average U- and average W-wind components during some time interval and $\overline{U'W'}$ is the average of the product of the U- and W-perturbations during that same time interval. Over any appreciable length of time $\overline{W} = 0$, so the second term drops out (that is, air is -Dviously escaping into space). Therefore, equation (5) reduces to:

$$\overline{UW} = \overline{U'W'} \tag{6}$$

The quantity $\overline{U'W'}$ is referred to as the eddy momentum flux. That is, $\overline{U'W'}$ is the flux of momentum that is caused by turbulent eddies in the atmosphere. When $\overline{U'W'} < 0$, the flux of momentum is to the surface (indicating the opportunity for pollutant deposition). The larger the value of $\overline{U'W'}$, the better the chances for deposition. When $\overline{U'W'} > 0$, the flux of momentum is away from the surface.

Turbulent eddies come in a large variety of sizes, ranging from centimeters in diameter to hundreds of meters. In order to properly measure the fluctuations caused by the smallest of these eddies, measurements must be taken of the wind direction and speed over very small time intervals. For this purpose, a set of "fast-response" instruments were utilized. These instruments were able to sample various fields at a rate of 10 Hz (that is, 10 times each second). The instruments used are explained in detail in the Methods section (Chapter 4). Calculations of U' and W' were made using a data analysis package written for this study. Ten-minute averages of the momentum flux were then calculated using the eddy correlation method described above.

The results of this analysis were unrealistic and alternated randomly from positive to negative values. It should be noted that, while it is possible to have instantaneous positive values of the momentum flux, the time-averaged values should always be negative when calculations are computed for the surface layer. The questionable results were not completely unexpected however, since the bow tower was constantly in motion due to the rocking of the R/V *Laurentian* in the waves. As a result, the measured "W" component of the wind was never truly just the "W" component. The data were contaminated by this motion in two ways. First, the tower was often tilting, such that it was never really vertical. For this reason, a true W-component was not measured. Rather, a combination of the W-component and a horizontal component was measured. Pond *et al.* (1971) found that without correction for an axis tilt of as little as 5°, such data were worthless. The tilt of the bow tower exceeded this limit. As noted earlier, equipment was ordered that would have allowed for corrections of these motions. However, the delivery of this equipment was delayed and it was unavailable for use during the data analysis.

The W-component data were also contaminated by the vertical bouncing of the boat and tower caused by the interaction of the ship with the waves on the lake surface. As waves passed under the ship, the ship (and the bow tower) would move up and down in response. This vertical motion was superimposed upon the actual W-component. It was originally felt that this effect could be eliminated by using a mathematical technique called spectral analysis. This technique is described below.

The turbulent motions of the atmosphere can be thought of as a series of fluctuations that repeat themselves with a certain frequency (e.g. once every second (1 Hz) or 5 times every second (5 Hz)). When the strength of the different fluctuations is plotted versus their frequency of occurrence on a log-log plot, the result is a plot similar to Figure 6-6. When these turbulent wind measurements are taken from a stable platform in





Frequency $(Hz = sec^{-1})$

a neutral boundary layer, these spectral energy values fall off with a slope of -5/3. Any variations to this -5/3 fall-off are said to be caused by external forcing. In this case, external forcing was due to the bouncing of the ship in the waves. Note that the external forcing in the data plot occurs at 0.3 Hz. This would represent an occurrence of once every three seconds. This matches the observed frequency of the waves on the lake during this particular measurement period.

The above analysis can be performed mathematically using a technique called Fourier transform. This type of analysis takes a time series plot of the wind data and mathematically transforms the plot into a sum of sine and cosine terms. These terms are based on the different frequencies of the various fluctuations. Mathematically, this is expressed as:

$$W(f) = \sum_{f} A_{f} \sin(ft) + \sum_{f} B_{f} \sin(ft)$$
(7)

where f is the "frequency" of the fluctuation and "A" and "B" describe the magnitudes of the fluctuations. Since the frequency of the external forcing is known, the terms that include this frequency or range of frequencies can be removed or filtered. A reverse transform can then be computed, resulting in a new time series that is theoretically the same as the original time series, minus the frequency caused by the external forcing.

A Fourier analysis was performed on the data for 24 and 25 July 91. The new time series was then used to compute the momentum flux using the eddy correlation technique described above. Again, the results were unrealistic. The values that were calculated continued to show an oscillatory trend by alternating randomly between positive and negative values. The magnitudes of the numbers were also quite small, indicating that the filtering technique had removed too much energy and did not generate realistic results.

Since both attempts at using the eddy correlation method did not result in reasonable values for the momentum flux, a decision was made to try several indirect methods for calculating the momentum flux. These methods are discussed below.

6.2.8. Energy Dissipation

At the beginning of this section, the generation of turbulence was attributed to mechanical and thermal processes. The intensity of turbulence is often expressed as the turbulent kinetic energy or (TKE). The turbulence that is often felt by airplane passengers is obviously quite strong if it can cause a plane to shake. This would be an example of turbulence with high TKE. Weaker turbulence would be classified as having lower TKE. Once formed, turbulent eddies will gradually break into smaller eddies due to their interactions with each other. Eventually, the eddies are small enough that molecular viscosity or friction will cause them to dissipate, transferring any remaining energy into heat. A range of middle-sized eddies exisits such that the change in the TKE of the eddies is not attributed to either the production processes mentioned earlier, or the effects of viscosity forces. Rather, the eddies exchange energy inertially from the larger eddies as This range of eddy sizes (and their corresponding frequencies of they break up. occurrence) is called the inertial subrange. The inertial subrange can been seen on the spectral power (spectral energy / sample size) plots in Figure 6-6 as the part of the plots that show a -5/3 fall-off. The "inertial subrange" plays a prominent role in the second analysis technique, energy dissipation.

The energy dissipation technique is based on the assumption that in near neutral conditions, the rate of production of turbulent energy at a particular height is equal to the rate of dissipation of turbulent energy at that same height. Mathematically, this is stated as:

$$-\overline{U'W'}\frac{dU}{dz} \text{ (production)} = \varepsilon \text{ (dissipation)}$$
(8)

where ε is the turbulent energy dissipation rate. Pond *et al.* (1971) showed that the dissipation rate can also be related to the momentum flux using the following relationship:

$$-\overline{\mathbf{U}'\mathbf{W}'} = (\kappa \varepsilon z)^{2/3}$$
(9)

where κ is the von Karman constant (≈ 0.40), ϵ is the dissipation rate, and z is the height at which the measurements were taken. Therefore, if the dissipation rate is known, the momentum flux can be inferred indirectly. The dissipation rate can be determined by returning to the spectral energy plots discussed previously (Figure 6-6). The energy dissipation rate for a period in time is related to the spectral power plot for that same period by the following relationship:

$$S(k) = \alpha_k^{2/3} \epsilon^{2/3} k^{-5/3}$$
(10)

where S(k) the spectral energy at a particular wave number, k is the wave number (= 2π n/ \overline{U} , with n = frequency) and α_k is the Kolmogorov constant (=0.55). To determine the dissipation rate for any given period, the following steps were undertaken:

- 1. a Fourier transform was performed on the data,
- 2. the inertial subrange was located,
- 3. any frequency within this range was picked and the corresponding value of S(k) were recorded, and
- 4. equation (10) was solved for values of ε .

Ten-minute average values of ε were computed and then substituted into equation (9) to acquire the ten minute average momentum flux values. A similar analysis can be performed to acquire dissipation rates for other scalar variables, such as moisture and heat. These dissipation rates can then be used to compute moisture and heat fluxes, respectively.

To compute the momentum flux, a spectral analysis on the horizontal component of the wind must be performed. Figure 6-6 shows such a plot (bottom). In the frequency range of 0.1-0.3 Hz, there is a slight deviation from the -5/3 slope. This is another signature of the ship motion. This signature is not as prominent as seen in the W- wind component plot (top-Figure 6-6). The advantage of the dissipation technique is that only the spectral energy for one frequency needs to be considered. Therefore, the analysis could be completed using a frequency outside the 0.1-0.3 Hz range (i.e. a frequency range that was much higher than the frequency of the water waves). Thus, the information used for this analysis was in a range unaffected by the bouncing of the ship. A frequency of 0.7 Hz was chosen for this analysis.

The results of the calculations were not consistent with previous research. While not shown here, the magnitudes of the momentum flux values calculated were much higher than the results published by other investigators for measurement programs similar to those during the LMUATS. One possible source of error in the data is that the bow tower was located only 3 meters ahead of the R/V *Laurentian*. As a result, the interaction of the horizontal wind with the wake of the ship likely distorted the horizontal wind flow. If this occurred, the horizontal turbulence field measured would not be representative of the actual turbulence field over the lake (per conversation with Tim Crawford, NOAA-ATDD, Oak Ridge National Lab, 1992).

As noted above, similar analysis was possible for scalar variables such as moisture. Since fast-response measurements of water vapor were made during the period 24-25 July 91, analysis was performed on this data using the energy dissipation method. The values of the moisture flux calculated from this analysis were much higher than other data published by other researchers. Upon further analysis of the moisture data, additional evidence indicated that the horizontal wind data were tainted. Computation of the moisture flux via the energy dissipation method requires use of both the energy dissipation rates for moisture and horizontal wind. When values of the energy dissipation rates for moisture were compared with those published by other researchers, the values compared rather favorably (e.g. Pond *et al.* (1971) during BOMEX). As a result, the difference between the moisture flux values and those from other studies can be traced back to erroneous values of energy dissipation rates for the horizontal wind.

6.2.9. Bulk Aerodynamic

The final method used to compute the momentum flux was the bulk aerodynamic method. This method computes the momentum flux from a bulk, aerodynamic quantity such as the five-minute average wind speed at the height in interest. While this method is a very indirect method of computing the momentum flux, the influence of ship motion is not a consideration. Over a long period of time (e.g. five minutes), these motions will be averaged out. The resulting data will not require that correction: be used. The momentum flux is calculated using the following relationship:

$$-\overline{\mathbf{U}'\mathbf{W}'} = \mathbf{C}_{\mathrm{D}}\overline{\mathbf{U}}^2 \tag{11}$$

where C_D is the momentum drag coefficient and \overline{U} is the mean horizontal wind (Arya, 1988).

One disadvantage of this simplistic approach is the value of C_D varies considerably as the characteristics of the underlying surface change. Therefore, the drag coefficient is

really a function of the roughness length (a relative measure of surface roughness). Values for the roughness length vary from 10⁻⁴ meters for a calm, open sea surface to 3 meters for urban areas. Arya (1988) uses the following relationship to calculate values of the drag coefficient:

$$C_{\rm D} = \kappa^2 / [\ln (Z/Z_0)]^2$$
(12)

where κ is the von Karman constant, Z is the height of the measured wind speed in equation (11) and Zo is the roughness length. For our calculations, a value of 2 x 10⁻⁴ was used for Zo, yielding a value of 0.0015 for CD.

The momentum flux results obtained with this method are given in the Appendix. Unlike the results using the previous two methods, the values obtained using the bulk aerodynamic method do compare favorably with values obtained by others who have carried out similar experiments. The results are shown in a graphical form in Figure 6-7 on the following page.

6.2.10. Interpretation of Bulk Aerodynamic Results

From Figure 6-7, it can be seen that the momentum flux values were quite small during the afternoon hours of 24 July, with values remaining less than 0.010 m²/sec² until approximately 6PM. Recalling previous discussions of deposition velocities, the deposition velocities of pollutants during afternoon hours can be inferred to be low. Therefore, long-range transport would have been likely throughout the afternoon. This hypothesis is supported by the chemical measurements made for the period of 9AM-9PM EDT, showing high levels of many pollutants at both the R/V *Laurentian* and South Haven sites.

That evening, a cold front approached the southern Lake Michigan Basin. A gradual increase in the momentum flux values was observed during the front's approach. Surface weather observations indicate that the front passed by the R/V *Laurentian*'s position between 8PM and 8:30PM EDT. Shortly after the front's passage, the values of the momentum flux increased dramatically. The flux values peaked near 0.110 m²/sec² around 1AM EDT on 25 July, before diminishing somewhat for the remainder of the measurement period (until 8PM EDT 25 July). During this period, deposition velocities were likely quite high.



Figure 6-7. Temporal Variation of the Momentum Flux Measured Aboard the R/V Laurentian 24-25 July, 1991.

It should be noted that the information inferred from the momentum flux measurements parallels the conclusions derived from stability data. However, it is difficult to draw any concrete conclusions without the support of results from other flux measurements of moisture, heat and CO_2 . Had attempts at using the eddy correlation method been more successful, these additional fluxes could have been calculated. While calculation of the momentum flux via the bulk method was possible, the measurement techniques used for the other variables prohibited the use of gradient or bulk methods to accurately calculate their respective fluxes.

6.2.11. Suggestions For Future Flux Measurements

Despite the difficulties encountered during the measurement campaign, the measurement of meteorological and chemical fluxes to and from the Great Lakes is a very attainable goal. However, special consideration must be given to several issues.

When the objective of a field program is to measure the small-scale structure of an atmospheric turbulence field, any motion experienced by the sensing instrument may well be of the same magnitude as the turbulence being measured. This problem is of special importance when trying to make direct, *in situ* measurements of a marine surface layer (as was the case for this project). The ideal situation would involve no instrument motion, but this is often unrealistic especially during ship borne measurements. The degree to which the data are contaminated by the motion of the sensing instrument depends on which flux measurement technique is being employed and to what type of platform the instrument is attached.

6.2.11.1. Ship Borne Platforms

If the flux measurements are being made from a ship borne platform, such as in this study, several precautions must be taken. It is inevitable that the sensing instrument will experience some form of motion. Even during nearly calm wind conditions some degree of wave action will be present, manifesting itself in the motion of the ship and affecting the sensing instruments.

If the bulk aerodynamic method is to be used, the effects of the ship motion will be averaged out by the time averaging of the data. This should be true whether the instrumentation used is either the fast or slow response variety. If the gradient method is used, the flux calculations of the variable of interest will require the accurate measurement of the vertical gradient (or change with height) of that variable. This task will be very difficult. As the instruments move vertically due to wave motions influencing the ship, the levels at which the measurements will actually be taken will be changing constantly. A great degree of instrument separation would be required to alleviate this effect which is usually not practical. As a result, this method is not suggested for use on ship borne platforms.

The energy dissipation method of flux calculation has been shown to be successful in previous field programs. As discussed above, this analysis technique allows the investigator to retrieve the flux from the fluctuations of a particular frequency **outside** the frequency range of the ship/sensor motions. The only requirement is that the chosen frequency resides within the inertial subrange. While zero ship/instrument movement would be preferred, the energy dissipation method allows for the measurement of meteorological and scalar fluxes under low to moderate wave conditions. The energy dissipation method was suggested as the most practical method for ship borne flux measurements by several investigators, including Dr. Ken Davidson (Naval Post-Graduate School) and Dr. Tim Crawford (Oak Ridge National Laboratory - ATDD). After completing analysis of the data collected during the LMUATS, it appears that this method would be the preferable method of analysis.

While the eddy correlation method is the most direct method of flux calculation, significant post-processing of the data will be necessary to remove the effects of the ship motion from the data. For this to be possible, it will be necessary to account for the position of the instrument sensor at all times. Pond *et al.* (1971) were able to use the eddy correlation method during BOMEX, though the floating platform that they used was said to be very stable compared to a surface ship. Post-processing procedures included use of a complicated mathematical scheme called coordinate rotation. According to Pond, this method was based on some strong assumptions, but seemed to produce values which compared favorably with calculations using the bulk and energy dissipation methods. The results from similar calculations on ship borne data would be suspect, at best.

In each of the above methods, significant consideration would have to be given to the physical placement of the instrumentation with respect to the ship and/or instrument platform. Any physical object will cause a distortion of wind flow. Care must be taken to place the sensing instrument in an area unaffected by platform or ship waking effects.

6.2.11.2. Stationary Platforms

The use of stationary platforms for the measurement of fluxes to and from the Great Lakes would greatly simplify the post measurement analysis of data. Depending on the stability of the platform, instrument motion effects could be virtually eliminated. However, several new problems would result. Few stationary platforms, if any, exist which would be suited for such an application. During this study, it was noted that several large, cement structures were located offshore of Chicago. These structures house the intake ducts for the city's water supply. Such structures could serve as sites for instrument towers for flux measurement instruments. However, these structures are not easily accessible and would likely cause considerable distortion of the wind flow. The tower would need to be constructed so as to place the instrumentation out of the area affected by the distortion.

A second idea would be to construct a tower on a sandbar just offshore. Such a structure would need to be strong enough to withstand the considerable force produced by the motion of the lake waters. If this could be accomplished, the platform would also allow for the measurement of fluxes using any of the previously described methods. One question that would need to be answered, however, is how representative the flux measurements would be of fluxes occurring over the center of the lake. Also, if such a lake shore platform were built, data collection might be limited to onshore flow conditions only. Depending on shoreline topography, flow from land to the measurement platform could contain motions induced by flow over the lake shore topography. Such flow would not be representative of conditions at mid-lake, though these results would be useful for studying near shore effects on fluxes and deposition.

Chapter 7

Source Apportionment/Receptor Modeling

7.1. Introduction

An understanding of the transport and fate of contaminants emitted to the atmosphere is crucial for determining potential impacts on human health and the environment. Source characterization is a powerful tool for the assessment of emissions from local sources. There are a number of methods available which identify sources or source regions contributing to the pollution load measured at a given receptor. These can be categorized into statistical methods, chemical and isotopic trace methods, individual particle analysis, meteorological methods including trajectory techniques, dispersion modeling and various combinations of these approaches. Some of these methods are briefly described by Zweidinger *et al.* (1990) and Sweet and Vermette (1992 and 1993) in their reports on VOCs and trace elements in Illinois and St. Louis. These are further expanded upon in their references as well as in Gordon (1988), Henry *et al.* (1991) and Hopke (1991).

7.1.1. Source Characterization Techniques

Traditionally, dispersion models have been the method of choice for calculating source-receptor relationships for air pollutants. These models require detailed emissions inventories for the sources of the pollutants of interest (e.g., SO_2 , HCs, NO_x , etc.). However, even if the dispersion modeling could be done accurately, it is very unlikely that the source emissions inventories for the pollutants of interest would be adequate. As discussed earlier in this document, emissions inventories for the criteria pollutants have many short-comings. These inadequacies are even more severe for hazardous pollutants or pollutants which have large contributions from fugitive emissions, natural sources and dusts.

The limitations of the dispersion-oriented methods led to the development of receptor-oriented models. These have been used effectively to identify the natural and anthropogenic sources of atmospheric particles in both urban and rural areas (Gordon, 1980, 1988). Receptor models assess contributions from various sources of atmospheric pollutants based on measurements at sampling or receptor sites. The measurement used most often and most successfully is the elemental composition of atmospheric particle matter (Dzubay *et al.*, 1988; Keeler *et al.*, 1990). Pollutant properties, such as particle morphology, particle size distribution, vapor to particulate partitioning, and elemental composition, can then be used to identify sources or source types. Meteorological information can also be used in conjunction with receptor models for assessing the contributions of distant sources. These are often referred to as hybrid models (Keeler, 1987).

Another method of source characterization is the chemical element balance, or chemical mass balance (CMB) method. It is based upon the premise that the emissions characteristics of various source types are different enough in chemical and elemental composition, as well as physical size and morphology so that one can identify their contributions by measuring these characteristics in samples collected at a receptor site. Thus, identifying the number and types of important sources of air pollutants is an important first step in the application of CMB models to apportion the sources of air pollutants measured in a specific urban area. The CMB models assume that the composition of all contributing source types are known. However, this is often not the case due to the fact that the sources are not easily sampled and/or the source classes have widely varying compositions (Henry, 1991). Thus, the lack of specific source profile information is an important limitation of the CMB method and this ultimately limits the application of this approach. Particularly, emissions data have been sparse in the past, particularly for SOCs, but the situation is improving.

While the CMB method has been applied primarily to urban-scale data, Rahn and Lowenthal (1984, 1985) applied this technique to the regional signatures they identified to apportion sulfate and trace metals observed on particulate matter. The application of receptor models to regional and global scale problems has been controversial and has yet to be fully developed to the level necessary for it to be definitive in nature. However, an independent verification of the appropriateness of the trace element ratio approach was performed, and it was indicated that this technique can be quite powerful (Keeler, 1987; Keeler and Samson, 1987).

7-2

Statistical methods have been developed that use information on the chemical composition of aerosols to study the contribution of sources or even source regions to the contamination at a given receptor. The APCA method, originally applied to total suspended particulate concentrations (particles measured in both the fine and coarse fractions), determines the composition of major source components, such as coal combustion, crustal, or sea-salt, which may have contributed to the measured concentrations at the receptors. Further improvement of this modeling method was realized when APCA was applied to aerosol elemental concentration measurements in separate particle size fractions (Li and Winchester, 1990). The results of this APCA application provided the basis for the interpretation of coupled chemical reactions and physical processes in remote locations. Also, information concerning atmospheric aging processes and, therefore, the history of the aerosols was obtained. For example, it was noticed that some crustal components were found in all particle size fractions. Carbonaceous fuel combustion pollutants were identified by the presence of S, Si and Cl and the absence of Al in all size fractions. This was the result of the release of volatile SiO from the reduction of silicon dioxide by carbon during the combustion of coal with high ash content. Since Al is non-volatile during coal combustion, its absence when Si and other metals were present indicates that the aerosol was generated from burning high-ashcontent coal.

Single or Individual Particle Analysis (IPA) has been applied in aerosol research to investigate the sources and morphology of the collected atmospheric particulate matter (Dzubay and Mamane, 1989; Mamane and Dzubay, 1987; Mamane, et al., 1986; Sheridan, 1989). Single Particle Analysis provides critical size distribution information that can be used directly to calculate the deposition of pollutants as a function of size. In a review by Sheridan (1989), it was observed that particles emitted by anthropogenic sources, such as carbon soot and coal combustion spheres, occurred simultaneously with the highest concentrations of H_2SO_4 droplets. Thus, IPA can be used to estimate the source apportionment, as well as physical and chemical processes occurring during long-range transport of air pollutants. One analytical method for IPA is the use of scanning electron microscopy (SEM). Mamane (1990) utilized this technique to estimate the contribution of refuse incinerators to the pollutant loadings of Philadelphia. SEM was also used in the analysis of atmospheric particles collected during the Green Bay Aerosol Study (Mamane et al., 1993). The particle size distributions and chemical compositions provided important information that was utilized in receptor modeling as well as deposition calculations.

The utility of back-trajectory analysis for identifying probable source regions contributing to elevated levels of atmospheric contaminants was illustrated over a decade ago (Samson, 1980). In that work, trajectories corresponding to high and low resultant sulfate concentrations measured at Allegheny Mountain were plotted separately to give a picture of the meteorological flow patterns associated with each of the two sulfate categories. Keeler (1987) also utilized this technique 6-years later to investigate the meteorological conditions associated with high and low sulfate concentrations measured at the same sites during the Allegheny-Laurel-Deep Creek Lake Experiment.

In order to assess atmospheric deposition to a receptor such as Lake Michigan, it is necessary to know the relative contribution of various sources to the total mass loading. Emissions to the atmosphere of the compounds discussed in this report are multitudinous. Most of the compound classes result from human activities, but in some cases, natural sources may make a contribution as well. For example, PAHs are released both by anthropogenic combustion and forest fires, while Hg is emitted during coal combustion and naturally from mines and soils. Techniques for deducing sources included in this section are trajectory and meteorological analyses, individual particle analysis, emissions inventories, multi-variate statistical methods, and chemical mass balance (CMB) models.

7.2 Meteorological and Trajectory Analysis

On-site meteorological parameters, such as wind speed and temperature (maximum and average over the 12-hour sampling period), were also used to investigate the simple chemical and elemental relationships in the measured data. The maximum 1-hour and the 12-hour average temperatures for each sampling period were calculated, and were found to be positively correlated at South Haven with the gas phase species ozone, HNO_3 (r > 0.75), SO_2 (r = 0.66), particulate SO_4^{2-} (r = 0.62), and aerosol acidity (r = 0.61). This is not surprising since the highest concentrations of these pollutants, mostly secondary in nature, were found when there was a strong flow from the southwest and higher temperatures. The average wind speed measured over the sampling period was also correlated with the pollutant measurements. Weaker correlations were observed for the same species (r=0.5), suggesting that wind speed was not as strong an influence on the observed concentrations during the study.

Attempts to understand the sources and transport of hazardous air pollutants are only fairly recent. To begin our analysis of the meteorological transport of the hazardous pollutants, it is instructive to investigate the meteorological conditions associated with both high and low levels of compounds or measurements for which we have some past understanding (i.e., PM10 or aerosol sulfate). Figures 7-1 through 7-3 show the mixed-layer trajectories associated with elevated PM10 concentrations (> 50 μ g/m³) measured at the three land-based measurement sites during the LMUATS.

Several interesting observations can be made from these figures. First, the highest concentrations of PM10 at each site are associated with transport from the southwest. Also, on all five days when PM10 > 50 μ g/m³ in South Haven, the PM10 at IIT and Kankakee also exceeded this amount.

In addition, both IIT and Kankakee recorded PM10 > 50 μ g/m³ on the same days except for one, 16 July. The fraction of the PM10 measured in the fine mode ($\leq 2.5 \mu$ m) decreased on the days when PM10 > 50 μ g/m³ at both Kankakee and IIT. This is due to the fact that the fine-fraction mass is comprised primarily of sulfate aerosol in various states of neutralization. On average, about 60% of the fine mass measured at all of the sites was sulfate, associated ions (e.g. NH₄⁺, H⁺) and water.

The trajectory analysis of the PM10 measurements at the 3 land-based sites forced a consideration of two large urban/industrial source regions that may actually contribute to substantial deposition of HAPs. The Chicago/Gary area was the initial focus of the study and is directly adjacent to Lake Michigan. The second important urban/industrial area is the East St. Louis-Granite City-St. Louis area which has similar insudtrial sources and magnitudes as the Chicago/Gary area. Both of these source regions contain a wide variety of industrial point sources including many known to emit HAPs. Emissions information for the important sources in the two regions was obtained to help us in interpreting the chemical data as well as for identifying source profiles for the subsequent CMB analysis.

The southeast Chicago source region is dominated by iron and steel and related industries (Table 7-1). These industries are concentrated along either side of the Calumet River. In addition to direct industrial point source emission, fugitive emissions from storage areas and stockpile operations have been determined to be of measurable significance (Figure 7-4). Large tracts of land are utilized for storage of coal, slag, scrap steel, limestone and other raw materials. Additional significant point sources include grain handling, landfills, chemical production and other miscellaneous manufacturing. The east St. Louis/Granite City source region is dominated by iron/steel related industries, metal smelting and organic chemical production (Table 7-2).

Figure 7-1. Mixed-layer Backward Trajectories Associated with PM10 Concentrations > 50µg/m³ in South Haven, MI.



Figure 7-2. Mixed-layer Backward Trajectories Associated with PM10 Concentrations > $50\mu g/m^3$ in Chicago, IL.



Figure 7-3. Mixed-layer Backward Trajectories Associated with PM10 Concentrations > 50µg/m³ in Kankakee, IL.



		1991
Source	Source Type	Particulate
		Emissions
Cargill, Inc.	Marketing Grain	54
Chicago Blast Furnace	Steel Manufacturing	324
Chicago Coke Plant	Steel Manufacturing	152
CID Landfill	Landfill Site	4
Cinders	Slag Processing	143
Con-Ed Peaking Units	Electric Utility	7
Continental-Elv B	Marketing Grain	121
Domtar Industries	Refining Sodium Chloride	13
Ford Motor Company	Auto Manufacturing	9
General Mills, Inc.	Milling Grain	154
Great Lakes Carbon	Petro & Coal Production	7
Heckett En. Harsco	Slag Processing	111
Heckett Eng.	Slag Processing	77
Heckett-Plant 27	Slag Processing	37
Inland Metals	Refining Nonferrous	1
Interlake-Riverdale	Steel Manufacturing	374
International Materials	Marine Cargo Handling	17
Jay's Foods	Food Preparation	12
LTV Steel	Steel Manufacturing	515
Marblehead Lime	Lime Manufacturing	130
Mississippi Line	Marine Cargo Handling	12
PVS Chemicals	Inorganic Chemicals	130
Rail-to-water	Marine Cargo Handling	12
Riverdale Plating	Plating	19
SCA Chemical	Refuse Disposal	16
Sherwin-Williams	Paint Manufacturing	2
Stauffer Chemical	Fertilizer Manufacturing	21
Stolt Terminals	Warehouse & Storage	7
U.S. Steel-Southworks	Steel Manufacturing	110

Table 7-1. Southeast Chicago Point Source Information.

Adapted From Sweet et al., 1990

Source Name	Source Type	1991 Particulate Emissions	
		Tons/Year	
Amax (Big River) Zinc	Zinc Smelter	120	
Archer Daniels Midland	Soybean Processing	107	
Bulk Service	Marine Cargo Handling	104	
Central Soya		45	
Cerro Copper Products	Secondary Copper Smelter	49	
Corn Sweeteners, Inc.	Grain Processing	2	
Ethyl Petroleum Products	Organic Chemicals	3	
Granite City Steel	Steel Manufacturer	2,282	
International Mill Service	Ground Minerals	49	
Jennison Wright Corporation	Wood Preserving	13	
Kerr-McGee	Wood Preserving	8	
Midwest Rubber Reclaiming	Reclaimed Rubber	376	
Monsanto	Organic Chemicals	168	
Nestle Company	Food Manufacturer	36	
Pfizer Pigments	Inorganic Pigments	157	
Phillips Pipeline Company	Petroleum Terminal	1	
Pillsbury	Grain Handling	132	
SCI	Secondary Aluminum Smelter	52	
St Louis Lead Recyclers	Lead Recycling	5	
St. Louis Slag Products	Slag Processing	242	
Tara Corporation	Secondary Lead Smelter	74	
Trade Waste Incinerator	Hazardous Waste Incineration	71	
U.S. Army	Construction	10	
Union Electric	Electric Utility	8	

 Table 7-2. East St. Louis and Granite City Point Source Information.

Adapted from Sweet et al., 1990



Figure 7-4. Selected Point Sources in Southeast Chicago.

(From Sweet et al., 1990)

As previously discussed herein, the highest measured pollutant concentrations at all of the land-based sites (Kankakee, IIT, and South Haven) were associated with air flow from the southwest. On 17 July 1991, air mass transport was from the southwest (Figure 7-1). The backward mixed-layer trajectories suggest that the regional air mass passed over both major source regions before passing over Lake Michigan. PM10 concentrations measured at the 3 land-based sites were above 60 μ g/m³ at both Kankakee and South Haven and above 80 μ g/m³ at IIT. Almost 50% of the PM10 on 17 July was particulate sulfate with 30 μ g/m³ measured at Kankakee.

Several Illinois State National Air Monitoring Stations (NAMS) are located between the East St. Louis and southeast Chicago source regions. On 17 July 1991, samples were taken at these non-continuous sites (a one-in-six day sampling day). PM10 and total suspended particulate results are shown for these sites in Figures 7-5a and 7-5b, respectively. The results indicate that total suspended particulate is predominantly influenced by strong local sources whereas PM10 and sulfate concentrations appear to be driven by the strong regional coal combustion sources. The spatial distribution of the coal-fired utilities is shown in Figure 7-6 and the point sources are listed in Section 404 of the 1990 CAAA. Five sites of importance to this analysis are listed in Table 7-3.

The Nilwood site, located in Macoupin County, has no local sources and is used as a background reference by the Illinois Environmental Protection Agency. The Peoria site in Peoria County and the Decatur site in Macon County have similar industrial point sources and correspondingly similar measured ambient concentrations. Oglesby, however; has two large cement manufacturing facilities that are major sources of particulate emissions. The total suspended particulate and PM10 concentrations observed at Oglesby were 328 μ g/m³ and 167 μ g/m³, respectively. The Joliet site in Will County had typical total suspended particulate values, but PM10 concentrations were elevated reaching 77 μ g/m³. This appears to be the result of transport from the Oglesby area.

Information from several Illinois State Special Purpose Monitoring Sites (SPMS) was examined to explain several observed concentration deviations. These SPMS are listed in Table 7-4. The Randolph County Sites are sited in a rural area to monitor a coal extraction and processing operation. The measured PM10 concentrations for these sites were 126 μ g/m³ and 91 μ g/m³ respectively. The remaining SPMS sites examined were the Chemetco sites in Madison County and the Chicago-Horsehead sites in Cook County. These sites appeared to contribute to the observed elevated Pb concentrations.



Figure 7-5a. PM10 Concentrations in the Study Region on 17 July 91.

Figure 7-5b. Total Particulate Concentrations in the Study Region on 17 July 91.



Monitoring Site	Source	Source Type	1991 Particulate Emissions* Tons/Year
Decatur	Archer Daniels Midland	Corn Milling	5,000
	Firestone	Tire Manufacturer	179
	A.E.Staleys Manufacturing	Corn Milling	6,800
	Wagner Casting	Iron Foundry	458
	Muller Company	Gray Iron Foundry	74
Joliet	Commonwealth Edison	Electric Utility	3,400
	Crosfield Chemicals, Inc.	Industrial Inorganic Chem.	12
	Desoto Inc.	Soap & Detergent	21
	Olin Corporation	Industrial Inorganic Chem.	1,220
Oglesby	Illinois Cement Company	Cement Manufacturer	42,621
	Lone Star Cement Co.	Cement Manufacturer	564
Peoria	Archer Daniels Midland	Corn Sweetener Plant	300
	Caterpillar	Assembly Plant	300
	Keystone Steel & Wire	Steel Wire & Related Prod.	200
Nilwood	None		

Table 7-3. Selected Illinois Air Monitoring Sites and Surrounding SourceInformation.

*Based on Illinois Environmental Protection Agency, Emissions Inventory

Monitoring Site	Source	Source Type	Particulate Emissions* Tons/Year	Lead Emissions* Tons/Year
Chemetco	Chemetco	Secondary Smelter	567	78
	Clark Oil & Refining	Oil Refinery	167	
	Shell Oil	Oil Refinery	16,174	
Chicago- Horsehead	Horsehead Resource Development Co.	Hazardous Waste Recycling	1,161	250
Randolph County	Illinois Power-Baldwin	Electric Utility	30,118	
	Peabody Coal Company	Open Pit Mine & Coal Prep. Plant	66,111	

Table 7-4. Selected Illinois Special Purpose Air Monitoring Sites andSurrounding Source Information.

*Based on 1992 & 1993 Illinois State Emission Inventory



Figure 7-6. Coal-Fired Power Utilities in the United States.

7.3. Scanning Electron Microscopy (SEM)

Six aerosol samples collected at the IIT site during the LMUATS were analyzed by Scanning Electron Microscopy and Energy-Dispersive X-ray spectroscopy (SEM/EDX). The objective of the SEM/EDX analyses was to characterize a representative number of individual aerosol particles for each sample in order to provide additional information about particulate sources impacting the IIT site. SEM/EDX analyses revealed significant differences in aerosol composition among the six samples which in turn reflected differing mixes of sources. The observed differences generally support results obtained by X-ray fluorescence (XRF) and by receptor modeling applied to the same sample set. The results are described in the following section.

7.3.1. SEM Results

Results of the SEM analyses for both coarse and fine particles are tabulated in the particle data tables in the Appendix. Examples of the tablulation are shown here for the sample collected on 21 July 1991 (Tables 7-5 and 7-6). Particles are sorted into three major classes: industrial, mineral, and organic with subclasses within each major class. These tables report the actual number of particles characterized for the given filter. The information provided in the header for each table includes the area of the filter scanned by SEM as well as the effective sample volume for the size fraction analyzed. Note however that the data have not been normalized to these parameters so that direct comparison of different samples on a number basis is not valid. It is however meaningful to compare the composition of different samples expressed as percentages.

Photomicrographs of selected industrial particles are shown in Figure 7-7(a-n). Fibrous strands in the background are Teflon filter material. The high der.sity of sulfate particles is clearly illustrated in Figure 7-7a which also includes an iron sphere of 1 μ m. Iron spheres, less than 0.5 μ m in diameter are evident in aggregated long chains in Figure 7-7b. Figures 7-7c, 7-7d, and 7-7e show an iron aggragate, an aluminum particle, and aluminum oxide. Mineral particles are shown in Figures 7-7f through 7-7j including ammonium sulfate, magnesium chloride, aluminosilicate flyash, silica spheres, and calcium aluminum oxide particles. Biological and other organic particles are shown in Figures 7-7k through 7-7n. These large particles include soot, spores and organic material. Aluminum oxide particles were found in abundance on the sample collected on 8 August 1991.

LAKE MICHIGAN URBAN AIR TOXICS STUDY								
SAMPLE ID: 1027 COARSE FRACTION SITE: IIT								
DATE OF SAMPLING: 7/21/91 VOLUME (m ³): 11.96 SEM AREA				A (μm ²):	19,200			
	PARTICLE SIZE (µm)							
MINERALS	1.5-2.1	<u><</u> 3.1	<5 1	<7.1	<u>≤1</u>	0 >10	Total	₱⁄₫
Silicate	19	12	7	3			41	31.8
Quartz	5	1					6	4.7
Ca-rich	4	4	3				11	8.5
Ca & S	13	2	5				20	15.5
Dolomite							0	0.0
Dol. Limestone	2	4					6	4.7
Other	2 ¹⁾		3 ²⁾				5	3.9
			M	INDRA	LS		89	69.1
ORGANICS								
Spores		1	2				3	2.3
Plant Debris							0	0.0
Soot		2	1				3	2.3
			0	RGANI	CS		6	4.6
INDUSTRIAL								
Fly Ash	3						3	2.3
Al-rich							0	0.0
Fe-rich	9 ³⁾						9	7.0
Zn-rich							0	0.0
S-rich	7						7	5.4
Other	8 ⁺⁾	7 ⁵⁾					15	11.6
INDUSTRIAL					34	26.3		
TOTALS	72	33	21	3	0	0	129	100 0
%	56	26	16	2	0	0	100	

Table 7-5. Tabulation of Coarse Fraction Particulate Matter Collected on 21 July 91Analyzed by SEM.

1) Includes (1) Si-S-Ca-Ti-Fe-K-Mg smooth particle surrounded by film.

2) (1) Iron-rich; (1) Ca-S-Cl-Mg-K; (1) Aluminum-rich.

3) Mostly spheres.

- 4) Mg-Cl-Fe-S-Mn; Fe & Zn; NaSO₄; S-P-K-Ca (possibly fertilizer); NaSO₄ & CaCO₃; Mn-Fe-Zn spheres (possibly smelter or blast furnace); possibly K phosphate
- 5) Mn & Fe; Zn-Cl-Fe-Ca-Si; Pb-Cl-K-Zn (incinerator); Al/Si-Mn-Cl-S-Ca-Ba-Fe-Zn-Pb; (NH₄)₂SO₄ & KSO₄; Na-Si-S-Ca-Ti-Fe-K-Mg.

LAKE MICHIGAN URBAN AIR TOXICS STUDY								
SAMPLE ID: 1027 FINE FRACTION SITE: IIT								
DATE OF SAMPLING: 7/21/91 VOLUME (m ³): 1.26 SEM AREA (μm ²): 12,000							2,000	
	PARTICLE SIZE (µm)							
MINERALS	<0.5	<0,7	<0.9	<1.1	<1.3	<1.5	Intal	9%
Silicate	1		1	4	1	4	11	12.9
Quartz		1		1	1		3	3.5
Ca-rich			1	1	2	2	6	7.1
Ca & S	3				1		4	4.7
Dolomite							0	0.0
Dol. Limestone							0	0.0
Other							0	0.0
					MIN	ERALS	24	28.2
ORGANICS								
Spores							0	0.0
Plant Debris							0	0.0
Soot			1	1		1	3	3.5
					ORG	ANICS	3	3.5
INDUSTRIALS								
Fly Ash							0	0.0
Al-rich							0	0.0
Fe-rich	171)	2	4	1	3 ²⁾	2	29	34.1
Zn-rich	6^{3}	1+)	13)			1	9	10.6
S-rich	$(6700)^{6}$	17)			 		1	1.2
Other	9 ⁸⁾	29)	1 ¹⁰⁾	$2^{(1)}$	$2^{(2)}$	3 ¹³⁾	19	22.4
INDUSTRIAL 58 68.3								
TOTALS	36	7	9	10	10	13	85	100.0
%	42	8	11	12	12	15	100	

Table 7-6. Tabulation of Fine Fraction Particulate Matter Collected on 21 July 1991 Analyzed by SEM.

1) Majority of Fe-rich particles are combustion spheres. 8) All contain Fe as well as Mn and/or Zn.

2) Fe & Mn; Fe & Cr (sphere); Fe-Ca-K-Ti-S.

- 3) Includes (4) Zn & S, (1) Zn & Pb, (1) Zn & Na.
- 4) Zn-Na-S-Cl.
- 5) Zn-S.
- 6) Avg. diameter ~ 0.3-0.4 μ m.
- 7) S & trace Zn.

- 9) Pb & trace of Fe and Zn; Fe-Zn.
- 10) K-S-Na.
- 11) Possible NH₄Cl sphere.
- 12) (1) Cl particle; (1) Na & C particle.
- 13) Pb-Zn-Cl; Si-Fe-S-Zn.

Table 7-7 below summarizes the results of the SEM analyses and highlights similarities or dissimilarities among the samples. Silicates and Ca-rich minerals (limestone, gypsum, dolomite) from soils, road dust, etc. dominate the coarse fraction of all samples except for the one collected on 8 August. Elements associated with these minerals include Mg, Al, Si, K, Ca, Ti, and Fe. The elements Cr, Mn, Cu, Zn, and Pb are associated almost exclusively with industrial-derived fine particles. Iron concentrations are generally split between silicate minerals and industrial sources - primarily mineral sources in the coarse fraction.

Samples collected on 21 July and 8 August were strongly impacted by industrial sources and have the least dolomite and dolomitic limestone content. The particulate sample from 2 August reflected the least impact from industrial sources as it was rich in guartz and Ca-containing minerals. Samples from 21 July, 6 August, and 8 August showed the greatest influence from industrial sources including many Fe combustion spheres, with the sample collected on 6 August particularly rich in Fe spheres. The relative concentration of these spheres changed dramatically over the 3-week sampling period revealing the changing impact of the iron and steel industry at the IIT site. In addition, samples collected on 21 July and 8 August were strongly impacted by a source or sources of Mn-Fe-Zn (apparently associated together, sometimes in combustion spheres). The sample from 21 July also had a number of Cl-rich and Pb-rich particles. The sample from 8 August, and to a lesser extent the sample from 19 July, reflected a combustion source of aluminum oxide particles which were observed only in the coarse fraction (Table 7-7). Aluminum silicate fly ash spheres from coal-fired power plants appeared much less frequently than Fe spheres, but were observed in the fine fraction of all samples. The sample collected on 19 July showed the highest concentration. Some Cu-rich particles were found in the fine fraction of samples collected on 6 August and 19 July. Samples collected on 6 and 8 August had relatively high concentrations of organic particles (soot, spores and pollens, and/or plant debris) in the coarse fraction. The sample collected on 6 August also had a relatively high percentage of fine fraction soot, possibly associated with diesel combustion sources. Samples collected on 21 July and 6 August showed a number of Na-rich particles of unknown origin in both size fractions. The sodium was observed to be sometimes associated with Zn, sometimes sometimes with S, and sometimes with no other metals (sodium carbonate or sodium hydroxide).

7.3.2. SEM Summary

SEM analyses of six air samples from the Lake Michigan Urban Air Toxics Study revealed significant differences between samples collected at the same site on different days. The observed differences reflect changes in the mixture of sources impacting the sampling site. Particles found in the samples could be associated with the following source categories: soil and/or road dust, coal-fired power plants, the iron and steel industry (combustion source), the alumina industry (combustion source), diesel combustion, and botanical (plant debris, spores, pollen). In addition, SEM provided evidence of an industrial source or sources of Mn-Fe-Zn that produced both combustion spheres and non-spherical particles. Other particles were identified that may represent an incineration source (particles rich in Zn, Cl, Zn-Cl) and a smelter (particles rich in Pb or Cu). The results obtained by SEM are generally consistent with the bulk XRF analyses. (SEM results on the 8 August sample did not however reflect the high Pb and Cl values measured by XRF in the fine fraction of this sample).

Some of the particulate samples chosen for SEM analysis were selected because of high particulate mercury concentrations seen during analysis by INAA. Among this subset, particulate mercury varied from 135 pg/m^3 to 290 pg/m^3 for samples collected on 18 and 19 July and 6 and 8 August. On 21 July, one of the highest particulate mercury concentrations measured at IIT, 720 pg/m^3 , occurred. Upon inspection by SEM, the particulate matter collected on 21 July contained a large percentage of Fe spheres, and other industrial/combustion source particulates in the coarse fraction (mainly in the 1.5-2.1 μ m size range) and predominantly industrial particles in the fine fraction (Table 7-7). SEM inspection of the sample collected on 8 August revealed many similarities in the coarse and fine fractions to the 21 July sample, with a couple of distinct differences: 1) The coarse fraction of the 8 August sample contained many Al_2O_3 spheres and 2) The size range of the fine fraction industrial components in the 8 August sample contained a significant fraction of particles in the 0.5 to 0.9 µm range compared to the predominance of industrial particles $< 0.5 \,\mu m$ in the 21 July sample. Absolute principal component scores for each of these days (detailed in Section 7.5.) indicate the iron and steel industry as a source for both 21 July and 9 August. However, individual particle examination revealed a large number of industrial particles in the 21 July sample, suggesting not only smelting and steel industry, but also incineration. The presence of significant numbers of Al₂SO₃ spheres in the 8 August sample also indicates that the alumina industry responsible for this emission may not be associated with high particulate mercury levels.

Figure 7-7. Industrial Particles.



a) Iron Sphere and Sulfate Particles



b) Aggregate of Iron Spheres


c) Iron Aggregate



d) Aluminum



Figure 7-7. Mineral Particles.

e) Magnesium Chloride



f) Aluminosilicate Flyash





g) Silica sphere



h) Calcium Aluminum Silicate Particles

1





i) Aluminum Sulfate



j) Aluminum Oxide



k) Soot



/) Spores

Figure 7-7. Organic Particles.



m) Organic Material



n) Spore

Sample Date	Coarse Fraction	Fine Fraction
18 July 91	 86% Mineral, 4% Industrial, 10% Organic (by number). Highest Organic content (many spores/pollens) and lowest Industrial content. No Fe spheres, 1 Fly ash sphere. Some large soot scattered over filter. 	 71% Mineral, 26% Industrial, 3% Organic, (excluding Sulfate). High % of Mineral particles. High Sulfate content. Some Al/Si Fly ash spheres, 1 Fe sphere, and several non-spherical Fe-rich particles. Several Zn & Cl particles.
19 July 91	 85% Mineral, 9% Industrial, 6% Organic (by number). Relatively high Quartz & Dolomitic Limestone content. Relatively high Soot component. Industrial particles include large Aluminum Oxide particles, some Al/Si Fly ash, some non-spherical Fe-rich particles. 	68% Mineral, 24% Industrial, 8% Organic, (excluding Sulfate). High % of Mineral particles. Relatively high Soot content and Sulfate content. Highest concentration of Fly ash spheres. Some Cu particles. Lowest Concentration of Zn-rich particles.
21 July 91	69% Mineral, 26% Industrial, 5% Organic (by number). Intermediate % (by number) as Minerals: High Gypsum & Calcite, but no Dolomite or Dolomitic Limestone. High number % of industrial particles including many Fe combustion spheres, some Al/Si Fly ash, and a large number of industrial "other" particles suggestive of smelting, steel industry, and/or incineration (Mn, Zn, Fe, Cl, Pb). <u>No Al₂O₃ particles. Similar coarse particle size distribution to 8 August sample.</u>	 28% Mineral, 68% Industrial, 4% Organic (excluding Sulfate). No Dolomite or Dolomitic Limestone. High % of Industrial particles (excluding S). Many Fe spheres, Zn-rich, and industrial "other" particles related to smelters, steel industry, and/or incineration. No Al/Si Fly ash however. Moderate concentration of Zn-rich particles. Some Pb & Cl particles.

Table 7-7.	Individual Particle Analysis Sum	mary.
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Sample	Coarse Fraction	Fine Fraction
2 August 91	 91% Mineral, 4% Industrial, 5% Organic (by number). Highest Mineral content, highest quartz. Sample has high Ca content in Calcite, Dolomite, and Dolomitic Limestone, but no Gypsum. Fair number of spores. Lowest % of Industrial particles: includes only 1 Al/Si Fly ash sphere, no Fe spheres, and some industrial Al₂O₃. Similar size distribution to coarse fraction of 18 July. 	 79% Mineral, 17% Industrial, 3% Organic, (excluding Sulfate). Highest % of Mineral particles. High Silicate content. Lowest % of Industrial particles. very few Fe spheres or Zn-rich particles. Some Aluminum Oxide particles and Al/Si Fly ash.
6 August 91	 62% Mineral, 23% Industrial, 15% Organic (by number). Intermediate % of Mineral particles. Highest % of Ca-rich class. High % of plant debris and spores/pollens. Moderately high % of Industrial particles. Highest concentration of Fe combustion spheres of all samples. <u>No</u> Al₂O₃ particles. 	 26% Mineral, 56% Industrial, 18% Organic (excluding Sulfate). Relatively high % of Soot. High concentration of Fe spheres but almost no Zn-rich particles. Some Cu particles. Several Na-rich particles. Sulfate particles are smaller than the typical sizes.
8 August 91	 37% Mineral, 40% Industrial, 23% Organic (by number). Lowest % of Mineral particles. Relatively little dolomite or Dolomitic Limestone. Relatively high % of spores, plant debris, and soot. Highest % of Industrial particles. Unusually high concentration of industrial Al₂O₃ particles. Many Fe combustion spheres. Some Fe-Zn particles. Most Coarse particles are in the smallest size bin (1.5-2.1µm) (similar to 21 July coarse fraction). 	 19% Mineral, 79% Industrial, 2% Organic (excluding Sulfate). Highest % of Industrial particles and lowest % of Mineral class. Relatively little Dolomite, Dolomite Limestone, Quartz; relatively high Ca & S. Industrial particles include some Al/Si Fly ash and the highest concentration of Fe spheres and Zn-rich particles. Only 1 Al₂O₃ particle. Many Fe-Mn-Zn particles.

Table 7-7. Individual Particle Analysis Summary (continued).

Note: The Fine fraction in all samples is dominated by number by Sulfate particles (typical diameter ~0.3 to 0.4 µm).

Since only about 100 particles could be examined in each size fraction per sample, one must be careful in assuming that the data are representative of the sample as a whole. In future studies, a larger number of particles should be quantified (at least 300 particles). This objective should be much more readily achieved with the use of a computer-controlled SEM/EDX (CCSEM) system in 1994 to replace the present manually-operated SEM.

The present study underscores the need for good source samples. Appropriate source signatures based on XRF or INAA are essential to chemical mass balance modeling. The same samples, if properly loaded, could also provide the microscopist with a particle library containing characteristic morphologies and compositions of source-specific particles. This would greatly enhance the source-apportionment capabilities of SEM/EDX.

7.4. Correlation Analysis of Observed HAPs

As a first approach for investigating potential relationships between the chemical compounds (both gaseous and particulate) and elements measured during the LMUATS, Pearson Correlation coefficients were calculated using the statistical software package, SAS (Cary, N.C.). Since the number of compounds measured during the study is quite large, the intra-site correlations within compound classes or analysis technique are shown first, followed by the correlations between classes (fine metals and rare earth elements $< 2.5 \mu m$ with PAHs, PCBs and pesticides). Correlations with p-values less than 0.05 were considered significant and are highlighted in Table 7-8, as well as in the tables in the Appendix. Only variables of importance to the present discussion will be presented.

7.4.1. Relationships at the Illinois Institute of Technology (IIT)

Three methods of analysis were used to determine the elemental composition of particulate matter in samples collected at IIT. XRF analysis was used to obtain data for fine mass, Al, Si, S, Cl, K, Ca, Ti, V, Mn, Fe, Ni, Cu, Zn, Se, Br, and Pb. INAA was used to obtain values for Na, Mg, Cr, As, Mo, Sb, La, and Sm while CVAFS was used to analyze particulate mercury. All elements used in these correlations are from fine-fraction concentrations, except for particulate Hg which is total particulate matter.

Correlations of fine-fraction elements at IIT utilized a total of 32 data points. The highest elemental correlation at IIT was between fine mass and sulfur (r=0.98). A subset

 Table 7-8. Pearson Correlations Among Fine Fraction Elements (and Total Particulate Mercury) Measured at IIT.

MASS	Al	Si	S	Cl	К	Ca	Ti	v	Mn	Fe	Ni	Cu	Zn	Se	Br	Pb	Na	Mg	Cr	As	Mo	Sb	La	Sm	HgV	
1.00	0.27	0.48	0.98	0.30	0.66	0.71	0.49	0.22	0.38	0.54	0.25	0.51	0.44	0.67	0.65	0.52	0.78	0.33	0.47	0.47	0.36	0.56	0.74	0.18	0.33	MASS
	1.00	0.54	0.18	0.01	0.36	0.46	0.54	0.30	0.03	0.24	0.31	0.02	0.06	0.10	0.36	0.20	0.23	0.06	-0.09	-0.02	-0.18	0.03	0.12	-0.05	0.14	Al
		1.00	0.39	-0.05	0.48	0.79	0.71	0.26	0.09	0.38	0.48	0.29	0.14	0.33	0.41	0.37	0.35	0.67	0.14	0.09	-0.05	0.15	0.29	0.33	0.07	Si
			1.00	0.24	0.58	0.65	0.39	0.17	0.29	0.44	0.17	0.46	0.36	0.61	0.60	0.43	0.76	0.26	0.43	0.42	0.33	0.57	0.75	0.19	0.26	S
				1.00	0.40	-0.03	0.02	0.12	0.87	0.63	0.22	0.18	0.76	0.58	0.47	0.55	0.14	0.20	0.66	0.80	0.72	0.24	0.30	0.01	0.76	Cl
					1.00	0.56	0.54	0.27	0.67	0.85	0.12	0.69	0. 72	0.81	0.70	0.85	0.64	0.25	0.52	0.60	0.46	0.45	0.56	0.01	0.61	K
						1.00	0.68	0.25	0.12	0.46	0.40	0.39	0.17	0.34	0.43	0.38	0.56	0.46	0.27	0.18	0.0 2	0.41	0.64	0.13	-0.05	Ca
							1.00	0.71	0.15	0.33	0.50	0.14	0.21	0.34	0.44	0.38	0.42	0.32	0.12	0.15	0.00	0.07	0.34	0.14	0.12	Ti
								1.00	0.12	0.12	0.47	-0.11	0.16	0.24	0.30	0.23	0.26	0.16	0.18	0.17	-0.01	0.05	0.18	0.21	0.14	V
									1.00	0.86	0.11	0.49	0.96	0.77	0.55	0.85	0.38	0.29	0.72	0.83	0.77	0.42	0.44	0.09	0.87	Mn
										1.00	0.11	0.69	0.83	0.81	0.64	0.90	0.50	0.35	0.63	0.77	0.64	0.61	0.52	0.01	0.68	Fe
											1.00	-0.09	0.07	0.10	0.16	0.10	0.13	0.43	0.28	0.16	0.00	0.06	0.22	0.24	-0.05	Ni
												1.00	0.54	0.68	0.50	0.67	0.59	0.31	0.35	0.41	0.38	0.50	0.40	0.06	0.39	Cu
													1.00	0.78	0.55	0.92	0.54	0.31	0.69	0.75	0.70	0.40	0.48	0.18	0.91	Zn
														1.00	0.71	0.82	0.64	0.40	0.61	0.74	0.69	0.53	0.45	0.20	0.70	Se
															1.00	0.60	0.61	0.26	0.34	0.53	0.42	0.45	0.41	0.00	0.53	Br
																1.00	0.65	0.43	0.65	0.71	0.59	0.53	0.54	0.22	0.78	Pb
																	1.00	0.36	0.40	0.32	0.29	0.51	0.61	0.22	0.42	Na
																		1.00	0.51	0.32	0.24	0.25	0.22	0.57	0.27	Mg
																			1.00	0.83	0.65	0.60	0.60	0.33	0.55	Cr
																				1.00	0.81	0.59	0.50	0.17	0.65	AS Ma
																					1.00	U.46	0.36	0.20	0.10	M0
		•																				1.00	U.00	0.18	0.19	30 Lo
		-																					1.00	1.00	0.27	1.4 Sm
																								1.00	1.00	SM M-V
																									1.00	ngv

of highly correlated fine elements at IIT included Fe, K, Mn, Zn, Se and Pb. These elements are good markers for iron-steel manufacturing and coal combustion. This group of elements also correlated with the sample-average temperature and with the sample-average ozone concentration. Ca showed the highest correlation with temperature and ozone at IIT with a correlation coefficient of 0.83 and 0.74, respectively. This is largely due to the coincident wind direction, southwest, that resulted in both elevated ozone and higher temperatures. Particulate Hg also showed a positive correlation with temperature, but the sample size was limited.

Since leaded gasoline is generally not used in motor vehicles, Pb is no longer a marker for emissions of that type. Other elements showing high correlations included Mn with Cl, and Hg with Mn, Zn, Cl, Fe, Se, and Pb. Elemental carbon may indicate a source from fuel combustion, including diesel truck emission and wood burning. Both elemental and organic carbon were significantly correlated with total fine mass, S, and Ca, supporting the suspected combustion source. Among the fine fraction elements analyzed by INAA, Na, Cr, As, Mo, Sb, and La were all correlated at least weakly, but in many cases with r>0.6, indicating mixed combustion sources. These potentially include incinerator emissions, steel industry, smelting as well as a regional background component. Each of these metals was also correlated with Ca, indicating a potential natural source. Both elemental carbon and organic carbon were significantly correlated with fine mass, S, and Ca at IIT.

Several PAHs were highly correlated (r>0.90, n=16). One group of PAHs with r=0.9or greater included chrysene, benz(a)anthracene, benzo(e)pyrene. benzofluoranthenes. indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene. and benzo(g,h,i)pervlene. These PAHs were also highly correlated with some PCBs and pesticides. A second highly correlated group of PAHs included fluoranthene, phenanthrene, and pyrene. Similar correlations were also found for this group with the PCBs and pesticides, but pyrene had lower correlation coefficients. The two compounds fluorene and acenaphthene were also highly correlated and had similar correlations with PCBs and pesticides. Acenaphthene, fluorene, phenanthrene, and fluorenone are all moderately to highly correlated with the maximum temperature and ozone at IIT. Acenaphthene showed the highest correlation with ozone with an r=0.86. Two PAHs, acenaphthylene and cyclopenta(c,d)pyrene were not significantly correlated with any other PAHs at IIT.

Ratios of selected PAHs with respect to benzo(e)pyrene were calculated in order to further characterize PAH sources. Benzo(e)pyrene, found in particulate form, generally is a more stable PAH. When compared to the other more volatile and reactive PAH species, ratios compared between sites indicate source composition. Compounds chosen for comparison to benzo(e)pyrene were pyrene, benz(a)anthracene, chrysene, cyclopenta(c,d)pyrene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and coronene. On days with similar prevailing wind directions, the ratio of these compounds to benzo(e)pyrene showed similar patterns.

PAH profiles for various source categories are not well characterized. In addition, PAH correlations and ratios are difficult to use for predicting sources because of differing emissions of PAHs from one source type and the reactivity of PAHs. Thus, the task of attributing specific sources based solely on PAH data is difficult. Another method of investigating sources of PAHs is to examine their relationship to specific tracer elements. Correlations between fine-fraction elements and PAHs at IIT revealed that PAHs which had very similar inter-correlation patterns also had similar correlations with fine-fraction elements. For example, chrysene, acenaphthene and fluoranthene were all correlated with Ca and Ni, while chrysene and fluoranthene were correlated with Al and Si as well. Three PAHs had highly significant correlations (r>0.80) with some metals. These include chrysene with Ca, acenaphthylene with Cl, Mn and Zn, and fluorenone with Ca. Chrysene also was significantly correlated with Al, Si, and Ni, while acenaphthylene was also correlated with Fe, Se, Pb, and Hg. These relationships may indicate coal combustion sources as well as smelting and the local iron and steel industry. Naphthalene and benzo(a)pyrene, which are indicative of some combustion types, did not show significant correlations with any of the elements at IIT.

Three subsets of PCB compounds were highly correlated (r>0.90) for the 16 samples analyzed. One group, consisting of total tri-, total tetra-, and total PCBs, had similar correlations with the PAHs and pesticides. The second group including total penta-, hexa-, hepta- and total PCBs, was also highly correlated with ozone. Total penta-PCBs were correlated with temperature (r=0.82) and ozone (r=0.85). The total hexa- and total hepta-PCBs also had similar correlations with the PAHs and pesticides. The third highly correlated group was the octa-PCBs which had similar correlations with the PAHs and pesticides and pesticides. All of these groups of PCBs were significantly correlated with each other as well (r>0.72).

Two PCB compounds had no correlations with other PCBs. These were the tri-PCB and the hexa-PCBs, both of which had concentrations within a very small range (0 - 0.74 pg/m^3 for the tri- and 0 - 1.11 pg/m^3 for the hexa-PCB). Other PCBs with a small range of values had only one or two significant correlations including the tetra-PCBs, the octa-PCBs, and the total nano- and deca-PCBs.

Analysis of PCB correlations with fine-fraction elements indicated no high correlations (r>0.9) between members of these two categories. The mono-PCBs were not significantly correlated with any of the elements, with the exception of a negative correlation with V (r=-0.63). The rest of the PCBs were significantly correlated with the same group of elements including fine mass, S, Si, and Ca. Two PCBs, total hepta- and total octa-PCBs, also had significant correlations with the INAA data for Na, Mg, Cr, Sb, La, and Sm.

Three pesticides, trans-Nonachlor, Dieldrin, and alpha-Chlordane, were highly correlated (r>0.80) for the 16 samples at IIT. Trans-Nonachlor and alpha-Chlordane had similar correlations with the PAHs and PCBs, but Dieldrin had different correlations. Three compounds were not correlated with other pesticides, HCB, Simazine, and p,p'-DDD. Of these, p,p'-DDD was also not significantly correlated with any PAHs or PCBs, and HCB was only significantly correlated with one PCB. Three other compounds, Atrazine, Alachlor and Metalachlor, had only one significantly correlated with any PAHs or PCBs.

Interesting groupings were seen when the pesticides measured at IIT were correlated with several different fine-fraction elements. However, these correlations were never greater than 0.80. The group of highly correlated pesticides mentioned above produced similar correlations with many elements, but each pesticide had additional elements with which it correlated significantly. Alpha and gamma-HCH did not correlate with any elements in common. Alpha HCH demonstrated only negative correlations with fine-fraction metals including Si, Ca, and Ni. Gamma-HCH was positively correlated with V. HCB demonstrated the only other significant negative correlation (-0.76, with V). Both DDT and Simazine were correlated with the same elements at IIT: Na, Mg, Cr. As, Mo, Sb, La, and Sm. Mirex, Dieldrin, Chlorpyrifos and p, p'-DDE were all correlated with Zn, Se and Pb among other elements. Three pesticides (p,p'-DDD, Alachlor and Metolachlor) had no significant correlations with any elements. Two pesticides had only negative correlations, alpha-HCH with Si, Ca, and Ni. and HCB with V.

7.4.2. Relationships at South Haven, MI

At South Haven, sulfate, nitrate, nitric acid, strong aerosol acidity (H^+), sulfur dioxide and ammonia were quantified in addition to fine-fraction elements. The strongest correlation was between fine mass and sulfur (r=0.98), which, as expected, was similar to the correlation between fine mass and sulfate. The dominant grouping of elements that correlated well at South Haven were S, Si, K, Ca, Mn, Fe, Zn, Se, Br, Pb, elemental carbon, organic carbon, SO_4^{-2} , NO_3^- , HNO₃, and SO_2 . A regional/transported combustion source is indicated by this combination of elements, as well as a natural component.

At South Haven, the majority of PAHs measured correlated with one another. Two slightly distinct groupings of highly correlated PAHs were: 1) fluoranthene, pyrene benz(a)anthracene, chrysene, cvclopenta(c,d)pyrene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and coronene; and 2) fluorene and phenanthrene were correlated with fluoranthene, benz(a)anthracene, chrysene, cyclopenta(c,d)pyrene, benzofluoranthenes. pyrene, benzo(e)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(a)pyrene, benzo(g,h,i)pervlene and coronene. This may represent an aged airmass that has undergone substantial reaction with other atmospheric components.

All PAHs except acenaphthylene and anthracene correlated ($r\geq0.5$) with fine mass, S, K, Ca (except for naphthalene), Mn, Fe, Zn (except for acenaphthene and retene), Se, Br (except for retene), Pb, SO₄⁻², HNO₃, and SO₂ (except for coronene), indicating a regional sulfate mixture and other potential combustion sources. In addition, H⁺ was correlated with acenaphthene, retene, fluoranthene and benz(a)anthracene.

Few PCBs at South Haven were correlated with one another. 2,2',3,4,5'-PCB was correlated with penta-PCBs, 2,2',3,4,5,6,6'-PCB, Hexa-PCBs, 2,2',3,4,5,6,6'-PCB, hepta-PCBs, 2,2',3,3',4,5,6-PCB, and octa-PCBs. Mono-PCBs had a weak negative correlation with di-PCBs, 2,2',3,4,5'-PCB, penta-PCBs, and hepta-PCBs. In general, the individual isomers quantified were correlated with the congener groups of which they are a member (for example, 2,2',4,6-PCB was correlated strongly, r=0.83, with tetra-PCBs). There was no surprise in that finding.

Several PCBs at South Haven were correlated with the same set of fine-fraction elements with which a large set of PAH compounds were correlated. Hexa-PCBs, hepta-

PCBs, octa-PCBs and penta-PCBs were correlated with fine mass, Si, S, K, Ca, Mn, Fe, Zn, Se, Br, Pb, SO_4^{-2} , HNO₃, and SO_2 . Several PCBs were also correlated with vapor phase mercury including nona-PCBs, di-PCBs, 2,2',3,4,5'-PCB, penta-PCBs, hexa-PCBs, octa-PCBs, and total PCBs.

Few pesticides at South Haven were correlated, and those compounds that did demonstrate a correlation, were generally weak ($r\sim0.5$). The few compounds that were highly correlated were trans-Nonachlor, alpha and gamma Chlordane and trans-Nonachlor with Dieldrin. The weaker correlations include hexachlorobenzene with alpha HCH, Alachlor with trans-Nonachlor, alpha and gamma Chlordane, DDT with DDE, and alpha and gamma Chlordane, and negative correlations between Aldrin and Dieldrin and DDT.

The same subset of fine-fraction metals that correlated with groupings of PAHs and PCBs measured at South Haven also correlated with a few of the pesticides. Alachlor, trans-Nonachlor and alpha and gamma-Chlordane were all correlated with fine mass, Si, S, K, Ca, Ti, Mn, Fe, Zn, Se, Br, Pb, strong acidity, SO_4^{-2} , HNO₃, and SO_2 . In addition, Dieldrin was correlated with all of these elements except for Ca, Zn, and Br. DDT was correlated with fine mass, Si, S, Ca, Ti, Fe, strong acidity, SO_4^{-2} , HNO₃, and SO₂. Simazine was correlated with a different set of elements, Al, Si, Ca, Ni, and Cu, while alpha HCH demonstrated a different correlation pattern as well with negative correlations with Si, Cl, K, Ni, and Cu.

Ozone correlated with many elements and compounds at South Haven. The highest correlation (r=0.91) was with HNO₃, followed by Cv or organic carbon (r=0.90), Ce or elemental carbon (r=0.89), and fine and coarse Fe (r=0.87 and 0.86, respectively). The relatively high correlation of ozone with coarse Fe is an interesting one. The correlation of coarse mass with the maximum hourly ozone measured during the sampling period (r=0.82) was slightly higher than the correlation observed with fine mas. (r=0.81). Coarse Ca was also correlated with the maximum hourly ozone (r=0.82). This interesting relationship between coarse particulate species and the maximum hourly ozone is largely due to the location of the iron and steel industry in the urban areas upwind of South Haven in the same direction. The correlation also reflects the temperature interdependence with mixed layer flow from the southwest to South Haven.

7.4.3. Relationships at Kankakee, IL

The correlations found between fine elements measured at Kankakee are generally weak, except for the correlation (r=0.96) between fine mass and S. Other correlations include S and Se, and moderate correlations between Al, Si, Cl, K, Ca, Ti, Fe, and Cu. This combination indicates a regional background with indication of an influence that may be attributed to combustion. In addition, Fe correlated with Al, Si, K, Ca, Ti, and Mn, while Cu correlated with fine mass, Al, Si, Cl, and slightly with S, K, Ca, and Ti.

Several PAHs quantified in samples collected at Kankakee were highly correlated. These include anthracene, fluoranthene, pyrene, benz(a)anthracene, chrysene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene and dibenzo(a,h)anthracene. Coronene was also significantly correlated with all of the same PAHs ($r\sim0.6$). In addition, acenaphthene, fluorene and phenanthrene were correlated with cyclopenta(c,d)pyrene, retene and fluorenone.

Very few PAHs quantified at Kankakee were correlated with fine-fraction elements measured at that site. This may be due to a lack of coincident sources or may indicate an aged airmass that has undergone extensive reaction and conversion resulting in relationships that cannot be attributed to specific source types. However, pyrene, benz(a)anthracene and benzofluoranthenes were correlated with S, phenanthrene was correlated with Cl, acenaphthene with K, acenaphthene and cyclopenta(c,d)pyrene with Mn, acenaphthene with Fe and acenaphthene, and fluorene and phenanthrene with Zn.

Several PCB isomers were highly correlated with quantified PCB congener groups. 2,2',3,4,5'-PCB and penta-PCBs were highly correlated with hexa-PCBs, hepta-PCBs, octa-PCBs and total PCB. 2,2',3,4,5,6,6'-PCB and 2,2',3,3',4,5,6-PCB were highly correlated with nona-PCBs and deca-PCBs, while nona-PCBs were highly correlated with deca-PCBs. Correlations between PCBs and fine-fraction elements were very sparse, as was the case for PAHs. Total mono-PCBs, total hexa-PCBs and total hepta-PCBs were correlated with fine mass, total hepta-PCBs were correlated with S, 2,2',4,6-PCB was highly correlated with Cl, total mono-PCB and 2,2',4,6-PCB were correlated with Cu, and negative correlations were observed for total mono-PCBs and 2,3-PCB with Ni, and tri-PCBs with Ti.

Pesticides measured in Kankakee samples revealed a correlation pattern in which Dieldrin, alpha and gamma Chlordane, DDE, DDD, gamma HCH, Alachlor and Mirex were all correlated. In addition, trans-Nonachlor was correlated with alpha and gamma Chlordane, Chlorpyrifos, Dieldrin, Alachlor and Mirex. Simazine was correlated with DDD, gamma HCH and Alachlor. DDT and Aldrin were only correlated with each other.

Correlations between fine-fraction elements and pesticides were stronger, in general, than those correlations at the other sites. Several pesticides were correlated with Mn, Zn, Se and Br (including Alachlor, Mirex, trans-Nonachlor, Dieldrin, gamma-Chlordane, alpha-Chlordane and DDE). In addition, certain pesticides such as Chlorpyrifos demonstrated a correlation pattern with a subset of fine-fraction elements, fine mass, Si, K, Ca, Ti, Fe and slightly with Al. Atrazine was correlated with Al, Si, K, Ca, Ti, Fe and slightly with Mn and Ni. DDD was correlated with Zn, Se, Br and Pb. DDT did not correlate positively with any of the fine-fraction metals. However, weak negative correlations were observed with fine mass, Al, Cl, K, Ca and Cu.

7.5. Principal Component Analysis

In order to investigate the sources and transport patterns for the hazardous air pollutants measured in the southern Lake Michigan Basin a receptor modeling technique, principal component analysis (PCA), was applied to selected measurements collected during LMUATS. Table 7-9 lists ten source categories and their known elemental 'fingerprint' or tracer species. The number of samples collected on the R/V *Laurentian* was too small to allow use of PCA. Consequently, this receptor model was used only to apportion sources in Kankakee. Chicago and in South Haven. Elements included in the statistical analysis were chosen on the basis of 1) quality of analytical data, and 2) use in apportioning sources (marker compound or element).

7.5.1. Absolute Principal Component Analysis Applied to Trace Elements

APCA was performed on the fine-fraction trace elemental and carbon data collected in Chicago (Table 7-10). The four factor model accounted for 91% of the variability in the data. A majority of the variance in the data was explained with model. Factor 1 explained the largest amount of variability in the data set (49%) and was dominated by elements generally associated with the iron and steel industry, and other metal production or manufacturing. Interestingly, when Hg vapor was included in the APCA, it was highly loaded on this factor as well, explaining 81% of the variability in the mercury concentrations measured. Factor 2 had moderate loadings of S, K, and elemental carbon, and high loadings for fine Si and Ca indicating a mixed component with soil

SOURCE	KEY ELEMENTS
Soil	Mg, Al, Si, K, Ca, Sc, Ti, Mn, Fe, Ga, Sr, La, Ce, Sm
Coal Combustion	Soil Elements & Fine B, Ge, As, Se, Sb, Ba, W, Hg, U
Oil Combustion	Fine Particle V, Ni, Mo
Petroleum Refinery	La, Ce, Nd
Motor Vehicles	Elemental Carbon
Smelters	Ni, Cu, As, Cd, In, Sn, Sb, Pb
Marine Aerosol	Na, Cl
Vegetative Burning	Organic and Elemental Carbon, Cl, K, Zn
Iron-Steel	Fine Particle Mg, Cr, Mn, Fe, Co, Ni
Incineration	Cl, Zn, Ag, In, Sb, Hg

Table 7-9. Atmospheric Tracer Elements and their Known Sources (Keeler, 1987).

	Factor 1	Factor 2	Factor 3	Factor 4
	Fe-Steel	Soil +	Metal Industry	Regional S
S	0.15	0.41	0.37	0.78
Si	0.14	0.95	-0.05	0.10
K	0.76	0.51	0.05	0.25
Ca	0.06	0.90	0.33	0.17
Mn	0.95	-0.03	0.20	0.01
Fe	0.8 7	0.34	0.28	-0.02
Zn	0.95	0.01	0.12	0.10
Se	0.81	0.15	0.15	0.48
Pb	0.91	0.27	0.16	0.08
EC	0.12	0.58	0.61	0.16
As	0.79	-0.05	0.46	0.15
Sb	0.32	0.17	0.83	0.15
Cr	0.66	0.01	0.61	0.16
Eigenvalue	5.84	2.73	2.1	1.2
% variance	49	23	18	10

 Table 7-10. Factor Loadings from Varimax-Rotated PCA of IIT Fine Fraction

 Elemental Data.

influence as well as a hint of cement industry. Factor 3 appears to represent a smelting or metals processing source with high factor loadings from Sb, Cr, and EC, and moderate loadings for As and S. Factor 4 appears to be the regional S component with high loadings of S and moderate loadings of Se and elemental carbon. S was found to be smeared onto all of the components at IIT.

The results of a three-factor model of the fine-fraction trace elemental and carbon data collected in Kankakee (Table 7-11) accounted for 86% of the variability in the data used in the analysis. Factor 1 explained the largest amount of variability in the data set (35%) and was highly loaded with elements generally of soil origin (Si, Ca, K, Fe). As discussed in Section 5 many of these elements were very enriched over their crustal abundance suggesting that iron-steel emissions may also be contributing to this factor.

Factor 2 appears to represent iron-steel emissions as well as Pb and Zn smelting or metal processing emissions with high factor loadings from Mn, Zn, and Pb. This factor is associated with northerly air mass transport from Chicago/Gary to Kankakee. Factor 3 represents the regional S component, which is dominated by coal combustion sources, with high loadings of S and Se. The mass contributions were calculated using APCA for Kankakee. The largest source of fine mass at this site was the regional S source, contributing on average, $14 \mu g/m^3$ of the 20 $\mu g/m^3$.

	Factor 1	Factor 2	Factor 3
S	0.11	-0.22	0.87
Si	0.91	-0.17	0.00
Ca	0.71	-0.17	0.02
K	0.8 7	0.39	0.12
Mn	0.44	0.74	-0.17
Fe	0.90	0.27	-0.15
Zn	-0.03	0.81	-0.07
Se	-0.11	0.21	0.85
Рb	-0.09	0.79	0.15
Eigenvalue	3.12	2.19	1.58
% variance	35	24	18

 Table 7-11. Factor Loadings from Varimax-Rotated PCA of Kankakee Fine

 Fraction Elemental Data.

In South Haven, the three-factor model for fine-fraction elements explained 93% of the variability in the data with 42% explained by the first factor (Table 7-12). This varimax-rotated model accounts for 92% of the variability in the fine mass as well. Factor 1 was found to have high loadings from several elements including Mn, Zn, Pb, elemental carbon. as well as moderate loadings for K, Fe, Ca, and Se. These elements represent emissions from the iron and steel industry and perhaps diesels. Factor 2 is highly loaded with fine Si and moderately loaded with K, Ca, Mn, Fe, and elemental carbon. This factor looks like a soil factor but the addition of elemental carbon suggests that soil is mixed with

other source influences. The highest mass contributions for this component were on 22 July and 2 August when air mass trajectories were from the southwest over the lake through Chicago and towards South Haven. Factor 3 indicates the regional S component with high loadings for S and Se, and moderate loadings for Pb, elemental carbon, Zn and K. Factor 3 was the dominant component during the pollution episode observed in South Haven and the other two sites from 16-22 July. This component was responsible for over half of the fine mass, on average, contributing 8.3 μ g/m³ out of 13.6 μ g/m³. The first and second factors contributed 2.7 and 3.4 μ g/m³ to the fine mass, respectively.

	Factor 1	Factor 2	Factor 3
-	Iron-Steel	Soil +	Regional S
S	0.39	0.25	0.85
Si	0.14	0.97	0.11
K	0.55	0.65	0.47
Ca	0.49	0.75	0.33
Mn	0.76	0.42	0.43
Fe	0.59	0.69	0.39
Zn	0.72	0.19	0.61
Se	0.44	0.22	0.83
Pb	0.76	0.32	0.52
EC	0.77	0.41	0.41
Eigenvalue	3,4	3.1	2.9
% variance	36	33	31

 Table 7-12. Factor Loadings from Varimax-Rotated PCA of South Haven Fine

 Fraction Elemental Data.

The blurring of several source types onto one component that is a large distance from the sources is not uncommon (Keeler *et al.*, 1991). As the distance from the source increases relative to the distance between sources, this blurring seems to increase. The second reason for several sources being loaded on the same factor has to do with the location of the sources and the magnitude of the source influence. The regional S component was the dominant fine mass contributor at all three land-based sites. This component represents coal combustion sources that are upwind of the Kankakee site and when transport connects the three sites, such as on 17-22 July, this regional S component dominates the source apportionment. Emissions are added to the regional plume as it is transported through the urban/industrial areas of Chicago/Gary and carried out over Lake Michigan. The combined emissions are then mixed and transported to South Haven together, building in a correlation due to wind direction. Since transport from the southwest also brings hot humid weather to the Lake Michigan Basin, elevated ozone and photochemical activity is observed during the same period.

7.5.2. Principal Component Analysis Applied to PCB Data

Principal component analysis was utilized to investigate the variability, potential source(s) and source impacts observed in the PCB congeners or homologue categories measured at the IIT site. The tri-, tetra-, penta-, hexa-, hepta- and octa-PCB homologues and Total PCBs are loaded on the same factor making source characterization difficult. The second factor is dominated by congener 50, total nona-PCBs and deca-PCBs, while the third factor is dominated by mono- and di-PCBs and congener 5. Only one PCB, congener 1, loaded strongly on factor 4, with a small contribution from total tetra-PCB. However, this may be an artifact of the data, since congener 1 was underestimated during sample collection due to its high volatility.

At the conclusion of their report on PCB congeners and potential source contributions, Manchester-Neevig and Andren (1989) stated that overall, the congener distributions were surprisingly similar between seasons despite different air trajectories. Consequently, source apportionment is a difficult task with these compounds.

7.5.3. Principal Component Analysis Applied to Pesticide Deca

In order to discern urban versus rural contributions to levels of pesticides measured over the lake or at any receptor site, chemical mass balance, pesticide isomeric ratio correlations (with tracer elements), and principal component analysis can be utilized. However, interpreting source signatures for pesticides measured in ambient samples is a difficult endeavor. Distinguishing revolatilization of previously applied or transported pesticides from recent applications or transport of recently applied pesticides poses a major challenge in attempting to discern sources. Use of APCA for pesticides measured at Kankakee did not prove fruitful since the four factor model used did not separate

contributions from several of the pesticides measured. Factor 1 was described by high loadings from γ -HCH, Alachlor, Mirex, Trans-Nonachlor, Dieldrin, α - and γ -Chlordane, DDE, and DDD.

At IIT, the four factor model separated sources for the α - and γ -HCH isomers. Factor 1 describes the majority of the variability in the data for γ -HCH, Mirex, Trans-Nonachlor, Dieldrin, Chlorpyrifos, α - and γ -Chlordane, and DDE. This separation of pesticide contributions is similar to the pattern observed at Kankakee. However, Factor 2 at IIT also has high loadings of α -Chlordane, DDT, Trans-Nonachlor, Aldrin, Atrazine and factor 2 is negatively correlated with α -HCH.

At South Haven, pesticides that loaded strongly on Factor 1 include Alachlor, Trans-Nonachlor, Dieldrin, α - and γ - Chlordane and, to a lesser degree, 4,4'-DDT. Factor 2 describes a common source for DDT and DDE as well as γ -HCH. Aldrin was negatively correlated with Factor 2 at South Haven. Factor 3 had large contributions from α -HCH, HCB, Aldrin and Factor 4 in the model is also described by high loading from HCB, but also with Metolachlor and a negative correlation with Simazine.

7.5.4. Principal Component Analysis Applied to PAH Data

Source apportionment of PAHs is plagued by some of the same attributes which make pesticides difficult to use as tracer species. Because of their reactivity and exchange between different phases in the atmosphere (gas-to-particle phase distribution), organic compounds behave less conservatively than elemental tracers. Thus, changes in the relative abundance of individual compounds occur in transit from source to receptor due to differential reactivity and rates of atmospheric deposition. The limitations imposed by alteration of profiles are not well understood (Keeler *et al.*, 1993). However, recent work has elucidated potential PAH tracer species.

In a recent paper by Li and Kamens (1993), ratios of specific tracer PAHs were calculated in order to determine source signatures for gasoline exhaust, diesel exhaust and wood combustion. Ratios of benzo(g,h,i)perylene/coronene, benzo(g,h,i)perylene/indeno(1,2,3-c,d)pyrene, benzofluoranthenes/indeno(1,2,3-c,d) pyrene. chrysene/benzo(e)pyrene, benz(a)anthracene/benzo(a)pyrene and benzofluoranthenes/coronene were calculated for the LMUATS and are shown in Table 7-13. The source contribution for the pattern observed by Li and Kamens and Tong and

Karasek (1984) attributed to diesel exhaust is also given with the LMUATS ratios. The ratios for gasoline exhaust were identified and are given in Table 7-14.

In order to further characterize PAH source signatures, ratios of selected PAHs were calculated with respect to benzo(e)pyrene (BeP). Benzo(e)pyrene, generally found in particulate form, is a more stable PAH. When contrasted with other more volatile and reactive PAH species, ratios to BeP compared between sites may indicate source composition and transport. Compounds chosen for comparison to BeP were pyrene, benz(a)anthracene, chrysene, cyclopenta(c,d)pyrene, benzofluoranthenes, benzo(e)pyrene, benzo(a)pyrene, indeno(1,2,3-c,d)pyrene, dibenzo(a,h)anthracene, benzo(g,h,i)perylene, and coronene. On days when there was similar prevailing wind direction, the ratio of these compounds to BeP showed similar patterns. For example, on 17 July 91 when the wind directly connected IIT and South Haven, the PAH ratio profiles are similar (Figure 7-8). However, the ratios for some PAHs at South Haven were higher than at IIT such as the ratios of retene and dibenzo(a,h) anthracene which might be due to the influence of local sources. The profiles on the R/V Laurentian were always very similar to the profiles at IIT, for example the profiles on 6 August 91 shown in Figure 7-9. This may be a result of the R/V Laurentian's position close to Chicago and to the influence of coke ovens southeast of the site in Chicago. Figure 7-10 reveals the striking similarities between the PAH ratios found in coke oven emissions reported by Daisey et al. (1986) compared to those measured on the Laurentian on the night of 6 August 1991. All of the ratios seen in Figure 7-10 are within a factor of two which is quite remarkable considering the potential modifications of the ratios caused by transformations en route to the sampling station. Only on 5 August 91 does the PAH profile on the Laurentian demonstrate substantial difference from the PAH profiles at IIT.

7.5.5. Source Attribution Using Combined Data Sets and Ratios

Elemental carbon is also a good indicator of diesel exhaust. Correlations were calculated between the PAH ratios above and elemental and organic carbon by site in order to determine the potential strength of these relationships as an additional indicator of source contribution. At Kankakee, significant correlations were observed for the benzo(g.h,i)perylene/coronene ratio with organic carbon, mass, Cu, ozone, and S. Benzo(g.h,i)perylene/indeno(1,2,3-c,d)pyrene was negatively correlated with Al, Ca, Cu, and mean-temperature. Benzofluoranthenes/indeno(1,2,3-c,d)pyrene was correlated only with organic carbon, ozone, and S. Chrysene/benzo(e)pyrene was correlated with Ni and

Zn. Benz(a)anthracene/benzo(a)pyrene was correlated with Ti, Mn, Fe, Se, K, and Ca, and benzofluoranthenes/coronene was correlated with organic carbon, mass, S, and ozone.

IIT. of the PAH ratios (chrysene/benzo(e)pyrene At two and benz(a)anthracene/benzo(a)pyrene) were not correlated significantly with any elements measured, and benzofluoranthenes/indeno(1,2,3-c,d)pyrene was correlated only with ozone. Benzo(g,h,i)pervlene/coronene was correlated with ozone, Ca, and negatively correlated with vapor phase mercury. Benzo(g,h,i) pervlene/indeno(1,2,3-c,d) pyrene was negatively correlated with ozone, Ca, and positively correlated with Cl, Mn, Zn, and vapor phase Hg. Benzofluoranthenes/coronene was correlated only with ozone and Ca. None of the PAH ratios at IIT were correlated with organic or elemental carbon.

On R/V the Laurentian. significant correlations with benzo(g,h,i)perylene/coronene were observed with K, Ca, Mn, Fe, Pb, and nitrate (similar for this The correlations observed at Kankakee ratio). to the benzo(g,h,i) pervlene/indeno(1,2,3-c,d) pyrene ratio was correlated only with V and Ni. Benzofluoranthenes/indeno(1,2,3-c,d)pyrene was correlated with S, K, Mn, Fe, Pb, and elemental carbon. Chrysene/benzo(e)pyrene was not correlated with any elements measured Benz(a)anthracene/benzo(a)pyrene on the Laurentian. and both correlated with K. Mn. and Fe. benzofluoranthenes/coronene were correlated with Benz(a)anthracene/benzo(a)pyrene was also nitrate. and benzofluoranthene/coronene was also correlated with Zn and Pb.

At South Haven, three of the PAH ratios were correlated with organic carbon (benzo(g,h,i)perylene/coronene. benzofluoranthenes/indeno(1,2,3-c,d)pyrene and benzofluoranthenes/coronene) and both benzo(g,h,i)pervlene/coronene and benzofluoranthenes/coronene were correlated with elemental carbon, mass. S, K, Ca, Mn, Fe. Se. Pb, H⁺, HNO_2 , SO_2 , ozone, and temperature. SO₄, Benzofluoranthenes/indeno(1,2,3-c,d)pyrene was also correlated with mass, S, Fe, H⁺, The three PAH HNO₃ ozone, and temperature. ratios SO₄ Benzo(g,h,i)perylene/Indeno(1,2,3-c,d)pyrene, Chrvsene/Benzo(e)pyrene and Benz(a)anthracene/benzo(a)pyrene were not correlated with any of the elements measured at South Haven.

PAH Ratios	Kankakee	IIT	R/V Laurentian	South Haven	Li and Kamens (1993)	Tong and Karasek (1984)
Benzo(g,h,i)perylene/ Coronene	1.7	2.4	1.6	2.1	2.5	1.9
Benzo(g,h,i)pereylene/ Indeno(1,2,3-c,d)pyrene	0.8	0.9	0.8	0.8	1.1	1.1
Benzofluoranthenes/ Indeno(1,2,3-c,d)pyrene	1.7	2.5	1.9	2.0	0.5	0.3
Chrysene/ Benzo(e)pyrene	1.8	2.1	2.0	1.9	1.6	1.6
Benz(a)anthracene/ Benzo(a)pyrene	0.9	1.6	0.8	1.1	1.0	1.7
Benzofluoranthenes/ Coronene	4.2	7.4	4.1	5.9	2.9	1.8

Table 7-13. Ratios of PAHs Observed at LMUATS Sites Compared to Other Sites.

Table 7-14. Reported Ratios of PAHs which Represent Gasoline Exhaust.

PAH Ratios	Li and Kamens (1993)	Grimmer (1977)
Benzo(g,h,i)perylene/ Coronene	1.5	1.2
Benzo(g,h,i)pereylene/ Indeno(1,2,3-c,d)pyrene	3.5	3.8
Benzofluoranthenes/ Indeno(1,2,3-c,d)pyrene	0.4	0.2
Chrysene/ Benzo(e)pyrene	2.5	2.2
Benz(a)anthracene/ Benzo(a)pyrene	0.5	0.7
Benzofluoranthenes/ Coronene	0.3	0.2



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Figure 7-9. Profiles of PAH Ratios with Benzo(e)pyrene on 6 August 1991.

7.6. Chemical Mass Balance Modeling

A subset of the samples collected at the IIT site were selected for a detailed source apportionment of both the fine and coarse fractions. Results of individual particle analyses by Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM/EDS) were used to supplement the CMB results. Particle morphology and elemental analysis has been shown to be useful in resolving source types which cannot be resolved by conventional means (Dzubay and Mamane, 1989).

The CMB model yields quantitative source contribution estimates for the major sources contributing to the mass for each sample. In practice, the model is limited by the availability and variability of the chemical composition of the potential sources. The source chemical compositions, i.e. source profiles, are used in the model in conjunction with ambient data and uncertainties in each to estimate the mass concentration, with uncertainties, contributed by each source at the sampling site during each sampling period. The uncertainties of profiles may not realistically represent the actual variability of the source categories they represent. This should be considered in the interpretation of the CMB results.

Fortunately, the PM-10 particulate pollutant source apportionment for Chicago is well characterized (Vermette *et al.*, 1991; Sweet *et al.*, 1993). Recently, Sweet et al. (1993) reported using locally obtained fugitive dust source profiles to supplement literature data to apportion the sources of particulate pollutants in southeast Chicago and East St. Louis. This work builds upon work reported previously by the same group (Vermette *et al.*, 1991). Among their most significant findings are that: 1) surface dust emissions are usually more important contributors to both fine- and coarse-particle mass than a. c stack emissions, and 2) some sources may contribute significantly to specific toxic metals without affecting overall PM-10 levels. The findings from these studies are based on samples collected near sources of many of the fugitive dusts sources. Stack emissions became important in the fine fraction only when winds were blowing directly from the stack. The IIT site is about 17 km NNW of the source profile collection sites. Nevertheless, these findings may still be applicable to the downtown Chicago samples being studied here and will be considered in this analysis.

Tables 7-15 and 7-16 list the samples selected for CMB and SEM/EDS analysis and the measured composition of their coarse and fine fractions, respectively. In the fine

fraction, some elemental concentrations were available from both XRF and INAA. INAA is clearly the better method for some elements, such as As. For other elements, the 2 methods are comparable. For CMB analysis, it is best to have source profiles and ambient data produced by the same analytical procedures. The researchers who produced the potentially important fugitive dust profiles (see discussion below) chose to report the INAA results for V, As, and La; therefore, the ambient data used in this CMB analysis will include the INAA results for those elements also.

Carbon data were available for the fine fraction only. While carbon may not be useful in the CMB model because of the lack of carbon data in many of the source profiles, it is important to include to illustrate the fraction of the mass accounted for by carbon. The fractions of elemental and organic carbon of the total fine mass are listed in Table 7-15. Organic carbon concentrations were multiplied by 1.4 to account for the hydrogen and oxygen which, together with carbon, comprise the average particulate organic compounds in the ambient air (Countess *et al.*, 1980). Organic and elemental carbon combined account for 36% to 58% of the fine mass. Since most of the source profiles available do not report carbon, the CMB analysis will not be able to yield quantitative estimates for all sources of carbon.

While carbon is certainly a substantial contributor to the fine mass, the largest constituent is sulfur in the form of sulfate, including sulfuric acid and ammonium sulfate (Dzubay *et al.*, 1982; Dzubay *et al.*, 1987; Stevens et al., 1980). In the absence of sulfur speciation for these samples, sulfur is represented by sulfuric acid in Table 7-15. This illustrates the minimum contribution of sulfur to fine mass, which ranges from 37% to 55%. Ammonium sulfate estimates would be about 25% higher than the sulfuric acid estimates. In addition, any sulfates present would have some amount of water associated with them which could substantially increase the mass. The amount of the increase depends on the form of the sulfate and the relative humidity history (Dzubay *et al.*, 1987; Vossler and Macias, 1986). Sulfate particles are the result of conversion of gaseous SO_2 emissions, largely from coal combustion, to the particulate sulfate and as such are regional and generally associated with long-range transport.

	18 July	19 July	20 July	21 July	2 August	6 August	8 August
MASS	36,748±1175	45,347±1354	30,291±1118	36,261±1191	30,616±1024	15.327±1008	29,620±1122
Na	97 ± 6	€0 ± 4	36 ± 2	120 ± 8	54 ± 4	41 ± 3	50 ± 4
Mg	320 ± 70	100 ± 20	39 ± 17	65 ± 40	82 ± 20	47 ± 25	190 ± 10
Al	69 ± 44	156 ± 54	94 ± 43	182 ± 51	173 ± 47	87 ± 41	27 ± 40
Si	387 ± 57	434 ± 64	233 ± 37	259 ± 41	293 ± 44	85 ± 19	131 ± 25
Р	10 ± 17	36 ± 20	18 ± 17	-13 ± 16	48 ± 16	19 ± 12	2 ± 15
S	5820 ± 396	7526 ± 512	5402 ± 367	5411 ± 369	4812 ± 326	1854 ± 127	3794 ± 259
Cl	5 ± 4	16 ± 5	9 ± 4	10 ± 4	12 ± 4	7 ± 4	74 ± 7
K	77 ± 6	79 ± 6	56 ± 5	175 ± 12	80 ± 6	9 8 ± 7	146 ± 10
Ca	177 ± 12	171 ± 12	83 ± 6	95 ± 7	198 ± 14	89 ± 7	63 ± 5
Ti	13 ± 5	2 ± 5	7 ± 4	11 ± 4	10 ± 4	-8 ± 5	6 ± 4
V	0.98 ± 0.18	1.30 ± 0.3	$1.30 \pm .80$	1.20 ± 0.20	$0.75 \pm .07$	$0.70 \pm .06$	0. 94 ± .11
Cr	1.6 ± 0.7	1.4 ± 0.7	-0.6 ± 0.6	0. 9 ± 0.6	0.4 ± 0.6	0.9 ± 0.6	2 .6 ± .7
Mn	5.1 ± 0.8	5.4 ± 0.8	1.6 ± 0.7	23.9 ± 1.9	4.6 ± 0.7	13.0 ± 1.2	59.3 ± 4.1
Fe	158 ± 14	154 ± 14	88 ± 8	336 ± 30	170 ± 15	393 ± 35	558 ± 50
Ni	0.6 ± 0.7	0.7 ± 0.7	0.0 ± 0.6	-0.6 ± 0.6	0.4 ± 0.6	-0.8 ± 0.6	0.7 ± 0.7
Cu	14.6 ± 1.6	14.3 ± 1.6	6.4 ± 1.0	22.3 ± 2.3	7.9 ± 1.0	21.0 ± 2.1	15.6 ± 1.7
Zn	40 ± 4	27 ± 3	16 ± 2	212 ± 19	42 ± 4	51 ± 5	294 ± 26
As	0.52 ± 0.05	0.46 ± 0.06	0.46 ± 0.05	0.66 ± 0.07	0.67 ± 0.07	0.93 ± 0.10	2.30 ± 0.20
Se	2.1 ± 0.5	1.4 ± 0.4	1.6 ± 0.4	3.2 ± 0.5	0.3 ± 0.3	1.7 ± 0.4	4.1 ± 0.6
Br	4.0 ± 0.6	4.0 ± 0.7	2.7 ± 0.6	4.4 ± 0.7	3.4 ± 0.6	3.1 ± 0.6	4.9 ± 0.7
Sr	0.8 ± 0.6	1. 2 ± 0.6	0.4 ± 0.5	0.4 ± 0.5	-0.4 ± 0.5	-0.4 ± 0.5	0.0 ± 0.6
Zr	-0.7 ± 3.0	2.1 ± 3.3	-8.1 ± 2.7	3.6 ± 3.1	-3.6 ± 2.6	-0.6 ± 3.0	3.6 ± 3.1
Мо	1.8 ± 3.0	5.9 ± 3.3	7.9 ± 3.1	-3.1 ± 2.8	-1.6 ± 2.6	4.4 ± 3.1	1.9 ± 3.0
Pd	-3.5 ± 2.1	-1.1 ± 2.3	-1.5 ± 2.1	2.6 ± 2.2	2.5 ± 2.0	1.6 ± 2.3	-2.0 ± 2.1
Cd	2.1 ± 2.8	0.2 ± 2.9	5.0 ± 2.9	2.2 ± 2.8	1.2 ± 2.5	-2.0 ± 2.8	-1.6 ± 2.8
Sn	20.1 ± 5.4	2.2 ± 5.1	3.0 ± 4.8	7.0 ± 4.8	-6.1 ± 4.3	6.6 ± 5.0	11. 7 ± 5.1
Sb	1.60 ± 0.10	1.40 ± 0.10	0.72 ± 0.06	1.10 ± 0.10	0.98 ± 0.07	3.00 ± 0.20	1.90 ± 0.10
Ba	21 ± 10	39 ± 11	11 ± 9	9 ± 9	9 ± 8	33 ± 10	18 ± 10
La	$0.140 \pm .01$	0.240 ± 0.020	0.098±.008	0.170 ± 0.01	0.240±0.02	0.093±.007	0.230±.020
Pb	23.3 ± 2.6	10.3 ± 1.7	8.7 ± 1.5	61.7 ± 5.8	11.9 ± 1.6	29.9 ± 3.1	62.1 ± 5.8
S as	17,823	23,049	16,543	16,570	14.736	5651	11,620
H_2SO_4							
$H_2SO_4/$	0.49	0.51	0.55	0.46	0.48	0.37	0.39
MASS							
EC	2420 ± 242	2210 ± 221	1010 ± 101	1270 ± 127	2050 ± 205	1170 ± 117	1870 ± 187
OC	$10,700 \pm 1070$	16,200±1620	6 87 0 ± 6 87	$10,020 \pm 100$	819 0 ± 81 9	5550 ± 555	6230 ± 623
EC/	0.07	0.05	0.03	0.04	0.07	0.08	0.06
MASS							
OC*1.4	0.40	0.50	0.32	0.38	0.37	0.50	0.30
MASS							

Table 7-15. Average Fine-Particle Concentrations (ng/m³) and Uncertainties ofElements Used in CMB Source Apportionment.

	18 July	19 July	20 July	21 July	2 August	6 August	8 August
MASS	31,785±1095	37,753±1248	22,845±995	10,997±898	48,282±1270	19,567±966	10,017±900
Na	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Mg	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Al	1097 ± 328	1865 ± 546	1330 ± 392	250 ± 109	2493 ± 716	413 ± 148	734 ± 223
Si	3971 ± 991	5552 ± 1380	4786± 1183	1182 ± 303	8368±2062	1556 ± 387	430 ± 115
Р	53 ± 27	34 ± 25	25 ± 20	0.7± 15.6	72 ± 34	5.8 ± 18	15 ± 16
S	259 ± 176	270 ± 222	208 ± 162	251± 165	304 ± 154	510 ± 98	290 ± 126
Cl	67 ± 9	42 ± 8	33 ± 6	126 ± 15	68 ± 10	175 ± 19	130 ± 16
Κ	396 ± 40	479 ± 48	409 ± 41	109 ± 14	777 ± 77	154 ± 17	55 ± 8
Ca	2888 ± 217	2458 ± 185	1514 ± 114	815 ± 62	4083 ± 306	1980 ± 149	537 ± 41
Ti	84 ± 14	123 ± 17	100 ± 14	32 ± 6	167 ± 25	47 ± 7	19 ± 5
V	2.6 ± 1.9	7.7 ± 2.1	2.0 ± 1.7	1.0 ± 1.5	3.2 ± 2.1	4.4 ± 1.7	3.1 ± 1.6
Cr	3.8 ± 1.0	7.9 ± 1.4	3.2 ± 0.9	0.5 ± 0.7	5.8 ± 1.1	4.6 ± 1.0	3.7 ± 0.9
Mn	24.8 ± 2.4	25.5 ± 2.6	23.7 ± 2.3	17.0 ± 2.0	49.3 ± 4.3	64.2 ± 5.6	23.2 ± 2.9
Fe	954 ± 96	1133 ± 113	854 ± 85	905 ± 93	1894 ± 188	1518 ± 153	884 ± 93
Ni	1.2 ± 0.7	5.4 ± 1.1	-0.6 ± 0.7	0.5 ± 0.7	0.7 ± 0.7	0.5 ± 0.7	1.1 ± 0.7
Cu	13.1 ± 1.8	93 ± 10	7.9 ± 1.2	9.6 ± 1.6	18.7 ± 2.3	8.5 ± 1.5	9.2 ± 1.5
Zn	29.5 ± 3.7	49.8 ± 5.7	21.2 ± 2.6	44.4 ± 7.6	55.1 ± 6.4	31.8 ± 4.1	67 ± 11
As	1.5 ± 0.9	0.0 ± 0.9	0.7 ± 0.8	-1.1 ± 0.8	2.0 ± 1.0	0.8 ± 0.8	0.0 ± 0.8
Se	-0.3 ± 0.4	-0.9 ± 0.4	0.0 ± 0.4	0.8 ± 0.4	0.0 ± 0.3	0.3 ± 0.4	-0.5 ± 0.3
Br	1.1 ± 0.5	0.4 ± 0.5	0.6 ± 0.5	1.1 ± 0.4	0.8 ± 0.5	0.6 ± 0.5	0.8 ± 0.5
Sr	5.1 ± 0.7	5.1 ± 0.8	3.1 ± 0.6	1.5 ± 0.5	6.5 ± 0.8	2.7 ± 0.6	1.3 ± 0.5
Zr	0.2 ± 2.8	9.4 ± 3.5	3.9 ± 3.0	-3.9 ± 2.6	1.5 ± 2.5	-0.9 ± 2.7	2.9 ± 3.1
Мо	-2.6 ± 2.6	8.3 ± 3.3	0.9 ± 2.8	0.8 ± 2.6	-0.8 ± 2.4	1.4 ± 2.8	0.8 ± 2.8
Pd	1.3 ± 2.0	-1.3 ± 2.1	-0.7 ± 2.0	0.0 ± 2.0	0.7 ± 1.8	0.3 ± 2.1	-1.9 ± 2.0
Cd	2.8 ± 2.7	0.9 ± 2.7	-0.5 ± 2.6	3.5 ± 2.6	1.1 ± 2.3	-0.5 ± 2.6	0.2 ± 2.6
Sn	5.2 ± 4.6	-4.1 ± 4.8	-4.6 ± 4.5	0.5 ± 4.3	6.1 ± 4.1	8.4 ± 4.7	1.9 ± 4.6
Sb	2.5 ± 3.9	-7.2 ± 4.1	0.0 ± 3.9	4.6 ± 3.8	-0.4 ± 3.4	11.3 ± 4.3	2.1 ± 4.0
Ba	31.3 ± 9.2	24.8 ± 9.7	20.9 ± 9.0	14.6 ± 8.4	41.7 ± 8.9	9.7 ± 8.8	16.3 ± 9.1
La	28 ± 21	6 ± 22	54 ± 22	0.7 ± 21.1	17 ± 19	33 ± 22	-5 ± 22
<u>Pb</u>	17.4 ± 2.2	21.7 ± 2.5	12.8 ± 1.8	11.4 ± 2.1	32.0 ± 3.3	9.0 ± 1.7	8.8 ± 2.0

Table 7-16. Average Coarse-Particle Concentrations (ng/m³) and Uncertainties ofElements used in CMB Source Apportionment.

A relationship can be observed between the meteorology described for these samples in Chapter 6 and the fraction of fine mass consisting of sulfates. Recall that in Chapter 6, the meteorology during the second week of the study (July 14 - 20) was described by regional flow from the S-SW. This likely explains the higher fraction of sulfate in the samples collected on 18-20 July 91 listed in Table 7-15. The sulfate fraction drops to below 40% for samples collected on 6 and 8 August 91 which were associated with local transport from the S.E. Chicago area. These samples plus the sample collected

on 21 July 91 had the largest fine-particle concentrations of K, Mn, Cr, Zn, Se and Pb. In the coarse fraction, these samples had the largest Cl concentration and the smallest soil-related element concentrations.

Comparison of ratios of soil-related elements (Al, K, Ca, Fe) as measured in the ambient air with ratios representative of crustal material can reveal whether these elements have non-crustal sources. It was assumed that Si in both the fine- and coarse-particle fraction is dominated by crustal sources. In Table 7-17, these ratios are compared with crustal ratios based on crustal shale and crustal limestone profiles obtained from U.S. EPA's Volatile Organic Compound (VOC)/Particulate Matter (PM) Speciation Data System (U.S. EPA, 1991) (henceforth referred to as SPECIATE). Again, the influence of local transport of pollutants is evident for samples 6 and 8 August 91 from the ratios of fine fraction Fe to Si which are much greater than crustal values.

Sample Date	Size Fraction	Al/Si	K/Si	Ca/Si	Fe/Si
18 July 91	Coarse	0.27 ± 0.11	0.100 ± 0.027	0.73 ± 0.19	0.24 ± 0.06
19 July 91	Coarse	0.36 ± 0.13	0.086 ± 0.023	0.44 ± 0.12	0.20 ± 0.05
20 July 91	Coarse	0.28 ± 0.11	0.085 ± 0.023	0.32 ± 0.08	0.18 ± 0.05
21 July 91	Coarse	0.21 ± 0.11	0.092 ± 0.026	0.69 ± 0.18	0.76 ± 0.21
2 August 91	Coarse	0.30 ± 0.11	0.093 ± 0.025	0.49 ± 0.12	0.23 ± 0.06
6 August 91	Coarse	0.27 ± 0.12	0.099 ± 0.027	1.27 ± 0.33	0.98 ± 0.26
8 August 91	Coarse	1.71 ± 0.69	0.127 ± 0.039	1.25 ± 0.35	2.06 ± 0.59
18 July 91	Fine	0.18 ± 0.12	0.20 ± 0.03	0.46 ± 0.07	0.41 ± 0.07
19 July 91	Fine	0.36 ± 0.13	0.18 ± 0.03	0.39 ± 0.06	0.36 ± 0.06
20 July 91	Fine	0.40 ± 0.20	0.24 ± 0.04	0.36 ± 0.06	0.38 ± 0.07
21 July 91	Fine	0.70 ± 0.23	0.68 ± 0.12	0.36 ± 0.06	1.30 ± 0.24
2 August 91	Fine	0.59 ± 0.18	0.27 ± 0.05	0.68 ± 0.11	0.58 ± 0.10
6 August 91	Fine	1.02 ± 0.54	1.16 ± 0.28	1.05 ± 0.25	4.64 ± 1.13
8 August 91	Fine	0.21 ± 0.31	1.12 ± 0.23	0.48 ± 0.10	4.26 ± 0.91
Crustal Shale	-	0.293	0.097	0.081	0.173
Crustal Limestone	_	0.175	0.112	12.58	0.158

Table 7-17. Ratios (± analytical uncertainty) of Soil-Related Elements to Si.

In general, all of the crustal elements in the fine fraction have some non-crustal component and, as stated above, this component appears to be quite substantial for some elements and samples. In the coarse fraction, K/Si is consistent with crustal estimates for every sample. Coarse fraction Al/Si is similar to crustal values with the exception of the sample collected on 8 August 91 which deviates substantially from the crustal value. The coarse Ca/Si is consistently higher than crustal shale values, indicating influence of some Ca-rich source, most likely limestone which is used in the steel-making process or in making cement and is abundantly present in exposed piles of raw materials. The influence of this Ca-rich source is especially evident for samples collected on 6 August 91 and 8 August 91. Coarse Fe/Si likewise indicates the influence of some non-crustal Fe source, especially for samples collected on 6 and 8 August 91. These observations shall be considered in the CMB analysis and interpretation.

7.6.1. The Chemical Mass Balance Model

The U.S. EPA/DRI Chemical Mass Balance Model, version 7 (Watson et al., 1990) was used to quantitatively apportion the major sources of fine and coarse-particle chemical species measured on the selected sampling days at IIT to their major sources. The CMB model consists of an effective variance least squares solution to a set of linear equations which expresses each measured chemical species concentrations as a linear sum of the contributions of each source to the chemical species. The effective variance solution gives the most weight to the source or ambient measurements with the lowest uncertainty estimates. Source contributions are expressed as the product of the abundance of the species as emitted by the source and the total mass concentration contributed by the source. The set of abundances of all species as emitted by a particular source represents the "source profile". In practice, it is not possible to apportion the total mass to every individual contributing source in an airshed. Individual sources may be too similar to one another, too numerous, or may not contribute significantly to the total mass loading or to individual species. Similar sources are generally considered as a single "source category" or "source type". Because there are many incinerators in the Chicago airshed, they were considered as one incineration source type and represented by a single profile.

In performing chemical mass balance calculation, it is assumed that: 1) the abundance of each species used in the fitting procedure is known for each source type, and 2) all major sources of each species used in the fitting procedure must be included in the CMB. Other assumptions made for the CMB model are listed in Watson *et al.*, (1990).

One of the performance goals of the CMB model was to account for the total mass of each element, within the uncertainties of the measurements involved. A complete apportionment of the PM10 mass measured in this study was made more difficult because few source profiles included carbon abundances, and total carbon concentrations were not determined for the coarse fraction ambient data. It should be noted that biological material (pollens, spores, plant debris) may comprise a significant portion of the coarseparticle mass. Also, organic and elemental carbon are important components of motor vehicle particulate emissions, especially for diesel vehicles. Apportionment of vehicle particulate emissions is more difficult since tetraethyl lead has been removed from the fuel supply. Historically, Pb has been used as a tracer for motor vehicle particulate emissions. It was postulated that volatile organic species measured during the LMUATS could be used as tracers for the motor vehicle particulate emissions (Zweidinger *et al.*, 1990). However, the VOC data collected has limited applicability to CMB modeling because it was found to be unreliable.

7.6.2. Source Profiles

A combination of profiles available in the literature and in the U.S. EPA Speciation Data System or "SPECIATE" (U.S. EPA, 1991) were used to predict ambient species concentrations. Sources considered in the CMB analysis were chosen based on the results of previous work and knowledge of emissions in the Chicago area, as well as on the examination of crustal element ratios and meteorological conditions. Much of the fine fraction was assumed to originate from regional sources and consist primarily of sulfate. A single constituent source profile for sulfur represented by sulfuric acid was included to account for the minimum contribution of sulfate to the fine-particle mass. A profile represented sulfur as ammonium sulfate would yield an estimate about 25% higher than the sulfuric acid estimates. While this assumption, accounts for the secondary sulfate, and thus a large portion of the fine mass, it does not yield any information on the specific source types that contributed to the secondary sulfate.

Sweet *et al.* (1993) reported that steel-mill stack emissions are large contributors to the ambient loadings of certain toxic elements. Furthermore, the PCA and SEM analysis, discussed earlier in this chapter, confirmed that iron-steel emissions are important sources in the southern Lake Michigan Basin. Unfortunately, the profiles available which represent steel-related stack emissions are poor quality. However, surface dust profiles associated with steel making (Vermette *et al.*, 1990) were be the only steel-related profiles

included in this analysis. A locally obtained lime dust profile (Vermette *et al.*, 1990) is included to account for the excess crustal calcium values. An urban road dust profile developed from S.E. Chicago samples (Vermette *et al.*, 1988) was also considered.

Incinerator emissions in urban areas can account for most of the Zn and Pb concentrations, although they do not contribute substantially to the overall particulate concentration (Sweet et al., 1993; Vermette et al., 1991; Conner et al., 1993). The best available incineration profile in terms of quality of sample collection and analysis is profile #17105 found in the U.S. EPA's SPECIATE data system. This profile was determined from samples collected at a municipal incinerator in Philadelphia (Olmez et al., 1988). A profile developed from samples collected in E. Chicago, IN was available (#17107), but the methods of collection and analysis were not consistent with the procedures employed during LMUATS (i.e. XRF analysis was not performed). In addition, fine and coarse fraction particle samples were not collected as they were for the Philadelphia incinerator. The Philadelphia incinerator profile demonstrates that the fine and coarse fractions differ substantially in their elemental composition. Despite the differences in the two incinerator profiles, the Philadelphia incinerator profile is similar to the E. Chicago incinerator profile for some important elements: 11.5% versus 11.4% for Zn, 8.1% versus 6.9% for Pb. From these results it was determined that the Philadelphia incinerator source profile would be used for the current application.

The SPECIATE profile for crustal shale (#43305) was used to account for crustal element sources. Some local industries burn oil to produce power and refineries burn residual oil. Both an oil power plant (#11501) and a residual oil profile (#13501) from SPECIATE are considered in the analysis to account for some of the Ni and V. The same sources were considered for the coarse fraction as for the fine fraction, with the exception of the single-constituent sulfate profile. Source profiles are listed in Table 7-18 along with literature references and abbreviations used in this analysis.
Profile ID	Profile Description	Abbreviation	Reference
N/A	Sulfuric acid	H ₂ SO ₄	N/A
05P014	Steel yard road dust	STLYARD	Vermette et al., 1990
06P001	Coke yard road dust	COKEYARD	Vermette et al., 1990
06U004	Coal yard road dust	COALYARD	Vermette et al., 1990
07 S 301	Limestone dust	LIMEDUST	Vermette et al., 1990
N/A	Urban Road Dust	URBDUST	Vermette et al., 1988
43305	Crustal shale	SHALE	SPECIATE (U.S. EPA, 1991)
17105	Incinerator emissions	INCIN	SPECIATE (U.S. EPA, 1991)
11501	Oil-fired power plant	OILPP	SPECIATE (U.S. EPA, 1991)
13501	Residual oil combustion	RESOIL	SPECIATE (U.S. EPA, 1991)

 Table 7-18.
 Chemical Mass Balance source profiles.

7.6.3. CMB Results

Results of the CMB analysis are discussed below. These results represent a preliminary approximation of an obviously complex airshed. It should be noted that all source types could not be included in the source estimates, but every effort was made to provide a complete apportionment for as many of the toxic elements as possible with the limited amount of information available. It should be noted that all source types could not be included in the source estimates. However, meteorology and knowledge of emissions are considered in the interpretation of results to establish a physical basis for source estimates. Results of the SEM/EDS analyses are discussed later in light of the CMB results to support or supplement those results. SEM/EDS may offer clues as to which types of sources need to be included in future CMB efforts in this airshed.

7.6.3.1. Coarse Fraction

The estimates of source contribution to the coarse fraction particulate samples are summarized in Table 7-13. The source contributions for samples collected on 18 - 20 July and 2 August include profiles for INCIN, SHALE, STLYARD and LIMEDUST. In addition, a RESOIL profile was included for the sample collected on 19 July to supplement the information for Ni and V. Also, an URBDUST profile was used to provide additional information for most of the elements for the sample collected on 6 August. A satisfactory apportionment was not obtained for the sample collected on 8 August using the available source profiles. The appropriate species that provided an optimum fit to the model were selected to maximize the degrees of freedom (number of species minus the number of sources) and minimize Chi² and maximize r^2 . These indicators were within the desired values established by Watson *et al.* (1991).

<u> </u>	SOURCE CATEGORY							
Sample Date	RESOIL	URBDUST	INCIN	SHALE	STLYARD	LIMEDUST	UN- EXPLAINED	
18 July 91	0	0	1.1±0.3	41.0±4.1	4.1±1.6	18.9±3.0	39.4 ± 5.3	
19 July 91	0.2±.07	0	2.0±0.4	44.7±4.4	2.7±1.6	13.3±2.2	37.1 ± 5.2	
20 July 91	0	0	1.2±0.4	64.1±7.6	5.2±2.4	12.1±2.3	17.4 ± 8.3	
21 July 91	0	0	2.6±0.9	30.6±4.4	26.8±3.4	8.0±2.6	32.0 ± 6.2	
2 Aug 91	U	0	1.2±0.4	51.3±6.2	7.4±1.5	16.6±3.0	23.5 ± 7.1	
6 Aug 91	0	13.6±3.6	0	21.3±3.4	31.2±4.7	10.0±3.4	23.9 ± 7.6	
8 Aug 91	-	0	-	-	-	-	-	

 Table 7-19.
 Summary of CMB Results for Coarse-particle Fraction in Percent of Measured Mass with Uncertainty Estimates.

The CMB results for 18-20 July 91 and 2 August 91 were similar. Also, the meteorological conditions were similar for these days. For each of those sampling days the PM10 concentration was > 50 μ g/m³ and the total coarse particle concentration was

> 20 μ g/m³. Mixed-layer backward trajectories for these days (see Figure 7-2) indicated long-range transport from the East St. Louis area. For each of these samples crustal material, represented by SHALE, comprises the largest fraction of the coarse mass (41%-69%), followed by LIMEDUST (12%-19%), STLYARD (3%-5%) and INCIN (1%-2%). The latter two profiles accounted for significant amounts of some elements but contributed very little to the total coarse mass concentration. The RESOIL applied to the sample collected on 19 July 91 accounted for a very small (0.2%) portion of the coarse particle mass but was necessary to account for the higher mass of V and Ni. These elements are characteristic of oil combustion sources. While most of the coarse mass was apportioned, it should be noted that a significant amount (17-39%) could not be apportioned using the CMB model.

The major source contribution for the sample collected on 21 July was STLYRD followed by SHALE and LIMEDUST. The winds were strong on this day coming from the SSW. The mixed-layer backward trajectory indicated that the air mass passed northward away from the East St. Louis area, and passed instead across the common border of Iowa, Missouri and Illinois. The coarse particle mass concentration for this day was $11 \ \mu g/m^3$, significantly lower than for the other samples measured. However, the local wind characteristics may provide some additional information.

The meteorological conditions were significantly different on 6 August 91 with winds generally from the ESE to SE. This difference was reflected in the change in the overall apportionment. Winds from the ESE to SE would result in greater influence of the industrial and fugitive sources associated with S.E. Chicago. Indeed, STLYARD is estimated to be the dominant source (31%) of the coarse mass for this sampling day, followed by SHALE (21%), URBDUST (14%) and LIMEDUST (10%). The URBDUST profile was needed to account for nearly half of the Cr and Mn. Howeva, the individual species apportionment indicates that some species, most notably Pb, were significantly overpredicted by STLYARD. However, the only stack-related steel emissions profiles available were of poor quality and thus were not included in any final apportionments, although unsuccessful attempts were made to include them in preliminary calculations.

7.6.3.2. Fine Fraction

The estimates for source contribution to the fine fraction particulate samples are summarized in Table 7-20. The steel-related fugitive dusts (STLYARD, COKEYARD, COALYARD) could be used interchangeably in the CMB calculations with equivalent mathematical fits to the data. There was not sufficient meteorological and emissions information available to determine which dust profile best represented the true source contributions, so the range of results is reported for each sample. These profiles cannot be included in the CMB simultaneously because they are collinear. The appropriate species that provided an optimum fit to the model were selected to maximize the degrees of freedom (number of species minus the number of sources) and minimize Chi^2 and maximize r^2 .

	SOURCE CATEGORY								
	H ₂ so ₄	RESOIL	INCIN	SHALE URBDUST (21 July 91)	STLYARD/ COKEYARD/ COALYARD	LIMEDUST	UN- EXPLAINED		
18 Jul <u>y</u> 91	47.8±5.8- 48.4±0.9	0	0.8±0.1- 0.9±0.1	0.7±1.0 - 3.1±0.6	$1.6 \pm 0.3 - 22.0 \pm 4.8$	0.5±0.3 - 1.3±0.2	28.2±7.6 - 45.2±5.9		
19 July 91	50.3±6.1- 50.7±6.1	0	$0.35 \pm .04 - 0.45 \pm 0.05$	1.2±0.9 - 3.2±0.6	$1.2 \pm 0.3 - 17.3 \pm 3.9$	0.4±0.2 - 1.0±0.2	30.5±7.3 - 43.8±6.1		
20 July 91	54.3±6.6- 54.6±6.6	0	$0.36 \pm .04 - 0.42 \pm 0.05$	1.6±0.8 2.8±0.5	$0.7 \pm 0.3 - 10.8 \pm 3.7$	0.3±0.2 - 0.7±0.1	32.6±7.6 - 41.0±6.6		
21 July 91	44.7±5.5- 45.3±5.5	0	2.3±0.2- 3.2±0.3	2.1±0.3 - 4.0±0.6	$6.1 \pm 0.9 - 26.4 \pm 4.2$	0	22.4±6.9 - 44.2±5.6		
2 Aug 91	47.3±5.7- 48.0±5.8	0	0.6±0.1- 1.0±0.1	0.2±0.9 - 3.2±0.6	$1.9 \pm 0.4 - 28.3 \pm 5.4$	0.8±0.3 - 1.8±0.3	22.8±7.9 - 44.9±5.9		

 Table 7-20.
 Summary of CMB Results for Fine-particle Fraction in Percent of Measured Mass with Uncertainty Estimates.

CMB source apportionment of the fine fraction proved more problematic than the coarse fraction. This may be attributed to the limited useful source profiles for non-fugitive steel mill emissions and to the overwhelming dominance of sulfate in the fine fraction. Also, the absence of a representative motor vehicle profile combined with the lack of carbon abundancies in some of the existing profiles further limit the fine fraction source apportionment.

The CMB results for samples collected on 18-20 July 91 and 2 August 91 were similar, which is consistent with the results obtained for the coarse fraction. As discussed previsously, the meteorological conditions were similar for these days. For each of these sampling days the total PM10 concentration was > 50 μ g/m³ and the total fine particle

concentration was > $30 \ \mu g/m^3$. Source contribution estimates were determined using profiles for H₂SO₄, RESOIL, INCIN, SHALE, LIMEDUST and steel-related fugitive dusts (STLYARD, COKEYARD, or COALYARD). Sulfur, represented by sulfuric acid in the CMB, contributed the largest fraction of the fine mass. The other sources accounted for most of the measured elements, but only a small portion of the total fine mass. The steel-related fugitive dust contribution was largest for COKEYARD and smallest for STLYARD. The SHALE estimate varied inversely to these estimates. Since each type of fugitive dust may be transported from the same general source region, more detailed profiles and meteorological information are needed to determine which, if any, is contributing to the fine mass. The individual species apportionments revealed that each of the fugitive dust profile was available to be included in the apportionment. Such a profile could significantly change the apportionment of the steel-related elements.

The sample collected on 21 July 91 could not be described well based on the source profiles utilized. This sample differed from the samples discussed above in several ways: 1) it had the smallest sulfate contributions and the largest INCIN contributions, 2) a locally-obtained urban dust profile (URBDUST) was required in place of SHALE to account for much of the soil-related elements, 3) Ca was overpredicted by the fugitive dust profiles and 4) diagnostics indicating that the apportionment may not be reliable as evidenced by the larger Chi² and the smaller r².

As previously discussed for the coarse fraction, the meteorological conditions during sample collection on 6 and 8 August 91 was significantly different from the other sampling periods. These samples indicated an increased impact of local pollutant sources contributing to the fine fraction samples. Because the profiles of the local sources may not have been adequate, these fine fraction samples were determined to be "unapportionable". This indicates a need for an improvement in the profiles of the local sources.

A characteristic of all of the fine-fraction CMB apportionments is the substantial overprediction of Cl. A loss of Cl after sample collection is seen frequently, and is presumed to be due to on-going reactions with atmospheric pollutants or volatilization. In addition, Cu could not be accounted for by the sources considered in the apportionments. Its underprediction could be caused by incorrect or inadequate local profiles. However, long-range transport of fine Cu from smelting operations in the East St. Louis area could account for the underprediction.

There was a relatively large fraction (22% - 45%) of the total fine mass which could not be accounted for by the sources included in the calculations. This may be due to the inadequate profiles for current motor vehicle emissions. However, this may also be due to water associated with sulfate particles.

7.6.4. Comparison of Individual Particle Analysis and CMB Results

Results of the SEM/EDS analyses are discussed to support or supplement the CMB results. SEM/EDS analysis was useful in providing clues as to which types of sources need to be included in future CMB efforts for this airshed. A detailed discussion of the SEM/EDS results are presented in section 7.3 of this chapter. It should be noted that the SEM/EDS results are reported as percent by number and not by mass, as are the CMB results. Thus, because of differences in particle size and density, the two results are not equivalent. Because of the time required for manual SEM/EDS analysis, only about 100 particles per size-fraction per sample could be examined, limiting the representativeness of each analysis.

7.6.4.1. Coarse Fraction

The SEM/EDS analysis reports that all coarse fraction samples were dominated by minerals, which includes both Si-rich and Ca-rich components. The mineral fraction was largest for samples collected on 18 and 19 July 91 and on 2 August 91. Results for these samples are discussed together because they are similar for both SEM/EDS and CMB results. SEM/EDS was not performed on the sample collected on 20 August 91. Silicates and quartz comprise 56-59% by number of the coarse fraction of these 3 samples, a little greater than the 41-51% source contribution estimate for SHALE. Some of the Si-rich particles may be associated with other fugitive dusts such as STLYARD. Particles containing Ca comprised 24-31% compared with 13-19% estimated for LIMEDUST by CMB. This disparity can be explained by the fact that some of the Ca-rich particles may occur in the SHALE, STLYARD, or other fugitive dusts. The carbonaceous particles account for 5-10% by number and could explain some of the unapportioned mass. These particles represent spores and plant debris (natural sources) and soot (combustion). Plant debris was generally the largest type of particle found (5-10 μ m) and could thus represent more mass than other types of particles. Industrial particles represented only a small fraction (4-9%) of the coarse particles, consistent with CMB results. However, individual particle analysis revealed a complexity which was not possible to show with CMB. For instance, some flv ash spheres were found, but this type of source could not be apportioned by CMB because they were similar in elemental composition to other sources. It should also be noted that the absence of some particles from the analysis does not indicate a lack of influence of the responsible source. However, this may indicate that an insufficient number of particles were examined.

The SEM/EDS results for 21 July 91 differed considerably from the 3 samples discussed above, as did the CMB results. Both individual particle analysis and CMB show that industrial emission were more important for this sample than the previous 3 samples. Particles identified as originating from industrial sources comprised 26% of the coarse particles; 7% were Fe spheres emitted from combustion sources and the remainder was a mixture of elements from industrial sources. The CMB yielded a remarkably similar result (27%) by representing Fe-rich sources with the STLYARD fugitive dust profile. This agreement may be fortuitous, as a dust profile implies that particles are not the result of combustion. On the other hand, some of the combustion products from the nearby stacks may have settled to the ground in the area where the STLYARD samples were collected. There is a disparity between the SEM/EDS estimate for Ca-rich particles (29%) and the CMB estimate for LIMEDUST (8%) which cannot be explained by the available evidence.

The sample collected on 6 August 91 had a significant amount of industrial particles (23%), more than half of which were Fe spheres from combustion sources. This is consistent with the winds blowing from the heavily industrial S.E. Chicago area on that day. In the CMB analysis, most of the Fe (71%) was attributed to STLYARD, a fugitive dust profile. The lack of information on the particle morphology of the source samples limited interpretation of these results. Twenty-five percent of the coarse particles were Sirich, compared with a SHALE source contribution estimate of 21%. SHALE is the source profile richest in Si. Again, the contribution of Ca-rich particles (29%) is higher than what would be expected from the CMB source contribution estimate for LIMEDUST (10%) which suggests that an additional source of the Ca impacted the sample. This sample contained the largest number of plant debris and spores/pollen (14%) which could explain much of the mass unaccounted for by the CMB calculation.

7.6.4.2. Fine Fraction

The SEM/EDS analysis reported that all fine fraction samples were dominated by sulfate. Because more than 99% of the fine particle identified in the SEM/EDS analysis were sulfate particles, a quantitative comparison with CMB results is impractical. For this reason, only a qualitative discussion is presented here. Any percentages reported refer to

the non-sulfate population of fine particles. The sulfate particles identified were all in the smallest size category (< 0.5 μ m) and appeared as round droplets. The droplet appearance supports the hypothesis that water is associated with the sulfate particles and could account for much of the mass not accounted for by the CMB calculations.

Samples identified as having large numbers of Fe-rich combustion spheres were those samples which were not apportionable (6 and 8 August 91) or which had problematic apportionments (21 July 91). Industrial particles accounted for 56 - 79% of the non-sulfate particles in the 3 samples which were difficult to apportion. Clearly, a proper apportionment of the fine fraction requires good source profile information for local industrial sources, which can be responsible for many of the toxic elements.

SEM/EDS results for samples collected on 18 and 19 July 91 and 2 August 91 were similar, as they were for the CMB results. These samples had the smallest percentage of industrial fine particles (17% -26% of the non-sulfate particles). Nevertheless, good industrial profiles are needed for these samples as well.

For all samples collected, the soot carbon comprised 2% - 8% of the non-sulfate fine particles. The size of the soot particles was variable. Since soot may comprise a substantial portion of motor vehicle emissions, the number and size of soot particles could potentially be used to estimate an upper limit for motor vehicle emissions.

Some particles were identified as originating from incineration, supporting the inclusion of the INCIN profile in the CMB calculations. Fly ash particles were also identified in some of the samples, but the profile for a coal combustion source did not provide an adequate apportionment in the CMB calculations.

The SEM/EDS results seem to support the conclusion that the source apportionment of the fine fraction was often problematic and that more source profile information is needed. Source profiles for the major sources in the southern Lake Michigan Basin should include measurements of carbon and mercury to better characterize the source impacts in this area.





Chapter 8

Estimating Atmospheric Deposition

8.1. Introduction

The transfer of trace metals from the atmosphere to a receptor surface via dry deposition of particles or gaseous contaminants has been the subject of many studies over the last twenty years (Slinn et al., 1978; Sehmel, 1980; Nicholson, 1988; Noll et al., 1988; Wu et al., 1992). However, an in-depth evaluation of the dry deposition flux of trace metals to large water bodies that considers the dynamics of micro-meteorological parameters has not been performed. Such an evaluation would have to account for influences on dry deposition such as particle size distribution, phoretic forces, electrostatic gradients, and/or the dynamics of water waves controlling the flux of particles at the airwater interface. The theoretical and experimental knowledge of particle dry deposition over a water surface is limited due to the inherent difficulties in making direct flux measurements over water (Wesely and Williams, 1981; Sievering, 1982). Past measurements of direct dry deposition fluxes made over Lake Michigan (Wesely and Williams, 1981) and the Atlantic Ocean (Sievering, 1982) were likely to have been affected by the large uncertainty caused by particle growth in the humidity gradient present over water. Furthermore, results using the gradient technique have not been reported in the literature due to the near impossibility in detecting small concentration gradients (usually 1%) at the air-water interface for particle diameters <1 μ m.

In order to estimate dry deposition fluxes of contaminants to land and water surfaces, ambient concentration measurements are typically combined with deposition velocities obtained from the literature. Another method that has been developed over the past 10 years is the use of surrogate surfaces (Noll *et al.*, 1985; Holsen *et al.*, 1993). However, there are only a few data points using this technique in the Lake Michigan Basin, and most of these are on land (Strachan and Eisenreich, 1988, 1992; Holsen *et al.*, 1993). Moreover, there are statistical uncertainties associated with these surrogate

surface estimates that may be significant due to the fact that (a) the measurements are not made directly on the water (the information may not be applicable to the air-water interface); and (b) the dry deposition sampler is operated at a distance above the water surface (at least 5-15 meters if it is located on board a ship) where the effect of critical parameters such as phoretic and electrostatic forces, particle growth in the humidity gradient at the air-water interface, and dynamics of water waves are not accounted for in the measured fluxes.

It is also difficult to determine the effect of changes in the meteorological conditions (wind speed, atmospheric stability, surface roughness) on the total dry deposition of trace metals from the atmosphere to the water surface and on the ambient concentrations as air masses cross the lake. A lagrangian process can not be easily implemented because of the small number of direct measurements made at a few fixed points. Furthermore, a simple extrapolation of the point estimates to the total surface area of Lake Michigan (about 57,800 km²) may provide highly uncertain results.

This section discusses a new hybrid receptor-deposition modeling approach used to evaluate the trace metal dry deposition over Lake Michigan during LMUATS. The dynamic model accounts for both temporal and spatial variations in the dry deposition fluxes over Lake Michigan for air masses traversing the lake. The variations in the dry deposition flux are the result of horizontal and vertical dispersion, variations in wind speed, the action of water waves, and the temperature gradient at the air-water interface.

The results calculated for this study are compared to direct measurements of dry deposition fluxes and ambient concentrations of trace metals made at land-based sampling sites as well as over-water measurements on Lake Michigan. Finally, the average dry deposition fluxes to Lake Michigan are presented for measured trace metals along with a discussion of the band of uncertainty related to the above mentioned parameters.

8.2. Methods

Dry deposition processes are affected by a wide range of meteorological parameters (i.e., wind speed, atmospheric stability, relative humidity), pollutant characteristics (i.e., chemical speciation, particle size and shape) and receptor surface characteristics (i.e., surface roughness, type of surface). Early attempts to evaluate the dry deposition flux to large water-bodies assumed that deposition velocities and ambient concentrations were constant in both time and space and did not explicitly take into

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account the effect of processes that influence the dynamics of particle transfer from the atmosphere to the water surface and vice versa. These processes include atmospheric dispersion, particle growth within the humidity gradient, diffusophoresis, thermophoresis, and wave breaking. Finally, atmospheric processes occur on many different time scales which also must be considered when evaluating the deposition flux to large water surfaces.

A combined dispersion-deposition modeling approach was developed to estimate the deposition flux of contaminants over Lake Michigan. The dry deposition flux, F, of trace metals is related to the ambient concentrations χ , the dry deposition velocity of particles, V_d, and the area, S, of the receptor surface through the following expression (Chamberlain, 1983).

$$F(t) = \chi(t) V_{d}(t) S$$
 (1)

The flux, F(t), is a function of χ and V_d which are not constant in time or space, but change during air mass transport over Lake Michigan. Mixed layer 72-hour backward and forward trajectories (Heffter, 1980) were calculated for each LMUATS monitoring site. The path of the air parcel and the transport layer depth were calculated using both routine upper-air observations from the National Weather Service (NWS) and supplementary data taken from selected periods of the Lake Michigan Ozone Study (LMOS) for air parcels crossing the lake to and from the monitoring sites.

Atmospheric concentrations of contaminants along a trajectory are affected by the dispersion and deposition of pollutants emitted from sources located in the basin. Since a complete emissions inventory was not available for all of the sources of hazardous air pollutants in the Lake Michigan Basin, a virtual source (VS) was constructed from measured concentrations at the sampling sites in order to estimate the variation of ambient concentrations due to atmospheric dispersion along the over water trajectory. The VS is defined as an area source, equivalent to all sources operating in the basin which are along the path of the calculated air mass trajectory in either the forward or backward direction from Lake Michigan. The distance of the VS from the lake shore is an important parameter which can significantly affect the calculated concentrations of contaminants in the air mass as it traverses the lake. Therefore, the distance of the VS from the coast was determined through an optimization process that minimized the ratio of the predicted to the observed concentrations at the monitoring stations. The sampling station where the

ratios are evaluated is used as a source (or receptor) with respect to the sampling station where the backward (or forward) trajectories end (or start).

Once the optimal distance of the VS from the lake was defined, the dispersion parameters were evaluated using the monitoring site as the end point for each backward trajectory (or the starting point for forward trajectories) crossing the lake and sampling site. The change in atmospheric concentration of a contaminant along a trajectory, assuming that the contaminant is uniformly distributed in the volume, dV=dx dy dz, is governed by the following differential equation:

$$dM(t) / dt = [\chi(t) dx(t) dy(y) dz(t) / dt] - Vd \chi(t) dx(t) dy(t)$$
(2)

where dM(t) is the mass of contaminant in the volume dV = dx dy dz. Assuming no loss of contaminant through the upper level of the transport layer, the variation of the ambient concentration along the trajectory is obtained from Eq.1 by the following mass balances:

$$\chi_{i,j} \left(x_{i,j} \, y_{i,j} \, z_{i,j} - \chi_{i,j} \, V_{d_{i,j}} \left(\Delta t \, x_{i,j} \, y_{i,j} \right) = \chi_{i,j-1} \left(x_{i,j-1} \, y_{i,j-1} \, z_{i,j-1} \right)$$
(3)

$$\chi_{i,i-1} (\mathbf{x}_{i,i-1} \ \mathbf{y}_{i,i-1} \ \mathbf{z}_{i,i-1}) - \chi_{i,i-1} \ \mathbf{V}_{\mathbf{d}_{i,i-1}} (\Delta t \ \mathbf{x}_{i,i-1} \ \mathbf{y}_{i,i-1}) = \chi_{i,i} (\mathbf{x}_{i,i} \ \mathbf{y}_{i,i} \ \mathbf{z}_{i,i})$$
(3')

Eqs.3 and 3' are for trajectories in the backward and forward mode, respectively. The index i represents the trajectory while j is the trajectory segment index which increases along the trajectory (for both forward and backward mode) beginning at the monitoring site. $\chi_{i,j}$ is the concentration of the contaminant in the volume $x_{i,j}$ $y_{i,j}$ $z_{i,j}$, $V_{di,j}$ is the deposition velocity of the particulate contaminant, and Δt is the time step which is constant ($\Delta t = 3$ hr) for each segment.

The first term of these mass balance equations represents the mass of contaminant in the volume $x_{i,j} y_{i,j} z_{i,j}$ and the second term is the mass of contaminant deposited over the water surface area, $x_{i,j} y_{i,j}$. The term on the right side is the mass of contaminant advected along the subsequent trajectory segment after accounting for the lateral spread of the plume and the depletion of the ambient mass by dry deposition during the previous time step. The time dependent pollutant concentrations along the backward or forward trajectories are determined by Eqs. 3 and 3' which leads to the following expressions:

$$\chi_{i,n} = \chi_{i,1} (\mathbf{x}_{i,1} \mathbf{y}_{i,1} \mathbf{z}_{i,1} / \mathbf{x}_{i,n} \mathbf{y}_{i,n} \mathbf{z}_{i,n}) \prod_{j=2,n} [1 - Vd_{i,j} \Delta t / \mathbf{z}_{i,j}]^{-1}$$
(4)

$$\chi_{i,n} = \chi_{i,1} \left(x_{i,1} \, y_{i,1} \, z_{i,1} \, / \, x_{i,n} \, y_{i,n} \, z_{i,n} \right) \prod_{j=1,n-1} \left[1 - V d_{i,j} \, \Delta t \, / \, z_{i,j} \right] \tag{4'}$$

where $\chi_{i,1}$ is the ambient concentration of the pollutant measured at the sampling site (j=1), $x_{i,j}$ is the distance traveled by the plume, $z_{i,j}$ is the transport layer depth, $y_{i,j}$ is the crosswind plume width, and n is the number of 3-hour trajectory segments. Equations 4 and 4' consider the sampling site as the receptor in backward mode and as the source in forward mode.

One of the earliest experiments that measured lateral dispersion over long distances was completed by Richardson and Proctor (1925) with a re-assessment by Sutton (1932). The data consisted mainly of the distance of balloons from release points as a function of time and distance in Brighton and Reagent Parks in London. Sutton's (1932) analysis concluded that the horizontal spread of the balloons varied with a power law: x^q (q = 0.875) for downwind distances greater than 500 km. This finding agrees fairly well with results obtained later by Braham et al. (1952), Crozier and Seely (1955) and Pasquill (1956). Data collected from the Mt. Isa smelter plumes in central Australia (Bigg et al., 1978) with a wider range of downwind distances (15 to 1000 km) provided an exponential law very close to that estimated by Sutton (1932) for the Richardson and Proctor (1925) data set. The analysis of data collected over the sea by Crabtree (1982) for a plume emitted by the Eggborough Power Station followed a power law with a coefficient (q = 0.5) which is lower than that estimated for plumes transported over land. The significant difference between sea and land data may be explained by the large reduction, if not complete absence, of thermally induced turbulence over the water. However, the observation of the constant power law behavior of plume width with distance is partially due to the wind directional shear across the boundary layer (Pasquill and Smith, 1983). Therefore, based on these previous results in the literature, a power law with coefficient q = 0.5 was chosen to estimate the lateral spread of the plume crossing the lake. The dispersion parameters for backward trajectories are given by:

$$y_{i,j} = \left(U_{i,j} \Delta t / 2\right)^{q} \qquad j = n \qquad (5)$$

$$y_{i,j} = \left[\sum_{k=j+1,n-1} U_{i,k} \Delta t + U_{i,j} \Delta t / 2 \right]^{q} \quad 1 \le j < n$$
(6)

The dispersion parameters for forward trajectories are given by:

$$y_{i,j} = (U_{i,j} \Delta t / 2)^{q}$$
 $j = 1$ (5')

$$y_{i,j} = \left[\sum_{k=j+1,n-1} U_{i,k} \Delta t + U_{i,j} \Delta t / 2 \right]^{q} \quad 1 < j \le n$$
 (6')

where $U_{i,j}$ is the wind speed (km/h) at the water level.

 $U_{i,j}$ are derived from wind data calculated for each trajectory segment. The analytical expression for the wind speed at a given level is deduced from the following iterative approach in which the friction velocity, U^{*}, is obtained by the surface layer similarity theory (McBean, 1979) given by:

$$U^* = \kappa U_{i,j}(z) / [\ln(z/z_0) - \Phi_m(z/L) + \Phi_m(z_0/L)]$$
(7)

Writing Eq.7 for two different altitudes and neglecting $\Phi_m(z_0/L)$ (second order term), the wind speed $U_{i,j}(z)$ at surface level $z_{0\le z} < L$ is

$$U_{i,j}(z) = U_{i,j}(z_t) \left[\left(\ln(z/z_0) - \Phi_m(z/L) \right) / \left(\ln(z_t/z_0) - \Phi_m(z_t/L) \right) \right]$$
(8)

$$z_0 = v / 9.1 \text{ U}^* + 0.016 \text{ U}^{*2}/\text{g}$$
 (9)

where κ is the von Karman constant, $U_{i,j}(z_t)$ is the geostrophic wind speed, z_t is the average terrain height at which the geostrophic wind speed is calculated and z_0 is roughness of the water surface related to the dynamic of water waves (Williams, 1982; Chamberlain, 1983). The quantity $\Phi_m(z/L)$ is the atmospheric stability function (Businger *et al.*, 1971; Yaglom, 1977; Wieringa, 1980a; Wieringa, 1980b; van Ulden and Holtslag, 1985) which is a function of the surface roughness and the reciprocal of the Monin-Oboukhov length (1/L) through the following expressions:

$$\Phi_{\rm m}(z/L) = 2 \ln[(1+x)/2] + \ln[(1+x^2)/2] - 2 \tan^{-1}(x) + \pi/2 \qquad L < 0 \tag{10}$$
$$x = (1 - 16z/L)^{0.25}$$
$$\Phi_{\rm m}(z/L) = -5z/L \qquad L \ge 0 \tag{11}$$

The Monin-Oboukhov length L was estimated using California Institute of Technology's linear approximation to Golder's plot (Golder, 1972).

The deposition velocity for fine and coarse particles along each trajectory segment was calculated using a deposition model formulated for water surfaces. The approach is based upon Williams' (1982) model which separates the atmosphere into two layers; the upper layer where particle transport is controlled by turbulent transfer and the lower layer where particle transport is controlled by gravitational settling. The transfer of particles is controlled by two parallel paths, one is from air to a smooth water surface while the other path is from air to a broken water surface with formation of spray and bubbles. The twolayer formulation then provides the following expression for the deposition velocity of particles over a water surface (similar to the electrical circuit analysis of Williams, 1982).

$$V_{di,i} = (A/B) \left[(1-\alpha) \left(K_{ss} + V_{gw} \right) + K_m \alpha \left(K_{bs} + V_{gw} \right) / \left(K_m + \alpha \left(K_{ab} + K_{bs} + V_{gw} \right) \right) \right]$$
(12)

where:

$$A = K_{m} [(1 - \alpha) K_{as} + \alpha K_{ab} + V_{gd}] + (1 - \alpha) (K_{as} + V_{gd}) \alpha (K_{ab} + K_{bs} + V_{gw})$$

$$B = K_{m} [(1 - \alpha) (K_{as} + K_{ss}) + \alpha (K_{ab} + K_{bs}) + V_{gw}] + (1 - \alpha) (K_{as} + K_{ss} + V_{gw}) \alpha (K_{ab} + K_{bs} + V_{gw})$$

and α is the fraction of water surface that becomes broken due to the action of wind speed (Wu, 1979). The settling velocity is calculated for dry V_{gd} and wet V_{gw} particle diameters. Further, A and B are related to turbulent transfer coefficients from the atmosphere to the smooth (K_{as}) and broken (K_{ab}) water surfaces formulated by Hess and Hicks (1975), and to the smooth surface transfer coefficient (K_{ss}) found in Slinn and Slinn, 1980. K_r is the lateral transfer coefficient and K_{bs} is the broken surface transfer coefficient that must be estimated empirically since a mathematical formulation is not widely accepted. The coefficients (K_{as}) and (K_{ab}) were used by Williams (1982) as constants with a range between 0 to ∞ and K_{ss} = 1000 cm/s. Later in this report, the values of K_{bs} and K_m are empirically defined using the ambient concentrations and dry deposition fluxes for fine (<2.5 µm) and coarse (2.5-10 µm) particles measured over Lake Michigan.

The model of Sehmel and Hodgson (1978) which has been used extensively for evaluating deposition velocities was used here. While this model was not specifically formulated for water surfaces, eddy diffusivity, gravitational settling and particle inertia, the main mechanisms influencing the dry deposition velocity of particles, were considered. Finally, the model combines these terms with the terminal settling velocity and Brownian diffusion to predict deposition velocities.

8.3. Modeling Results

Aerosol samples were collected on 37-mm Teflon filters using dichotomous samplers at each monitoring site. Trace element concentrations in the fine and coarse fractions were determined using X-Ray fluorescence (XRF) analysis (Dzubay *et al.*, 1982). Tables 5-3 and 5-4 list the mean concentrations of selected trace metals in the fine (<2.5 μ m) and coarse (2.5-10 μ m) fractions of the PM10 measured at Chicago, IL and South Haven, MI. Concentrations of fine fraction elements were generally lower at South Haven than at Chicago with the exception of Al which was more abundant in South Haven on the average. In the coarse fraction, crustal elements were found to be 2 to 3 times lower in concentration at South Haven. The concentrations of primarily anthropogenically derived elements such as Cd, Cr and Se were found at similar level at both sites, while Al, Mn, Zn, and Pb were found to be 2 to 5 times lower at South Haven than those measured at Chicago.

The deposition velocities of trace metals over Lake Michigan were calculated using the particle size distributions for specific elements found in Holsen *et al.* (1993). These were measured at Chicago (IIT) during the LMUATS. The size distributions were used to calculate mass median diameters (MMD) in the fine (< 2.5 μ m) and coarse (2.5-10 μ m) fractions. MMDs for elements not measured by Holsen, such as Hg, S, K, Ni, As, Se, and Br, were taken from the literature (Milford and Davidson, 1985; Sadisivan, 1978). Table 8-1 shows the MMDs used in this study for trace metals in both size fractions.

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	Fine	Coarse	Reference
	(< 2.5 µm)	(2.5-10 µm)	<u></u>
Al	0.75	4.0	1
Si	1.30	5.0	1
S	0.50	4.0	2
K	1.30	5.0	2
Ca	1.30	5.0	· · 1
Cr	0.75	4.0	1 .
Mn	0.75	4.0	1
Fe	1.30	5.0	1
Ni	0.75	4.0	2
Cu	0.75	4.0	1
Zn	0.75	4.0	1
As	0.75	4.0	2
Se	0.50	4.0	2
Br	0.50	4.0	2
Cd	0.75	4.0	1
Hg (*)	0.61		2
Pb	0.50	4.0	1

Table 8-1. Mass Median Diameter (µm) for Selected Trace Elements.

(1) Holsen *et al.* (1993)

(2) Milford and Davidson (1985); Sadisivan (1978); Dodd et al. (1991)

Figure 8-1 shows the mixed layer trajectories from Chicago for 14 and 15 July 1991, moving backwards in time in 3-hour time-steps. The temporal trends in the calculated deposition velocities for fine particles along the trajectories that crossed Lake Michigan from north \star_{2} south are shown in Figure 8-2. The variations in the calculated deposition velocities over water are quite large for micron and submicron particles.

Figure 8-1. Mixed Layer Backward Trajectories that Crossed Lake Michigan on 14 and 15 July, 1991.



(IIT = Chicago. Small squares indicate the position of the air mass as it moves backward from the site in 3-hour increments)





Dry Deposition Velocity (cm/s)



The dry deposition fluxes of trace metals associated with fine particles are affected by large variations in the deposition velocity. The variations are about a factor of 3 for a $0.5 \mu m$ particle diameter (Figure 8-2a), 10 for a $0.75 \mu m$ particle diameter (Figure 8-2b) and 15 for a 1.3 μm particle diameter (Figure 8-2c). Variations of 10 to 20% in deposition velocity occur for a 4 μm particle diameter and 3 to 10% for a 6 μm particle diameter along trajectories such as those calculated for the 14 and 15 July.

Table 8-2 gives the model parameters utilized for three different MMDs along the trajectory calculated for 15 July (shown in Figure 8-1). The coefficient j denotes the trajectory segment starting at the receptor site (IIT) and moving backwards in time away from the starting point. The estimated deposition velocities agree fairly well with those of Williams (1982) and Slinn (1983), whose predicted deposition velocities were 10- to 100-fold greater for particle diameters > 0.8 μ m.

Figures 8-3 and 8-4 show the measured/calculated ratios for both fine and coarse particles obtained for trajectories that traversed Chicago, Lake Michigan and South Haven on the 19, 20 and 21 of July 1991 (Figure 8-5). The measured/calculated ratios were obtained assuming a VS operating at 30 km from Lake Michigan with a power law coefficient of q = 0.5 to account for the lateral spread of the plume crossing the lake. The measured/calculated (m/c) concentration ratios for fine particles are generally in the range of 0.75 to 2. The exceptions to this were Al and total Hg, which had m/c ratios of 4.6 and 8, respectively on 21 July. On 19 July, Si had a m/c ratio of 6.8 while Pb had a m/c equal of 3.6 for the trajectory on July 19. Measured/calculated ratios for coarse particles range from 0.5 to 3.6 with the exception of Pb, Zn and Mn which have ratios of 5, 8 and 6.5 respectively, for the trajectories on July 19, 20 and 21.

The high ratios obtained for some elements in the fine and coarse fraction may be explained by (a) an increase in the horizontal spread of the plume (the power-law coefficient was greater than the value used) caused by unstable atmospheric conditions yielding lower concentrations in the air parcel crossing the lake; and (b) significant fumigation leading to higher depletion rates of contaminants from the plume.

Next, the calculated dry deposition fluxes for trace metals are compared with annual estimates made by Holsen *et al.* (1993) using surrogate surfaces mounted on the R/V Laurentian. These surfaces were approximately 5 meters above the water surface, the same level that the other aerosol measurements were performed.

j	Ws	U*	Φ_{m}	10 ⁻³ α	Km	Kbs	Kas	Kab	K _{SS}	Vgd	Vd
	(m/s)	(cm/s)			(cm/s)	(cm/s)	(cm/s)	(cm/s)	(cm/s)	(cm/s)	(cm/s)
						Dp =	0.5 mm				
1	1.0	0.84	-36.82	0.002	1.0	7	0.0060	0.0071	0.00001	0.0011	0.0012
2	0.9	0.65	-44.41	0.001	1.0	7	0.0041	0.0048	0.00001	0.0011	0.0012
3	1.7	2.61	-14.06	0.010	1.0	7	0.0294	0.0387	0.00020	0.0011	0.0014
4	1.6	2.32	-15.72	0.010	1.0	7	0.0251	0.0326	0.00020	0.0011	0.0014
5	2.6	5.51	-6.32	0.060	1.0	7	0.0759	0.1063	0.00060	0.0011	0.0020
6	2.5	5.17	-6.81	0.050	1.0	7	0.0703	0.0980	0.00050	0.0011	0.0019
7	3.3	7.93	-3.96	0.150	1.0	7	0.1172	0.1672	0.00100	0.0011	0.0025
8	3.3	7.93	-3.96	0.150	1.0	7	0.1172	0.1672	0.00100	0.0011	0.0025
9	4.6	12.74	-2.00	0.520	1.0	7	0.2008	0.2895	0.00180	0.0011	0.0037
10	4.5	12.36	-2.09	0.480	1.0	7	0.1941	0.2797	0.00170	0.0011	0.0036
				·····	·	Dp =	0.75 mm				
1	1.0	0.84	-36.82	0.002	1.1	50	0.0060	0.0073	0.00001	0.0026	0.0026
2	0.9	0.65	-44.41	0.001	1.1	50	0.0042	0.0049	0.00001	0.0026	0.0026
3	1.7	2.61	-14.06	0.010	1.1	50	0.0298	0.0413	0.00020	0.0026	0.0033
4	1.6	2.32	-15.72	0.010	1.1	50	0.0254	0.0347	0.00010	0.0026	0.0031
5	2.6	5.51	-6.32	0.060	1.1	50	0.0767	0.1159	0.00050	0.0026	0.0058
6	2.5	5.17	-6.81	0.050	1.1	50	0.0710	0.1067	0.00040	0.0026	0.0054
7	3.3	7.93	-3.96	0.150	1.1	50	0.1181	0.1839	0.00080	0.0026	0.0101
8	3.3	7.93	-3.96	0.150	1.1	50	0.1181	0.1839	0.00080	0.0026	0.0101
9	4.6	12.74	-2.00	0.520	1.1	50	0.2012	0.3208	0.00140	0.0026	0.0259
_10	4.5	12.36	-2.09	0.480	1.1	50	0.1946	0.3099	0.00140	0.0026	0.0243
						<u>Dp</u> =	1.3 mm			·····	
1	1.0	0.84	-36.82	0.002	6.0	800	0.0061	0.0077	0.00001	0.0077	0.0082
2	0.9	0.65	-44.41	0.001	6.0	800	0.0042	0.0052	0.00001	0.0077	0.0080
3	1.7	2.61	-14.06	0.010	6.0	800	0.0304	0.0457	0.00010	0.0077	0.0140
4	1.6	2.32	-15.72	0.010	6.0	800	0.0259	0.0382	0.00010	0.0077	0.0127
5	2.6	5.51	-6.32	0.060	6.0	800	0.0785	0.1331	0.00030	0.0077	0.0361
6	2.5	5.17	-6.81	0.050	6.0	800	0.0727	0.1222	0.00030	0.0077	0.0327
7	3.3	7.93	-3.96	0.150	6.0	800	0.1207	0.2145	0.00060	0.0077	0.0655
8	3.3	7.93	-3.96	0.150	6.0	800	0.1207	0.2145	0.00060	0.0077	0.0655
9	4.6	12.74	-2.00	0.520	6.0	800	0.2050	0.3795	0.00100	0.0077	0.1404
10	4.5	12.36	-2.09	0.480	6.0	800	0.1983	0.33664	0.00100	0.0077	0.1314

 Table 8-2. Model Parameters Obtained for Three MMDs along Backward

 Trajectory Segments over Lake Michigan on 15 July 1991.

Figure 8-3. Ratio of the Measured / Calculated Concentration of Trace Metals Associated with Fine Particles Obtained from Backward Mixed-layer Trajectories for South Haven on 19, 20 and 21 July 1991.



Figure 8-4. Ratio of the Measured Calculated Concentration of Trace Metals Associated with Coarse Particles obtained from Backward Mixed-layer Trajectories for South Haven on 19, 20 and 21 July 1991.



Figure 8-5. Backward Mixed-layer Trajectories for South Haven that Traversed Lake Michigan on the 19- 21 July, 1991.



(IIT = Chicago, SHA = South Haven. Small squares indicate the position of the air mass as it moves backward from the site in 3-hour increments)

Holsen *et al.* (1993) estimated that fine particles are responsible for about 2% and 0.6% of the total dry deposition flux of Pb and Ca, respectively, at the Chicago site. The Pb and Ca dry deposition flux associated with coarse particles with aerodynamic diameters in the range of 2.5 to 10 μ m accounted for about 11.5 and 8% of total fluxes of Pb and Ca, respectively. Based on these estimates, the dry flux deposited to Lake Michigan by the fine and coarse fractions of the PM10 were calculated for this study (Table 8-3) and also by Holsen *et al.* (1993). The higher ratios for the coarse fraction may be due to (a) particle growth in a humidity gradient (not considered in this study) yielding submicron particles in the inertial deposition range (and therefore higher dry deposition fluxes); (b) position of the sampling station in the plume; (c) statistical uncertainty related to dry deposition measurements; (d) small representativeness of measured fluxes at one point for the whole lake area; (e) a different dry deposition flux distribution for particle sizes measured in Chicago (used in this comparison) versus those found directly on Lake Michigan.

	PM10 F	raction	PM10		
	Fine	Fine	Coarse	Coarse	
·····	Pb	Ca	Pb	Ca	
(1) Holsen et al. (10)	0.0019	0.294	0.010	4.6	
(2) This Study	0.0020	0.216	0.022	5.5	
Ratio (2) / (1)	1.00	0.74	2.20	1.2	

Table 8-3. Comparison of Calculated Dry Deposition Flux (µg/m²-h) with that Determined by Holsen *et al.* (1993).

The previous results obtained for ambient concentrations and dry deposition fluxes were used to define the optimal values for K_m and K_{bs} . Both of these or efficients in the work by Williams (1982) work ranged from 0 to ∞ cm/s for K_m , and 0 to 1000 cm/s for K_{bs} . Figure 8-6 displays the K_m and K_{bs} curves obtained by cubic spline interpolations of estimated values for aerodynamic particle diameters in the range of 0.5 to 6 μ m. Obviously, the previous results are not thought to represent the real physical situation that occurs at the air-water interface, since they were validated with measurements made using surrogate surfaces not directly on the water surface. However, the high uncertainty in the direct measurements of dry deposition fluxes to water surface using gradient and eddy flux techniques (Wesely and Williams, 1981; Sievering, 1982) would not provide results any more reliably.

Figure 8-6. Curves of K_m and K_{bs} Coefficients vs. Particle Aerodynamic Diameters.



Dry deposition fluxes over Lake Michigan are estimated for trajectories crossing Lake Michigan, Chicago, and South Haven for trace metals associated with the fine and coarse PM10 particles. Figure 8-7 shows the average dry deposition loadings for trace metals in the fine fraction obtained from trajectories crossing South Haven and Lake Michigan. The dry deposition loads for trace metals primarily of crustal origin range from 26 tons for Si to 9.5 tons for K. Trace metals primarily of anthropogenic origin have a dry deposition load in the range of 18.86 tons for S to 0.04 tons for Br. In the coarse fraction (Figure 8-8), the dry deposition load for crustal or soil elements ranges from 333 tons for Si to 48.8 tons for K, while elements of anthropogenic origin are in the range of 146.5 tons for Al to 0.31 tons for Br.

To evaluate the variability of the dry deposition fluxes over a 24-hour period, the deposition fluxes obtained from the daytime (18Z) backward trajectories were compared to nighttime (beginning at 6Z) backward trajectories. Ambient concentrations measured for the 12-hour nighttime sample and for the 12-hour daytime period were used to evaluate the dry deposition fluxes of trace elements. Figure 8-9 shows the ratio of the trajectory dry deposition fluxes calculated for the night/day (6Z/18Z) for trace metals associated with fine and coarse particles for the South Haven site. The variability of the dry deposition fluxes associated with fine particles ranged from 0.6 to 1.0 for most elements with the exception of Se 1.4 and Al 1.65. The coarse fraction showed a dry deposition flux ratio for most trace metals in the range of 0.6 to 1.4 with the exception of Al (2.2), Br (0.3) and Pb (0.3).

Figures 8-10 and 8-11 show the dry deposition loading of trace metals associated with fine and coarse particles over Lake Michigan obtained using the backward trajectories starting in Chicago. Crustal elements are slightly more abundant than those estimated from South Haven trajectories with the exception of K which gave lower values using the Chicago trajectories. Anthropogenic elements are again more abundant than that estimated from South Haven trajectories with the exception of Al (2.04 tons), Cd (0.08 tons), As (0.06 tons), Se (0.01 tons) and Cr (0.1 tons). Deposition loads associated with coarse particles (Figure 8-12) are two to three times higher than that obtained from the South Haven trajectories for both crustal and anthropogenic elements, with the exception of Al and S which were similar at both sites.

Figure 8-7. Dry Deposition Load of Trace Metals Associated with Fine Particles obtained from South Haven Measurements and Trajectories.



Figure 8-8. Dry Deposition Load of Trace Metals Associated with Coarse Particles obtained from South Haven Measurements and Trajectories.







Figure 8-10. Dry Deposition Load of Trace Metals Associated with Fine Particles obtained from Chicago Measurements and Trajectories.



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Figure 8-12. Chicago To South Haven Dry Deposition Flux Ratio.

In order to evaluate the dependence of the type of sampling site (i.e., rural, industrial) and location in the basin on the dry deposition estimates, the ratios between Chicago and South Haven dry deposition loads for trace metals associated with fine and coarse particles were calculated. The ratios for most of the fine fraction trace metals (Figure 8-12) were in the range of 0.6 to 3 with the exception of Cr 0.1 and total Hg 16. The high ratio for total Hg was probably due to strong local sources in the Chicago area, as ambient Hg concentrations measured in Chicago were about 5-15 times higher than those measured for vapor and particulate Hg in South Haven.

Table 8-4 gives the dry deposition load estimated to Lake Michigan for the LMUATS period. The estimated dry deposition flux to Lake Michigan was computed by Holsen et al. (1993) using the average elemental flux measured over the water and assuming that this measured flux was typical for the southern one-half of the lake. The average flux over the northern one-half of the lake was 25% of this amount. The difference in the dry flux between the northern and southern portions of Lake Michigan is roughly equivalent to the difference in total fluxes measured by Eisenreich (1980) with bulk deposition collectors from September 1975 to December 1976. The value reported for this study is the average of the drv deposition flux calculated from the data at South Haven and Chicago (IIT). The spatial averaging is implicitly included in the hybridreceptor modeling approach described in this chapter. Surprisingly, the results from the two approaches still agree within a factor of 2-4 for the two elements, Pb and Ca, given below. The estimates based on the hybrid-receptor modeling approach can be applied to any pollutant species and may be improved using additional sampling sites on both sides of the lake.

		PM10	PM10			
	Fine Pb	Fine Ca	Coarse Pb	Coarse Ca	Total Pb	Total Ca
(1) Holsen <i>et al.</i> (1993)	49.6	7673	261	120,060	311	112,073
(2) This Study	83.5	9020	919	229,680	1002	238,700
Ratio (2)/(1)	1.7	1.2	3.5	1.9	3.2	2.1

Table 8-4. Comparison of Calculated Dry Deposition Loads (kg) with thatEstimated by Holsen et al. (1993).

8.4. Discussion

Modeling the dry deposition flux may best be performed by invoking a strictly lagrangian framework since the concentration profile, aerosol size distribution, atmospheric chemistry, and meteorological conditions characterizing an air mass change as a function of transport time. Dry deposition fluxes over Lake Michigan may vary by several orders of magnitude due to variations in the aerodynamic particle diameter and meteorological conditions en route. Deposition velocities for submicron particles may vary by a factor of 3 to 10, while particles slightly larger than 1 μ m are found to have variations in deposition velocities of a factor of 15. Particles with an aerodynamic diameter greater than 4 μ m can have variations of 3 to 20% with respect to the mean. The large range in deposition velocities suggests that dry deposition fluxes measured at one point near the lake will have a large uncertainty.

Fluxes measured at one sampling point do not account for the effect of variations of meteorological parameters, particle size and ambient concentrations which occur when the air mass crosses the lake. Further, the deposition velocity of particles over a water surface is affected by the dynamics of water wave breaking and spray formation which are included in estimates reported here through the coefficients K_m and K_{bs} . Based on the comparison of calculated with measured dry deposition fluxes and ambient concentrations, optimal values of K_m and K_{bs} are derived for particles in the size range of 0.5 to 6 μ m. One must be careful, however, not to over-interpret the ratio of the calculated/measured dry deposition flux in the light of the assumptions made in calculating the dry deposition flux in this study. Furthermore, this caution should also be applied when considering that the measured fluxes are from one point on the lake and can not provide statistically meaningful results for the large surface area of Lake Michigan.

The results presented in this work were also compared to those obtained using the Sehmel and Hodgson (1978) model. The total flux ratio (S and H model / this study) obtained for most of the trace metals was in the range of 0.85 to 1.72 with a mean ratio of 1.35. The good agreement suggested by these ratios is surprising considering that the Sehmel and Hodgson (1978) formulation was not originally intended for a water surface, as it does not take into account the effect of wave breaking or spray formation on the transfer of particles from the atmosphere to the water surface and vice versa. On the other hand, in optimizing the K_m and K_{bs} coefficients, the role played by diffusophoretic and
thermophoretic forces on the downward and upward motion of particles was not considered, since direct measurement data are not available to validate the result.

The range in the dry deposition velocity caused by particle size and meteorological conditions and, hence, its influence on the dry deposition flux becomes smaller for particles in the inertial deposition range. Therefore, to account for the effect of all of the previously defined parameters, average values of the dry deposition fluxes calculated along each trajectory crossing Lake Michigan are presented. Figure 8-13 shows the distribution of dry deposition fluxes for several trace metals in the fine and coarse fraction for trajectories crossing Lake Michigan during LMUATS. The dry deposition flux is plotted on a log scale to allow the large variations in flux from element to element to be displayed on the same figure. The average dry deposition fluxes are calculated for each backward and forward trajectory crossing the lake. Table 8-5 gives the average dry deposition flux to Lake Michigan calculated for both fine and coarse particles during the LMUATS period. The dry deposition flux for trace metals typically of crustal or soil origin in the fine fraction ranges from 0.214 μ g/m²-h for K to 0.58 μ g/m²-h for Si, while in the coarse fraction the dry deposition flux ranges from 1.1 μ g/m²-h for K to 8.5 μ g/m²-h for Si. Trace elements primarily of anthropogenic origin associated with fine particles have a dry deposition flux in the range of 0.001 μ g/m²-h for Br and Se to 0.425 μ g/m²-h for S; in the coarse fraction the dry deposition fluxes range from 0.007 μ g/m²-h for Br to 3.3 μ g/m²-h for Al.

Figure 8-13. Dry Deposition Flux for Selected Crustal and Anthropogenic Elements for Backward Trajectories that Traversed Lake Michigan.



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Element	Fine	Coarse
	(< 2.5 µm)	(2.5-10 µm)
Al	0.086	3.3
Si	0.581	7.5
S	0.425	0.82
Κ	0.214	1.1
Ca	0.216	5.5
Cr	0.002	0.01
MN	0.003	0.05
Fe	0.288	3.3
Ni	0.002	0.018
Cu	0.004	0.045
Zen	0.013	0.075
As	0.002	0.010
Se	0.001	0.020
Br	0.001	0.007
Cd	0.003	0.020
Total Hg	0.001	
Pb	0.002	0.022

Table 8-5. Average Dry Deposition Fluxes (µg/m²-h) of Trace Metals to Lake Michigan.

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