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Results of the Lake Michigan Mass Balance Study: Atrazine Data Report

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Great Lakes National Program Office (G-17J)
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Chicago, IL 60604

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Results of the Lake Michigan Mass Balance Study:
Atrazine Data Report

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Executive Summary

The U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO) and partners instituted the Lake Michigan Mass Balance (LMMB) Study to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. The goal of the LMMB Study was to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. Objectives of the study were to: 1) estimate pollutant loading rates, 2) establish a baseline to gauge future progress, 3) predict the benefits associated with load reductions, and 4) further understand ecosystem dynamics. The LMMB Study measured the concentrations of polychlorinated biphenyls (PCBs), *trans*-nonachlor, atrazine, and mercury in the atmosphere, tributaries, lake water, sediments, and food webs of Lake Michigan. This document summarizes the atrazine data collected as part of the LMMB Study, and is one in a series of data reports that documents the project. Future documents will present the results of mass balance modeling.

Atrazine is a triazine herbicide that is widely used in the U.S. to control broadleaf weeds in the production of corn and sorghum. Approximately 64 to 75 million pounds of atrazine are applied per year in the U.S., much of which is used in the "Corn Belt" region that includes the upper midwest surrounding Lake Michigan. Atrazine is generally applied to soil pre-planting or pre-emergence, but is sometimes also applied to the foliage post-emergence. Atrazine can enter surface waters, including Lake Michigan, through runoff, spray drift, discharge of contaminated groundwater to surface water, wet deposition (dissolution of atrazine vapor in rainfall and washout of particulate bound atrazine), dry deposition (dry settling of particulate bound atrazine), and sorption from the vapor phase. For human health protection, EPA has set a maximum contaminant level of 3 μg/L in drinking water. EPA also has set draft ambient aquatic life criteria at 350 μg/L for protection from acute effects and 12 μg/L for protection from chronic effects.

In the LMMB Study, atrazine and atrazine metabolites (deethyl-atrazine [DEA] and deisopropyl-atrazine [DIA]) were measured in atmospheric, tributary water column, and open-lake water column samples. From March 1994 through October 1995, over 1000 samples were collected and analyzed by gas chromatography/mass spectrometry. Atmospheric vapor, particulate, and precipitation samples were collected from eight stations surrounding Lake Michigan and three background stations outside the Lake Michigan basin. Tributary water column samples were collected from 11 tributary rivers that flow into Lake Michigan. Open-lake water column samples were collected from 35 sampling stations in Lake Michigan, 2 stations in Green Bay, and 1 station in Lake Huron. While sediment and biological tissue were sampled for mercury, PCBs, and *trans*-nonachlor, these compartments were not sampled for atrazine, because atrazine is relatively water soluble, degradable, and does not accumulate in these compartments.

Atrazine in Atmospheric Components

The predominant atmospheric source of atrazine, DEA, and DIA measured in this study was precipitation. In atmospheric samples, atrazine was seldom detected in the vapor phase. Only 3.7% of vapor phase samples were above sample-specific detection limits that averaged 32 pg/m^3 and 20.7 pg/m^3 for samples analyzed at the Illinois Water Survey and Indiana University, respectively. Atrazine was more frequently detected in the particulate phase and in precipitation, with 23% and 50% of sample concentrations reported above sample-specific detection limits, respectively. The presence and concentration of atrazine in both the particulate phase and in precipitation was highly seasonal. Atrazine was generally not detectable in atmospheric samples during the fall and winter, but atmospheric concentrations peaked during the spring in connection with the agricultural application of the herbicide. Maximum monthly atrazine concentrations in the particulate phase ranged from 160 pg/m^3 to 1400 pg/m^3 among atmospheric sampling stations, and mean atrazine concentrations during the spring and summer (March 20 through September 23) ranged from 25 pg/m^3 to 370 pg/m^3 among atmospheric sampling stations. In precipitation, maximum monthly atrazine concentrations ranged from 100 ng/L to 2800 ng/L among atmospheric sampling stations, and monthly volume-weighted mean concentrations during the spring and summer ranged from 19 ng/L to 120 ng/L among atmospheric sampling stations. Concentrations of atrazine metabolites (DEA and DIA) were well correlated with atrazine concentrations and generally followed the same patterns.

In general, atrazine in the particulate phase was higher at atmospheric sampling stations surrounding the southern Lake Michigan basin than at those stations surrounding the northern basin. This is consistent with agricultural land use that decreases in intensity from south to north in the Lake Michigan region. Atrazine concentrations in precipitation were less reflective of local land use conditions and suggest long-range transport of the herbicide in addition to local inputs. Atrazine concentrations in precipitation were not consistently higher surrounding the southern Lake Michigan basin, and in fact, atrazine concentrations in precipitation were often higher at remote sampling stations in the far north than at stations surrounding the southern basin.

Atrazine in Tributaries

Atrazine was detected above the method detection limit of 1.25 ng/L in 99% of tributary samples. Maximum atrazine concentrations in Lake Michigan tributaries ranged from 6.4 ng/L in the Manistique River to 2700 ng/L in the St. Joseph River, and mean atrazine concentrations ranged from 3.7 ng/L to 350 ng/L in these same two rivers, respectively. Concentrations of atrazine in tributaries were strongly influenced by geographical location and corn crop acerage. Mean atrazine concentrations in the Manistique, Pere Marquette, and Menominee Rivers were statistically lower than in the remaining eight measured tributaries except for the Muskegon River. The watersheds of these three tributaries are more forested and contain fewer agricultural influences than the other monitored tributaries. Atrazine concentrations were highest in the St. Joseph, Grand, and Kalamazoo Rivers, where agricultural influences were much stronger and atrazine use rates were 52 to over 160 lbs/mi^2. For these three tributaries with the highest atrazine levels, distinct peaks in atrazine were observed in mid to late May, corresponding with the agricultural application of the herbicide. Distinct seasonal patterns of atrazine concentrations were not observed for the other tributaries. Concentrations of atrazine metabolites (DEA and DIA) in tributaries were well correlated with atrazine concentrations and generally followed the same patterns.

Atrazine in the Open-lake Water Column

Within Lake Michigan, atrazine concentrations in open-lake water column samples were relatively consistent. Average atrazine concentrations at open-lake sampling stations within Lake Michigan ranged from 33.0 to 48.0 ng/L. Atrazine concentrations within Lake Michigan were statistically greater than those measured at the reference station on Lake Huron and were statistically lower than concentrations measured at one Green Bay sampling station. Because the open lake was well-mixed with respect to atrazine, lake-wide averages could be calculated. Over the course of the study, lake-wide average atrazine concentrations increased from 37.0 ng/L in April/May 1994 to 39.7 ng/L in March/April 1995. During this same time period, DEA concentrations increased by 14.9% and DIA concentrations increased by 54.0%. While atrazine concentrations increased slightly during the study, open-lake average atrazine levels remained more than 50 times below the maximum contaminant level for drinking water and more than 300 times less than the proposed ambient water quality criterion for protection of aquatic life from chronic effects.

Chapter 1
Project Overview

The U.S. Environmental Protection Agency's Great Lakes National Program Office (GLNPO) and partners instituted the Lake Michigan Mass Balance (LMMB) Study to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. The LMMB Study measured the concentrations of polychlorinated biphenyls (PCBs), *trans*-nonachlor, atrazine, and mercury in the atmosphere, tributaries, lake water, sediments, and food webs of Lake Michigan. This document summarizes the atrazine data collected as part of the LMMB Study, and is one in a series of data reports that documents the project. Future documents will present the results of mass balance modeling.

1.1 Background

The Great Lakes, which contain 20% of the world's freshwater, are a globally important natural resource that are currently threatened by multiple stressors. While significant progress has been made to improve the quality of the lakes, pollutant loads from point, non-point, atmospheric, and legacy sources continue to impair ecosystem functions and limit the attainability of designated uses of these resources. Fish consumption advisories and beach closings continue to be issued, emphasizing the human health concerns from lake contamination. Physical and biological stressors such as invasion of non-native species and habitat loss also continue to threaten the biological diversity and integrity of the Great Lakes.
The United States and Canada have recognized the significance and importance of the Great Lakes as a natural resource and have taken steps to restore and protect the lakes. In 1978, both countries signed the Great Lakes Water Quality Agreement (GLWQA). This agreement calls for the restoration and maintenance of the chemical, physical, and biological integrity of the Great Lakes by developing plans to monitor and limit pollutant flows into the lakes.

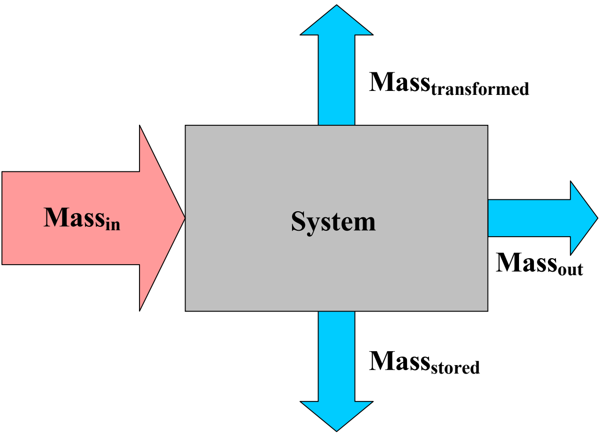
The GLWQA, as well as Section 118(c) of the Clean Water Act, required the development of Lake-wide Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing inputs of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. To assist in developing these LaMPs and to monitor progress in pollutant reduction, Federal, State, Tribal, and local entities have instituted Enhanced Monitoring Plans. Monitoring is essential to the development of baseline conditions for the Great Lakes and provides a sound scientific base of information to guide future toxic load reduction efforts.

The LMMB Study is a part of the Enhanced Monitoring Plan for Lake Michigan. The LMMB Study was a coordinated effort among Federal, State, and academic scientists to monitor tributary and atmospheric pollutant loads, develop source inventories of toxic substances, and evaluate the fates and effects of these pollutants in Lake Michigan. A mass balance modeling approach provides the predictive ability to determine the environmental benefits of specific load reduction scenarios for toxic substances and the time required to realize those benefits. This predictive ability will allow Federal, State, Tribal, and local agencies to make more informed load reduction decisions.

1.2 Description

The LMMB Study used a mass balance approach to evaluate the sources, transport, and fate of contaminants in the Lake Michigan ecosystem. A mass balance approach is based on the law of conservation of mass, which states that the amount of a pollutant accumulating in a system is equal to the amount entering the system, less the amount of that pollutant leaving or chemically changed in the system. If the system is defined as the Lake Michigan/Green Bay water column, then pollutants may enter the system via tributaries, direct runoff, the atmosphere (wet deposition, dry deposition, and sorption from the vapor phase), the sediment, and the Straits of Mackinac. Pollutants may leave the system through volatilization to the atmosphere, loss to the sediment, or discharge through the Straits of Mackinac and the Chicago water diversion. The law of conservation of mass also can be applied to other systems such as biota, sediment, or air.

What is Mass Balance?



$$Mass_{in} = Mass_{transformed} + Mass_{stored} + Mass_{out}$$

The LMMB Study measured contaminant concentrations in various inputs and ecosystem compartments over spatial and temporal scales. Mathematical models that track the transport and fate of contaminants within Lake Michigan are being developed and calibrated using these field data. The LMMB Study is the first lake-wide application of a mass balance determination for toxics in the Great Lakes and will serve as the basis of future mass budget/mass balance efforts.

1.3 Scope

1.3.1 Modeled Pollutants

When EPA published the *Water Quality Guidance for the Great Lakes System* (58 FR 20802), the Agency established water quality criteria for 29 pollutants. Those criteria are designed to protect aquatic life, terrestrial wildlife, and human health. PCBs, *trans*-nonachlor, and mercury are included in the list of 29 pollutants. The water quality criteria and values proposed in the guidance apply to all of the ambient waters of the Great Lakes system, regardless of the sources of pollutants in those waters. The proposed criteria provide a uniform basis for integrating Federal, State, and Tribal efforts to protect and restore the Great Lakes ecosystem.

The number of pollutants that can be intensively monitored and modeled in the Great Lakes system is limited by the resources available to collect and analyze thousands of samples, assure the quality of the results, manage the data, and develop and calibrate the necessary models. Therefore, the LMMB Study focused on constructing mass balance models for a limited group of pollutants. PCBs, *trans*-nonachlor, atrazine, and mercury were selected for inclusion in the LMMB Study because these pollutants currently or potentially pose a risk to aquatic and terrestrial organisms (including humans) in the Lake Michigan ecosystem. These pollutants also were selected to cover a wide range of chemical and physical properties and represent other classes of compounds which pose current or potential problems. Once a mass budget for selected pollutants is established and a mass balance model is calibrated, additional contaminants can be modeled with limited data and future resources can be devoted to activities such as emission inventories and dispersion modeling.

1.3.1.1 Polychlorinated Biphenyls

PCBs are a class of man-made, chlorinated, organic chemicals that include 209 congeners, or specific PCB compounds. The highly stable, nonflammable, non-conductive properties of these compounds have made them useful in a variety of products including electrical transformers and capacitors, plastics, rubber, paints, adhesives, and sealants. PCBs were produced for such industrial uses in the form of complex mixtures under the trade name "Aroclor" and were commercially available from 1930 through 1977, when EPA banned their production due to environmental and public health concerns. PCBs also may be produced by combustion processes, including incineration, and can be found in stack emissions and ash from incinerators.

Seven Aroclor formulations were included in the Priority Pollutant List developed by the EPA Office of Water under the auspices of the Clean Water Act because they were found by EPA in the effluents from one or more wastewater treatment facilities. Aroclors may have entered the Great Lakes through other means, including spills or improper disposal of transformer fluids, contaminated soils washing into the watershed, or discharges from ships. The PCBs produced by combustion processes may be released to the atmosphere, where they are transported in both vapor and particulate phases and enter the lakes through either dry deposition or precipitation events (e.g., rain).

The stability and persistence of PCBs, which made them useful in industrial applications, have also made these compounds ubiquitous in the environment. PCBs do not readily degrade and thus accumulate in water bodies and aquatic sediments. PCBs also bioaccumulate, or buildup, in living tissues. Levels of PCBs in some fish from Lake Michigan exceed U.S. Food and Drug Administration tolerances, prompting closure of some commercial fisheries and issuance of fish consumption advisories. PCBs are a probable human carcinogen, and human health effects of PCB exposure include stomach, kidney, and liver damage, liver and biliary tract cancer, and reproductive effects, including effects on the fetus after exposure of the mother.

PCB congeners exhibit a wide range of physical and chemical properties (e.g., vapor pressures, solubilities, boiling points), are relatively resistant to degradation, and are ubiquitous. These properties make them ideal surrogates for a wide range of organic compounds from anthropogenic sources.

In the LMMB Study, PCBs were selected as a model for conservative organic compounds (USEPA, 1997c).

1.3.1.2 Trans-Nonachlor

Trans-nonachlor is a component of the pesticide chlordane. Chlordane is a mixture of chlorinated hydrocarbons that was manufactured and used as a pesticide from 1948 to 1988. Prior to 1983, approximately 3.6 million pounds of chlordane were used annually in the U.S. In 1988, EPA banned all production and use of chlordane in the U.S.

Like PCBs, chlordane is relatively persistent and bioaccumulative. *Trans*-nonachlor is the most bioaccumulative of the chlordanes. *Trans*-nonachlor is a probable human carcinogen. Other human health effects include neurological effects, blood dyscrasia, hepatoxicity, immunotoxicity, and endocrine system disruption.

Historically, *trans*-nonachlor may have entered the Great Lakes through a variety of means related to the application of chlordane, including improper or indiscriminate application, improper cleaning and disposal of pesticide application equipment, or contaminated soils washing into the watershed.

In the LMMB Study, *trans*-nonachlor was selected as a model for the cyclodiene pesticides (USEPA, 1997c).

1.3.1.3 Atrazine

Atrazine is a herbicide based on a triazine ring structure with three carbon atoms alternating with three nitrogen atoms. Atrazine is the most widely used herbicide in the U.S. for corn and sorghum production. Atrazine has been used as an agricultural herbicide since 1959, and 64 to 75 million pounds of atrazine are used annually in the U.S. Atrazine is extensively used in the upper Midwest, including the Lake Michigan watershed, where it is primarily associated with corn crops.

Unlike PCBs and *trans*-nonachlor, atrazine is not extremely persistent or bioaccumulative. Atrazine is moderately susceptible to biodegradation, with a half-life in soils of about 60-150 days. Atrazine may persist considerably longer in water and is relatively non-reactive in the atmosphere. Atrazine rarely exceeds the maximum contaminant level (MCL) set by USEPA as a drinking water standard, but localized peak values can exceed the MCL following rainfall events after atrazine application. Atrazine can cause human health effects such as weight loss, cardiovascular damage, muscle and adrenal degeneration, and congestion of heart, lungs, and kidneys. Atrazine is also toxic to aquatic plants.

In the LMMB Study, atrazine was selected as a model for more reactive, biodegradable compounds in current use (USEPA, 1997c).

1.3.1.4 Mercury

Mercury is a naturally-occurring toxic metal. Mercury is used in battery cells, barometers, thermometers, switches, fluorescent lamps, and as a catalyst in the oxidation of organic compounds. Global releases of mercury in the environment are both natural and anthropogenic (caused by human activity). It is estimated that about 5,500 metric tons of mercury are released annually to the air, soil, and water from anthropogenic and natural sources (USEPA 1997e). These sources include combustion of various fuels such as coal; mining, smelting and manufacturing activities; wastewater; agricultural, animal and food wastes.

As an elemental metal, mercury is extremely persistent in all media. Mercury also bioaccumulates with reported bioconcentration factors in fish tissues in the range of 63,000 to 100,000. Mercury is a possible human carcinogen and causes the following human health effects: stomach, large intestine, brain, lung, and kidney damage; blood pressure and heart rate increase, and fetus damage.

In the LMMB Study, mercury was selected as a model for bioaccumulative metals (USEPA, 1997c).

Table 1-1. Characteristics of Lake Michigan Mass Balance Modeled Pollutants

Pollutant	Sources	Uses	Toxic Effects	Bioconcentration Factor[a]	EPA Regulatory Standards[b]
PCBs	• Waste incinerators (unintentional byproducts of combustion) • Industrial dischargers • Electrical power	• Electrical transformers and capacitors • Carbonless copy paper • Plasticizers • Hydraulic fluids	• Probable human carcinogen • Hearing and vision impairment • Liver function alterations • Reproductive impairment and deformities in fish and wildlife	1,800 to 180,000	MCL = 0.5 µg/L CCC = 14 ng/L HH = 0.17 ng/L
trans-Nonachlor[c]	• Application to crops and gardens	• Pesticide on corn and citrus crops • Pesticide on lawns and gardens	• Probable human carcinogen • Nervous system effects • Blood system effects • Liver, kidney, heart, lung, spleen, and adrenal gland damage	4,000 to 40,000	MCL = 2 µg/L CMC = 2.4 µg/L CCC = 4.3 ng/L HH = 2.1 ng/L
Atrazine	• Application to crops	• Herbicide for corn and sorghum production	• Weight loss • Cardiovascular damage • Muscle and adrenal degeneration • Congestion of heart, lungs, and kidneys • Toxic to aquatic plants	2 to 100	MCL = 3 µg/L CMC[d] = 350 µg/L CCC[d] = 12 µg/L
Mercury	• Waste disposal • Manufacturing processes • Energy production • Ore processing • Municipal and medical waste incinerators • Chloralkali factories • Fuel combustion	• Battery cells • Barometers • Dental fillings • Thermometers • Switches • Fluorescent lamps	• Possible human carcinogen • Damage to brain and kidneys • Adverse affects on the developing fetus, sperm, and male reproductive organs	63,000 to 100,000	MCL = 2 µg/L CMC = 1.4 µg/L CCC = 0.77 µg/L HH = 50 ng/L FWA[e] = 2.4 µg/L FWC[e] = 12 ng/L Wildlife[f] = 1.3 ng/L

[a] From: USEPA. 1995a. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Inorganic Chemicals, Technical Version*. EPA 811/F-95/002-T. U.S. Environmental Protection Agency, Office of Water, Washington, D.C.; and USEPA. 1995b. *National Primary Drinking Water Regulations, Contaminant Specific Fact Sheets, Synthetic Organic Chemicals, Technical Version*. EPA 811/F-95/003-T. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[b] MCL = Maximum Contaminant Level for drinking water. CMC = Criterion Maximum Concentration for protection of aquatic life from acute toxicity. CCC = Criterion Continuous Concentration for protection of aquatic life from chronic toxicity. HH = water quality criteria for protection of human health from water and fish consumption. Data from: USEPA. 1999. *National Recommended Water Quality Criteria-Correction*. EPA 822/Z-99/001. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[c] Characteristics presented are for chlordane. *trans*-nonachlor is a principle component of the pesticide chlordane.

[d] Draft water quality criteria for protection of aquatic life. From: USEPA. 2001a. *Ambient Aquatic Life Water Quality Criteria for Atrazine*. U.S. Environmental Protection Agency, Office of Water, Washington, DC.

[e] FWA = Freshwater acute water quality criterion. FWC = Freshwater chronic water quality criterion. From National Toxics Rule (58 FR 60848).

[f] Wildlife criterion. From the Stay of Federal Water Quality Criteria for Metals (60 FR 22208), 40 CFR 131.36 and the Water Quality Guidance for the Great Lakes System (40 CFR 132).

1.3.2 Other Measured Parameters

In addition to the four chemicals modeled in the LMMB Study, many other chemicals and parameters were measured in the LMMB Study as part of the Enhanced Monitoring Program. A survey of these chemicals and parameters will aid in understanding the overall ecological integrity of Lake Michigan. These additional parameters include various biological indicators, meteorological parameters, and organic, metal, and conventional chemicals in Lake Michigan. A complete listing of all parameters included in this study is provided in Table 1-2.

Table 1-2. Lake Michigan Mass Balance Study Parameters

Organics	
acenaphthene	*p,p'*-DDT
acenaphthylene	endosulfan sulfate
aldrin	endosulfan I
anthracene	endosulfan II
atrazine	endrin
α-BHC	endrin aldehyde
β-BHC	endrin ketone
δ-BHC	fluoranthene
γ-BHC (Lindane)	fluorene
benzo[*a*]anthracene	heptachlor
benzo[*g,h,i*]perylene	heptachlor epoxide
benzo[*b*]fluoranthene	hexachlorobenzene (HCB)
benzo[*k*]fluoranthene	indeno[1,2,3-*cd*]pyrene
benzo[*e*]pyrene	mirex
benzo[*a*]pyrene	*trans*-nonachlor
α-chlordane	oxychlordane
γ-chlordane	PCB congeners
chrysene	phenanthrene
coronene	pyrene
p,p'-DDE	retene
p,p'-DDD	toxaphene
Metals	
aluminum	magnesium
arsenic	manganese
calcium	sodium
cadmium	nickel
chromium	lead
cesium	selenium
copper	thorium
iron	titanium
mercury	vanadium
potassium	zinc

Table 1-2. Lake Michigan Mass Balance Study Parameters

Conventionals	
alkalinity	particulate organic carbon
ammonia	percent moisture
bromine	pH
chloride	phosphorous
chlorine sulfate	silica
conductivity	silicon
dissolved organic carbon	temperature
dissolved oxygen	total Kjeldahl nitrogen
dissolved phosphorous	total organic carbon
dissolved reactive silica	total phosphorous
dry weight fraction	total suspended particulates
elemental carbon	total hardness
nitrate	turbidity
ortho-phosphorous	
Biologicals	
fish species	fish weight
fish age	fish length
fish maturity	fish taxonomy
chlorophyll *a*	fish diet analysis
fish lipid amount	primary productivity
Meteorological	
air temperature	wind direction
relative humidity	wind speed
barometric pressure	visibility
weather conditions	wave height and direction

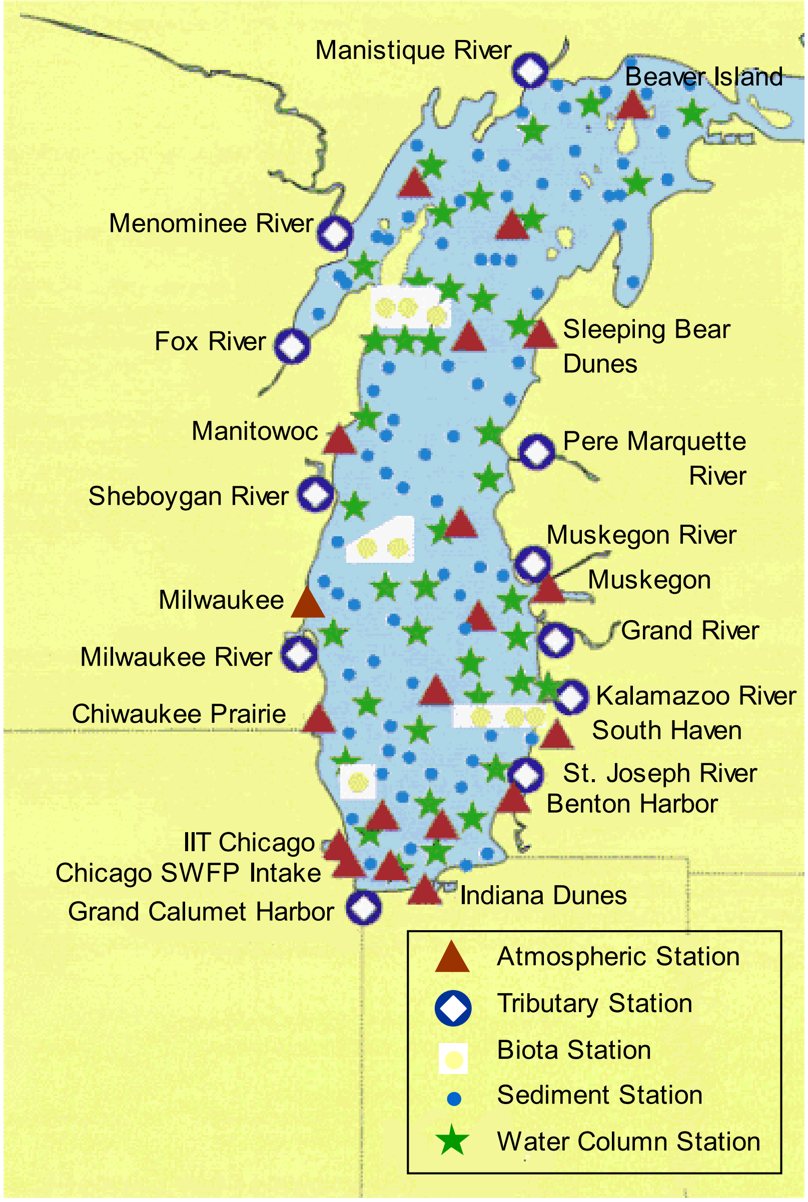
1.3.3 Measured Compartments

In the LMMB Study, contaminants were measured in the following compartments:

- **Open-Lake Water Column** — The water column in the open lake was sampled and analyzed for the modeled pollutants
- **Tributaries** — Tributary water columns were sampled and analyzed for the modeled pollutants
- **Fish** — Top predators and forage base species were sampled and analyzed for diet analysis and contaminant burden. Fish were not analyzed for atrazine, because atrazine is not bioaccumulative.
- **Lower Pelagic Food Web** — Phytoplankton and zooplankton were sampled and analyzed for species diversity, taxonomy, and contaminant burden. The lower pelagic food web was not analyzed for atrazine, because atrazine is not bioaccumulative.
- **Sediments** — Cores were collected and trap devices were used to collect Lake Michigan sediment for determination of contaminants and sedimentation rates. Sediments were not analyzed for atrazine, because atrazine is relatively water soluble, degradable, and does not generally accumulate in sediments.
- **Atmosphere** — Vapor, particulate, and precipitation phase samples were collected and analyzed for the modeled pollutants

For the modeled pollutants, more than 20,000 samples were collected and analyzed, including more than 9000 quality control (QC) samples, at more than 300 sampling locations (Figure 1-1). Field data collection activities were initially envisioned as a one-year effort. However, it became evident early into the project that a longer collection period would be necessary to provide a full year of concurrent information on contaminant loads and ambient concentrations for modeling purposes. Therefore, field sampling occurred from April, 1994 to October, 1995.

Figure 1-1. Lake Michigan Mass Balance Study Sampling Locations



1.4 Objectives

The goal of the LMMB Study was to develop a sound, scientific base of information to guide future toxic load reduction efforts at the Federal, State, Tribal, and local levels. To meet this goal, the four following LMMB Study objectives were developed:

- **Estimate pollutant loading rates** — Environmental sampling of major media will allow estimation of relative loading rates of critical pollutants to the Lake Michigan Basin.
- **Establish baseline** — Environmental sampling and estimated loading rates will establish a baseline against which future progress and contaminant reductions can be gauged.
- **Predict benefits associated with load reductions** — The completed mass balance model will provide a predictive tool that environmental decision-makers and managers may use to evaluate the benefits of specific load reduction scenarios.
- **Understand ecosystem dynamics** — Information from the extensive LMMB monitoring and modeling efforts will improve our scientific understanding of the environmental processes governing contaminant cycling and availability within relatively closed ecosystems.

1.5 Design

1.5.1 Organization

The Great Lakes National Program Office proposed a mass balance approach to provide coherent, ecosystem-based evaluation of toxics in Lake Michigan. GLNPO served as the program sponsor for the LMMB Study. GLNPO formed two committees to coordinate study planning, the Program Steering Committee and the Technical Coordinating Committee. These committees were comprised of scientists from Federal, State, academic, and commercial institutions (see Section 1.5.2, Study Participants). The committees administered a wide variety of tasks including: planning the project, locating the funding, designing the sample collection, coordinating sample collection activities, locating qualified laboratories, coordinating analytical activities, assembling the data, assuring the quality of the data, assembling skilled modelers, developing the models, and communicating interim and final project results. The National Exposure Research Laboratory (NERL) at Duluth, in cooperation with the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory and the Atmospheric Sciences Modeling Division are supporting the modeling component of the mass balance study by developing a suite of integrated mass balance models to simulate the transport, fate, and bioaccumulation of the study target analytes.

1.5.2 Study Participants

The LMMB Study was a coordinated effort among Federal, State, academic, and commercial institutions. The following agencies and organizations have all played roles in ensuring the success of the LMMB Study. Except for the three organizations indicated with an asterisk (*), all of the participants were members of the LMMB steering committee.

Federal and International

- USEPA Great Lakes National Program Office (*Program Sponsor*)
- USEPA Region 5 Water Division
- USEPA Office of Research and Development — Large Lakes Research Station
- USEPA Atmospheric Research and Environmental Analysis Lab
- US Geological Survey
- US Fish and Wildlife Service
- US Department of Energy
- National Oceanic and Atmospheric Administration
- USEPA Office of Air and Radiation*
- USEPA Office of Water*
- Environment Canada*

State

- Illinois Department of Natural Resources
- Illinois Water Survey
- Indiana Department of Environmental Management
- Michigan Department of Environmental Quality
- Wisconsin Department of Natural Resources
- Wisconsin State Lab of Hygiene

Academic and Commercial

- Indiana University
- Rutgers University
- University of Maryland
- University of Michigan
- University of Minnesota
- University of Wisconsin
- Battelle Labs
- Grace Analytical

1.5.3 Workgroups

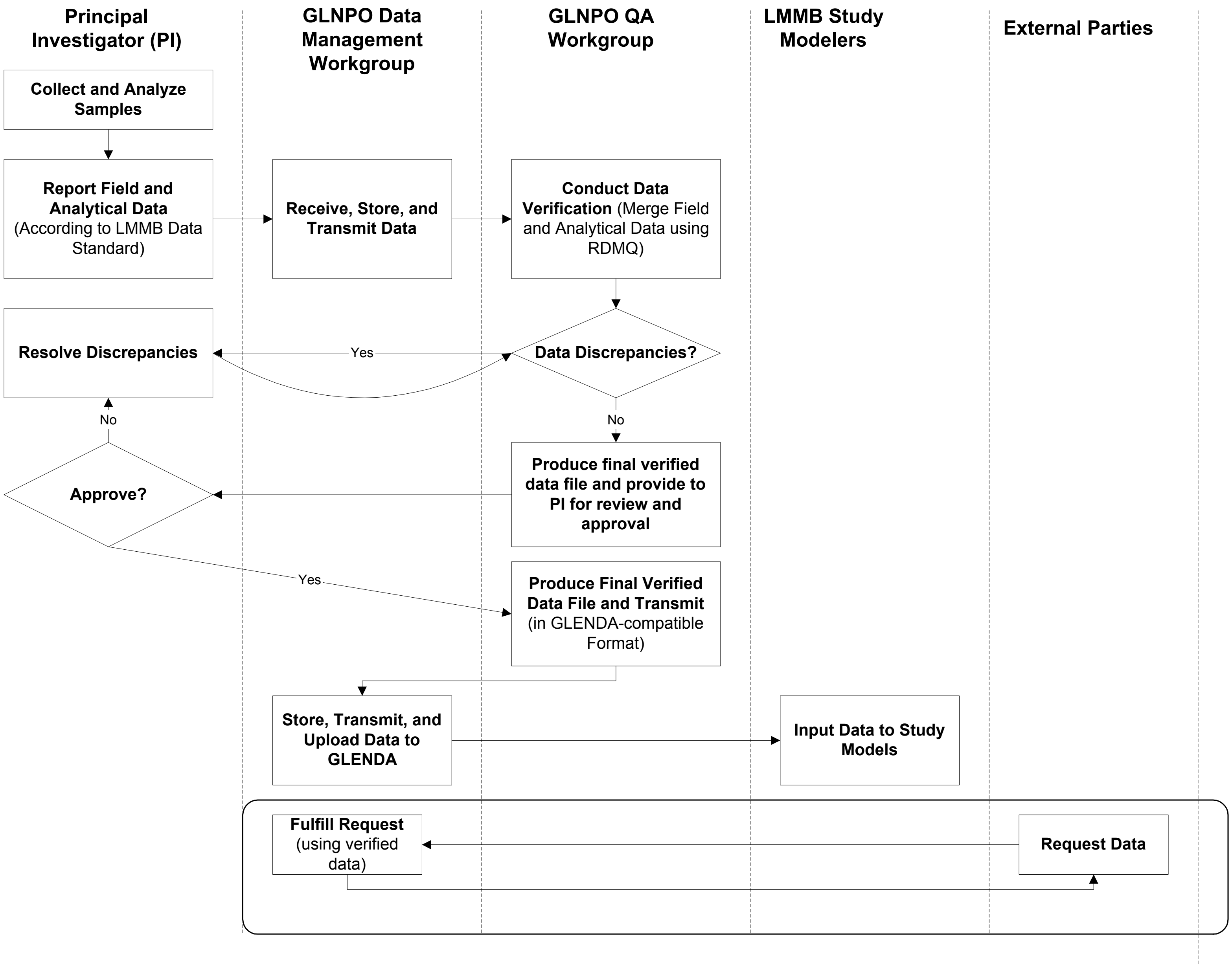
Eleven workgroups were formed to provide oversight and management of specific project elements. The workgroups facilitated planning and implementation of the study in a coordinated and systematic fashion. The workgroups communicated regularly through participation in monthly conference calls and annual "all-hands" meetings. Workgroup chairs were selected and were responsible for managing tasks under the purview of the workgroup and communicating the status of activities to other workgroups. The workgroups and workgroup chairs are listed below.

- Program Steering Committee — Paul Horvatin
- Technical Coordinating Committee — Paul Horvatin
- Modeling Workgroup — William Richardson
- Air Monitoring Workgroup — Jackie Bode
- Biota Workgroup — Paul Bertram and John Gannon
- Chemistry Workgroup — David Anderson
- Data Management Workgroup — Kenneth Klewin and Philip Strobel
- Lake Monitoring Workgroup — Glenn Warren
- Tributary Monitoring Workgroup — Gary Kohlhepp and Robert Day
- Quality Assurance Workgroup — Louis Blume and Michael Papp
- Sediment Monitoring Workgroup — Brian Eadie

1.5.4 Information Management

As program sponsor, GLNPO managed information collected during the LMMB Study. Principal investigators (PIs) participating in the study reported field and analytical data to GLNPO. GLNPO developed a data standard for reporting field and analytical data and a database for storing and retrieving study data. GLNPO also was responsible for conducting data verification activities and releasing verified data to the study modelers and the public. The flow of information is illustrated in Figure 1-2.

Figure 1-2. Flow of Information in the Lake Michigan Mass Balance Study



1.5.4.1 Data Reporting

More than twenty organizations produced LMMB data through the collection and analysis of more than 20,000 samples. In the interest of standardization, specific formats (i.e., file formats and codes to represent certain data values) were established for reporting LMMB data. Each format specified the "rules" by which data were submitted, and, in many cases, the allowable values by which they were to be reported. The data reporting formats were designed to capture all pertinent sampling and analytical information from the field crews and laboratory analysts. Data reporting formats and the resulting Great Lakes Environmental Monitoring Database (GLENDA, see Section 1.5.4.2,) were designed to be applicable to projects outside the LMMB as well. For the LMMB Study, special conditions were applied for reporting analytical results. Because the data were being used for input to study models, principal investigators were asked to report analytical results as measured even when measurements were below estimated detection limits. The quality assurance program discussed in Section 1.5.5 included identifying (i.e., flagging) all analytical results that were below estimated detection limits.

Principal investigators (including sampling crews and the analytical laboratories) supplied sample collection and analysis data following the standardized reporting formats if possible. LMMB data were then processed through an automated SAS-based data verification system, Research Data Management and Quality Control System (RDMQ), for quality assurance/quality control checking. After verification and validation by the PI, the datasets were output in a form specific for upload to GLENDA. Finally, these datasets were uploaded to GLENDA.

1.5.4.2 Great Lakes Environmental Monitoring Database

Central to the data management effort is a computerized database system to house LMMB Study and other project results. That system, the Great Lakes Environmental Monitoring Database (GLENDA), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

Development of GLENDA began in 1993 with a logical model based on the modernized STORET concept and requirements analysis. GLENDA was developed with the following guiding principles:

- **True multi-media scope** — water, air, sediment, taxonomy, fish tissue, fish diet, and meteorology data can all be housed in the database
- **Data of documented quality** — data quality is documented by including results of quality control parameters
- **Extensive contextual indicators** — ensures data longevity by including enough information to allow future or secondary users to make use of the data
- **Flexible and expandable** — the database is able to accept data from any Great Lakes monitoring project
- **National compatibility** — GLENDA is compatible with STORET and allows ease of transfer between these large databases

In an effort to reduce the data administration burden and ensure consistency of data in this database, GLNPO developed several key tools. Features including standard data definitions, reference tables, standard automated data entry applications, and analytical tools are (or will soon be) available.

1.5.4.3 Public Access to LMMB Data

All LMMB data that have been verified (through the QC process) and validated (accepted by the PI) are available to the public. Currently, GLNPO requires that written requests be made to obtain LMMB data.

The datasets are available in several formats including WK1, DBF, and SD2. More information about the datasets is available on the LMMB web site at: http://www.epa.gov/glnpo/lmmb/datafaqs.html.

The primary reason for requiring an official request form for LMMB data is to keep track of requests. This allows GLNPO to know how many requests have been made, who has requested data, and what use they intend for the data. This information assists GLNPO in managing and providing public access to Great Lakes data and conducting public outreach activities. As of November 2000, 38 requests for LMMB data have been made: 8 from EPA, 5 from other federal agencies, 5 from state agencies, 5 from universities, 10 from consultants, 3 from international agencies, and 2 from non-profit or other groups. In the future, after all data are verified and validated, GLNPO intends to make condensed versions of the datasets available on the LMMB web site for downloading. This will allow easy public access to LMMB data.

Additional details of the information management for the LMMB study can be found in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i).

1.5.5 Quality Assurance Program

At the outset of the LMMB Study, managers recognized that the data gathered and the models developed from the study would be used extensively by decision makers responsible for making environmental, economic, and policy decisions. Environmental measurements are never true values and always contain some level of uncertainty. Decision makers, therefore, must recognize and be sufficiently comfortable with the uncertainty associated with data on which their decisions are based. In recognition of this requirement, LMMB Study managers established a QA program goal of ensuring that data produced under the LMMB Study would meet defined standards of quality with a specified level of confidence.

The QA program prescribed minimum standards to which all organizations collecting data were required to adhere. Data quality was defined, controlled, and assessed through activities implemented within various parameter groups (e.g., organic, inorganic, and biological parameters). QA activities included the following:

- **QA Program** — Prior to initiating data collection activities, plans were developed, discussed, and refined to ensure that study objectives were adequately defined and to ensure that all QA activities necessary to meet study objectives were considered and implemented.
- **QA Workgroup** — EPA established a QA Workgroup whose primary function was to ensure that the overall QA goals of the study were met.
- **QA Project Plans (QAPPs)** — EPA worked with PIs to define program objectives, data quality objectives (DQOs), and measurement quality objectives (MQOs) for use in preparing QAPPs. Principal investigators submitted QAPPs to EPA for review and approval. EPA reviewed each QAPP for required QA elements and soundness of planned QA activities.
- **Training** — Before data collection activities, PIs conducted training sessions to ensure that individuals were capable of properly performing data collection activities for the LMMB Study.
- **Monthly Conference Calls and Annual Meetings** — EPA, PIs, and support contractors participated in monthly conference calls and annual meetings to discuss project status and objectives, QA issues, data reporting issues, and project schedules.
- **Standardized Data Reporting Format** — Principal investigators were required to submit all data in a standardized data reporting format that was designed to ensure consistency in reporting and facilitate data verification, data validation, and database development.
- **Intercomparison Studies** — EPA conducted studies to compare performance among different PIs analyzing similar samples. The studies were used to evaluate the comparability and accuracy of program data.

- **Technical Systems Audits** — During the study, EPA formally audited each PI's laboratory for compliance with their QAPPs, the overall study objectives, and pre-determined standards of good laboratory practice.
- **Data Verification** — PIs and EPA evaluated project data against pre-determined MQOs and DQOs to ensure that only data of acceptable quality would be included in the program database.
- **Statistical Assessments** — EPA made statistical assessments of the LMMB study data to estimate elements of precision, bias, and uncertainty.
- **Data Validation** — EPA and modelers are evaluating the data against the model objectives.

Comparability of data among PIs participating in the LMMB Study was deemed to be important for successful completion of the study. Therefore, Measurement Quality Objectives (MQOs) for several data attributes were developed by the PIs and defined in the QAPPs. MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. MQOs were defined in terms of six attributes:

- **Sensitivity/Detectability** — The determination of the low-range critical value that a method-specific procedure can reliably discern for a given pollutant. Sensitivity measures included, among others, method detection limits (MDLs) as defined at 40 CFR Part 136, system detection limits (SDLs), or instrument detection limits (IDLs).
- **Precision** — A measure of the degree to which data generated from replicate or repetitive measurements differ from one another. Analysis of duplicate samples was used to assess precision.
- **Bias** — The degree of agreement between a measured and actual value. Bias was expressed in terms of the recovery of an appropriate standard reference material or spiked sample.
- **Completeness** — The measure of the number of samples successfully analyzed and reported compared to the number that were scheduled to be collected.
- **Comparability** — The confidence with which one data set can be compared to other data sets.
- **Representativeness** — The degree to which data accurately and precisely represent characteristics of a population, parameter variations at a sampling point, a process condition, or an environmental condition.

The PI-defined MQOs also were used as the basis for the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for conducting review of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If a result failed to meet predefined criteria, the QC Coordinator contacted the PI to discuss the result, verify that it was correctly reported, and determine if corrective actions were feasible. If the result was correctly reported and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Data that met all predefined requirements were flagged to indicate that the results had been verified and were determined to meet applicable MQOs. In this way, every data point was assigned one or more validity flags based on the results of the QC checks. GLNPO also derived data quality assessments for each LMMB study dataset for a subset of the attributes listed above, specifically sensitivity, precision, and bias. The LMMB study modelers and the Large Lakes Research Station Database Manager also perform data quality assessments prior to inputting data into study models. Such activities include verifying the readability of electronic files, identifying missing data, checking units, and identifying outliers. A detailed description of the quality assurance program is included in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i). A brief summary of quality implementation and assessment is provided in each of the following chapters.

1.6 Project Documents and Products

During project planning, LMMB participants developed study tools including work plans, a methods compendium, quality assurance project plans, and data reporting standards. Through these tools, LMMB participants documented many aspects of the study including information management and quality assurance procedures. Many of these documents are available on GLNPO's website at http://www.epa.gov/glnpo/lmmb.

LMMB Work Plan

Designers of the LMMB Study have documented their approach in a report entitled *Lake Michigan Mass Budget/Mass Balance Work Plan* (USEPA, 1997c). The work plan describes the essential elements of a mass balance study and the approach used to measure and model these elements in the Lake Michigan system. This document was developed based upon the efforts of many Federal and State scientists and staff who participated in the initial planning workshop, as well as PIs.

Quality Assurance Program/Project Plans

The Lake Michigan Mass Balance Project Quality Assurance Plan for Mathematical Modeling, Version 3.0 (USEPA, 1998) documents the quality assurance process for the development and application of LMMB models, including hydrodynamic, sediment transport, eutrophication, transport chemical fate, and food web bioaccumulation models.

The Enhanced Monitoring Program Quality Assurance Program Plan

The Enhanced Monitoring Program Quality Assurance Program Plan (USEPA, 1997d) was developed in 1993 to ensure that data generated from the LMMB study supports its intended use.

LMMB Methods Compendium

The *Lake Michigan Mass Balance Project (LMMB) Methods Compendium* (USEPA, 1997a, 1997b) describes the sampling and analytical methods used in the LMMB Study. The entire three volumes are available on GLNPO's website mentioned above.

LMMB Data Reporting Formats and Data Administration Plan

Data management for the LMMB Study was a focus from the planning stage through data collection, verification, validation, reporting, and archiving. The goal of consistent and compatible data was a key to the success of the project. The goal was met primarily through the development of standard formats for reporting environmental data. The data management philosophy is outlined on the LMMB website mentioned above.

Lake Michigan LaMP

"Annex 2" of the 1972 Canadian-American Great Lakes Water Quality Agreement (amended in 1978, 1983, and 1987) prompted development of Lakewide Area Management Plans (LaMPs) for each Great Lake. The purpose of these LaMPs is to document an approach to reducing input of critical pollutants to the Great Lakes and restoring and maintaining Great Lakes integrity. The Lake Michigan LaMP calls for basin-wide management of toxic chemicals.

GLENDA Database

Central to the data management effort is a computerized data system to house Lake Michigan Mass Balance and other project results. That system, the Great Lakes Environmental Monitoring Database (GLENDA), was developed to provide data entry, storage, access and analysis capabilities to meet the needs of mass balance modelers and other potential users of Great Lakes data.

LMMB Data Reports

This report is one in a series of data reports that summarize the data from monitoring associated with EPA's Lake Michigan Mass Balance Study. In addition to this data report on atrazine, data reports are being published for PCBs and *trans*-nonachlor (USEPA, 2001f) and mercury (USEPA, 2001g).

Future Documents and Products

Following the completion of modeling efforts associated with the LMMB Study, GLNPO anticipates publishing reports summarizing the modeling results. In 2005, GLNPO also anticipates conducting a reassessment of Lake Michigan to calibrate and confirm modeling results with data collected 10-years after the initial LMMB sampling.

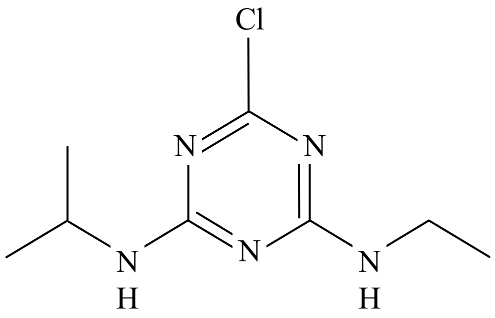
Chapter 2
Atrazine Study Overview

2.1 Atrazine Introduction

2.1.1 Physical/Chemical Properties

Atrazine, or 6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine, is a triazine herbicide with a chemical formula of $C_8H_{14}ClN_5$ and the chemical structure displayed in Figure 2-1. Atrazine is a white crystalline solid with a molecular weight of 215.7, a melting point of 171-174°C, and a boiling point of 279°C. The vapor pressure of atrazine is 0.04mPa (at 20°C), the solubility of atrazine in water is 30 mg/L (at 20°C), and the octanol-water partition coefficient (log K_{ow}) for atrazine is 2.34 (Worthing, 1991).

Figure 2-1. Chemical Structure of Atrazine

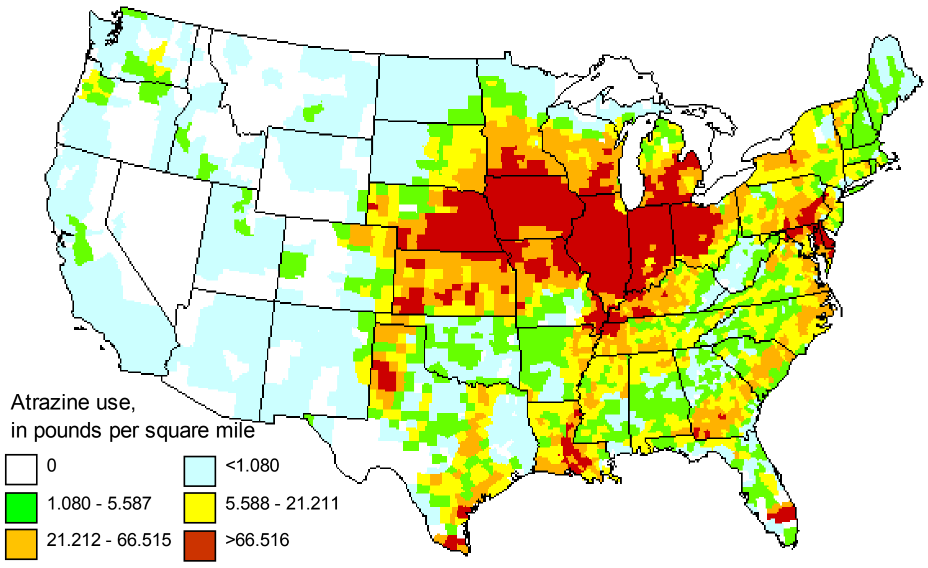


2.1.2 Atrazine Use

Atrazine is a systemic herbicide that inhibits photosynthetic electron transport and is used for control of broadleaf weeds and some grassy weeds. Atrazine is the most widely used herbicide in the U.S. for corn and sorghum production, with approximately three-fourths of all field corn and sorghum treated with atrazine (USEPA, 2001h). Atrazine is also used for weed control on crops of sugarcane, wheat, guava, macadamia nuts, orchard grass and hay, range grasses, and southern turf grasses. Atrazine is primarily applied directly to the soil during pre-planting or pre-emergence. Less commonly, atrazine may be applied post-emergence by foliar application directly to target plants.

Approximately 64 to 75 million pounds of atrazine are applied per year in the U.S. (USEPA, 2001h). It is primarily used in the "Corn Belt," the region stretching from eastern Nebraska to Ohio, immediately south and west of the Great Lakes (Goolsby *et al.*, 1997). Some of the most intensive use of atrazine is in the upper Midwest directly surrounding Lake Michigan (Figure 2-2). In total pounds of atrazine applied to corn crops, Illinois ranks first and Indiana ranks third (Ribaudo and Bouzaher, 1994). Michigan and Wisconsin, which also border Lake Michigan, rank seventh and eighth, respectively, in total pounds of atrazine applied to corn crops.

Figure 2-2. Estimated Annual Usage Rates of Atrazine in the United States for 1991-1995 (from U.S. Geological Survey, Pesticide National Synthesis Project, 1998)



2.1.3 Regulatory Background

Atrazine was initially registered as an herbicide in 1958 by Ciba-Geigy and has been used in the U.S. for over 40 years. Due to the extensive use of this herbicide and potential ecological and human health effects, EPA began to institute controls in the early nineties. In 1990, atrazine was classified as a restricted-use pesticide, application rates were reduced, most non-crop land uses were prohibited, application through irrigation systems was prohibited, and well-head protection plans were instituted. These controls were strengthened in 1992 through further reductions in application rates, expansion of setback requirements, and institution of construction requirements for bulk storage facilities (USEPA, 2001h).

To provide human health protection, EPA set a maximum contaminant level of 3 µg/L for atrazine in drinking water. Atrazine was originally classified as a possible human carcinogen, and based on this cancer risk, EPA initiated a special review for atrazine, simazine, and cyanazine in 1994. EPA has completed a preliminary risk assessment for atrazine including ecological and human health risks (USEPA, 2001b). As part of this review and assessment, the Health Effects Division's Cancer Assessment Review Committee recently concluded that atrazine is "not likely to be carcinogenic to humans" (USEPA, 2001h).

To protect aquatic life, EPA recently proposed ambient water quality criteria for atrazine (USEPA, 2001a; USEPA, 2001d). The draft criterion for protection against acute toxicity in freshwater (Criterion Maximum Concentration) was set at 350 µg/L. The draft criteria for protection against chronic toxicity in freshwater (Criterion Continuous Concentration) was set at 12 µg/L.

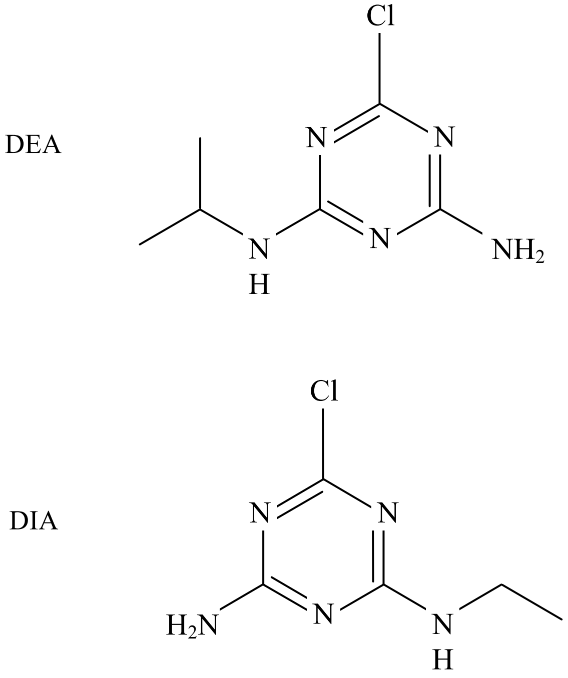
2.1.4 Fate and Effects

Applied atrazine may reach surface water resources through spray drift, runoff, contaminated groundwater discharge to surface water, or atmospheric deposition in precipitation, vapor, or particulate phases. The relatively low adsorption characteristics of atrazine and its solubility in water make it relatively mobile and susceptible to leaching and transport in runoff (USEPA, 2001e). Atrazine loadings from runoff are highest on highly sloped lands and when intense rain events directly follow herbicide application. Atrazine concentrations in agricultural field runoff have been measured in the low mg/L range, but these concentrations are typically diluted to the µg/L range once they enter receiving streams (USEPA, 2001a). Atmospheric sources of atrazine can originate from spray drift during application, airborne transport with associated soil particles suspended by wind erosion or planting and tilling operations, and volatilization from soil or foliage surfaces (Glotfelty *et al*., 1989). In agricultural regions, atrazine is generally present in the atmosphere throughout the growing season and available for removal via wet and dry deposition (Goolsby *et al*., 1997; Williams *et al*., 1992).

Atrazine is moderately susceptible to aerobic degradation in soils, with a half-life of 60-150 days (Ribaudo and Bouzaher, 1994). Under anaerobic conditions, this degradation rate slows dramatically to a half-life of 660 days. Studies on the persistence of atrazine in water have produced varied results with half-lives of several days reported in some experimental wetland systems and artificial streams to half-lives of over 300 days in larger lake systems (USEPA, 2001a). The persistence of atrazine in surface waters with relatively long hydraulic residence times and relatively low microbial activity is due to its resistence to abiotic hydrolysis and direct aqueous photolysis, its limited volatilization potential, and its moderate susceptibility to biodegradation (USEPA, 2001c).

Degradation products of atrazine include deethyl-atrazine (DEA), deisopropyl-atrazine (DIA), diaminochloro-triazine (DACT), and hydroxy-atrazine (HA). The relative concentration of these degradates in soil is atrazine >> DEA > DIA > DACT ~ HA. In surface water, the relative concentrations are similar, with atrazine >> DEA > DIA ~ DACT (USEPA, 2001c). The chemical structures of the two most common degradation products (DEA and DIA), which were studied in the Lake Michigan Mass Balance Study, are shown in Figure 2-3. These same metabolites are also produced in the atmosphere, where abiotic degradation of atrazine is primarily carried out by OH radical attack (Van Dijk and Guicherit, 1999).

Figure 2-3. Chemical Structure for Atrazine Breakdown Products, Deethyl-atrazine (DEA) and Deisopropyl-atrazine (DIA)



In general, atrazine is not very toxic to aquatic animals. Species mean values for acute toxicity ranged from 720 µg/L of atrazine for the midge, *Chironomus tentans*, to 49,000 µg/L for *Daphnia magna* (USEPA, 2001a). Species mean values for chronic toxicity ranged from 88.32 µg/L for brook trout, *Salvelinus fontinalis,* to 2935 µg/L for *Ceriodaphnia dubia* (USEPA, 2001a). Because atrazine inhibits photosynthesis, atrazine is considerably more toxic to aquatic plants than aquatic invertebrates and vertebrates. Toxicity to aquatic plants, including algae and macrophytes, commonly occurs at 10 µg/L of atrazine and above (USEPA, 2001a). Recent studies also have suggested that atrazine may cause endocrine disruption and reproductive abnormalities in amphibians at doses as low as 0.1 µg/L (Hayes *et al.*, 2002).

Preliminary environmental risk assessments for atrazine, conducted by the EPA Office of Pesticides Program's Environmental Fate and Effect Division, have indicated the possibility of chronic effects on mammals, birds, fish, aquatic invertebrates, and non-target plants at maximum, and in some cases, typical use rates (USEPA, 2001e). The data strongly suggest that atrazine will have direct negative impact on freshwater and estuarine plants as well as indirect effects on aquatic invertebrate and fish populations that rely on aquatic plants for habitat and a food chain base (USEPA, 2001e).

2.2 Study Design

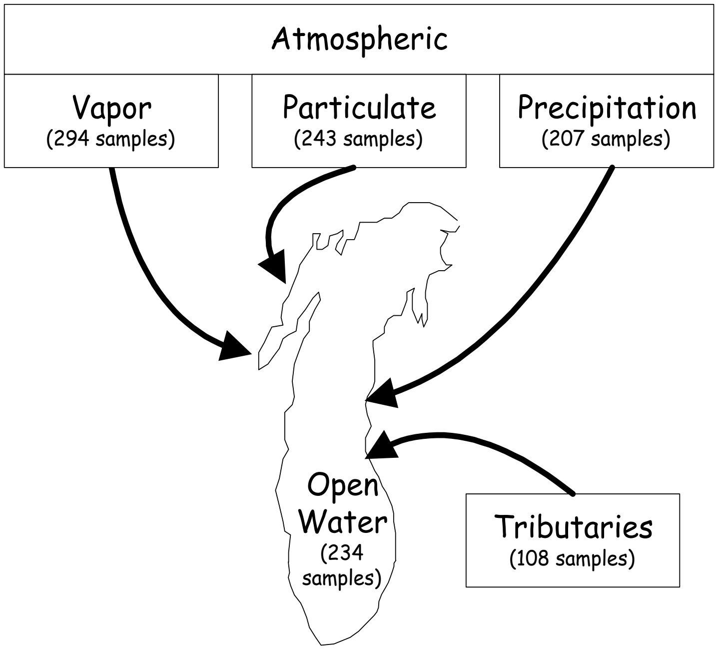
2.2.1 Description

Atrazine was selected as one of four contaminants to be modeled in the Lake Michigan Mass Balance Study. In this study, atrazine and atrazine metabolites (DEA and DIA) were measured in atmospheric, tributary, and open-lake water column components of the Lake Michigan ecosystem from March 1994 through October 1995. The data generated from this study was used to estimate an overall mass balance of atrazine in Lake Michigan and meet the defined objectives of the LMMB Project (see Section 1.4).

2.2.2 Scope

To develop a mass balance of atrazine in Lake Michigan, all significant sources and stores of atrazine in the environment were measured. Significant sources included tributary inputs and atmospheric inputs from the vapor phase, particulate phase, and precipitation (Figure 2-4). The open-lake water column compartment was determined to be the only significant store of atrazine. The sediment compartment was not included in this study because atrazine is relatively water soluble. Atrazine also does not bioaccumulate in living tissue, so biotic compartments were not included.

Figure 2-4. Sources and Stores of Atrazine Measured in the LMMB Study



Atmospheric samples were collected from March 15, 1994 to October 20, 1995. These atmospheric samples were collected from 8 shoreline sampling stations, 3 out-of-basin sampling stations, and 18 open-lake sampling stations. Atmospheric samples were collected in three separate sampling mediums or phases: vapor, particulate, and precipitation. A total of 294 vapor phase samples, 226 particulate samples, and 207 precipitation samples were collected and analyzed for atrazine. All but 64 of these samples were analyzed for DEA and DIA as well as atrazine. Samples from Sleeping Bear Dunes that were processed at Indiana University were not analyzed for DEA and DIA.

Tributary samples were collected from April 4, 1995 to October 31, 1995. A total of 108 samples were collected from 11 tributaries that flow into Lake Michigan. Open-lake water column samples from Lake Michigan were collected from April 25, 1994 to April 17, 1995. A total of 234 open-lake samples were collected from 35 sampling stations located throughout Lake Michigan, 2 sampling stations located in Green Bay, and 1 sampling station located on Lake Huron. All tributary and open-lake samples were analyzed for atrazine, DEA, and DIA.

2.2.3 Organization/Management

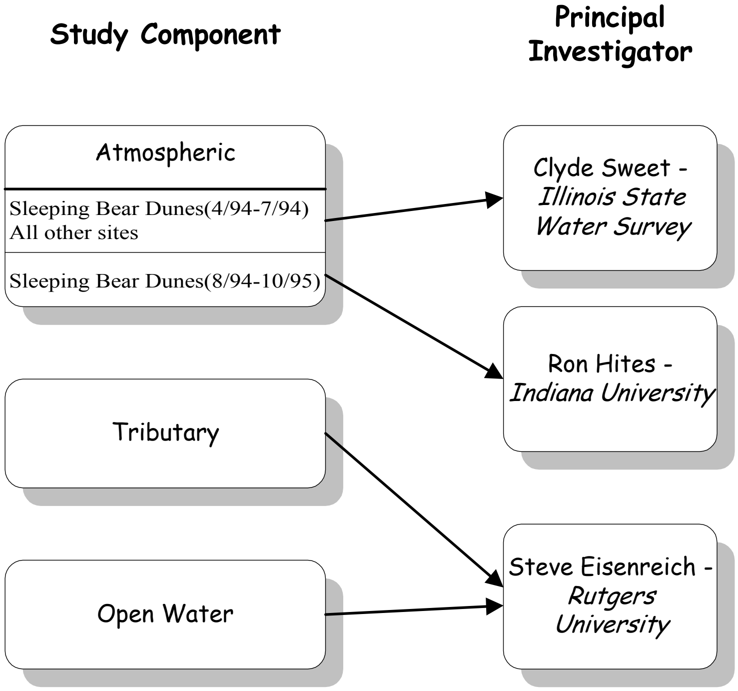
The responsibility for collecting and analyzing atrazine samples from the various components was divided among several principal investigators (Figure 2-5). All tributary and open-lake samples were collected and analyzed at the University of Minnesota Gray Freshwater Biological Institute and Rutgers University under the supervision of principal investigator, Steve Eisenreich. From April 1994 through July 1994, atmospheric samples from the Sleeping Bear Dunes site were collected and analyzed at the Illinois State Water Survey under the supervision of principal investigator, Clyde Sweet. From August 1994 through October 1995, atmospheric samples from the Sleeping Bear Dunes site were collected and analyzed at Indiana University under the supervision of principal investigator, Ron Hites. Atmospheric samples from all other sites also were collected and analyzed at the Illinois State Water Survey.

Each principal investigator developed a Quality Assurance Project Plan (QAPP) that was submitted to EPA's Great Lakes National Program Office. The QAPPs detailed the project management, study design, and sampling and analysis procedures that would be used in the study and the quality control elements that would be implemented to protect the integrity of the data. The LMMB quality assurance (QA) program is further discussed in Section 2.6, and detailed information on the quality assurance activities and data quality assessment specific to each ecosystem component are discussed in Chapters 3-5.

2.3 Sampling Locations

2.3.1 Atmospheric Components

Figure 2-5. Principal Investigators Responsible for Sampling and Analysis of Atrazine in Atmospheric, Tributary, and Open-lake Water Column Components

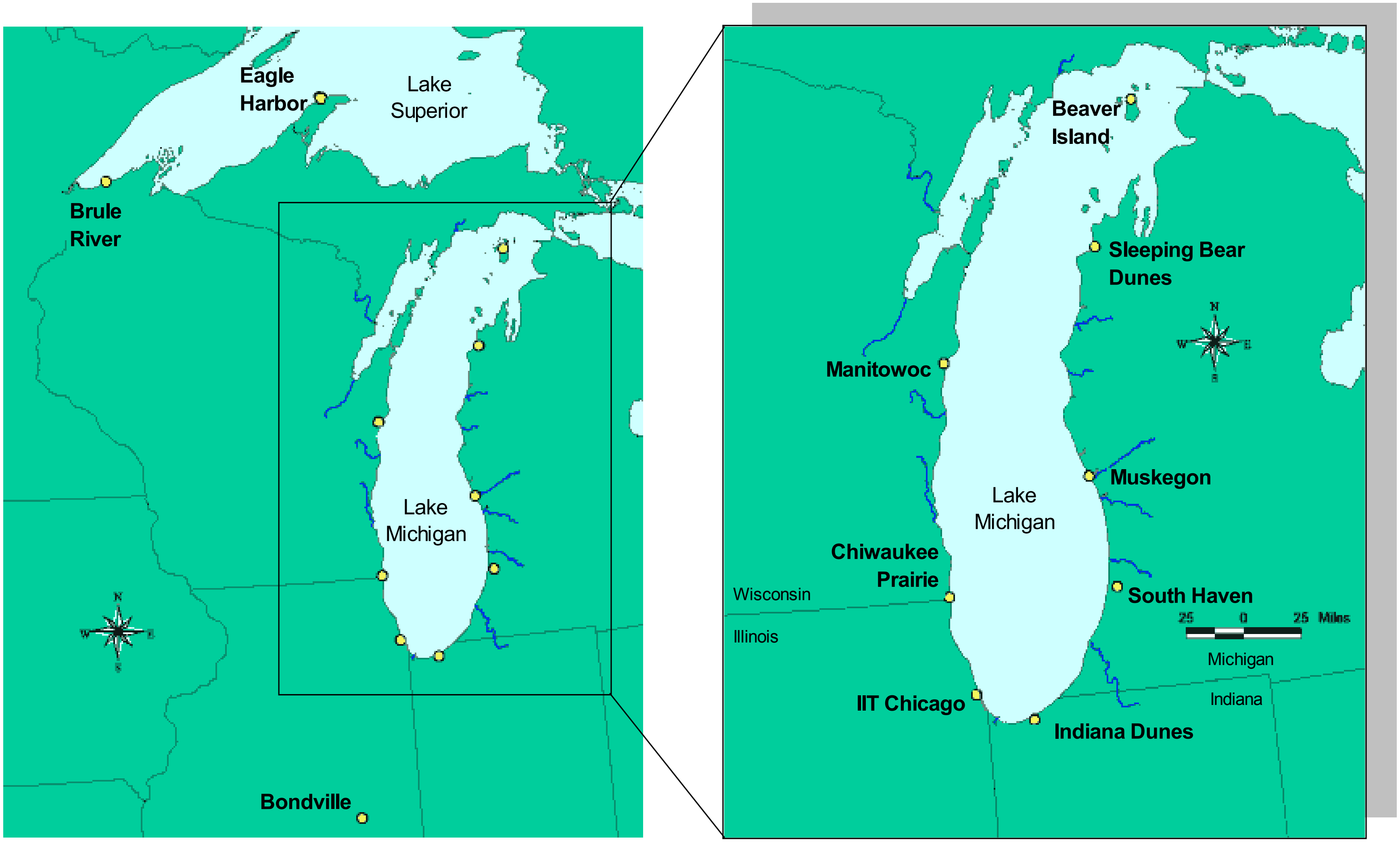


Eight shoreline sampling stations were established on Lake Michigan for the collection of atmospheric samples. In addition, three out-of-basin sampling stations were established as regional background sites to represent air coming over Lake Michigan during periods of southwest or northwest prevailing winds. Figure 2-6 shows the location of each of these sampling locations. Sampling locations for the LMMB Project were selected through workshop discussions. Site selection criteria considered predominant annual wind directions, source areas, and episodic summer events. In general, sites were selected to be regionally representative of the following land use categories:

- **remote** - no urban areas or major sources of air pollutants within 50 km (Beaver Island, Sleeping Bear Dunes, Eagle Harbor, and Brule River sites)
- **urban** - major urban sources within 1 km (Chicago IIT site)
- **urban-influenced** - major urban sources within 10 km (Muskegon, Manitowoc, Chiwaukee Prairie, and Indiana Dunes sites)
- **rural** - urban sources generally more than 10 km away, but agriculture sources within 1 km (South Haven and Bondville sites)

Sampling at the shoreline and background sites was conducted on a regular schedule between April, 1994 and October, 1995. Atrazine, DEA, and DIA also were measured in air and precipitation collected at 14 locations over Lake Michigan during periodic cruises of the *Research Vessel (R/V), Lake Guardian* (April-May, 1994; June, 1994; August, 1994; October-November, 1994; January, 1995; March-April, 1995; August, 1995; September-October, 1995).

Figure 2-6. Atmospheric Sampling Stations



2.3.2 Tributaries

Tributary water column samples were collected from eleven rivers that flow into Lake Michigan (Figure 2-7). These tributaries included the Menoninee, Fox, Sheboygan, and Milwaukee Rivers in Wisconsin; the Grand Calumet River in Indiana; and the St. Joseph, Kalamazoo, Grand, Muskegon, Pere Marquette, and Manistique Rivers in Michigan. With the exception of the Pere Marquette River, these tributaries were selected for the LMMB Study because of elevated concentrations of PCBs and mercury in resident fish. The Pere Marquette River was selected because it has a fairly large and pristine watershed. The 11 monitored tributaries represent greater than 90% of the total river flow into Lake Michigan and an even higher percentage of the total tributary load of pollutants into Lake Michigan.

Table 2-1 describes specific watershed characteristics and impairment information for each of the monitored tributaries. Of the 11 tributaries, 6 (the Kalamazoo, Manistique, Menominee, Fox, Sheboygan, and Grand Calumet Rivers) are classified as Great Lakes areas of concern (AOCs). Areas of concern are severely degraded geographic areas within the Great Lakes Basin. They are defined by the US-Canada Great Lakes Water Quality Agreement (Annex 2 of the 1987 Protocol) as “geographic areas that fail to meet the general or specific objectives of the agreement where such failure has caused or is likely to cause impairment of beneficial use or the area’s ability to support aquatic life.” Most of the 11 tributaries are also listed on the Clean Water Act Section 303(d) list of impaired water bodies due to contamination from mercury, PCBs, and other pollutants.

Figure 2-7. Tributary Sampling Stations

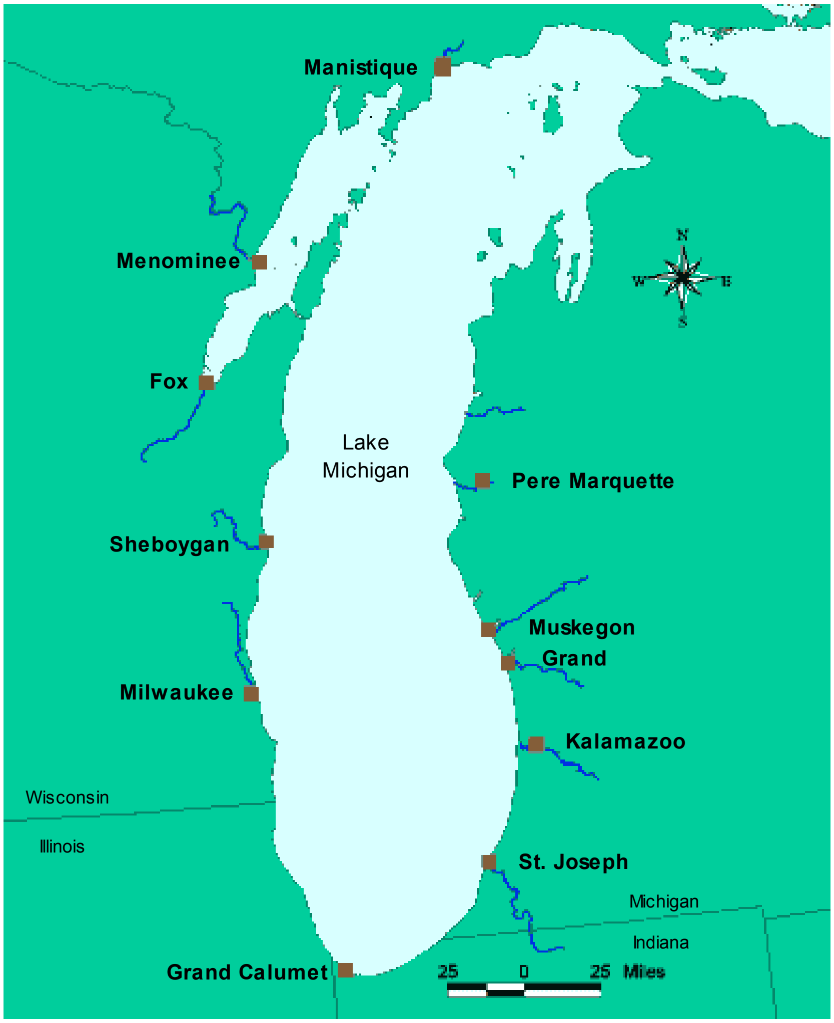


Table 2-1. Watershed Characteristics for Tributaries Monitored in the LMMB Study

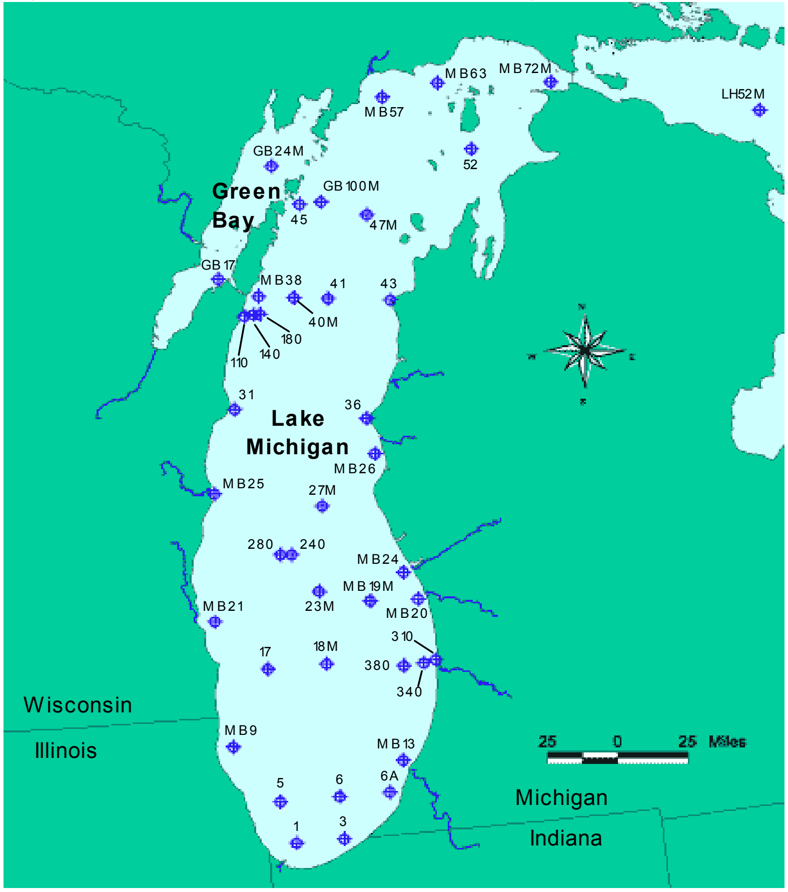
Tributary	Watershed area (mi^2)	Total river miles in watershed	Riparian Habitat		IWI Score[a]	Impaired for[b]	Area of Concern
			Forested	Agricultural / Urban			
St. Joseph	4685	3743	25-50%	>50%	3- less serious problems, low vulnerability	E. coli, mercury, PCBs, pathogens, macro-invertebrate community	
Kalamazoo	2047	1560	25-50%	>50%	3- less serious problems, low vulnerability	mercury, PCBs	X
Grand (lower)	2003	2014	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, pathogens	
Muskegon	2686	1886	25-50%	>50%	5- more serious problems, low vulnerability		
Pere Marquette	2644	1356	25-50%	>50%	3- less serious problems, low vulnerability	mercury, PCBs	
Manistique	1464	1061	>75%	20-50%	1- better quality, low vulnerability	mercury, PCBs, pathogens	X
Menominee	2306	1660	>75%	20-50%	1- better quality, low vulnerability	dioxin, PCBs, mercury, pathogens	X
Fox (lower)	442	700	25-50%	>50%	6- more serious problems, high vulnerability	PCBs, organic enrichment, dissolved oxygen	X
Sheboygan	2201	1699	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, mercury	X
Milwaukee	864	802	25-50%	>50%	5- more serious problems, low vulnerability	PCBs	
Grand Calumet	1039	760	25-50%	>50%	5- more serious problems, low vulnerability	PCBs, pesticides, lead, mercury, dissolved oxygen, cyanide, chlorides, impaired biotic community, oil and grease, copper	X

[a] EPA's Index of Watershed Indicators Score for assessing the health of aquatic resources.

[b] Based on 1998 listing of Clean Water Act Section 303(d) impaired waters.

2.3.3 Open Lake

Figure 2-8. Open-lake Water Column Sampling Stations



Open-lake water column samples were collected from 35 sampling locations on Lake Michigan, 2 sampling locations in Green Bay, and 1 sampling location on Lake Huron (Figure 2-8). Ten of these stations were identified as master stations where increased resolution sampling was conducted. Open-lake stations were selected to represent good spatial coverage throughout the lake and to include both nearshore (<25-30 meters in depth) and offshore locations. Many of the open-lake sampling stations were located at existing NOAA (National Oceanic and Atmospheric Administration) weather buoys or sites where additional information had previously been collected.

Open-lake samples were collected during six cruises of the *R/V Lake Guardian*. These cruises were conducted from April 25, 1994 to April 17, 1995. The first survey occurred in the early spring just after ice out (April/May 1994). The second survey was in early summer (June 1994) after the onset of stratification and following the spring runoff period of agricultural chemicals from cropland. The third survey was in late summer (August 1994) during later stages of stratification. The fourth and fifth surveys, conducted in October 1994 and January 1995, sampled only a few of the Lake Michigan sites. The final survey occurred in March/April 1995 just after ice out.

2.4 Sampling Methods

Full details of the sampling methods used in the LMMB Study have been published by EPA in a Methods Compendium (USEPA, 1997a; USEPA, 1997b). A brief summary is provided below.

2.4.1 Atmospheric Components

Twenty-eight-day composite precipitation samples were collected using a MIC-B wet only sampler (Meterological Instruments of Canada, Thornhill, ONT) with a 0.212 m^2 stainless steel catch basin. The sampler was modified for all-weather operation by enclosing and insulating the space underneath the sampler. The temperature in the enclosure was maintained at 10 to 15°C during the winter using a small space heater. The collector also was fitted with a precipitation sensor and a retractable cover. The catch basin remained covered to prevent evaporation until precipitation was detected by the sensor. Rain or melted snow collected in the catch basin passed by gravity flow through a 30-cm XAD-2 resin column that absorbed atrazine in the precipitation sample. Glass wool plugs inserted before and after the XAD-2 resin trapped any particles in the sample. Resin columns and plugs were changed at 28-day intervals and shipped to the lab for analysis. At this time, the precipitation collection funnel was rinsed with water and wiped with a piece of clean quartz fiber filter paper to remove adhering particles. The filter paper and rinsings were then included as part of the sample. Samples were sealed with Teflon^{TM} caps, transported to the testing laboratory, and stored in air-tight containers at -18°C until analysis.

Twenty-four-hour composite air samples for atrazine analysis were collected every 3 to 12 days using a modified high-volume sampler. The sampler was modified to include an aluminum tube behind the filter holder that accommodated a vapor trap consisting of a stainless steel cartridge of XAD-2 resin. Air flow was maintained at a rate of 34 m^3/hr during sampling. Particulate phase atmospheric samples were collected on pre-fired quartz fiber filters, and vapor phase atmospheric samples were collected in the XAD-2 resin vapor trap. Samples were wrapped in aluminum foil, sealed in air tight metal cans, transported to the testing laboratory, and stored at -18°C until analysis.

For most atmospheric sampling sites, individual 24-hour samples were combined in the laboratory to provide monthly composite vapor trap and filter samples. This monthly composite sample, which consisted of multiple 24-hour composites, was then analyzed at the testing laboratory. At the Sleeping Bear Dunes site and occasionally at other sites, individual 24-hour XAD-2 samples were analyzed without compositing. In these cases, the results from individual 24-hour samples were mathematically composited (by volume weighting) to obtain monthly atrazine values.

Each shoreline site had a 10-meter meteorological tower and a number of meteorological instruments including wind speed and wind direction sensors at a height of 10 m (Met-One, Grants Pass, OR), a solar radiation sensor (LI-Cor, model LI 200S, Lincoln, NE), temperature and relative humidity sensors (Campbell Scientific, Logan, UT), and a standard Belfort rain gauge (Belfort Instrument, Baltimore, MD) with a Nipher wind shield. All of the meteorological sensors were automatically recorded every six seconds using a datalogger (Campbell Scientific, model 21X, Logan, UT).

2.4.2 Tributaries

The number and timing of sampling events were dependent upon the stability of the tributary and the timing of increased flow events. Tributaries with greater stability (i.e., those that are less responsive to precipitation events) were sampled less frequently than those that were more variable. Sampling was also timed to collect approximately one-third of samples during base flow conditions and approximately two-thirds of samples when flows were above the 20th percentile.

Tributary samples were collected as near to river mouths as possible without being subject to flow reversals that are common near river mouths in Lake Michigan. Composite samples were obtained using the USGS quarter-point sampling procedure. In this procedure, the stream is visually divided into three equal flow areas. At the center of each flow area, samples were collected from 0.2 and 0.8 times the depth. All six samples were then composited and pumped (using a peristaltic pump) through a 0.7 µm glass fiber filter. The filtrate was then passed through a large, 250 g, XAD-2 resin column to trap dissolved organics. Samples were then chilled and delivered to the testing laboratory. While the measured atrazine concentrations in tributary samples represent the filtered phase, these concentrations should generally approximate total atrazine concentrations due to the solubility of atrazine.

2.4.3 Open Lake

Open-lake samples were collected from various depths depending upon the stratification conditions. During stratification, open-lake stations were sampled at the mid-epilimnion and mid-hypolimnion. During non-stratified periods, samples were collected at mid-water column depth and two meters below the surface. Master stations, during times of non-stratification, were sampled at mid-water column depth, one meter below the surface, and two meters off the bottom. During times of stratification, master stations were sampled at one meter below the surface, mid-epilimnion, mid-hypolimnion, and two meters off the bottom. In addition, stations 18 and 41 were sampled at the thermocline and 2 meters below the surface during stratification.

Water samples were collected using a General Oceanics (Model 1015) rosette sampler on board the *R/V Lake Guardian*. Water was transferred from individual rosette canisters to amber one liter bottles, and stored at 4°C until processing at the testing laboratory.

2.5 Analytical Methods

Full details of the analytical methods used in the LMMB Study have been published by EPA in a methods compendium (USEPA, 1997a; USEPA 1997b). The sample collection, extraction, and analysis methods for the atmospheric components and water samples from the tributaries and open lake are modifications of the methods used for the PCBs and chlorinated pesticides. These modifications include the changes to the extraction conditions needed to extract more polar analytes like atrazine, DEA, and DIA, and changes to chromatographic conditions such as columns and temperature programs necessary for the instrumental analysis. A brief summary is provided below.

2.5.1 Atmospheric Components

Atrazine and atrazine metabolites were extracted from XAD-2 resin or filter samples by Soxhlet extraction with 300 mL of a 1:1 hexane and acetone mixture. The extract was concentrated by rotary evaporation to about 3 mL and then the solvent was exchanged to hexane with rotary evaporation. The concentrated extract was subjected to clean-up on 3% deactivated silica with a sodium sulfate cap to remove most of the non-target, interfering compounds. Atrazine, DEA, and DIA were eluted in a methanol fraction. The volume of each fraction was reduced to between 0.3 and 1 mL by rotary evaporation and concentrated in a stream of high-purity nitrogen. Samples were transferred to vials, capped, and stored at -20°C. Analysis of atrazine, DEA, and DIA was conducted using gas chromatography coupled to a mass spectrometer detector.

2.5.2 Tributaries and Open Lake

Atrazine, DEA, and DIA were isolated from filtered water samples using 250 mg Carbopack (Supelco Corp) solid-phase extraction (SPE) cartridges. Analytes were eluted from the SPE using 7 mL of a 90% dichloromethane, 10% methanol solution (vol:vol), followed by 5 mL of methanol. The eluent was then passed through clean anhydrous sodium sulfate to remove excess water. Extracts were concentrated to <100 µL under a nitrogen gas stream. Analysis of atrazine, DEA, and DIA was conducted using gas chromatography coupled to a mass spectrometer detector.

2.6 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The goal of the QA program was to ensure that all data gathered during the LMMB Study met defined standards of quality with specified levels of confidence. Data quality was defined, controlled, and assessed through activities that included development of study QAPPs, use of SOPs, and data verification. These activities are described in detail in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i). Specific quality control elements implemented in the sampling and analysis of atrazine included:

- use of Standard Operating Procedures and trained personnel for field sampling and laboratory analysis;
- determination of method sensitivity through calculation of method detection limits;
- establishment and maintenance of sample holding times;
- preparation and analysis of a variety of blanks to characterize contamination associated with specific sample handling, storage, and analysis processes including field blanks, lab reagent blanks, bottle blanks, trip blanks, and lab procedural blanks;
- collection and analysis of field or laboratory duplicate samples;
- preparation and analysis of a variety of quality control samples including performance standards;
- use of a standardized data reporting format; and
- for atmospheric samples, preparation and analysis of matrix spike samples to characterize the applicability of the analytical method to the study sample matrices.

Performance or intercomparison studies were not conducted for the atrazine analyses. However, all of the PIs obtained the atrazine calibration standard from the same vendor and the sample preparation, extraction, and instrumental analysis (GC/MS with Selected Ion Monitoring) procedures were similar among all PIs. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data. Prior to data submission, each researcher submitted electronic test files containing field and analytical data according to the LMMB data reporting standard. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers.

Prior to sample collection, Quality Assurance Project Plans (QAPPs) were developed by the PIs and submitted to GLNPO for review. Because the open-lake and tributary monitoring were conducted by the same PI, a separate QAPP was not prepared for the tributary monitoring, and GLNPO and the PI agreed to implement the procedures outlined in the open-lake QAPP for the tributary sampling and analysis. In the QAPPs, the PIs defined MQOs in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. The MQOs were designed to control various phases of the measurement process and to ensure that the total measurement uncertainty was within the ranges prescribed by the DQOs. The MQOs for atrazine are listed in Section 4 of *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i).

The PI-defined MQOs also were used in the data verification process. GLNPO conducted data verification through the LMMB QA Workgroup. The workgroup was chaired by GLNPO's Quality Assurance Manager and consisted of quality control coordinators that were responsible for verifying the quality of specific data sets. Data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. If the results failed to meet MQOs and corrective actions were not feasible, the results were flagged to inform data users of the failure. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. In this data report, the summary and analysis of atrazine data represent all results with the exception of those flagged as "invalid" by the QC coordinator in concert with the PI.

In addition to flags related to the evaluation of MQOs, a wide variety of flags were applied to the data to provide detailed information to data users. For example, the flag LAC (laboratory accident, no result reported) was applied to sample results to document that a sample was collected, but no result was reported due to a laboratory accident. The frequencies of flags applied to atrazine study data are provided in the Quality Implementation Sections of each of the following chapters. The flag summaries include the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but do not include all flags applied to the data to document sampling and analytical information (such as LAC). In order to provide detailed quality information to data users, the study data are maintained in the GLENDA database with all applied flags. Detailed definitions of the flags can be found in the *Allowable Codes Table* on GLNPO's website at: www.epa.gov/glnpo/glenda/codes/codes.html under *Result Remark, List of QC flags* (lab_rmrk).

The PIs participating in the study also conducted real-time data verification. PIs applied best professional judgement during sampling, analysis, and data generation, based on their experience monitoring atrazine in the environment. In most cases, when sample results were questionable, the PI reanalyzed the sample or clearly documented the data quality issues in the database through the application of data quality flags or by including comments in the database field, "Exception to Method, Analytical." Because the flags and comments are maintained in the database for each sample result, data users are fully informed of data quality and can evaluate quality issues based on their intended use of the data. The level of documentation that GLNPO is maintaining in the study database is unprecedented for a database of this size and will serve as a model for future efforts.

GLNPO also conducted data quality assessments in terms of three of the six attributes used as the basis for the MQOs, specifically sensitivity, precision, and bias. These three attributes could be assessed from the results of QC samples analyzed in the study. For example, system precision was estimated as the mean relative percent difference (RPD) between results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between results for laboratory duplicate pairs. Bias was estimated using the mean recovery of spiked field samples or other samples of known concentration such as laboratory performance standards. A summary of data quality assessments is provided for the atrazine study data in the Quality Implementation Section of each of the following chapters.

Chapter 3
Atrazine in Atmospheric Components

3.1 Results

From March 15, 1994 to October 20, 1995, atmospheric samples were collected from 8 shoreline sampling stations, 3 out-of-basin sampling stations, and 18 sampling stations in the open lake (over-water) (Table 3-1). Atmospheric samples were collected, analyzed, and results reported in three separate sampling mediums or phases: vapor (in pg/m^3), particulate (in pg/m^3), and precipitation (in ng/L). A total of 294 vapor phase samples, 226 particulate samples, and 207 precipitation samples were collected and analyzed for atrazine. All but 64 of these samples also were analyzed for deethyl-atrazine (DEA) and 6-deisopropyl-atrazine (DIA). Samples from Sleeping Bear Dunes that were processed at Indiana University were not analyzed for DEA and DIA.

Table 3-1. Number of Atmospheric Samples Analyzed for Atrazine, DEA, and DIA

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Shoreline Atmospheric Stations	Beaver Island	3/15/94 - 10/8/95	17	17	20	54
	Indiana Dunes	3/15/94 - 10/20/95	29	29	21	79
	IIT Chicago	3/15/94 - 10/2/95	25	24	17	66
	Muskegon	3/15/94 - 10/13/95	17	16	20	53
	Manitowoc	3/15/94 - 10/8/95	18	18	20	56
	Sleeping Bear Dunes[a]	4/1/94 - 10/19/95	45[b]	19[c]	18[d]	82
	South Haven	3/15/94 - 10/8/95	21	18	21	60
	Chiwaukee Prairie	3/15/94 - 10/2/95	20	20	20	60
Out-of-basin Atmospheric Stations	Brule River	4/1/94 - 10/8/95	17	17	19	53
	Bondville	3/15/94 - 10/20/95	21	20	21	62
	Eagle Harbor	4/1/94 - 7/31/94	8	4	4	16

Sampling Station		Sampling Dates	Vapor Samples Analyzed	Particulate Samples Analyzed	Precipitation Samples Analyzed	Total Samples Analyzed
Over-water Atmospheric Stations	1	5/10/94 - 10/11/95	4	1	1	6
	11	5/8/94	1			1
	110	4/8/95 - 9/23/95	3			3
	18M	5/6/94 - 10/9/95	5			5
	23M	5/4/94 - 10/3/95	4	1	1	6
	27M	5/2/94 - 9/27/95	5			5
	280	10/26/94 - 10/1/95	4			4
	310	3/28/95 - 10/8/95	3			3
	380	10/31/94 - 1/23/95	1		1	2
	40M	10/18/94 - 9/25/95	4	1		5
	41	4/30/94 - 8/12/94	2	1		3
	47M	8/7/94 - 9/19/95	5			5
	5	11/4/94 - 10/10/95	6	3	1	10
	6	8/25/94 - 10/12/95	4	1		5
	GB17	4/12/95			1	1
	GB24M	10/17/94 - 9/20/95	4	2	1	7
	MB19M	1/24/95	1			1
	geographical composite[e]	4/30/94 - 10/11/95		14		14
Total			294	226	207	727

[a] Samples from Sleeping Bear Dunes that were processed at Indiana University (8/2/94 - 10/19/95) were not analyzed for DEA and DIA.

[b] 45 samples were analyzed for atrazine, and 10 samples were analyzed for DEA and DIA.

[c] 19 samples were analyzed for atrazine, and 4 samples were analyzed for DEA and DIA.

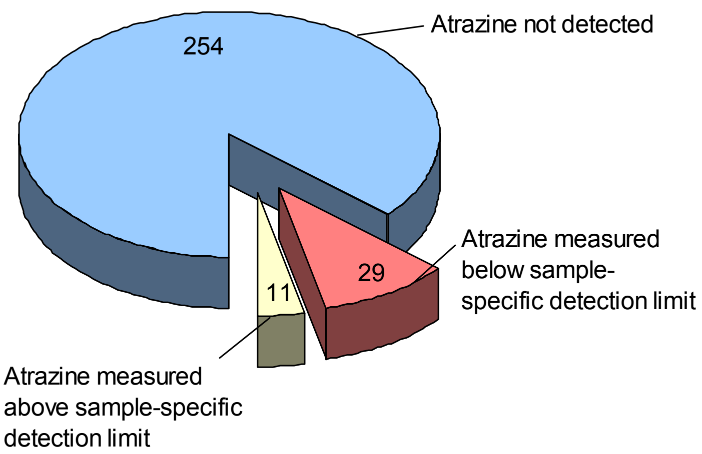
[d] 18 samples were analyzed for atrazine, and 4 samples were analyzed for DEA and DIA.

[e] Samples were collected while the *R/V Lake Guardian* was traveling between stations. These samples are considered geographical composites.

3.1.1 Vapor Fraction

Atrazine was not detected in the vapor fraction of most atmospheric samples collected during the 1994-1995 sampling campaign. Of 294 vapor samples tested, atrazine was detected (i.e., measured above zero) in only 40 samples (14%), and measured atrazine concentrations were above sample-specific detection limits in only 11 (3.7%) samples (Figure 3-1). Method detection limits (MDLs) were calculated from results of seven spiked samples according to the procedures specified at 40 CFR part 136, Appendix B.

Figure 3-1. Detection Frequency of Atrazine in Vapor Phase Samples



The MDL was then adjusted for each sample based on the analyzed sample volume and surrogate recovery factors to obtain sample-specific detection limits. Sample-specific detection limits ranged from 13 to 104 pg/m^3 for samples analyzed at the Illinois Water Survey, and from 8.89 to 49.7 pg/m^3 for samples analyzed at Indiana University. Sample-specific detection limits averaged 32 pg/m^3 and 20.7 pg/m^3 for samples analyzed at the Illinois Water Survey and Indiana University, respectively.

Table 3-2 lists the 11 vapor samples that contained measured atrazine concentrations above sample-specific detection limits. These samples included one individual sample from South Haven, four composite samples from Bondville, and six individual samples from Sleeping Bear Dunes. Four of the six samples from Sleeping Bear Dunes that contained atrazine above sample-specific detection limits (those collected on 10/23/94, 11/4/94, 8/8/95, and 10/7/95) were flagged for contamination of corresponding field or laboratory blanks. The concentrations measured in these four samples were only 1.0, 3.6, 1.4, and 4.5 times the concentration measured in corresponding blanks, so results for these four samples are likely biased high.

Table 3-2. Atrazine Concentrations in the Vapor Fraction Measured Above Sample-specific Detection Limits

Sampling Location	Sampling Date	Sample Description	Atrazine Concentration (pg/m^3)
South Haven	7/7/94 - 7/8/94	single 24-hr composite sample	70
Bondville	5/7/94 - 5/21/94	manual composite of 2, 24-hr composite samples	330
	6/1/94 - 6/26/94	manual composite of 3, 24-hr composite samples	420
	6/9/95 - 6/22/95	manual composite of 2, 24-hr composite samples	480
	7/3/95 - 7/28/95	manual composite of 3, 24-hr composite samples	160
Sleeping Bear Dunes	10/23/94 - 10/24/94	single 24-hr composite sample	18.6
	11/4/94 - 11/5/94	single 24-hr composite sample	71.1
	11/16/94 - 11/17/94	single 24-hr composite sample	22.1
	8/8/95 - 8/9/95	single 24-hr composite sample	11.6
	9/13/95 - 9/14/95	single 24-hr composite sample	31.5
	10/7/95 - 10/8/95	single 24-hr composite sample	34.5

3.1.1.1 Seasonal Variation

Atrazine was detected in an insufficient number of samples to evaluate seasonal trends of atrazine concentrations in the atmospheric vapor fraction. Atrazine in the vapor fraction was measured above sample-specific detection limits in only 11 samples, which were collected during the months of May, June, July, August, September, October, and November (Table 3-2).

3.1.1.2 Geographical Variation

Atrazine was detected in an insufficient number of samples to evaluate geographical trends of atrazine concentrations in the atmospheric vapor fraction. During the March 1994 through October 1995 sampling campaign, atrazine was not detected above sample-specific detection limits in any vapor phase samples from the following stations: Beaver Island, Eagle Harbor, Brule River, Indiana Dunes, IIT Chicago, Muskegon, Manitowoc, and Chiwaukee Prairie. Vapor-phase atrazine concentrations were measured above sample-specific detection limits only in samples from South Haven, Bondville, and Sleeping Bear Dunes (Table 3-2). Atrazine concentrations in these samples ranged from 11.6 to 480 pg/m^3, and maximum detected concentrations were 70, 480, and 71.1 pg/m^3 at the South Haven, Bondville, and Sleeping Bear Dunes sites, respectively.

Two of the three sites where atrazine was detected in the vapor phase were classified as rural sampling locations (South Haven and Bondville), where local agricultural influences were prevalent. The third site (Sleeping Bear Dunes) was classified as a remote site, however, four of the six samples from this site that had atrazine concentrations above sample-specific detection limits were likely biased high due to laboratory or field contamination (see Section 3.1.1). The two remaining samples from Sleeping Bear Dunes that contained detectable levels of atrazine (those collected on 11/16/95 and 9/13/95) were not influenced by blank contamination, but were only slightly above (1.2 and 1.4 times) sample-specific detection limits. Only samples from Bondville were greater than five times sample-specific detection limits. These samples from Bondville also represented monthly composites of multiple 24-hr samples, whereas samples from South Haven and Sleeping Bear Dunes that contained atrazine above sample-specific detection limits were individual 24-hr samples. This indicates that atrazine concentrations well above detection levels may be typical in May, June, and July at the Bondville site. At all other sites, atrazine concentrations are generally below detection, but occasional peaks in atrazine concentration above detection levels may be experienced in individual samples.

3.1.1.3 Analysis of Breakdown Products

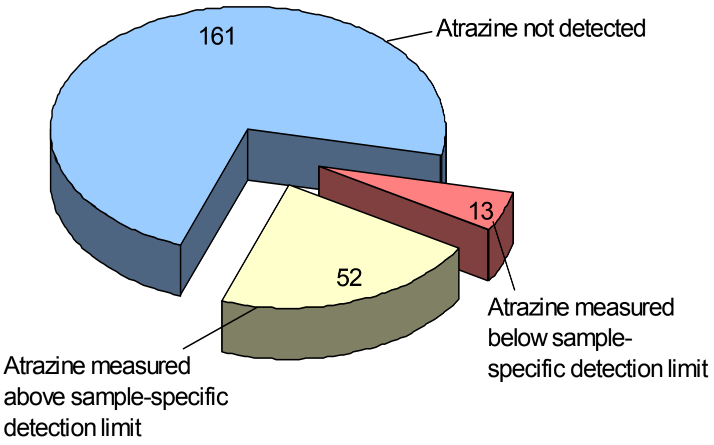
DEA and DIA were not detected in any of the 259 vapor samples analyzed. Sample-specific detection limits for DEA in the vapor phase ranged from 24 to 199 pg/m^3 and averaged 62 pg/m^3 for samples analyzed at the Illinois Water Survey. Sample-specific detection limits for DIA in the vapor phase ranged from 24 to 204 pg/m^3 and averaged 63 pg/m^3 for samples analyzed at the Illinois Water Survey. Samples processed at Indiana University were not analyzed for DEA or DIA.

3.1.2 Particulate Fraction

Of 226 particulate samples tested, atrazine was detected (i.e., measured above zero) in 65 samples (29%), and measured atrazine concentrations were above sample-specific detection limits in 52 (23%) samples (Figure 3-2). Method detection limits (MDLs) were calculated from results of seven spiked samples according to the procedures specified at 40 CFR part 136, Appendix B. The MDL was then adjusted for each sample based on the analyzed sample volume and surrogate recovery factors to obtain sample-specific detection limits. Sample-specific detection limits ranged from 3.0 to 68 pg/m^3 for samples analyzed at the Illinois Water Survey, and from 26.8 to 284 pg/m^3 for samples analyzed at Indiana

University. Sample-specific detection limits averaged 17 pg/m^3 and 70.7 pg/m^3 for samples analyzed at the Illinois Water Survey and Indiana University, respectively. Particle size distribution analysis was not conducted to identify the size of atmospheric particles associated with the detection of atrazine.

Figure 3-2. Detection Frequency of Atrazine in Particulate Phase Samples



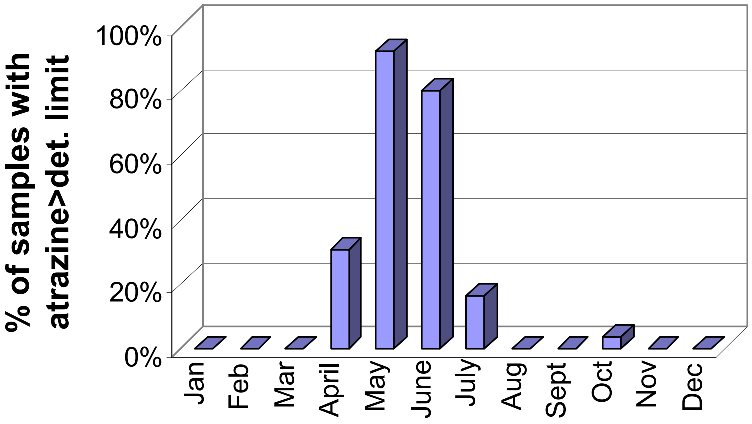
3.1.2.1 Seasonal Variation

The presence and concentration of atrazine in the particulate phase was highly influenced by season. Of the 52 particulate phase samples that contained atrazine above sample-specific detection limits, 51 were collected during the months of April through July (Figure 3-3). Only one particulate phase sample collected from August through March contained atrazine levels above method detection limits. During the late spring, a majority of samples contained atrazine. Atrazine was detected above sample-specific detection limits in 92% of particulate samples collected in May and 80% of samples collected in June (Figure 3-3).

Atrazine concentrations in the particulate phase peaked during both the spring of 1994 and the spring of 1995 at all shoreline and out-of basin sampling stations (Figure 3-4). For all sampling stations except for two (Indiana Dunes and South Haven), peak particulate phase atrazine concentrations were higher in the spring of 1994 than the spring of 1995. Peak concentrations were observed during the month of May at 9 of the 11 sampling stations. Peak concentrations were observed in April and June at the IIT Chicago and Bondville stations, respectively.

Due to the dramatic seasonal variation in atrazine concentrations, station averages were calculated only for measurements during the spring and summer growing season, when atrazine was primarily detected in atmospheric samples. Spring/summer mean atrazine concentrations were calculated by averaging monthly composite samples that were collected between March 20 (the first day of spring) and September 23 (the first day of fall), based on the midpoint of the compositing period. When individual samples were collected during a month, rather than monthly composite samples, the results were mathematically composited (by volume weighting) to obtain monthly composite results, which were then used to calculate spring/summer mean atrazine concentrations. All results were included in mean calculations as reported, meaning that measurements

Figure 3-3. Frequency Distribution of Atrazine Detection in Particulate Phase Atmospheric Samples



below sample-specific detection limits were included and not censored. Results reported as zero also were included in mean calculations.

Particulate atrazine concentrations in the spring/summer of 1994, 1995, and both years combined are presented in Table 3-3. For all sampling stations except for two (Sleeping Bear Dunes and South Haven), mean spring/summer atrazine levels in the particulate phase were higher in 1994 than 1995.

3.1.2.2 Geographical Variation

Atrazine was detected in the particulate phase at all shoreline and out-of-basin sampling stations. Maximum monthly atrazine concentrations at these locations ranged from 160 pg/m^3 at Sleeping Bear Dunes to 1400 pg/m^3 at Bondville. Mean spring/summer atrazine levels for the two-year sampling campaign (1994-1995) ranged from 25 pg/m^3 at Beaver Island to 370 pg/m^3 at Bondville (Table 3-3). Mean particulate atrazine concentrations differed by more than a factor of 10 among sites, but these differences were not statistically significant (based on a Kruskal-Wallis test ($p = 0.395$)), due to the high variability of measured concentrations at each station.

While mean atrazine concentrations did not differ significantly among stations, it was observed that atrazine levels in the particulate phase were generally higher at shoreline sampling stations surrounding the southern Lake Michigan basin than shoreline sampling stations surrounding the northern basin. Mean spring/summer atrazine levels at all of the southern basin sampling stations (Chiwaukee Prairie, IIT Chicago, Indiana Dunes, South Haven, and Muskegon) were higher than at any of the northern basin sampling stations (Manitowoc, Sleeping Bear Dunes, and Beaver Island) (Figure 3-5). This trend is consistent with the increased use of atrazine in the southern Lake Michigan basin compared to the northern basin (Figure 2-2). Out-of-basin sampling stations also fit this trend with the exception of the Eagle Harbor site. The southern out-of-basin sampling station (Bondville), which is in the center of an intensive corn-growing region, had the highest mean particulate atrazine concentration of any site. The remote, northern Brule River sampling station had a lower mean atrazine concentration than any of the southern sites. The northern Eagle Harbor sampling station was the only site that did not fit this trend. The mean atrazine concentration at the Eagle Harbor sampling station was higher than at three of the southern basin sampling stations (Chiwaukee Prairie, Muskegon, and South Haven), however, only four monthly composite samples were collected from the Eagle Harbor site (between April and July 1994), and atrazine was detected in only one of those monthly composites (530 pg/m^3 in May 1994). In a 1995 study, Foreman *et al.* (2000) detected atrazine in 35% of weekly composite air samples collected at the Eagle Harbor site.

In addition to samples collected at land-based sampling stations, atmospheric particulate samples were collected from seven sampling locations in the open lake (over-water). A total of 10 samples were collected from the following over-water sites: 1, 5, 6, 41, 23M, 40M, and GB24M. Fourteen additional samples were geographical composites that were collected as the *R/V Lake Guardian* traveled between open-lake sampling stations. Of the 24 analyzed samples, atrazine was detected in only two samples. In May 1994, an atrazine concentration of 560 pg/m^3 was measured at station 1, and in May 1995, an atrazine concentration of 280 pg/m^3 was measured at station 5. Both of these stations are relatively close to the shore, and measured concentrations are comparable to the nearest shoreline stations (IIT Chicago and Indiana Dunes).

Figure 3-4. Seasonal Trend of Atrazine Concentrations in the Particulate Phase

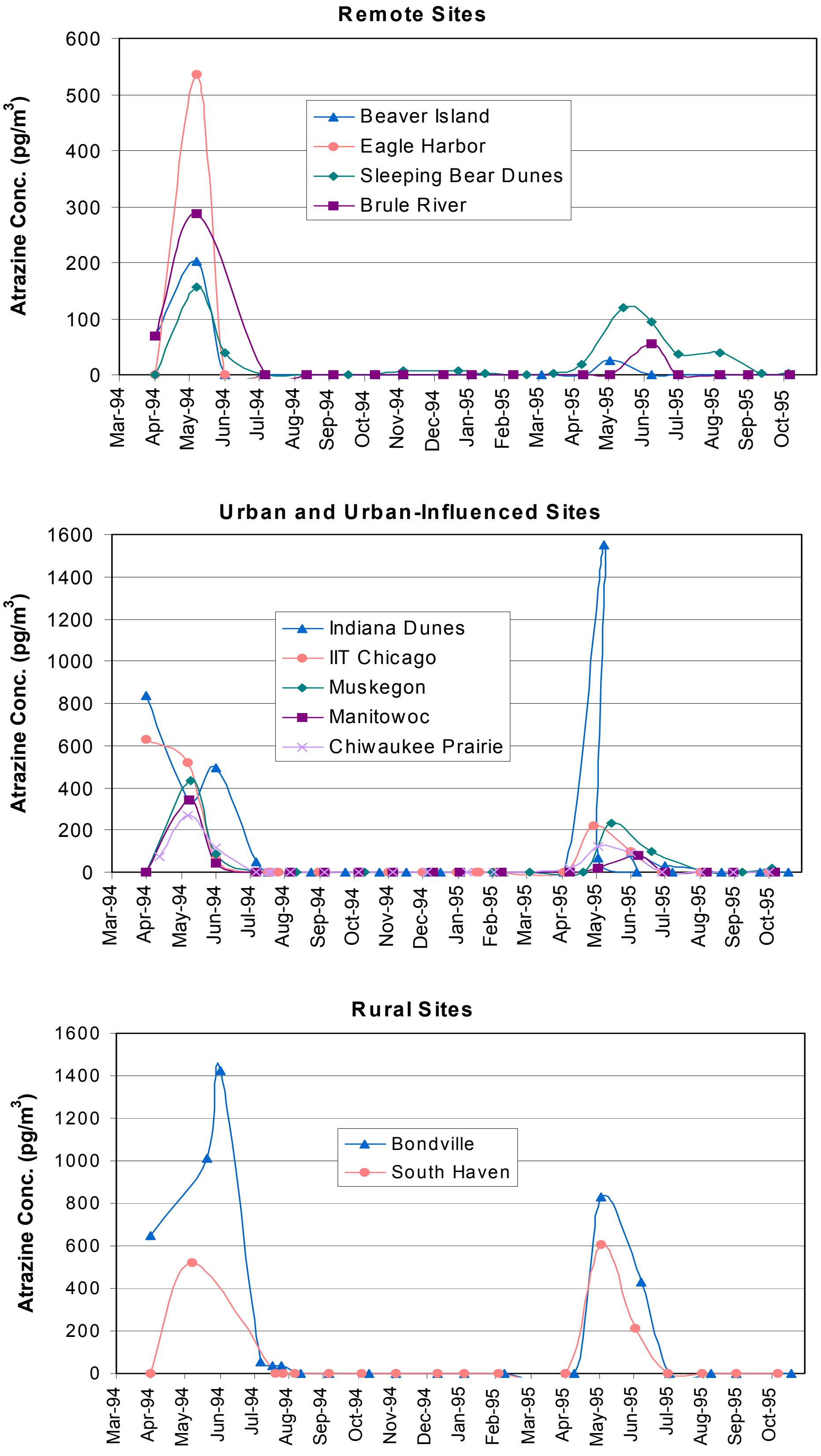
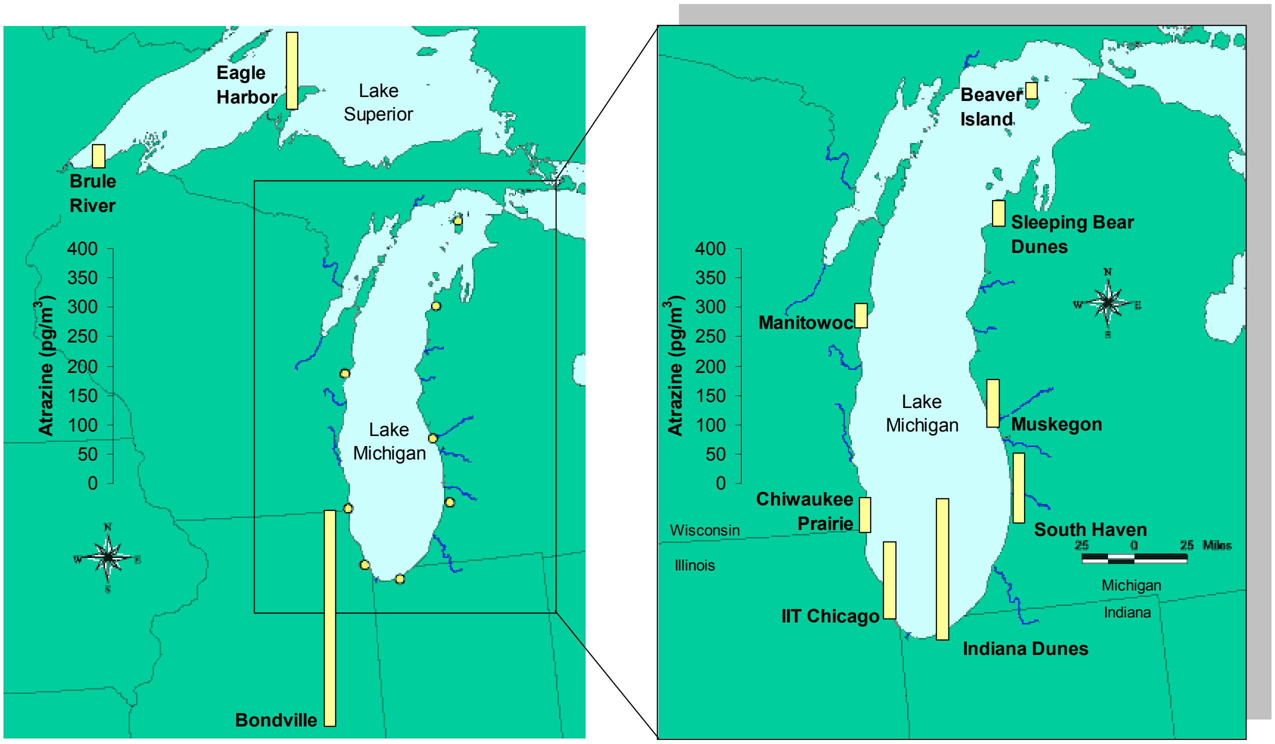


Table 3-3. Mean Spring/Summer Atrazine Concentrations Measured in the Particulate Phase

Sampling Location	Spring/Summer 1994[a]					Spring/Summer 1995[b]					Spring/Summer 1994-1995[c]				
	N[d]	Mean (pg/m^3)	Range (pg/m^3)	SD[e] (pg/m^3)	RSD[f] (%)	N[d]	Mean (pg/m^3)	Range (pg/m^3)	SD[e] (pg/m^3)	RSD (%)	N[d]	Mean (pg/m^3)	Range (pg/m^3)	SD[e] (pg/m^3)	RSD[f] (%)
Beaver Island	6	45	0.0-200	82	180	6	4.1	0.0-25	10	240	12	25	0.0-200	60	240
Eagle Harbor	4	130	0.0-530	270	200	-	-	-	-	-	4	130	0.0-530	270	200
Sleeping Bear Dunes	5	39	0.0-160	67	170	7	44	1.5-120	46	100	12	42	0.0-160	53	130
Brule River	5	71	0.0-290	120	180	6	9.1	0.0-54	22	240	11	37	0.0-290	87	230
Indiana Dunes	6	280	0.0-840	340	120	6	200	0.0-1200	470	240	12	240	0.0-1200	400	160
IIT Chicago	6	200	0.0-630	290	140	6	53	0.0-220	91	170	12	130	0.0-630	220	170
Muskegon	6	87	0.0-440	170	200	5	66	0.0-230	100	150	11	78	0.0-440	140	180
Manitowoc	6	64	0.0-340	140	210	6	16	0.0-78	31	200	12	40	0.0-340	98	240
Chiwaukee Prairie	6	76	0.0-270	110	140	6	38	0.0-120	53	140	12	57	0.0-270	82	140
Bondville	6	520	0.0-1400	610	120	6	210	0.0-830	350	170	12	370	0.0-1400	500	140
South Haven	5	100	0.0-520	230	220	6	140	0.0-610	250	180	11	120	0.0-610	230	190

[a] Samples collected from March 20, 1994 through September 23, 1994, based on the midpoint of the compositing period.
[b] Samples collected from March 20, 1995 through September 23, 1995, based on the midpoint of the compositing period.
[c] Samples collected from March 20 through September 23, 1994 and March 20 through September 23, 1995, based on the midpoint of the compositing period.
[d] N = number of monthly composite samples.
[e] SD = standard deviation.
[f] RSD = relative standard deviation.

Figure 3-5. Mean Spring/Summer Atrazine Concentrations Measured in the Particulate Phase



3.1.2.3 Analysis of Breakdown Products

DEA was only detected above sample-specific detection limits in five particulate phase samples. Sample-specific detection limits for DEA in the particulate phase ranged from 4.5 to 102 pg/m^3 and averaged 25 pg/m^3 for samples analyzed at the Illinois Water Survey. DEA was detected above sample-specific detection limits in the June 1995 monthly composite sample from Bondville (67 pg/m^3); the June 1994 monthly composite sample from Indiana Dunes (78 pg/m^3); the May 1995 monthly composite sample from Indiana Dunes (230 pg/m^3); a 12-hour composite sample from over-water station 1 on May 10, 1994 (230 pg/m^3); and a 12-hour composite sample from over-water station 5 on May 11, 1995 (100 pg/m^3). All samples that contained detectable amounts of DEA corresponded to samples containing >280 pg/m^3 atrazine. In those samples with DEA above sample-specific detection limits, DEA/atrazine ratios averaged 0.25.

DIA was not detected in any particulate phase samples analyzed. Sample-specific detection limits for DIA in the particulate phase ranged from 4.5 to 102 pg/m^3 and averaged 25 pg/m^3 for samples analyzed at the Illinois Water Survey. Samples processed at Indiana University were not analyzed for DEA or DIA.

3.1.3 Precipitation Fraction

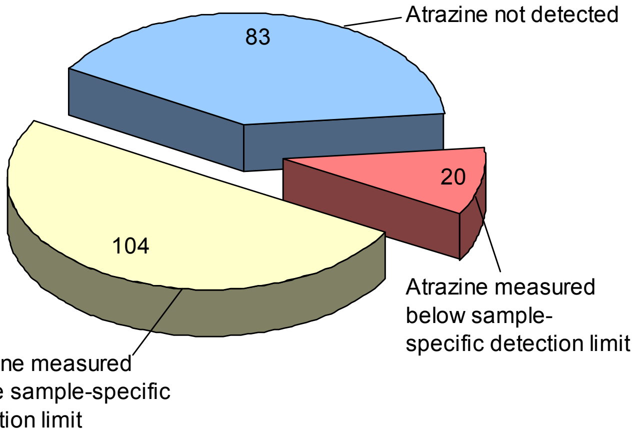
Of 207 precipitation samples tested, atrazine was detected (i.e., measured above zero) in 124 samples (60%), and measured atrazine concentrations were above sample-specific detection limits in 104 (50%) samples (Figure 3-6). Method detection limits (MDLs) were calculated from results of seven spiked samples according to the procedures specified at 40 CFR part 136, Appendix B. The MDL was then adjusted for each sample based on the analyzed sample volume and surrogate recovery factors to obtain sample-specific detection limits. Sample-specific detection limits ranged from 0.37 to 20 ng/L for samples analyzed at the Illinois Water Survey, and from 0.726 to 47.6 ng/L for samples analyzed at

Indiana University. Sample-specific detection limits averaged 3.0 ng/L and 8.96 ng/L for samples analyzed at the Illinois Water Survey and Indiana University, respectively.

3.1.3.1 Seasonal Variation

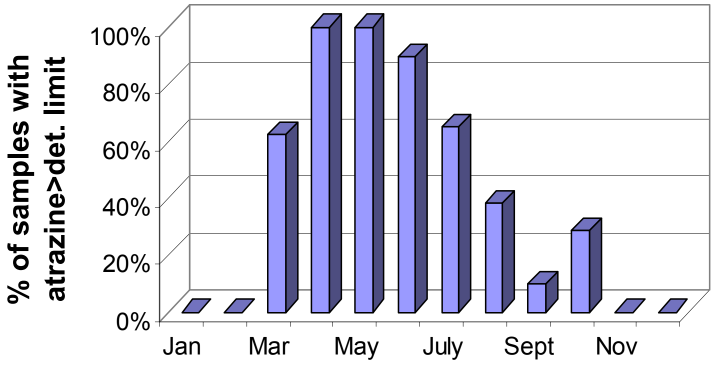
The presence and concentration of atrazine in precipitation samples was strongly influenced by season. Atrazine was primarily detected during the spring and summer months (Figure 3-7). All precipitation samples collected during April and May contained atrazine above the sample-specific detection limits, and a majority of samples collected in March, June, and July contained atrazine above sample-specific detection limits. Atrazine was detected in less than half of precipitation samples collected in August, September, and October; and atrazine was not detected in any samples collected from November through February.

Figure 3-6. Detection Frequency of Atrazine in Precipitation Samples



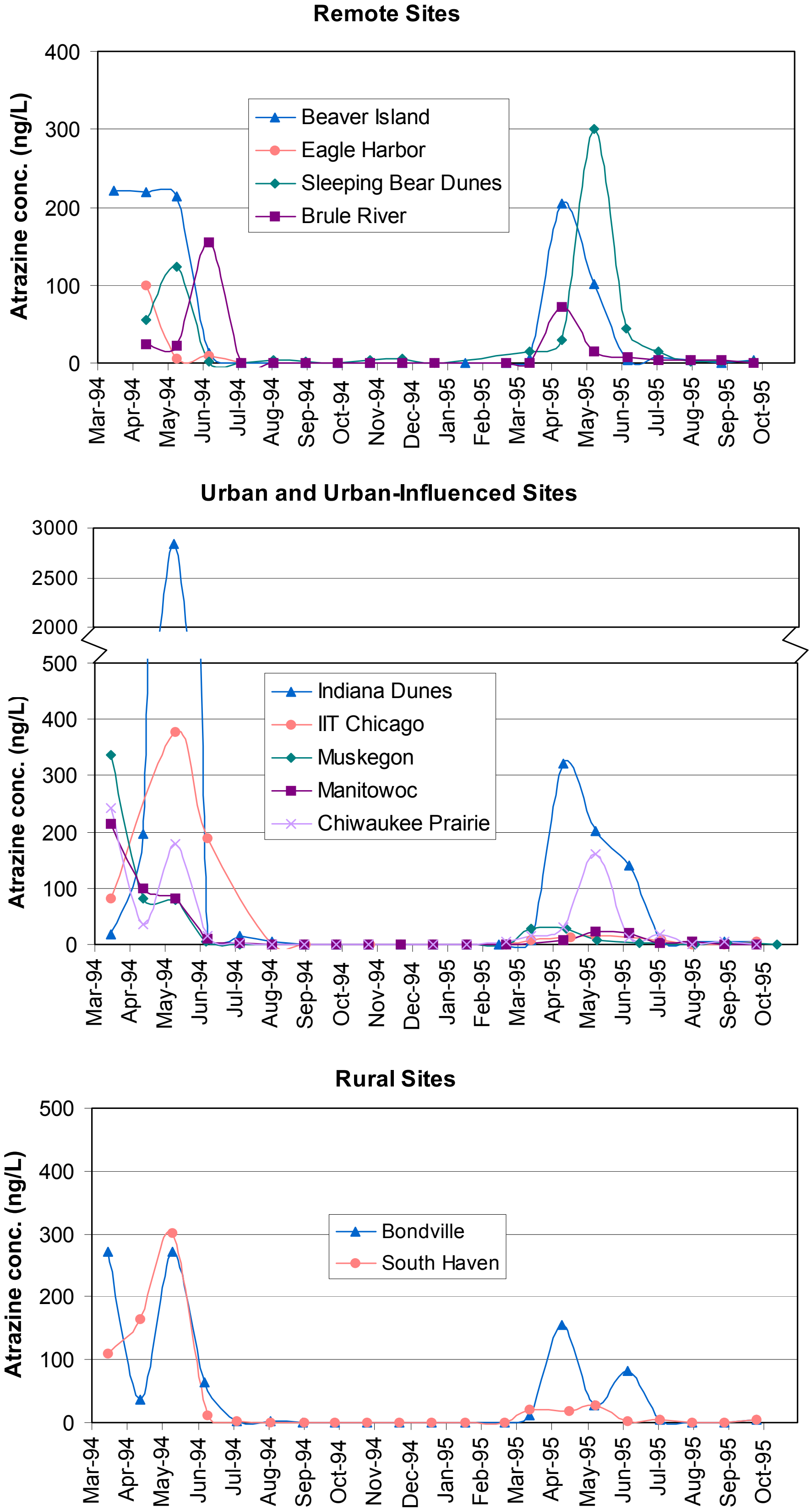
Atrazine concentrations in precipitation peaked during both the spring of 1994 and the spring of 1995 at all shoreline and out-of basin sampling stations (Figure 3-8). For all sampling stations except for Sleeping Bear Dunes, peak atrazine concentrations in precipitation were higher in the spring of 1994 than the spring of 1995. Peak concentrations were observed during the month of March at five sampling stations (Beaver Island, Muskegon, Manitowoc, Chiwaukee Prairie, and Bondville). At four sampling stations (Sleeping Bear Dunes, Indiana Dunes, IIT Chicago, and South Haven), peak concentrations were observed in May. Peak concentrations were observed in April and June at Eagle Harbor and Brule River, respectively.

Figure 3-7. Frequency Distribution of Atrazine Detection in Precipitation Samples



DEA and DIA concentrations followed the same seasonal pattern as atrazine concentrations, with detection frequency and concentrations peaking in the spring and summer months. DEA was only detected in samples collected from March through August, and DIA was only detected in samples collected from April through June. Similarly to seasonal trends for atrazine, DEA and DIA concentrations peaked in the early spring. Peak concentrations of DEA and DIA at all sampling stations were higher in the spring of 1994 than the spring of 1995.

Figure 3-8. Seasonal Trend of Atrazine Concentrations in Precipitation



Remote Sites

Urban and Urban-Influenced Sites

Rural Sites

Due to the dramatic seasonal variation in atrazine, DEA, and DIA concentrations, station averages were calculated only for measurements during the spring and summer growing season, when atrazine and atrazine metabolites were primarily detected in atmospheric samples. Spring/summer mean atrazine concentrations were calculated by volume-weighted averaging of 28-day composite samples that were collected between March 20 (the first day of spring) and September 23 (the first day of fall), based on the midpoint of the compositing period. Station averages were calculated as volume-weighted means to avoid bias from small precipitation events with very high measured concentrations or large precipitation events with low measured concentrations. Volume-weighted mean concentrations were calculated as:

$$\frac{\sum_{i=1}^{n} c_i \times v_i}{\sum_{i=1}^{n} v_i}$$

where:

c_i = measured concentration in the ith sample,
v_i = volume of the ith sample, and
n = number of samples.

All results were included in volume-weighted mean calculations as reported, meaning that measurements below sample-specific detection limits were included and not censored. Results reported as zero also were included in volume-weighted mean calculations.

Volume-weighted mean atrazine concentrations measured in precipitation during the spring/summer of 1994, 1995, and both years combined are presented in Table 3-4. For all sampling stations except for Chiwaukee Prairie and Sleeping Bear Dunes, volume-weighted mean spring/summer atrazine levels in the precipitation phase were higher in 1994 than 1995 (Table 3-4). Volume-weighted mean spring/summer DEA and DIA concentrations were higher in 1994 than 1995 at all sites (Table 3-5).

Table 3-4. Volume-weighted Mean Spring/Summer Atrazine Concentrations Measured in Precipitation

Sampling Location	Spring/Summer 1994[a]					Spring/Summer 1995[b]					Spring/Summer 1994-1995[c]				
	N[d]	Mean[e] (ng/L)	Range (ng/L)	SD[f] (ng/L)	RSD[g] (%)	N[d]	Mean[e] (ng/L)	Range (ng/L)	SD[f] (ng/L)	RSD[g] (%)	N[d]	Mean[e] (ng/L)	Range (ng/L)	SD[f] (ng/L)	RSD[g] (%)
Beaver Island	7	85	0.0-220	120	120	7	46	0.0-210	79	170	14	67	0.0-220	98	140
Eagle Harbor	4	19	0.0-100	48	170	-	-	-	-	-	4	19	0.0-100	48	170
Sleeping Bear Dunes	6	17	0.84-120	50	160	7	47	1.4-300	110	190	13	35	0.84-300	84	180
Brule River	6	31	0.0-160	61	180	7	19	0.0-72	26	170	13	25	0.0-160	44	190
Indiana Dunes	7	130	0.0-2800	1100	240	7	110	4.0-320	130	130	14	120	0.0-2800	750	280
IIT Chicago	5	53	0.0-380	160	120	6	8.2	0.0-17	6.5	88	11	24	0.0-380	120	190
Muskegon	7	43	0.84-340	120	170	6	8.5	0.0-29	13	120	13	26	0.0-340	92	210
Manitowoc	7	40	0.0-210	80	140	6	7.4	0.79-22	9.1	98	13	26	0.0-210	62	180
Chiwaukee Prairie	7	29	0.0-240	100	150	7	34	0.0-160	57	160	14	32	0.0-240	80	160
Bondville	7	120	0.0-270	120	130	7	56	0.0-160	59	150	14	83	0.0-270	97	150
South Haven	7	39	0.0-300	120	140	7	12	0.0-28	12	110	14	28	0.0-300	88	190

[a] Samples collected from March 20, 1994 through September 23, 1994, based on the midpoint of the compositing period.

[b] Samples collected from March 20, 1995 through September 23, 1995, based on the midpoint of the compositing period.

[c] Samples collected from March 20 through September 23, 1994 and March 20 through September 23, 1995, based on the midpoint of the compositing period.

[d] N = number of 28-day composite samples.

[e] Mean was calculated as a volume-weighted mean by dividing the total mass of atrazine measured at a site (individual concentrations x sample volumes) by the total precipitation volume collected at the site.

[f] SD = standard deviation.

[g] RSD = relative standard deviation.

Table 3-5. Volume-weighted Mean Spring/Summer DEA and DIA Concentrations Measured in Precipitation[a]

Sampling Location	N[b]	DEA				DIA			
		Mean[c] (ng/L)	Range (ng/L)	SD[d] (ng/L)	RSD[e] (%)	Mean[c] (ng/L)	Range (ng/L)	SD[d] (ng/L)	RSD[e] (%)
Beaver Island	14	18	0.0-110	36	170	3.7	0.0-50	14	300
Eagle Harbor	4	9.7	0.0-19	7.9	73	1.2	0.0-6.4	3.2	200
Sleeping Bear Dunes	4	13	0.0-80	38	140	0.0	0.0-0.0	0.0	0.0
Brule River	13	4.7	0.0-21	6.2	140	0.38	0.0-3.0	0.97	250
Indiana Dunes	14	20	0.0-620	160	310	3.5	0.0-150	39	350
IIT Chicago	11	2.3	0.0-85	25	270	0.96	0.0-92	28	330
Muskegon	13	20	0.0-190	65	190	2.6	0.0-32	9.9	250
Manitowoc	13	17	0.0-220	60	230	0.28	0.0-9.3	2.6	360
Chiwaukee Prairie	14	12	0.0-280	78	220	1.5	0.0-95	25	360
Bondville	14	9.2	0.0-100	27	210	0.81	0.0-18	4.9	330
South Haven	14	12	0.0-640	170	330	1.2	0.0-110	28	370

[a] Samples collected from March 20 through September 23, 1994 and March 20 through September 23, 1995, based on the midpoint of the compositing period.
[b] N = number of 28-day composite samples.
[c] Mean was calculated as a volume-weighted mean by dividing the total mass of DEA or DIA measured at a site (individual concentrations x sample volumes) by the total precipitation volume collected at the site.
[d] SD = standard deviation.
[e] RSD = relative standard deviation.

3.1.3.2 Geographical Variation

Atrazine was detected in precipitation samples from all shoreline and out-of-basin sampling stations. Maximum atrazine concentrations at these locations ranged from 100 ng/L at Eagle Harbor to 2800 ng/L at Indiana Dunes. The maximum concentration measured at Indiana Dunes in May 1994 is a suspected outlier. The high concentration in this sample, which is more than six times the value for other samples, may be due to a relatively small precipitation event (low volume) that may have coincided with emissions from nearby fields. To avoid bias of station averages by such events, station averages were compared on a volume-weighted basis.

Volume-weighted mean spring/summer atrazine levels for the two-year sampling campaign (1994-1995) ranged from 19 ng/L at Eagle Harbor to 120 ng/L at Indiana Dunes (Table 3-4 and Figure 3-9). Differences in mean atrazine levels among sites were not statistically significant due to the high variability of measured concentrations at each station, based on the Kruskal-Wallis test (p=0.913).

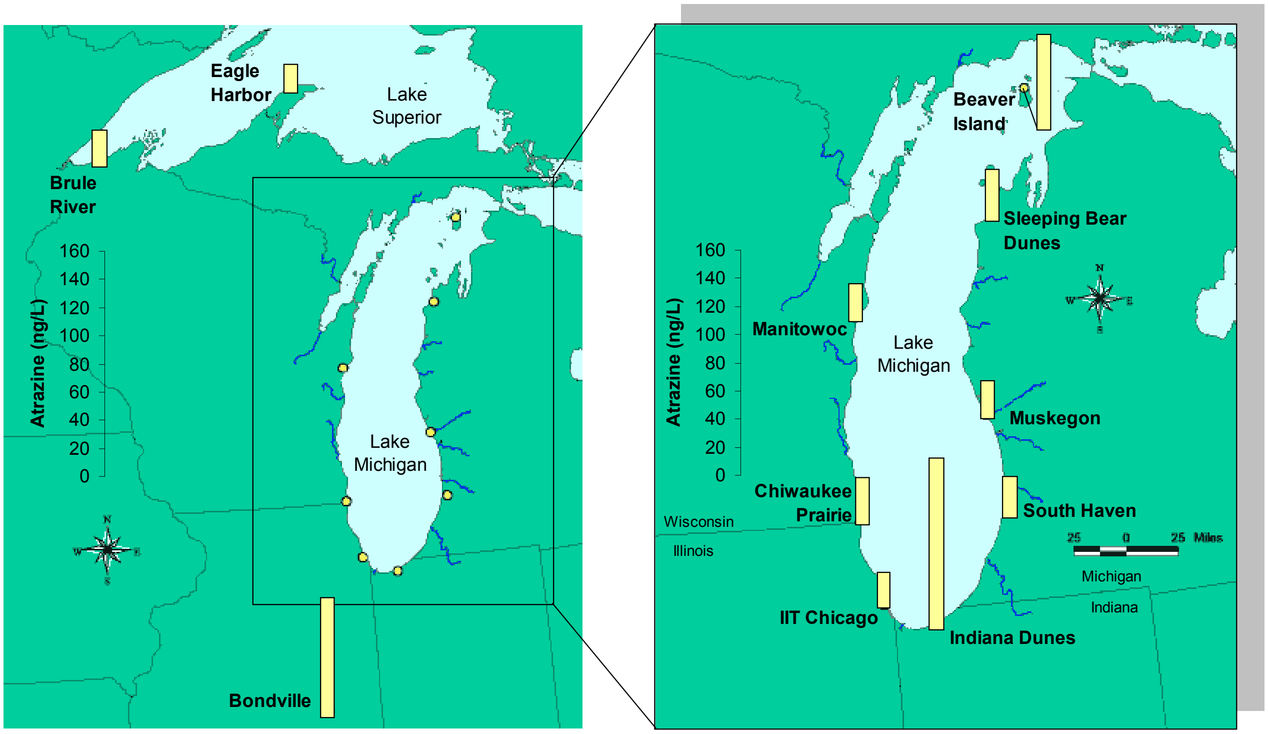
While particulate atrazine levels were generally higher at shoreline sampling stations surrounding the southern Lake Michigan basin than shoreline sampling stations surrounding the northern basin, this trend was not observed for atrazine levels in precipitation. In fact, the volume-weighted mean spring/summer atrazine concentrations at Beaver Island and Sleeping Bear Dunes, the two northern-most shore-line sampling station, were higher than at any of the southern basin sampling stations except for Indiana

Dunes (Figure 3-9). Volume-weighted mean spring/summer atrazine concentrations at the remote out-of-basin sampling stations (Eagle Harbor and Brule River) were comparable to concentrations at the shoreline stations. At the agricultural Bondville station, atrazine was higher than shoreline sampling stations, except for Indiana Dunes.

Similarly to atrazine in precipitation, DEA was detected in precipitation at all shoreline and out-of-basin sampling stations. Maximum DEA concentrations at each site ranged from 19 ng/L at Eagle Harbor to 640 ng/L at South Haven. Volume-weighted spring/summer DEA concentrations ranged from 2.3 ng/L at IIT Chicago to 20 ng/L at both Indiana Dunes and Muskegon (Table 3-5). Differences in mean DEA levels among sites were not statistically significant, based on the Kruskal-Wallis test (p=0.957), and did not represent any distinct geographical trends.

DIA was detected at all shoreline and out-of-basin sampling locations with the exception of the Sleeping Bear Dunes site, which was not sampled for DEA or DIA during the 1995 sampling campaign. Maximum non-zero DIA concentrations ranged from 3.0 ng/L at Brule River to 150 ng/L at Indiana Dunes. Volume-weighted spring/summer DIA concentrations ranged from 0.0 ng/L at Sleeping Bear Dunes to 3.7 ng/L at Beaver Island (Table 3-5). Differences in mean DIA levels among sites were not statistically significant, based on the Kruskal-Wallis test (p=0.994), and did not represent any distinct geographical trends.

Figure 3-9. Mean Spring/Summer Atrazine Concentrations Measured in Precipitation



Six precipitation samples were collected from the following over-water sampling stations: 1, 5, 380, 23M, GB24M, and GB17. Atrazine was detected in only two of these samples. The precipitation sample collected on August 20, 1994 at station 23M contained 7.5 ng/L atrazine, and the precipitation sample collected on April 12, 1995 at station GB17 contained 29 ng/L atrazine. Atrazine was not detected in any other precipitation samples from over-water stations, however, the remaining samples were collected in October and November, when atrazine also was not detected at shore-line sampling stations. DEA and DIA were not detected in precipitation samples collected from over-water sampling stations, however, four of these six samples were collected in October and November, when DEA and DIA also were not detected at shore-line sampling stations.

3.1.3.3 Analysis of Breakdown Products

Of 193 precipitation samples tested, DEA was detected (i.e., measured above zero) in 76 samples (39%), and measured DEA concentrations were above sample-specific detection limits in 58 (30%) samples (Figure 3-10). DIA was only detected in 17 of 193 (8.8%) samples (Figure 3-11). Sample-specific detection limits for DEA and DIA ranged from 0.55 to 30 ng/L and averaged 4.5 ng/L for samples analyzed at the Illinois Water Survey. Samples processed at Indiana University were not analyzed for DEA or DIA.

Figure 3-10. Detection Frequency of DEA in Precipitation Samples

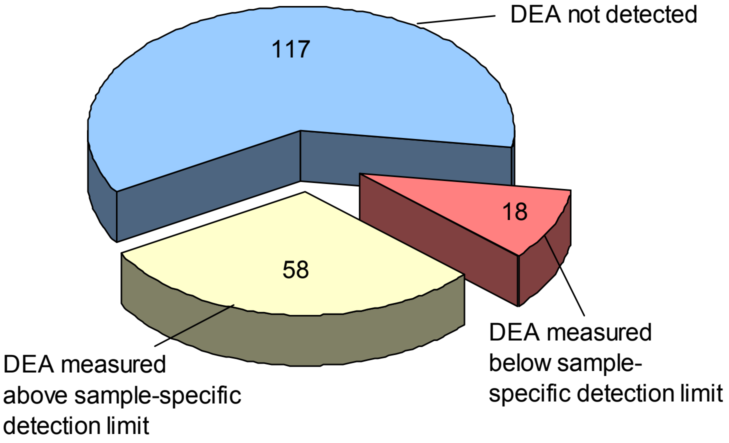
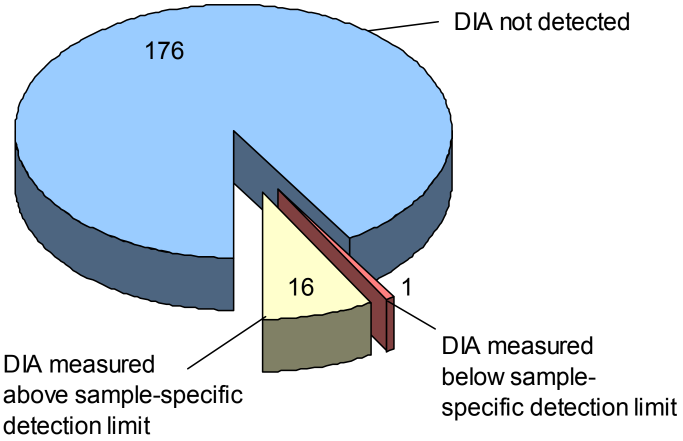
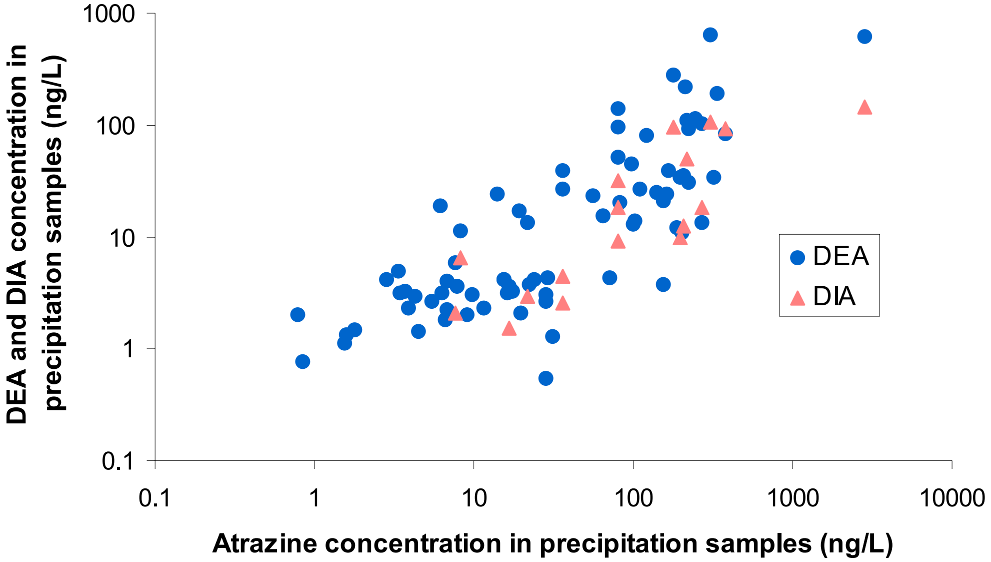


Figure 3-11. Detection Frequency of DIA in Precipitation Samples



DEA and DIA concentrations were highly correlated with atrazine concentrations in precipitation samples (Figure 3-12). All samples that contained detectable levels of DEA or DIA also contained detectable levels of atrazine, and as atrazine concentrations in precipitation samples increased, DEA and DIA concentrations also generally increased. Correlations between atrazine and DEA concentrations and between atrazine and DIA concentrations were statistically significant at the 95% confidence level. Pearson correlation coefficients for log transformed data were 0.80 and 0.84 for atrazine concentrations compared to DEA and DIA concentrations, respectively. For samples with concentrations greater than sample-specific detection limits, DEA/atrazine ratios in precipitation averaged 0.52. DIA/atrazine ratios averaged 0.22 among samples with concentrations greater than sample-specific detection limits.

Figure 3-12. Correlation of DEA and DIA Concentrations with Measured Atrazine Concentrations in Precipitation Samples



3.2 Data Interpretation

3.2.1 Atmospheric Sources and Concentrations

Atmospheric sources of atrazine and atrazine metabolites to Lake Michigan can include air/water exchange from the vapor phase, dry deposition of particulate-associated contaminants, and precipitation. This report summarizes the concentrations of atrazine in each of these atmospheric phases: vapor, particulate, and precipitation. This information will be used in the LMMB modeling effort to evaluate the fluxes and loads of contaminants from each of these sources.

Atrazine, DEA, and DIA were generally not detectable in the vapor phase of atmospheric samples collected in this study. Only 3.7% of samples contained atrazine above sample-specific detection limits. This is not surprising due to the relatively low vapor pressure of atrazine (0.04 mPa at 20°C). These data suggest that atrazine fluxes from the vapor phase are a minimal contributor to the total load of atrazine to Lake Michigan. This finding is consistent with previous mass balance modeling efforts, which have either neglected air/water exchange of atrazine as minimal (Rygwelski *et al.*, 1999) or estimated the load to Lake Michigan from air/water exchange to be less than 1% of the total load (Schottler and Eisenreich, 1997).

Atrazine was much more frequently detected in the particulate phase of atmospheric samples than the vapor phase. Schottler and Eisenreich (1997) estimated that over 90% of the total air concentration (vapor and particulate) is in the particulate phase. In this study, 91% of the mass of atrazine measured in atmospheric samples was in the particulate phase. Atrazine was detected above sample-specific detection limits in 29% of particulate phase samples, compared to the 3.7% of samples containing atrazine in the vapor phase. Detection frequency of atrazine in the particulate phase was even higher during spring and summer months (up to 92% in May). Similarly, Foreman *et al.* (2000) found that atrazine was detected in approximately 50 to 85% of spring/summer air samples collected at agricultural sites throughout the Mississippi River valley.

The predominant atmospheric source of atrazine, DEA, and DIA measured in this study was precipitation. Atrazine was detected in 50% of precipitation samples overall and up to 100% of precipitation samples collected during spring and summer months for a given station. Goolsby *et al.* (1997) found that atrazine was the most frequently detected herbicide in rainfall collected from the midwest and northeast in 1990-91, with 30.2% of precipitation samples containing detectable levels of atrazine. This compares well to the 50% of samples with detectable atrazine in this study, since this study focused on the midwest, where Goolsby *et al.* cited more frequent detection of atrazine. Goolsby *et al.* detected DEA and DIA in 17.4% and 2.6% of samples, respectively. This also is comparable to the 30% and 8.8% of samples collected in the LMMB Study that contained DEA and DIA, respectively.

Atrazine concentrations as high as 2.8 µg/L were measured in precipitation at the Indiana Dunes sampling station. This is similar to the maximum concentration of 3 µg/L measured by Goolsby *et al.* (1997) in individual samples collected from the midwest in 1990-91, and the maximum concentration of 2.9 µg/L measured by Capel *et al.* (1997) in Minnesota from 1989-1994. Nations and Hallberg (1992) measured considerably higher maximum atrazine concentrations (up to 40 µg/L) in precipitation from intense agricultural areas in Iowa. Goolsby *et al.* (1997) also found that volume-weighted mean concentrations of 0.2 - 0.4 µg/L were common in the midwest during mid-April through mid-July. These reported mean values were slightly higher than the volume-weighted mean concentrations observed in the LMMB Study. Volume-weighted mean atrazine concentrations measured in the LMMB Study ranged from 0.019 to 0.12 µg/L, however, these means were calculated for the March 20 through September 23 time period while Goolsby *et al.* (1997) reported means just for a 13-week period during peak atrazine detection. Volume-weighted mean atrazine concentrations calculated in the LMMB Study could also be lower due to the significant number of non-detect results that were reported and factored into mean calculations.

3.2.2 Seasonality

Atrazine, DEA, and DIA concentrations in all atmospheric phases were highly seasonal. Atrazine and atrazine metabolites were generally not detectable in winter air and precipitation samples. Atrazine detection frequency and concentrations peaked in the late spring to early summer corresponding to the agricultural application of atrazine during spring planting of corn and sorghum crops. Atrazine concentrations then generally decreased to below detection by mid-August.

This finding agrees with other researchers who have identified the absence of atrazine in winter samples (Williams *et al.*, 1992) and the increase in atrazine detection frequency in mid-April with peaks in May or June (Goolsby *et al.*, 1997; Nations and Hallberg, 1992; Capel *et al.*, 1997; Thurman and Cromwell, 2000). This highly seasonal nature of atmospheric atrazine concentrations suggests that atmospheric loadings to Lake Michigan can be quickly affected by alterations in use patterns. The general absence of atrazine in winter atmospheric samples indicates that atrazine is not extremely persistent in the atmosphere nor is it appreciably transported to the atmosphere during periods of non-use.

3.2.3 Regional Considerations

Atrazine concentrations in the particulate phase appeared to be higher in areas of more intensive agricultural land use, where atrazine usage is greater (see Figure 2-2). The highest mean concentration of atrazine in the particulate phase was measured at the Bondville sampling station, which is in the center of an intensive corn-growing region, where atrazine usage is greater than 163.73 pounds per square mile. In addition, atmospheric sampling stations surrounding the southern Lake Michigan basin, where atrazine use is highest, had higher mean particulate atrazine levels than stations surrounding the northern basin (Figure 3-9). Mean particulate atrazine concentrations at the more northern and remote Beaver Island, Sleeping Bear Dunes, and Brule River sites were lower than at any of the stations surrounding the southern Lake Michigan basin and were only 7-11% of the mean particulate atrazine concentration at the

Bondville site. These findings indicate that while long-range (e.g., regional) transport of atrazine in the particulate phase does occur, as demonstrated by the detection of particulate-phase atrazine at remote sites, atrazine concentrations in the particulate phase are generally reflective of local conditions. As suggested by Miller *et al.* (2000), airborne particles associated with atrazine are likely suspended by mechanical processes such as farm machinery and are likely to be in the larger size range (3-20 µm diameter). These larger particles are less likely to undergo long-range (e.g., regional) atmospheric transport and are generally deposited locally. Particle size distribution analysis was not conducted to confirm this hypothesis, but this explanation is consistent with the finding that particulate phase atrazine concentrations are reflective of local conditions.

In contrast, concentrations of atrazine in precipitation were less reflective of local conditions. While concentrations of atrazine in precipitation were highest at the Bondville and Indiana Dunes sites that are located in highly agricultural areas, precipitation at remote sites also contained high concentrations of atrazine. Concentrations of atrazine exceeding 100 ng/L were measured in individual precipitation samples collected at all of the LMMB sampling stations including those in remote areas hundreds of kilometers away from areas of intensive atrazine use. Volume-weighted mean atrazine concentrations in precipitation at the remote Beaver Island and Sleeping Bear Dunes sites were higher than all other stations except for Indiana Dunes and Bondville. This suggests that precipitation samples do not only reflect the atrazine from local sources that is scavenged by rainfall, but also may reflect atrazine that is brought into cloud formations and transported over long distances. Similarly, Capel *et al.* (1997) concluded that there is a significant content of pesticides in rain regionally in the Midwest, and that superimposed on this regional background is a local influence.

In addition, peak atrazine concentrations at Chiwaukee Prairie, Manitowoc, and Beaver Island in 1994 were observed in mid-March, even though corn planting had not yet begun in southern Wisconsin during this period (Wisconsin Department of Agriculture, 1994). Nations and Hallberg (1992) also observed that atrazine presence in precipitation began before application in the local area. Both the early appearance of atrazine around Lake Michigan and its detection in samples at remote sites on northern Lake Michigan and on Lake Superior (Brule River), far removed from agricultural source areas, suggest long-range (e.g., regional) transport. This conclusion is consistent with the findings of other researchers who have also detected atrazine in precipitation at sites remote from cropland. Goolsby *et al.* (1997) found atrazine in precipitation samples from Maine, Isle Royale in northern Lake Superior, and 4% of background sites in the Rocky Mountains and Alaska. Majewski *et al.* (2000) detected atrazine in 76% of samples collected from April through September 1995 at the remote Eagle Harbor site. Thurman and Cromwell (2000) measured atrazine concentrations as high as 1.8 µg/L in precipitation at the Isle Royale National Park in northern Lake Superior.

3.2.4 Atrazine Breakdown Products

Almost no DEA or DIA residues were detected in samples of airborne particles while detection of these breakdown products was common in rain samples containing atrazine. This may be simply due to the differences in methodologies used to collect, concentrate, and extract atrazine and atrazine metabolites from the different atmospheric phases. This finding may also suggest more efficient scavenging of atrazine metabolites by precipitation. Van Dijk and Guicherit (1999) agreed that atrazine metabolites are more polar than their parent compound, more water soluble, and more readily removed by wet deposition processes.

Goolsby *et al.* (1997) also suggested that significant degradation of atrazine could be occurring in the atmosphere. This hypothesis was based on the finding that DEA to atrazine ratios in precipitation samples (median of 0.5) were higher than these ratios in streams draining cornbelt states (<0.1 to 0.4). DEA to atrazine ratios calculated in precipitation samples from the LMMB Study (median of 0.18), however, were somewhat lower than ratios reported by Goolsby (median of 0.5), and ratios in stream samples from the LMMB Study (median of 0.77) were higher than reported by Goolsby.

Conclusions concerning the breakdown of atrazine are difficult to make simply from measured atrazine and DEA concentrations. Inputs, outputs, and transformations of atrazine and DEA all affect measured concentrations. To fully assess atrazine degradation, specific studies using labeled compounds would be required.

3.3 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the atrazine monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB QA program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i). A brief summary of data quality issues for the atmospheric atrazine data is provided below.

As discussed in Section 2.5, the sample collection, extraction, and analysis methods for atrazine monitoring in this study are modifications of the methods used for the PCBs and chlorinated pesticides. PIs used surrogate spikes to monitor the bias of the analytical procedure. Surrogate recoveries were reported with the data generated at Indiana University, but were not reported with the data generated at the Illinois Water Survey. The Illinois Water Survey PI noted that spike recoveries for atrazine were generally 70 to 120%, similar to those obtained for PCBs. In a few cases, however, atrazine recoveries were in the range of 10 to 25%, well below the normal recovery range of 70 to 120%. This occurrence is documented for each affected sample in the database in the field “Exception to Method, Analytical.” DEA and DIA recoveries were usually less than 50%, and sometimes as low as 20%. As a consequence, the PI characterized DEA and DIA results as semi-quantitative. For the Indiana University data, surrogate correction was applied to a subset of the atrazine data. Approximately 25% of the study samples were already extracted when the use of a surrogate was included in the analytical procedure. Sample results that were not surrogate corrected are indicated as such in the database in the field “Exception to Method, Analytical.”

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 3-6 provides a summary of flags applied to the atmospheric atrazine data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. In this data report, the summary and analysis of atrazine data represent all results with the exception of those flagged as “invalid” by the QC coordinator in concert with the PI.

As illustrated in Table 3-6 and discussed in previous sections, atrazine was not detected in the majority of atmospheric samples. Ninety eight percent of vapor samples analyzed at Illinois Water Survey and 86% of vapor samples analyzed at Indiana University contained atrazine at concentrations below detection limits and were flagged MDL (less than method detection limit) or UND (analyte not detected). Precipitation samples most frequently contained atrazine concentrations above detection, with only 43% of precipitation samples analyzed at Illinois Water Survey and 50% of precipitation samples analyzed at Indiana University containing atrazine below detection and flagged MDL or UND. As discussed in previous sections, the presence and concentration of atrazine was highly influenced by season with peak concentrations in spring corresponding to agricultural application and the lowest observed concentrations (below detection) throughout the winter months.

A significant portion of study samples for some fractions were flagged for exceeding sample holding times. For example, 71% of vapor samples and 53% of particulate samples analyzed at Indiana University exceeded the established holding time. Overall, only 16% of atmospheric samples exceeded holding times because samples analyzed at the Illinois Water Survey rarely exceeded holding times. However, the holding times for atrazine, and many other environmental pollutants, are not well-characterized and the effects on the sample results are unknown.

To characterize contamination associated with field and analytical activities, field blanks were obtained for precipitation and high-volume samples at a subset of monitoring stations. In each case, filters and/or absorbent were installed in the samplers for the normal sampling period but were not exposed to precipitation or air flow. The precipitation field blank included a water rinse of the collector surfaces to check for contamination by dry-deposition that might have penetrated the cover and seal on the precipitation collector. Atrazine was reported in three particulate field blanks. Laboratory blanks analyzed at Indiana University (and associated with samples collected from Sleeping Bear Dunes from August 1994-October 1995) showed consistent contamination. Fourteen precipitation blanks and 13 particulate blanks contained atrazine at concentrations ranging from 62.2 to 912 pg/L and 0.437 to 5.19 pg/m^3. Of the 18 vapor phase laboratory blanks, 17 contained detectable atrazine at concentrations ranging from 0.590 to 9.54 pg/m^3. The source of this contamination was never identified. Project samples associated with contaminated blanks were qualified with the FBS (Failed Blank Sample) flag and also as likely biased high (HIB) when the sample concentration was less than five times the concentration found in the associated blank. Only 6% of vapor samples and 7% of precipitation samples were flagged HIB. No particulate samples required this flag. Blank contamination is an issue when evaluating vapor sample results at Sleeping Bear Dunes that showed concentrations above the detection limit. As discussed in Section 3.1.1, four of the six detected atrazine concentrations from Sleeping Bear Dunes (those collected on 10/23/94, 11/4/94, 8/8/95, and 10/7/95) were flagged for contamination of corresponding field or laboratory blanks.

Table 3-6. Summary of Routine Field Sample Flags for the Analysis of Atrazine in Atmospheric Samples

Fraction	FLAGS[a]											
	Sensitivity		Holding Time	Contamination		Precision		Bias				
	MDL	UND	EHT	FBS	FFR	FDL	FFD	FPC	FSS	FMS	LOB	HIB
Vapor (Illinois)	NA	98% (254)	21% (55)	0	0	0	NA	0	NA	0	0	0
Precipitation (Illinois)	NA	43% (83)	8% (15)	0	0	0	NA	14% (27)	NA	5% (9)	11 % (21)	0
Particulate (Illinois)	NA	76% (161)	6% (13)	0	0	0	NA	0	NA	4% (8)	4% (8)	0
Vapor (Indiana)	86% (30)	NA	71% (25)	69% (24)	NA	NA	14% (5)	NA	6% (2)	0	0	6% (2)
Precipitation (Indiana)	50% (7)	NA	21% (3)	29% (4)	NA	NA	21% (3)	NA	21% (3)	21% (3)	0	7%(1)
Particulate (Indiana)	87% (13)	NA	53% (8)	60% (9)	NA	NA	20% (3)	NA	20% (3)	7% (1)	0	0

[a] The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

MDL= Less than method detection limit (analyte produced an instrument response but reported value is below the calculated method detection limit). Validity of reported value may be compromised.
UND= Analyte not detected (analyte produced no instrument response above noise).
EHT= Exceeded holding time (sample or extract was held longer than the approved amount of time before analysis). Validity of reported value may be compromised.
FBS= Failed blank sample (a blank sample associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FFR= Failed field blank (a field blank sample associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FDL= Failed laboratory duplicate (a laboratory duplicate associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FFD= Failed field duplicate (a field duplicate associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FPC= Failed performance check (a laboratory performance check sample associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FSS= Failed surrogate (surrogate recoveries associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
FMS= Failed matrix spike (a matrix spike associated with this analysis failed the acceptance criteria). Validity of reported value may be compromised.
LOB= Likely biased low (reported value is probably biased low as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery or other internal lab QC data). Reported value is not considered invalid.
HIB= Likely biased high (reported value is probably biased high as evidenced by LMS (lab matrix spike) results, SRM (standard reference material) recovery, blank contamination, or other internal lab QC data). Reported value is not considered invalid.
NA= Not applicable. This flag was not applied to this data set or this type of QC sample was not prepared.

Matrix spike samples results showed acceptable results for the majority of study samples, where 5% of precipitation samples, 4% of particulate samples, and no vapor samples analyzed at Illinois Water Survey failed the matrix spike MQO criteria. For samples analyzed at Indiana University, 21% of precipitation samples, 7% of particulate samples, and no vapor samples failed the MQO criteria.

Based on the evaluation of multiple QC sample results and surrogate recoveries, the PI and the QC coordinator assigned HIB and low bias (LOB) flags to sample results. From Illinois Water Survey, 11% of precipitation samples and 4% of particulate samples were flagged LOB. No samples analyzed at Indiana University were flagged LOB, but 6% of vapor samples and 7% of precipitation samples were flagged HIB. No samples analyzed at Illinois Water Survey were flagged HIB.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD between the results for laboratory duplicate pairs. Table 3-7 provides a summary of data quality assessments for several of these attributes for the atmospheric atrazine study data.

System precision, estimated as the mean RPD between field duplicate results varied greatly by fraction. For example, particulate samples analyzed at Illinois Water Survey had a mean RPD of 11% and precipitation samples analyzed at Illinois Water Survey had a mean RPD of 115%. This may reflect the difficulty in collecting precipitation samples, however, the mean RPD for precipitation samples analyzed by Indiana University was 28.1%. Duplicate pair samples with a reported concentration of zero for either one of both samples could not be used in this assessment. Because of the large number of results reported as zero, the system precision estimate is based on only a small number of field duplicates and may not accurately reflect the system. Analytical precision, estimated as the mean RPD between laboratory duplicates, could only be estimated for precipitation samples analyzed at Indiana University (due to the large number of zero results in the Illinois Water Survey data). The mean RPD between laboratory duplicates of precipitation samples was 23%. Analytical precision was lower, but not much lower, than the mean RPD of 28.1% for system precision. This suggests the majority of the variability associated with the measurement system, as implemented at Indiana University, was associated with the analytical process and less variability was associated with the sampling process. This is not uncommon for environmental monitoring activities. Analytical precision at Indiana University also can be evaluated by the variability in surrogate correction factors. The standard deviations of surrogate correction factors for vapor, precipitation, and particulate samples were 0.227, 0.411, and 0.188, respectively. This suggests that the analytical results are highly reproducible.

Evaluation of matrix spike sample (LMS) results and surrogate recoveries shows a slight low bias overall for all phases of atmospheric samples. In most cases, the PI and QC coordinator determined that the bias was not strong enough to warrant flagging the data as HIB or LOB. A small portion of samples generated at Illinois Water Survey were flagged LOB, due in part to low surrogate recoveries, and a small portion of samples generated at Indiana University were flagged HIB, due in part to contamination in laboratory blanks.

Table 3-7. Data Quality Assessment for the Analysis of Atrazine in Atmospheric Samples[a]

Fraction	Number of Routine Samples Analyzed	Number of Field Duplicates Analyzed	System Precision Mean Field Duplicate RPD (%)		Analytical Precision		Analytical Bias		Analytical Sensitivity
			< MDL	>MDL	Mean Lab Duplicate RPD (%), <MDL	SCF Variability (SD)	Mean SCF Recovery (%)	Mean LMS Recovery (%)	Samples reported as <MDL (%)
Vapor (Illinois)	259	26	all results=0	all results=0	all results=0 (4)	-- (0)	-- (0)	83% (36)	98%
Precipitation (Illinois)	193	10	123% (2)	115% (3)	-- (0)	-- (0)	-- (0)	82% (24)	50%
Particulate (Illinois)	211	15	-- (0)	11% (2)	all results=0 (3)	-- (0)	-- (0)	83% (27)	76%
Vapor (Indiana)	35	13	67.8% (13)	-- (0)	-- (0)	0.227 (25)	932.8% (25)	82.5% (17)	83%
Precipitation (Indiana)	14	12	61.6% (5)	28.1% (5)	23.0% (2)	0.411 (13)	95.7% (13)	110% (14)	50%
Particulate (Indiana)	15	8	76.2% (6)	51.3% (2)	-- (0)	0.188 (10)	59.1% (10)	80.4% (13)	87%

[a] The number of QC samples/duplicate pairs used in the assessment is provided in parentheses.

RPD =	Relative percent difference.
MDL =	Sample-specific detection limit.
SCF =	Surrogate correction factor (unitless).
LMS =	Laboratory matrix spike.

Chapter 4
Atrazine in Tributaries

4.1 Results

From April 4, 1995 to October 31, 1995, filtered samples were collected from 11 tributaries that flow into Lake Michigan. A total of 108 filtered samples were collected and analyzed for atrazine, DEA, and DIA (Table 4-1). Unlike atmospheric samples that often did not contain detectable levels of atrazine and atrazine breakdown products, most tributary samples contained detectable levels of atrazine, DEA, and DIA. All tributary samples except for one (collected on October 18, 1995 from the Pere Marquette River) contained atrazine above method detection limits (MDLs). DEA was measured above the MDL in all but 10 (9.3%) tributary samples (2 from the Pere Marquette River, 2 from the Menominee River, and 6 from the Manistique River). DIA was measured above the MDL in all but 16 (14.8%) tributary samples (1 from the Kalamazoo River, 1 from the St. Joseph River, 4 from the Manistique River, 5 from the Menominee River, and 5 from the Pere Marquette River). Method detection limits were calculated from results of seven spiked samples according to the procedures specified at 40 CFR part 136, Appendix B. The calculated MDLs were 1.25 ng/L for atrazine, 2.46 ng/L for DEA, and 8.27 ng/L for DIA.

Table 4-1. Tributary Samples Collected and Analyzed for Atrazine, DEA, and DIA

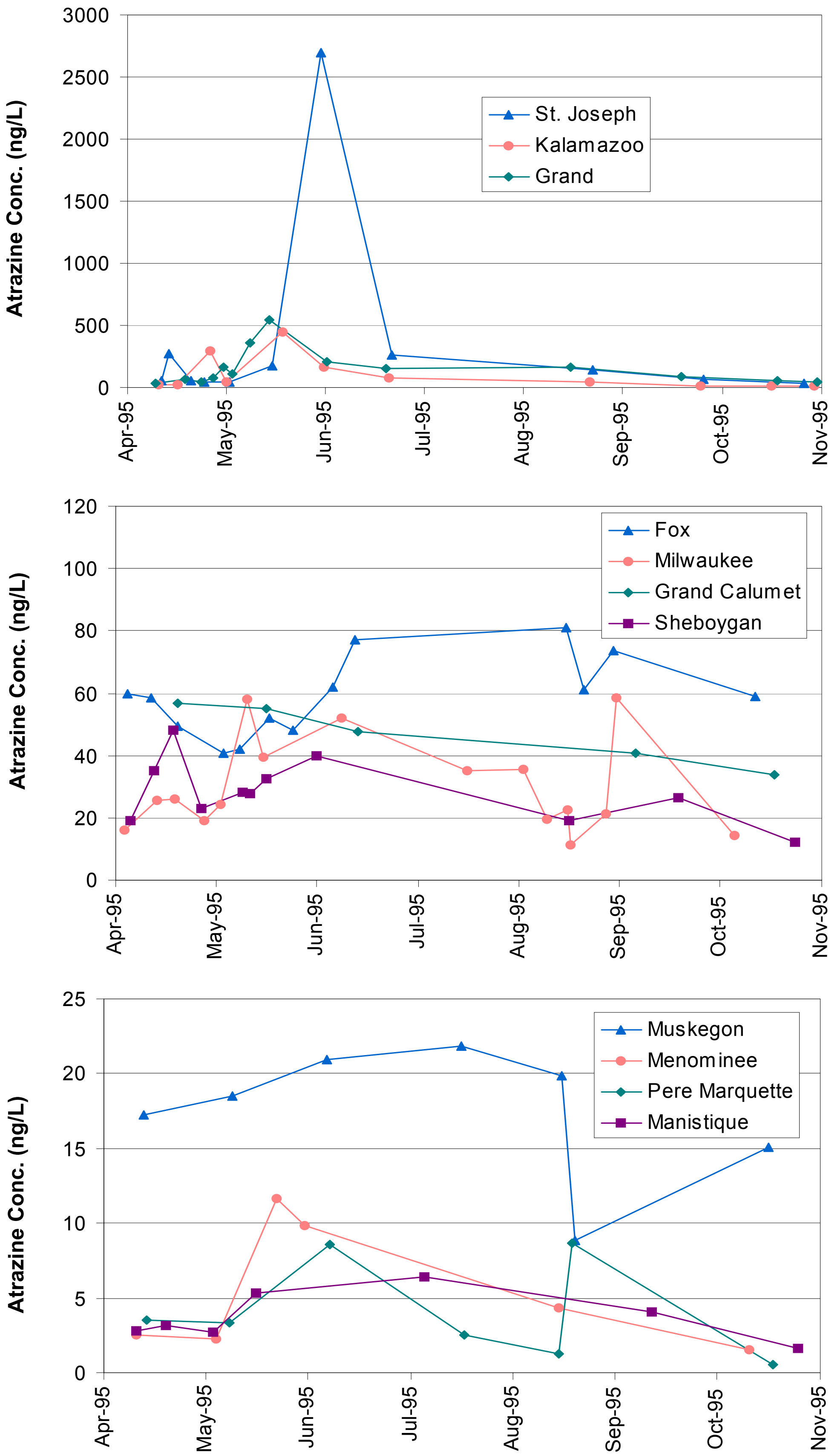
Tributary	Sampling Dates	Number of Samples
Fox	4/5/95 - 10/12/95	13
Grand Calumet	4/20/95 - 10/18/95	5
Grand	4/10/95 - 10/31/95	14
Kalamazoo	4/11/95 - 10/30/95	11
Manistique	4/11/95 - 10/26/95	7
Menominee	4/11/95 - 10/11/95	6
Milwaukee	4/4/95 - 10/6/95	16
Muskegon	4/13/95 - 10/17/95	7
Pere Marquette	4/14/95 - 10/18/95	7
Sheboygan	4/6/95 - 10/24/95	11
St. Joseph	4/12/95 - 10/27/95	11
	Total	108

4.1.1 Seasonal Variation

Tributary samples were only collected over a seven month period, so seasonal trends could not be fully evaluated. For the three tributaries with the highest mean atrazine concentrations (the St. Joseph River, the Kalamazoo River, and the Grand River), peaks in atrazine concentration were observed during mid to late May (Figure 4-1). Peaks in atrazine concentration were much less distinct for the remaining tributaries and occurred in April, May, July, or August (Figure 4-1). Seasonal patterns of DEA and DIA concentrations were very similar to those for atrazine. DEA concentrations in the St. Joseph and Grand Rivers peaked in mid to late May, and DEA concentrations in the Kalamzaoo River peaked in April. DIA concentrations in the St. Joseph and Kalamazoo Rivers peaked in mid to late May, and DIA concentrations in the Grand River peaked in April. For other tributaries, peaks in DEA and DIA concentrations were less defined and occurred in May, June, August, September, or October.

To statistically evaluate seasonal trends, monthly log-transformed atrazine, DEA, and DIA concentrations were compared using a two-way ANOVA model that considered station variability and monthly variability. Atrazine concentrations were significantly higher in June than in most other months

Figure 4-1. Seasonal Trend of Atrazine Concentrations in Lake Michigan Tributaries



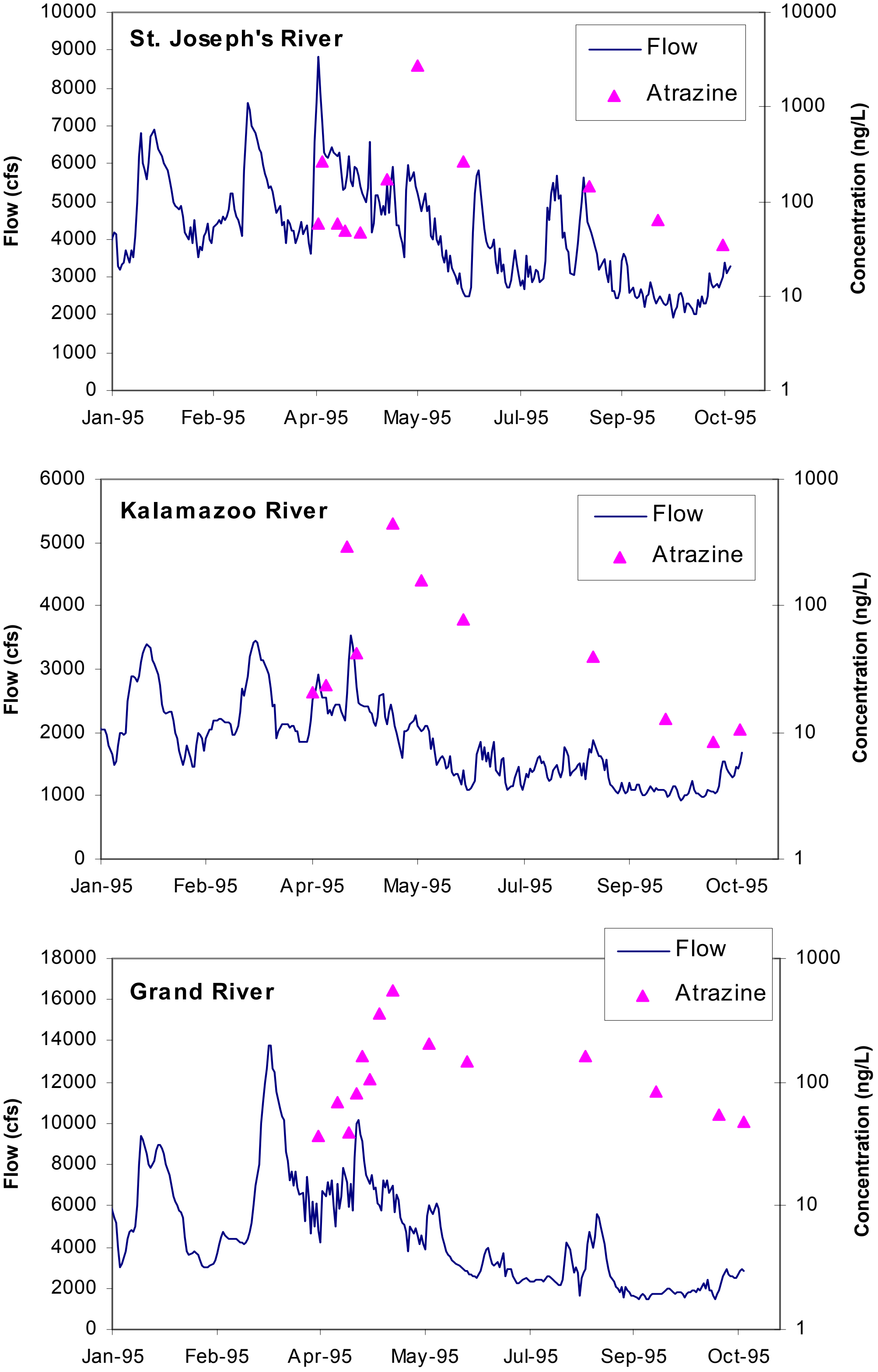
(April, July, August, and October), and atrazine concentrations were significantly lower in October than in most other months (April, May, June, and August). This finding of higher tributary atrazine concentrations in June and lower tributary atrazine concentrations in October (the last month sampled in the study) is consistent with application of the herbicide in the spring and degradation of the herbicide throughout the summer. A similar pattern was seen for DEA, with DEA concentrations significantly higher in June than in most other months (April, May, July, and October), and DEA concentrations significantly lower in October than in most other months (April, May, June, and August). DIA concentrations in June were significantly higher than concentrations in two other months (October and July), and DIA concentrations in October were significantly lower than concentrations in two other months (June and August). There was no significant interaction between month and station for any of the three analytes (atrazine: $p = 0.975$; DEA: $p = 0.973$; DIA: $p = 0.568$).

In addition to season, tributary atrazine concentrations are potentially affected by tributary flows. Higher flows associated with runoff events may increase atrazine concentrations as atrazine is flushed from the watershed. Conversely, during longer duration high flow events, atrazine concentrations could decrease as a result of dilution. The correlations between tributary atrazine concentrations and flow are presented in Table 4-2. In only one tributary (the Manistique River) was atrazine concentration significantly correlated with flow, and in this tributary, the correlation was negative (i.e., atrazine decreasing with increasing flow). Associations between flow and atrazine are difficult to make with such small data sets (n of 5 to 16), but in general, atrazine peaks appear to be much more influenced by the timing of atrazine application than tributary flows. Figure 4-2 shows the flow patterns and atrazine concentrations for the three tributaries with the highest atrazine levels. Peaks in atrazine occurred in the spring after atrazine application in the watershed. These peaks were often associated with small peaks in flow during the spring but were relatively independent of the magnitude of flow peaks. As Richards and Baker (1993) noted for Lake Erie tributaries, the annual pattern of atrazine concentrations is one of storm event peaks modified by an annual pattern of availability of the pesticide in late spring.

Table 4-2. Correlation of Tributary Atrazine Levels with Tributary Flow

Tributary	N	Correlation Coefficient	r^2	*p*-value
Manistique	7	-0.76	0.57	0.048
Muskegon	7	-0.52	0.27	0.230
Milwaukee	16	-0.33	0.11	0.210
Grand Calumet	5	0.019	0.00036	0.976
St. Joseph	11	0.060	0.0036	0.862
Grand	14	0.27	0.073	0.350
Fox	13	0.33	0.11	0.274
Menominee	6	0.47	0.22	0.347
Kalamazoo	11	0.53	0.28	0.091
Sheboygan	11	0.58	0.34	0.062
Pere Marquette	7	0.73	0.53	0.063

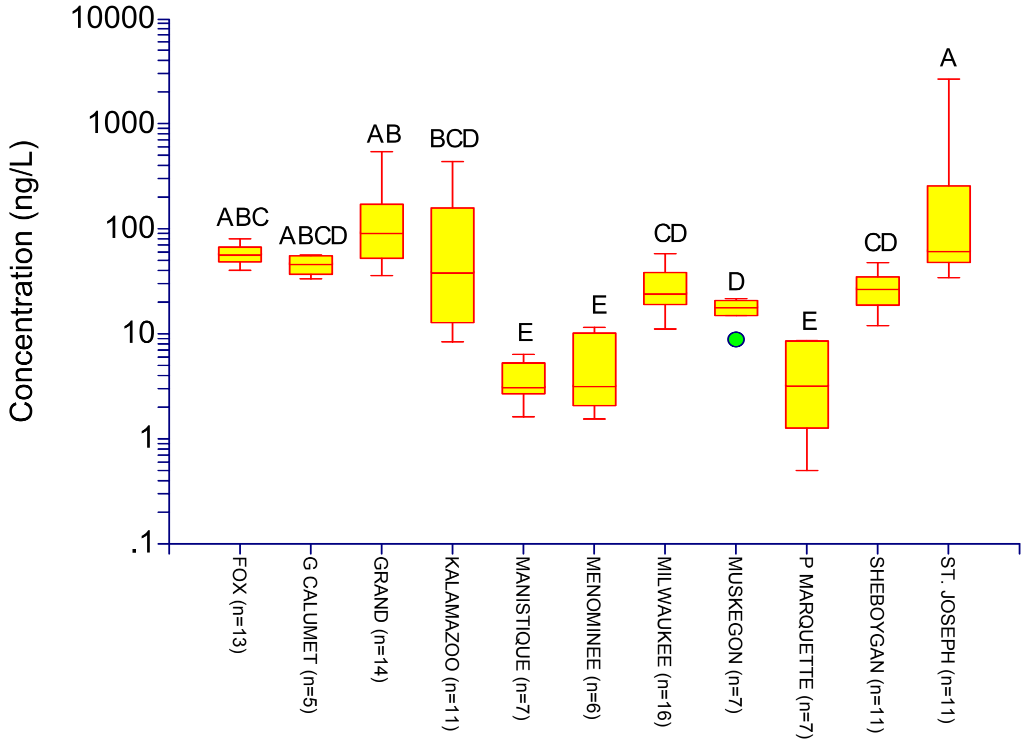
Figure 4-2. Seasonal Flow Patterns and Atrazine Concentrations in Selected Lake Michigan Tributaries



4.1.2 Geographical Variation

Atrazine concentrations measured in tributaries ranged nearly 4 orders of magnitude, from 0.50 ng/L in the Pere Marquette River to 2700 ng/L in the St. Joseph River (Figure 4-3). With the exception of one sample from the St. Joseph River that measured 2700 ng/L of atrazine, all other tributary samples contained 550 ng/L atrazine or less. Eighty-six percent of tributary samples contained less than 100 ng/L of atrazine, and all samples above 100 ng/L of atrazine were from the St. Joseph, Kalamazoo, or Grand Rivers.

Figure 4-3. Atrazine Concentrations Measured in Lake Michigan Tributaries[a]



[a] Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Tributaries with the same letter were not statistically different (at alpha = 0.05).

Mean atrazine concentrations during the 1995 sampling campaign ranged from 3.7 ng/L in the Manistique River to 350 ng/L in the St. Joseph River (Table 4-3 and Figure 4-4). The St. Joseph, Grand, and Kalamazoo Rivers had the highest mean atrazine concentrations (103 - 350 ng/L); and the Menominee, Manistique, and Pere Marquette Rivers had the lowest atrazine concentrations (3.7 - 5.3 ng/L). Those tributaries with the highest mean atrazine levels are located along the shore of the southern Lake Michigan basin, where agricultural influences are greatest. Those tributaries with the lowest mean atrazine levels are located in the northern portions of the lake, where land use is less dominated by agriculture (Figure 4-4).

Table 4-3. Mean Atrazine Concentrations Measured in Lake Michigan Tributaries

Tributary	N[a]	Mean (ng/L)	Range (ng/L)	SD[b] (ng/L)	RSD[c] (%)
Fox	13	59	41-81	13	22
Grand Calumet	5	47	34-57	9.7	21
Grand	14	150	36-550	140	96
Kalamazoo	11	103	8.5-440	140	140
Manistique	7	3.7	1.6-6.4	1.6	44
Menominee	6	5.3	1.6-12	4.3	80
Milwaukee	16	30	11-58	15	51
Muskegon	7	17	8.9-22	4.4	25
Pere Marquette	7	4.1	0.50-8.7	3.3	82
Sheboygan	11	28	12-48	10	36
St. Joseph	11	350	35-2700	780	220

[a] N = number of samples.
[b] SD = standard deviation.
[c] RSD = relative standard deviation.

Two-way analysis of variance controlling for month performed on log transformed tributary atrazine concentrations revealed that mean atrazine concentrations differed significantly (at the 95% confidence level) among tributaries. Results of Tukey's Studentized Range Test for multiple comparisons showed that mean atrazine concentrations in the St. Joseph and Grand Rivers were significantly higher (at the 95% confidence level) than mean concentrations in the Milwaukee, Sheboygan, Muskegon, Menominee, Manistique, and Pere Marquette Rivers and St. Joseph was greater than Kalamazoo (Figure 4-3). The mean atrazine concentration in the Fox River was significantly higher (at the 95% confidence level) than mean concentrations in the Muskegon, Menominee, Manistique, and Pere Marquette Rivers. These later three tributaries (the Menominee River, the Manistique River, and the Pere Marquette River) exhibited significantly lower (at the 95% confidence level) mean atrazine concentrations than any other site. Mean atrazine concentrations in these three rivers were from 3.3 to 94 times lower than mean atrazine concentrations in any other tributary.

DEA concentrations in tributary samples ranged from 1.1 ng/L in the Manistique River to 220 ng/L in the St. Joseph River. Mean DEA concentrations ranged from 1.7 ng/L to 55 ng/L in these same tributaries (Table 4-4). Similarly to atrazine concentrations, DEA concentrations were significantly lower (at the 95% confidence level) in the Menominee, Manistique, and Pere Marquette Rivers than in all other tributaries (Figure 4-5). Mean DEA concentrations were from 3.4 to 33 times lower in these three tributaries than in any other tributary. DEA concentrations in the Muskegon River were also significantly lower (at the 95% confidence level) than in the remaining tributaries (Figure 4-5).

DIA concentrations ranged from below detection to as high as 130 ng/L in the St. Joseph River. Mean DIA concentrations ranged from 6.1 ng/L in the Pere Marquette River to 45 ng/L in the Grand Calumet River (Table 4-4). DIA concentrations also were lower in the Manistique, Menominee, and Pere Marquette Rivers than in all other tributaries, however, the difference between the Pere Marquette River and the St. Joseph, Fox, and Kalamazoo were not statistically significant (at the 95% confidence level)

(Figure 4-5). Mean DIA concentrations in the Manistique, Menominee, and Pere Marquette Rivers were from 3.1 to 7.4 times lower than in other tributaries.

Figure 4-4. Mean Atrazine Concentrations Measured in Lake Michigan Tributaries

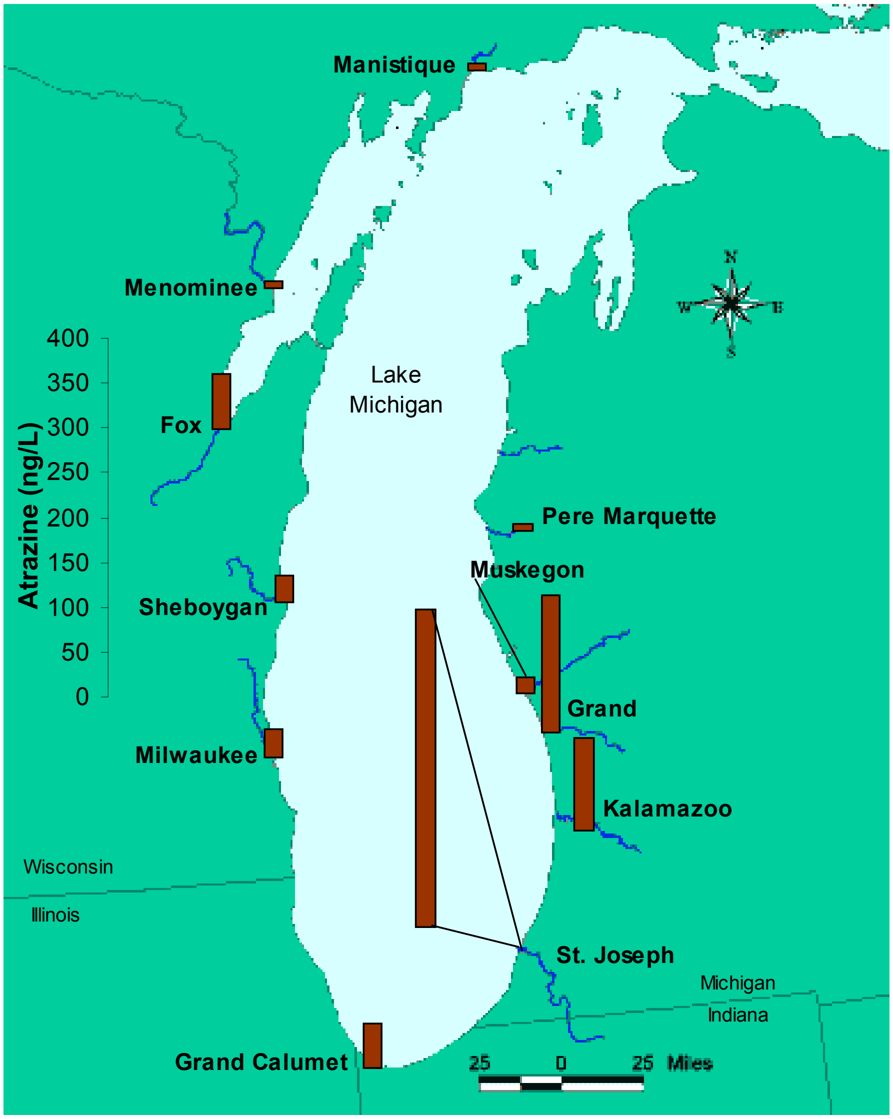


Table 4-4. Mean DEA and DIA Concentrations Measured in Lake Michigan Tributaries

Tributary	N[a]	DEA				DIA			
		Mean (ng/L)	Range (ng/L)	SD[b] (ng/L)	RSD[c] (%)	Mean (ng/L)	Range (ng/L)	SD[b] (ng/L)	RSD[c] (%)
Fox	13	47	37-62	6.5	14	23	14-34	6.0	27
Grand Calumet	5	31	24-39	6.5	21	45	27-94	27	60
Grand	14	49	26-88	19	40	41	26-60	11	27
Kalamazoo	11	28	13-50	13	46	20	7.9-37	10	51
Manistique	7	1.7	1.1-2.6	0.62	37	6.5	0.0-23	8.3	130
Menominee	6	4.0	1.6-6.9	2.2	56	6.3	0.0-23	8.5	140
Milwaukee	16	29	17-60	10	34	28	15-56	11	39
Muskegon	7	14	6.0-23	5.8	43	40	17-84	23	56
Pere Marquette	7	4.0	1.8-8.3	2.2	56	6.1	0.0-19	7.0	110
Sheboygan	11	32	28-44	4.4	14	38	25-47	7.2	19
St. Joseph	11	55	23-220	55	99	35	3.0-130	35	100

[a] N = number of samples.
[b] SD = standard deviation.
[c] RSD = relative standard deviation.

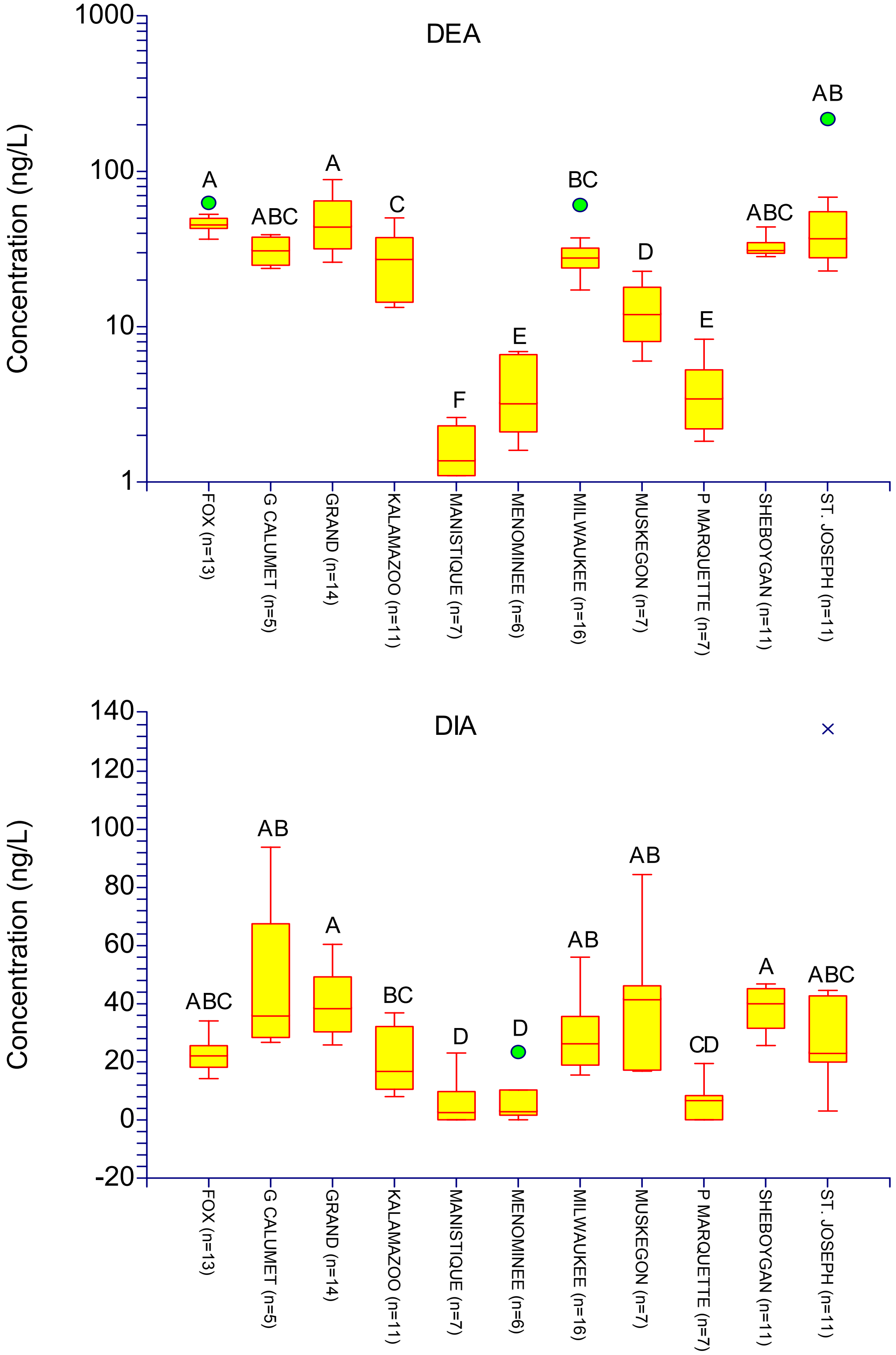
4.1.3 Analysis of Breakdown Products

DEA and DIA concentrations were highly correlated with atrazine concentrations in tributary samples. As atrazine concentrations increased, DEA and DIA concentrations also generally increased (Figure 4-6). Correlations between atrazine and DEA concentrations and between atrazine and DIA concentrations were statistically significant ($p< 0.0001$). Pearson correlation coefficients for log transformed data were 0.88 and 0.66 for atrazine concentrations compared to DEA and DIA concentrations, respectively.

The ratio of DEA to atrazine in surface water samples has been used to evaluate the degradation of atrazine in receiving systems. The median DEA/atrazine ratio calculated for tributary samples in this study was 0.77. Ratios ranged from 0.08 to 3.7. Two-way analysis of variance was performed on log-transformed DEA/atrazine ratios to evaluate the effect of month and tributary. This analysis revealed that DEA/atrazine ratios differed significantly among tributaries and differed significantly among months. The interaction of month and tributary did not account for a significant portion of the variance ($p=0.777$).

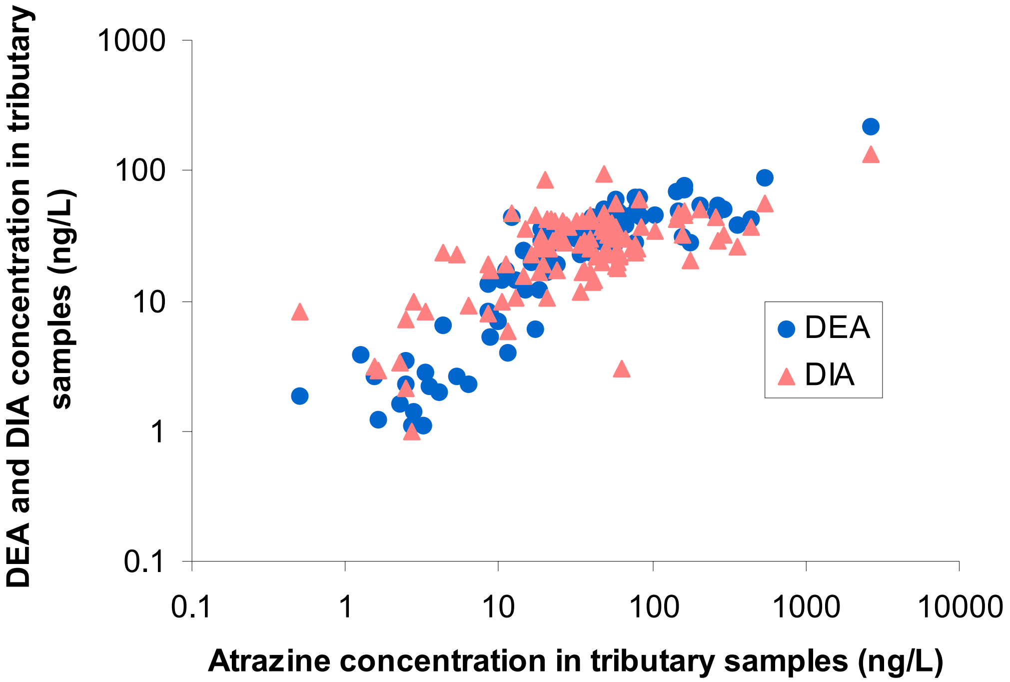
Mean DEA/atrazine ratios were the highest in the Pere Marquette, Sheboygan, and Milwaukee Rivers. Mean ratios were above 1.0 at each of these sites and were significantly greater than DEA/atrazine ratios in the Kalamazoo, Manistique, Grand, and St. Joseph Rivers. Mean DEA/atrazine ratios were 0.76 in the Kalamazoo River and below 0.5 in the Manistique, Grand, and St. Joseph Rivers. Higher DEA/atrazine ratios, especially those exceeding 1.0, indicate significant degradation of atrazine within the watershed or the tributary itself. Significant differences between DEA/atrazine ratios among tributaries suggest that either average residence times of atrazine within the watershed differ among tributaries, or degradation rates in those watersheds differ.

Figure 4-5. DEA and DIA Concentrations Measured in Lake Michigan Tributaries[a]



[a] Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Tributaries with the same letter were not statistically different (at alpha = 0.05).

Figure 4-6. Correlation of DEA and DIA Concentrations with Measured Atrazine Concentrations in Tributary Samples



Statistically significant differences in DEA/atrazine ratios also were observed among samples collected in various months (April through October). The mean DEA/atrazine ratio of 1.4 measured in October was significantly greater than the mean ratios in April (0.75), May (0.63), or June (0.87). The mean DEA/atrazine ratio of 1.1 measured in August also was significantly greater than mean ratios in April, May and June. Atrazine is typically applied in the late spring or early summer, so DEA/atrazine ratios are lowest during this time period. As atrazine degrades in soils, groundwater, or surface water throughout the summer, DEA/atrazine ratios increase. Results from this study, which showed the highest DEA/atrazine ratios in October and the lowest ratios in the spring, support this conclusion. Ratios in this study were the highest in October, however, sampling was not continued past October.

4.2 Data Interpretation

4.2.1 Atrazine Levels in Lake Michigan Tributaries

Atrazine, DEA, and DIA were detected more often in tributary samples than in atmospheric samples. Atrazine was above the method detection limit of 1.25 ng/L in 99% of tributary samples, compared to only 3.7%, 22%, and 50% of atmospheric vapor, particulate, and precipitation samples that exceeded sample specific detection limits, respectively. In this study, atrazine concentrations measured in Lake Michigan tributaries ranged from 0.5 to 2700 ng/L and averaged 3.7 to 350 ng/L. This is comparable to other tributaries in the Great Lakes region. Schottler *et al.* (1994) measured maximum atrazine concentrations of 2100 ng/L and base-flow concentrations of 20 to 65 ng/L in the Minnesota River in 1990 and 1991. Richards and Baker (1993) measured median atrazine concentrations of 90 to 660 ng/L in Lake Erie tributaries. In the St. Lawrence River and its tributaries, Lemieux *et al.* (1995) measured average atrazine concentrations of 10.4 to 31.1 ng/L.

Other studies that have focused on smaller, more agriculturally influenced streams or that have focused on measuring atrazine concentrations in storm events following herbicide application, have found much higher concentrations of atrazine than measured in this study. Kolpin and Kalkhoff (1993) measured atrazine concentrations as high as 8940 ng/L in small Iowa streams, and Stamer *et al.* (1994) estimated atrazine levels of 19,000 to 62,000 ng/L in Nebraska streams. In a 1989-1990 survey of mid-western streams, Thurman *et al.* (1992) measured a maximum concentration of 108,000 ng/L and a median concentration of 3800 ng/L during post-planting. Similarly, in a 1998 survey of mid-western streams, Battaglin *et al.* (2000) measured a maximum concentration of 224,000 ng/L and a median of 3970 ng/L shortly after herbicide application. As previously mentioned, several of these studies focused on the collection of samples in storm events following herbicide application. As Thurman *et al.* (1992) noted, median atrazine levels in mid-western streams dropped to 230 ng/L during pre-planting and harvest time periods. Atrazine concentrations also are more moderated in large river systems than in small streams that directly drain agricultural fields. For instance, Pereira and Hostettler (1993) measured atrazine concentrations ranging from 54 to 4735 ng/L in the Mississippi River and its major tributaries, and Clark *et al.* (1999) measured a median concentration of approximately 500 ng/L in the Mississippi River.

4.2.2 Comparison to Regulatory Limits

Measured atrazine concentrations in Lake Michigan tributaries were below regulatory limits for human health concerns and proposed ambient water quality criteria. The highest mean atrazine concentration in a tributary (350 ng/L) was approximately 10 times below the maximum contaminant level for drinking water (MCL) of 3000 ng/L. This contrasts with a 1989 survey of mid western streams, which found that 55% of streams exceeded the MCL during post-planting (Thurman *et al.,*1992).

When compared to the proposed ambient water quality criterion maximum concentration of 350 μg/L, maximum atrazine concentration measured in this study were more than 100 times less than the criterion. Mean atrazine concentrations were more than 34 times less than the proposed ambient water quality criterion continuous concentration of 12 μg/L.

4.2.3 Seasonality

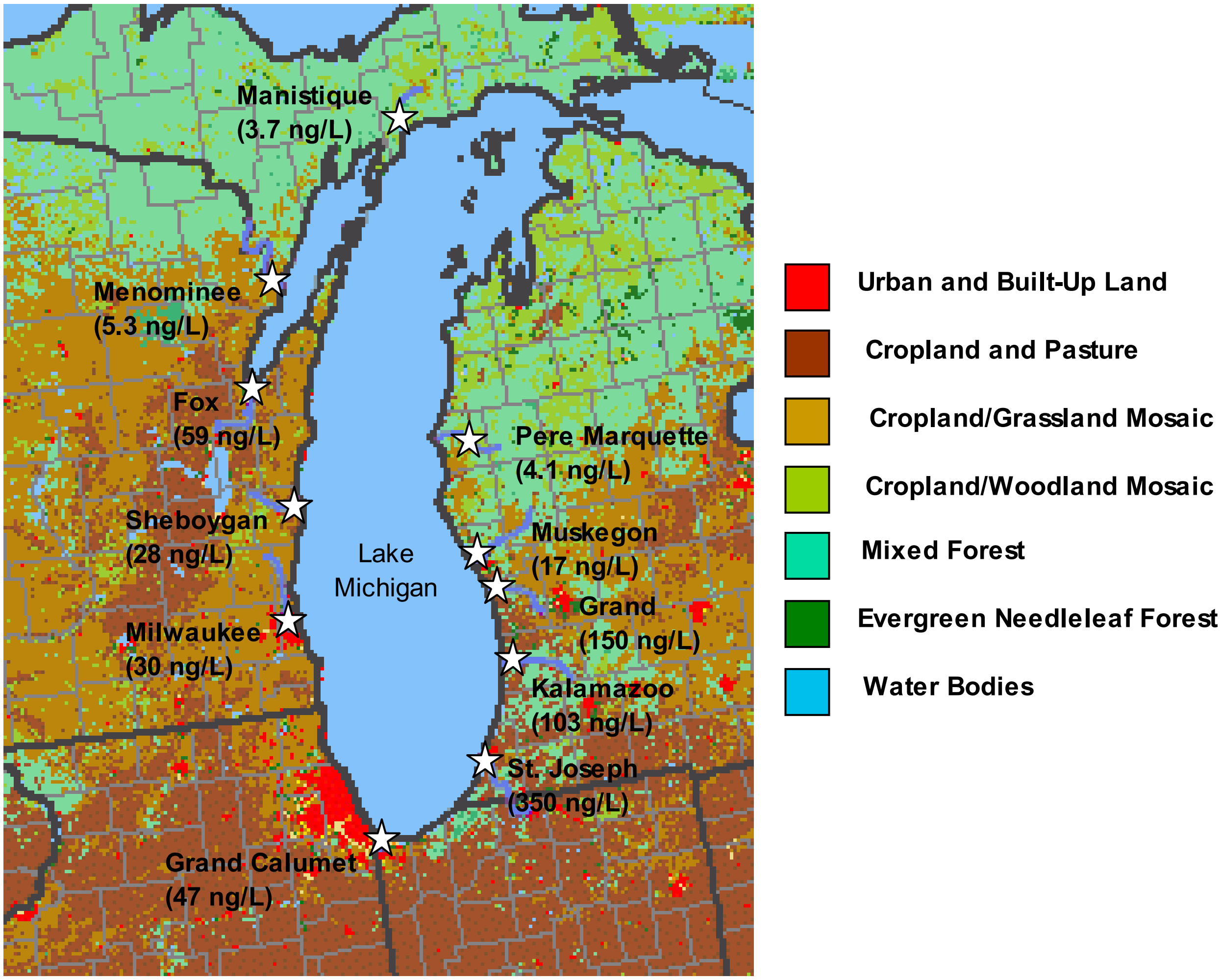
For the three tributaries with the highest atrazine levels (St. Joseph River, Kalamazoo River, and Grand River), distinct peaks in atrazine concentrations were observed in mid to late May. Distinct peaks in atrazine concentrations were not observed in other tributaries, however, it should be noted that measured tributary concentrations reflect not only atrazine levels but tributary flows as well. While tributary concentrations may be relatively constant, atrazine loads may peak in the late spring due to higher tributary flows. The modeling phase of the LMMB Study will combine atrazine concentration data with tributary flow data to estimate atrazine loads and the seasonal timing of these loads.

Most researchers have noted that the bulk of total atrazine loads in tributaries occurs during the early summer just after atrazine application and in correlation with major rain events (Muller *et al.*, 1997; Schottler and Eisenreich, 1997; Thurman *et al.*, 1992; Lemieux *et al.*, 1995; Clark *et al.*, 1999). Richards and Baker (1993) noted that the annual pattern of atrazine concentrations in Lake Erie tributaries was one of storm event peaks modified by an annual pattern of availability of the pesticide in late spring. Schottler and Eisenreich (1997) estimated the monthly contribution to annual atrazine loads to be 50% in June, 20% in May, 15% in July, 5% in April, 3% in August, and 1% in all other months.

4.2.4 Regional Considerations

Concentrations of atrazine and atrazine metabolites in tributaries were strongly influenced by geographical location and regional land use patterns. Atrazine, DEA, and DIA concentrations were significantly lower in the Menominee River, the Manistique River, and the Pere Marquette River than any other tributaries. This finding is consistent with land use and atrazine use patterns in these watersheds. These watersheds generally consist of less cropland and are more forested (Figure 4-7). In fact, EPA has listed the riparian habitat for the Manistique and Menominee Rivers as greater than 75% forested (Table 2-1). The lower percentage of cropland in the Manistique, Menominee, and Pere Marquette River watersheds also translates into lower atrazine use rates for these watersheds (Figure 4-8) and lower tributary atrazine levels (Figure 4-4). These rivers flow through counties with some of the lowest estimated atrazine use rates in the Lake Michigan region (estimated below 2.32 pounds per square mile in 1987-1989). The Muskegon River, which had the fourth lowest mean tributary atrazine concentration flows through counties with estimated atrazine use rates of less than 52.35 pounds per square mile. The remaining tributaries all flow through counties with estimated atrazine use rates of greater than 52.35 pounds per square mile. The St. Joseph River, which had the highest measured atrazine concentrations, flows through Indiana counties with estimated atrazine use rates of greater than 163.73 pounds per square mile. In conclusion, tributary atrazine concentrations are reflective of land use and atrazine use rates within the watershed. In a study of Nebraska streams, Stamer *et al.* (1994) similarly found that the largest yields and mean concentrations of atrazine in surface water were associated from drainage areas with the highest percentage of cropland, and the smallest was associated with the smallest amount of cropland. Richards and Baker (1993) also found that atrazine peak concentrations were strongly affected by land use and by soil type. Capel and Larson (2001) added that the load of atrazine to receiving streams as a

Figure 4-7. Mean Tributary Atrazine Concentrations (in parenthesis) and Land Use Patterns in the Lake Michigan Watershed



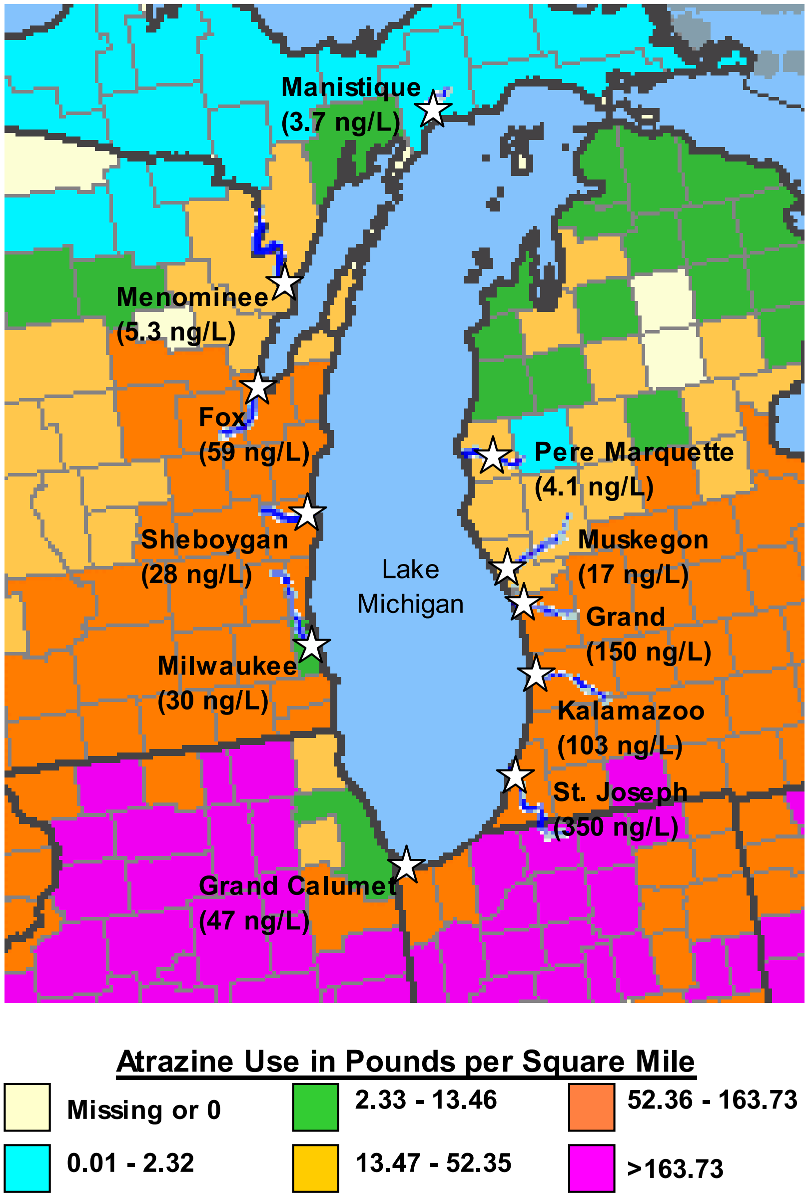
percentage of atrazine use within the basin was relatively constant regardless of the scale of the watershed. Lastly, seasonal and annual weather patterns and the timing of precipitation events in relation to agricultural activities are important in influencing tributary concentrations and loads of atrazine (Richards *et al.*, 1996).

4.2.5 Atrazine Breakdown Products

Ratios of DEA to atrazine in tributary samples measured in this study indicated significant degradation of atrazine. DEA/atrazine ratios averaged as high as 1.6 for some tributaries (Pere Marquette River). This is higher than mean DEA/atrazine ratios reported by Thurman *et al.* (1992) for mid-western tributaries.

Ratios of DEA to atrazine also increased over the summer months (from 0.63 in May to 1.4 in October) as spring-applied atrazine degraded within the watershed. Thurman *et al.* (1992) also reported an increase in DEA/atrazine ratios from <0.1 shortly after application to 0.4 later in the year. Thurman *et al.* (1992) hypothesized that increases in DEA/atrazine ratios later in the season were due to an influx of groundwater, which contains more degraded atrazine metabolites, during stream base flow conditions. Schottler *et al.* (1994) also found that late in the season, subsurface transport of atrazine and atrazine metabolites was predominant and led to increased DEA/atrazine ratios.

Figure 4-8. Mean Tributary Atrazine Concentrations (in parenthesis) and Atrazine Use in the Lake Michigan Watershed Estimated for 1987 to 1989 (graphic modified from Battaglin, U.S. Geological Survey, 1994)



4.3 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the atrazine monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB QA program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i). A brief summary of data quality issues for the tributary atrazine data is provided below.

Because the open-lake and tributary monitoring were conducted by the same PI, a separate QAPP was not prepared for the tributary monitoring, and GLNPO and the PI agreed to implement the procedures outlined in the open-lake QAPP for the tributary sampling and analysis. Field or trip blanks were not collected for tributary atrazine, however, a wide variety of blanks were prepared and analyzed for the open-lake water column data sets. As mentioned above, a single PI was responsible for collecting and analyzing the open-lake and tributary samples and these samples were extracted and analyzed together. Therefore, the results of the blank samples for the open-lake data may provide some information regarding system and analytical contamination (see Section 5.3). Six laboratory blanks were extracted and analyzed with the open-lake and tributary samples and are reported with both data sets. Results for atrazine for all of the six laboratory blanks were reported as zero.

As discussed in Section 2.5, the sample collection, extraction, and analysis methods for atrazine monitoring in this study are modifications of the methods used for the PCBs and chlorinated pesticides. In addition, during an audit of analytical procedures, two changes to the analytical method described in the approved QAPP were observed: addition of sodium sulfate to the extract in the centrifuge tube to remove interfering water, and use of d_5-ethylatrazine rather than d_{10}-anthracene as the internal standard. These changes improved analyte recovery and quantitation and were included in the analytical SOP (USEPA, 1997a; USEPA, 1997b).

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 4-5 provides a summary of flags applied to the tributary atrazine data. The summary provided below includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. In this data report, the summary and analysis of atrazine data represent all results with the exception of those flagged as “invalid” by the QC coordinator in concert with the PI.

All of the tributary samples contained detectable concentrations of atrazine so none of the tributary samples were flagged as “analyte not detected” (UND). Eighteen percent of tributary samples were flagged for exceeding the sample holding time of 30 days to extraction. However, the holding times for atrazine, and many other environmental pollutants, are not well-characterized and the effects on the sample results are unknown. All of the results for the field duplicate pairs were within acceptance criteria (i.e., none of the sample results were flagged as failed field duplicate), and only 8% of tributary sample results showed surrogate recoveries outside acceptance criteria. Based on the evaluation of multiple QC sample results and surrogate recoveries, the PI and the QC coordinator did not assign high bias (HIB) or low bias (LOB) flags to any sample results.

Table 4-5. Summary of Routine Field Sample Flags for the Analysis of Atrazine in Tributary Samples

Flag[a]	Percentage of Samples Flagged (%)[b]
UND, Analyte not detected	0
EHT, Exceeded holding time	18% (19)
FSS, Failed surrogate	8% (9)
FFD, Failed field duplicate	0

[a] The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.
[b] The number of routine field samples flagged is provided in parentheses.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on four of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results for laboratory duplicate pairs. Table 4-6 provides a summary of data quality assessments for several of these attributes for the tributary atrazine study data.

System precision, estimated as the mean RPD between field duplicate results, was 9%. Analytical precision, estimated as the standard deviation of surrogate correction factors, was 0.3. These measures suggest that analytical results are highly reproducible. Analytical bias, estimated as the mean surrogate recovery for the study samples, was 87% suggesting an overall slight low bias.

Table 4-6. Data Quality Assessment for the Analysis of Atrazine in Tributary Samples

Parameter[a]	Assessment[b]
Number of Routine Samples Analyzed	108
Number of Field Duplicates Analyzed	5
System Precision, Mean Field Duplicate RPD (%), >MDL	8.5 % (5)
Analytical Precision, SCF Variability (SD)	0.25 (108)
Analytical Bias, Mean Surrogate Recovery (%)	87 % (108)
Analytical Sensitivity , Samples Reported as < MDL (%)	0 .9 %

[a] RPD = Relative percent difference.
MDL = Method detection limit.
SCF = Surrogate correction factor.

[b] Number of sample/duplicate pairs used in the assessment is provided in parentheses.

Chapter 5
Atrazine in the Open-Lake Water Column

5.1 Results

Open-lake water column samples were collected during six cruises of the *R/V Lake Guardian* (Table 5-1). These cruises were conducted from April 25, 1994 to April 17, 1995. Open-lake samples were collected from 35 sampling locations on Lake Michigan, 2 sampling locations in Green Bay, and 1 sampling location on Lake Huron. Samples were collected at depths ranging from 1 to 257 m.

A total of 234 samples were collected and analyzed for atrazine, DEA, and DIA. All open-lake samples contained levels of atrazine and DEA above method detection limits (MDLs), and all but 12 samples (5.1%) contained DIA above the MDL. MDLs were calculated from results of seven spiked samples according to the procedures specified at 40 CFR part 136, Appendix B. The calculated MDLs were 1.25 ng/L for atrazine, 2.46 ng/L for DEA, and 8.27 ng/L for DIA.

Table 5-1. Summary of Open-lake Samples Collected

Cruise	Sampling Dates	Number of Sites Sampled	Total Number of Samples
1	4/25/94 - 5/11/94	25	54
2	6/17/94 - 6/25/94	8	25
3	8/4/94 - 8/26/94	31	64
4	10/18/94 - 10/30/94	3	10
5	1/17/95	1	2
6	3/23/95 - 4/17/95	26	79
	Total	38	234

5.1.1 Geographical Variation

Mean atrazine concentrations were calculated for each individual open-lake sampling station. Analysis of variance revealed that mean atrazine levels differed significantly among stations (at the 95% confidence level), however, these differences were primarily due to the inclusion of sampling stations located on Lake Huron and Green Bay. Atrazine concentrations at the Lake Huron sampling station (LH54M) were significantly lower than atrazine concentrations at all but three Lake Michigan sampling stations (MB63, MB72M, and 280), based on Tukey pairwise comparisons. Atrazine concentrations in southern Green Bay (station GB17) were significantly higher than atrazine concentrations at 18 Lake Michigan sampling stations.

Within Lake Michigan, atrazine concentrations were relatively consistent. Individual sample results ranged from 22.0 to 58.0 ng/L, and sampling station mean atrazine concentrations only ranged from 33.0 to 48.0 ng/L. Analysis of variance and Tukey's Studentized Range Test for multiple comparisons revealed that the only statistically significant difference in atrazine concentrations was between site 52 and three other sites. Atrazine concentrations at site 52 in northern Lake Michigan (near Beaver Island) were significantly greater than atrazine concentrations at sites 18M (located in south central Lake Michigan), 23M (located in south central Lake Michigan), MB72M (located near the Straits of Mackinac), and 280 (located in central Lake Michigan). While this difference may be statistically significant, it may be of little environmental significance. The mean atrazine concentration at site 52 was calculated from only two samples (42.0 and 54.0 ng/L atrazine).

Similar patterns of consistency among sampling stations were observed for DEA and DIA concentrations. The only statistically significant differences in DEA or DIA concentrations were between stations in

Green Bay and stations in Lake Michigan. Sampling station GB17 in Green Bay contained significantly higher DEA concentrations than three Lake Michigan sites (18M, 23M, and 280). Sampling stations GB17 and GB24M in Green Bay contained significantly higher DIA concentrations than five Lake Michigan sites (18M, 23M, 41, 3, and 5). Within Lake Michigan proper, no statistically significant differences were observed in DEA or DIA concentrations among sites. Individual DEA concentrations in Lake Michigan ranged from 14.0 to 36.0 ng/L, and sampling station means ranged from 18.5 to 30.3 ng/L. Individual DIA concentrations in Lake Michigan ranged from 0.00 to 30.3 ng/L, and sampling station means ranged from 9.00 to 20.6 ng/L.

Due to the geographical consistency of atrazine, DEA, and DIA concentrations within Lake Michigan, lake-wide mean concentrations can be calculated to reliably represent the lake. Lake-wide mean concentrations calculated for the study were 38.1, 25.8, and 14.9 ng/L for atrazine, DEA, and DIA, respectively. These concentrations represent average values for the entire April 1994 through April 1995 LMMB sampling campaign, however, it was found that average lake-wide concentrations differed significantly over time during the campaign (see Section 5.1.2 below).

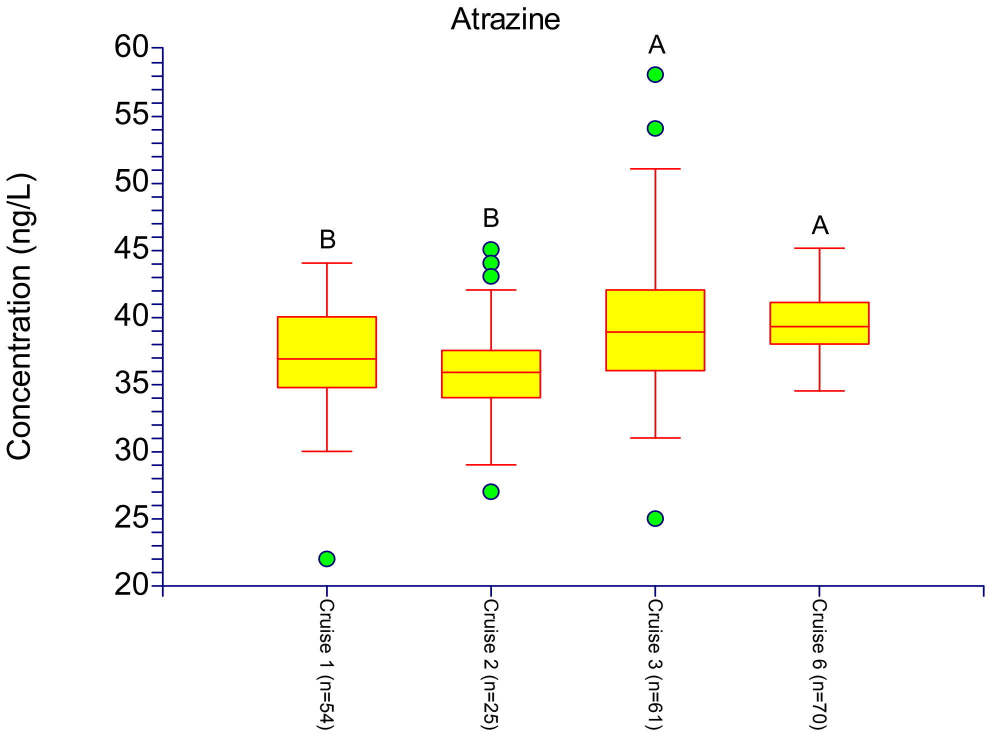
5.1.2 Seasonal Variation

Seasonal evaluations of open-lake atrazine concentrations are limited by the timing and intensity of sampling conducted in the LMMB Study. Open-lake atrazine concentrations were measured during six sampling cruises, however, limited data was collected during two of these cruises. Only ten samples from three sites were collected during the fourth cruise in October 1994, and only two samples from one site were collected during the fifth cruise in January 1995. Due to the limited number of samples and sites evaluated during the fourth and fifth cruises, data from these cruises were not deemed to be representative of the entire lake and were not used to evaluate seasonal trends. Sufficient data were present from the remaining four cruises (April/May 1994, June 1994, August 1994, and March/April 1995) to adequately compare mean Lake Michigan atrazine concentrations (Figure 5-1) over time.

An analysis of variance was conducted to test for statistical differences in mean atrazine concentrations measured during cruises one, two, three, and six. Statistically significant differences among cruises were identified at the 95% confidence level. Tukey's Studentized Range Test for multiple comparisons showed that mean atrazine concentrations measured during cruises three and six were significantly higher than atrazine concentrations measured during cruises one and two (Figure 5-1). Mean atrazine concentrations during cruises one (April/May 1994) and two (June 1994) were 37.0 and 36.0 ng/L, respectively; and mean atrazine concentrations during cruises three (August 1994) and six (March/April 1995) were 39.2 and 39.7 ng/L, respectively. Mean atrazine concentrations during cruises four and five, which were not included in this analysis, were 35.8 and 39.3 ng/L, respectively.

Similar patterns of increasing concentrations also were observed for DEA and DIA. Mean DEA concentrations measured during cruises three and six were significantly higher than DEA concentrations measured during cruises one and two (Figure 5-2). Mean DEA concentrations during cruises one (April/May 1994) and two (June 1994) were 24.1 and 22.2 ng/L, respectively; and mean DEA concentrations during cruises three (August 1994) and six (March/April 1995) were 26.9 and 27.7 ng/L, respectively. Mean DEA concentrations during cruises four and five, which were not included in this analysis, were 24.6 and 22.0 ng/L, respectively.

Figure 5-1. Atrazine Concentrations Measured in Lake Michigan During Four Sampling Cruises (Cruise 1 = April/May 1994, Cruise 2 = June 1994, Cruise 3 = August 1994, Cruise 6 = March/April 1995)[a]

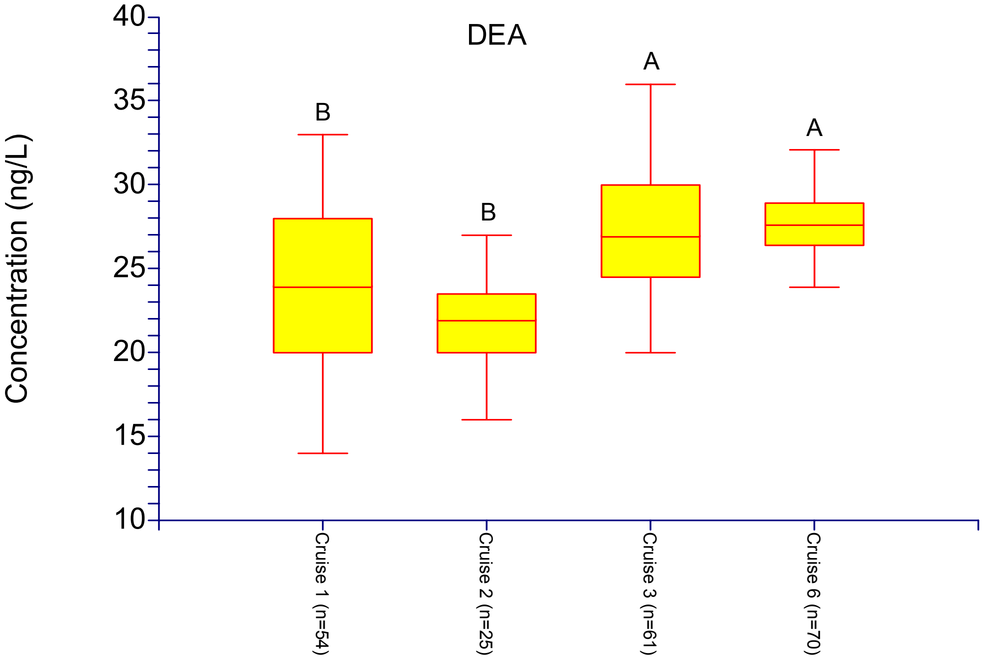


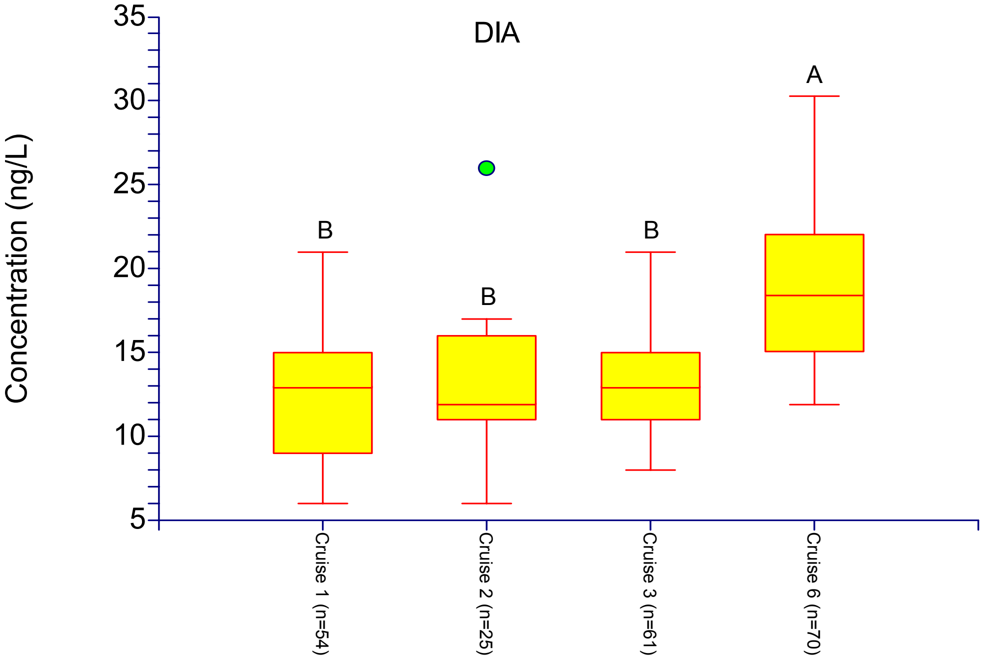
[a] Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

The mean DIA concentration measured during cruise six was significantly higher than mean DIA concentrations measured during cruises one, two, or three (Figure 5-2). Mean DIA concentrations during cruises one (April/May 1994), two (June 1994), and three (August 1994) were 12.4, 12.9, and 13.1 ng/L, respectively; the mean DIA concentration during cruise six (March/April 1995) was 19.1 ng/L. Mean DIA concentrations during cruises four and five, which were not included in this analysis, were 17.6 and 6.90 ng/L, respectively.

In conclusion, open-lake atrazine, DEA, and DIA concentrations increased during the one year sampling campaign. Increases from April/May 1994 to March/April 1995 were statistically significant for each analyte. During this period, lake-wide mean atrazine concentrations increased by 2.7 ng/L or 7.30%. Mean DEA concentrations increased by 3.6 ng/L or 14.9%, and mean DIA concentrations increased by 6.7 ng/L or 54.0%.

Figure 5-2. DEA and DIA Concentrations Measured in Lake Michigan During Four Sampling Cruises (Cruise 1 = April/May 1994, Cruise 2 = June 1994, Cruise 3 = August 1994, Cruise 6 = March/April 1995)[a]





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[a] Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

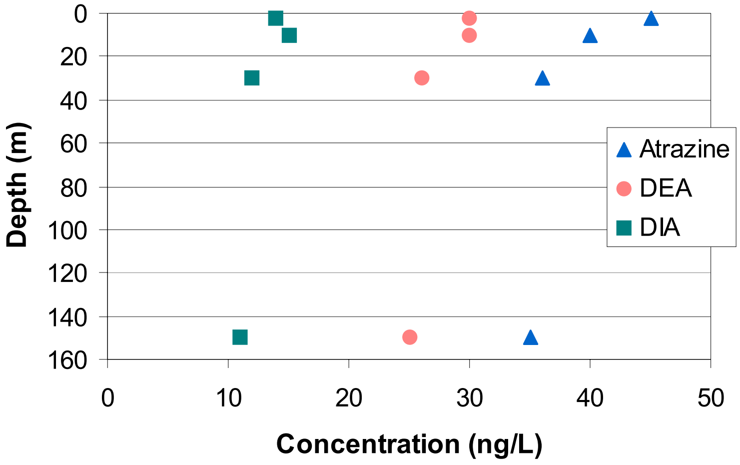
5.1.3 Vertical Variation

Open-lake samples were collected at various depths ranging from 1 to 257 m. Overall, there was no correlation between atrazine concentrations and depth of samples collected. This is not surprising, considering that the majority of samples collected during the LMMB Study were not collected during periods of thermal stratification in Lake Michigan. Only cruise three in August 1994 was conducted during highly stratified conditions.

Further investigation of vertical trends during stratified conditions revealed a statistically significant trend within the northern Lake Michigan basin (p=0.034, based on a two-sample t-test). Within the northern basin (above approximately 44˚ N latitude), atrazine concentrations were significantly higher (at the 95% confidence level) in the epilimnion than in the hypolimnion. The mean atrazine concentration in the epilimnion (at 20 m depth and above) was 42.0 ng/L, and the mean atrazine concentration in the hypolimnion (below 20 m depth) was 35.9 ng/L. Figure 5-3 shows depth profiles for atrazine, DEA, and DIA at site 41 in the northern Lake Michigan basin. This trend of increased concentrations in the epilimnion during stratified conditions was not observed in the southern basin. Within the southern basin, the mean atrazine concentration in the epilimnion (38.8 ng/L) was not significantly different from the mean atrazine concentration in the hypolimnion (39.0 ng/L) (p=0.873, based on a two-sample t-test).

Vertical trends of DIA were similar to those for atrazine. Within the northern basin, the mean DIA concentration in the epilimnion (15.7 ng/L) was significantly (at the 95% confidence level) higher than the mean DIA concentration in the hypolimnion (13.3 ng/L) (p=0.046). Within the southern basin, the mean DIA concentration in the epilimnion (12.0 ng/L) was not significantly different from the mean DIA concentration in the hypolimnion (12.1 ng/L) (p=0.873). Vertical trends in DEA concentrations were not statistically significant in either basin (Northern: p=0.143; Southern: p=0.478).

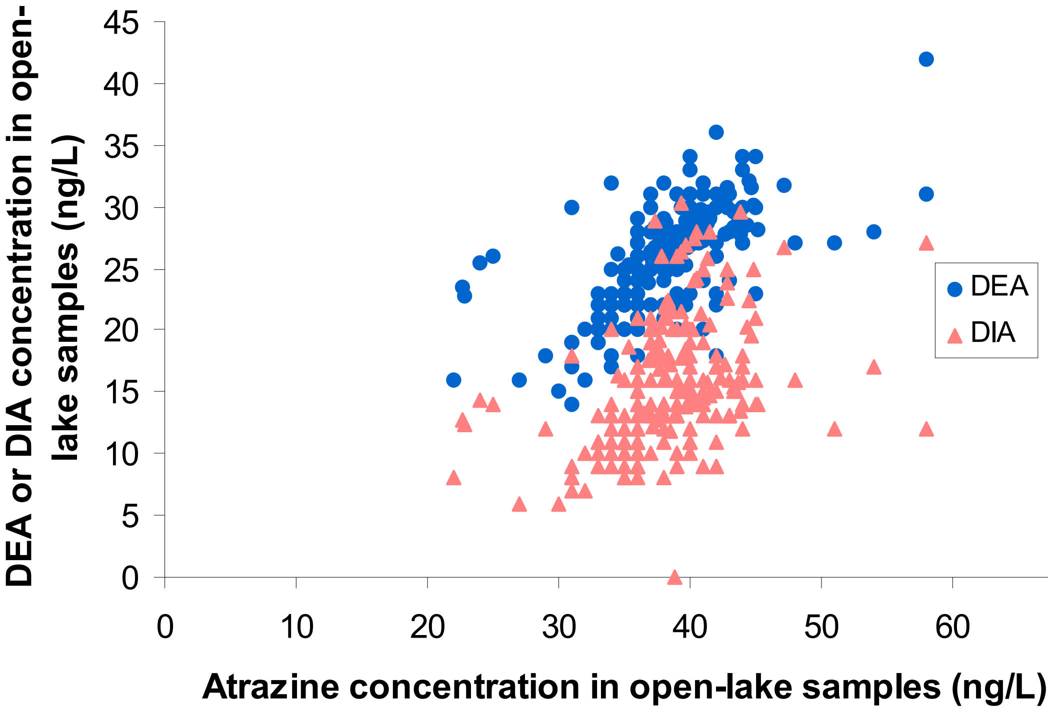
Figure 5-3. Depth Profile of Atrazine, DEA, and DIA Concentrations at Station 41 in Lake Michigan on August 12, 1994



5.1.4 Analysis of Breakdown Products

DEA and DIA concentrations were correlated with atrazine concentrations in open-lake samples. As atrazine concentrations in open-lake samples increased, DEA and DIA concentrations also generally increased (Figure 5-4). This correlation was significant at the 95% confidence level, but the correlations among atrazine, DEA, and DIA were not as strong in open-lake samples as observed for these analytes in precipitation and tributary samples. This is most likely due to the smaller range of concentrations measured in open-lake samples. Pearson correlation coefficients were 0.61 and 0.32 for atrazine concentrations in open-lake samples compared to DEA and DIA concentrations, respectively.

Figure 5-4. Correlation of DEA and DIA Concentrations with Measured Atrazine Concentrations in Open-lake Samples



The ratio of DEA to atrazine in open-lake samples was similar to that in tributaries. The median DEA/atrazine ratio in open-lake samples was 0.684, compared to 0.77 in tributary samples. DEA to atrazine ratios ranged from 0.429 to 1.04 in open-lake samples. Analysis of variance was performed on DEA/atrazine ratios to evaluate this variable over time. This analysis revealed that mean DEA/atrazine ratios during cruise three (0.693) and cruise six (0.698) were significantly higher than mean DEA/atrazine ratios during cruise one (0.648) and cruise two (0.619). This finding is consistent with the finding that DEA concentrations increased by 14.9% during the study, while atrazine concentrations increased by only 7.30%.

5.2 Data Interpretation

5.2.1 Atrazine Levels in Lake Michigan

A lake-wide mean atrazine concentration of 38.3 ng/L was calculated for Lake Michigan in this 1994-1995 study. This is slightly higher than the average lake-wide atrazine concentrations of 34 ng/L and 37 ng/L calculated for Lake Michigan by Schottler and Eisenreich (1994) in 1991 and 1992, respectively. Among the Great Lakes, Lake Michigan had the third highest lake-wide average atrazine concentration. Lake-wide atrazine concentrations in 1992 averaged 97 ng/L in Lake Ontario; 75 and 93 ng/L in Lake Erie's western and eastern basins, respectively; 37 ng/L in Lake Michigan, 23 ng/L in Lake Huron, and 3 ng/L in Lake Superior. Studies of smaller lakes in agricultural regions have shown higher lake-wide atrazine levels. Muller *et al.* (1997) measured average atrazine concentrations of 113 to 245 ng/L in much smaller (about 1/1000th the surface area of Lake Michigan) Swiss Lakes. Spalding *et al.* (1994) measured average concentrations of 7470 and 270 ng/L in two small Nebraska lakes, and Fallon *et al.*

(2002) measured atrazine concentrations of 1000 to 4000 ng/L in a Kansas reservoir (Perry Lake). Even remote lakes in the Midwest with presumably only atmospheric inputs of atrazine have measurable atrazine concentrations. In lakes on the Isle of Royale (an island in northern Lake Superior), Thurman and Cromwell (2000) measured 5 to 22 ng/L of atrazine in August 1992.

5.2.2 Comparison to Regulatory Limits

Measured atrazine concentrations in Lake Michigan were well below regulatory limits for human health concerns and proposed ambient water quality criteria. The lake-wide mean atrazine concentration of 38.3 ng/L was more than 75 times below the 3000 ng/L maximum contaminant level for drinking water. When compared to the proposed ambient water quality criterion maximum concentration of 350 µg/L, maximum atrazine concentrations measured in this study were more than 6000 times less than the criterion. Mean atrazine concentrations were more than 300 times less than the proposed ambient water quality criterion continuous concentration of 12 µg/L.

5.2.3 Lateral Variation

Atrazine concentrations measured at stations located in Green Bay were statistically higher than several Lake Michigan stations. This is likely due to the smaller volume of water available for dilution of pollutants in Green Bay and the limited mixing between the bay and Lake Michigan. Within Lake Michigan itself, atrazine concentrations were relatively consistent throughout the lake. Station averages only ranged from 33.0 to 48.0 ng/L. Schottler and Eisenreich (1994) also found no lateral variation in atrazine concentrations in Lake Michigan. They concluded that the lake was well mixed spatially with respect to atrazine. This study confirms that conclusion.

5.2.4 Temporal Trends

This study found that atrazine, DEA, and DIA concentrations in Lake Michigan all increased from the spring of 1994 to the spring of 1995. The measured increases of 7.30% in atrazine concentrations, 14.9% in DEA concentrations, and 54.0% in DIA concentrations were all statistically significant. This agrees with the increasing trend in atrazine concentrations reported by Schottler and Eisenreich (1994), who found that Lake Michigan atrazine concentrations were statistically greater in 1992 than in 1991. Combining results from the two studies, lake-wide atrazine concentrations in Lake Michigan have increased from 34 ng/L in 1991 to 39.4 ng/L in 1995.

While significantly longer studies are needed to confirm long-term trends of increasing Lake Michigan atrazine concentrations, the increases observed over the short 1991-1995 time period is consistent with the modeling efforts of Rygwelski *et al.* (1999). Rygwelski *et al.* (1999) estimated that if continued use of atrazine is sustained, atrazine concentrations in Lake Michigan would continue to rise until a concentration of approximately 160 ng/L is reached in about 300 years. Depending upon atrazine degradation half-life estimates ranging from two years to no degradation, Tierney *et al.* (1999) estimated achievement of steady state conditions in 11 to 307 years. Tierney *et al.* (1999) estimated that steady state concentrations would be 33, 77, 140, or 710 ng/L using degradation half-lives of 2 years, 5 years, 10 years, and no degradation, respectively. The two-year degradation half-life estimate is likely an underestimate, based on Lake Michigan atrazine concentrations measured in this study, which have already increased past 33 ng/L. In contrast to models that predict long-term increases in Lake Michigan atrazine concentrations, Schottler and Eisenreich (1997) estimated that atrazine concentrations in Lake Michigan are currently near steady state.

5.2.5 Vertical Trends

This study found that in the northern Lake Michigan basin, atrazine concentrations during stratification were significantly higher in the epilimnion than in the hypolimnion. This pattern was not observed in the southern Lake Michigan basin or when data from all sites (northern and southern basins) were combined. In previous studies, Schottler and Eisenreich (1994) concluded that concentration profiles demonstrated no consistent vertical trends, and epilimnetic atrazine concentrations were not statistically different from hypolimnetic concentrations. The findings of these two studies do not necessarily contradict one another. Both studies found that when all sites were combined, atrazine concentrations in the epilimnion were not statistically different than hypolimnetic atrazine concentrations. The LMMB study went on to observe that in just the northern basin, epilimnetic atrazine concentrations were statistically different from hypolimnetic atrazine concentrations. This observation may have been allowed by the greater coverage of lake stations in the current study (29 sites evaluated in the August 1994 cruise). Schottler and Eisenreich (1994) investigated only ten Lake Michigan sites, six of which were in the southern basin. Additional investigations are likely needed to determine if the observed trend in the northern basin observed in this study is a statistical anomaly or environmentally relevant.

Muller *et al.* (1997) also observed increased atrazine concentrations in the epilimnion of small Swiss lakes during stratification, and attributed this finding to increased atrazine loadings into the epilimnion during spring and summer months when the lake was stratified.

5.3 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the atrazine monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB QA program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001i). A brief summary of data quality issues for the open lake water column atrazine data is provided below.

As discussed in Section 2.5, the sample collection, extraction, and analysis methods for atrazine monitoring in this study are modifications of the methods used for the PCBs and chlorinated pesticides. In addition, during an audit of analytical procedures, two changes to the analytical method described in the approved QAPP were observed: addition of sodium sulfate to the extract in the centrifuge tube to remove interfering water, and use of d5-ethylatrazine rather than d10-anthracene as the internal standard. These changes improved analyte recovery and quantitation and were included in the analytical SOP (USEPA, 1997a; USEPA, 1997b).

Bottle blanks, laboratory blanks, field blanks, and trip blanks were prepared and analyzed. Atrazine, DEA, and DIA were not detected in any of these blanks, indicating that contamination of study samples did not occur from these sources. Field blanks and trip blanks were not collected at all study sites, and therefore, sample contamination from site-specific sources cannot be evaluated. However, the variety of blanks collected and the fact that all blank samples contained undetectable levels of atrazine, DEA, and DIA suggests that contamination of study samples may be unlikely.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 5-2 provides a summary of flags applied to the open-lake atrazine data. The summary provided below includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. In this data report, the summary and analysis of atrazine data represent all results with the exception of those flagged as "invalid" by the QC coordinator in concert with the PI.

Table 5-2. Summary of Routine Field Sample Flags for the Analysis of Atrazine in Open-lake Samples

Flag[a]	Percentage of Samples Flagged (%)[b]
UND, Analyte not detected	0
EHT, Exceeded holding time	42% (99)
FSS, Failed surrogate	9% (21)
FFD, Failed field duplicate	0

[a] The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

[b] The number of routine field samples flagged is provided in parentheses.

All of the open-lake samples contained detectable concentrations of atrazine so none of the open-lake samples were flagged as "analyte not detected". Forty-two percent of open-lake samples were flagged for exceeding the sample holding time of 30 days to extraction. However, the holding times for atrazine, and many other environmental pollutants, are not well-characterized and the effects on the sample results are unknown. All of the results for the field duplicate pairs were within acceptance criteria (i.e., none of the sample results were flagged as failed field duplicate), and only 9% of open-lake sample results showed surrogate recoveries outside acceptance criteria. . Based on the evaluation of multiple QC sample results and surrogate recoveries, the PI and the QC coordinator did not assign high bias (HIB) or low bias (LOB) flags to any sample results.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on four of these attributes. For example, system precision was estimated as the mean relative percent difference (RPD) between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean relative percent difference (RPD) between the results from laboratory duplicate pairs. Table 5-3 provides a summary of data quality assessments for several of these attributes for the open-lake atrazine study data.

System precision, estimated as the mean RPD between field duplicate results, was 6.08%. Analytical precision, estimated as the standard deviation of surrogate correction factors, was 0.250. These measures suggest that analytical results are highly reproducible. Analytical bias, estimated as the mean surrogate recovery for the study samples, was 91.3% suggesting an overall slight low bias.

Table 5-3. Data Quality Assessment for the Analysis of Atrazine in Open-lake Samples

Parameter[a]	Assessment[b]
Number of Routine Samples Analyzed	234
Number of Field Duplicates Analyzed	59
System Precision, Mean Field Duplicate RPD (%), >MDL	6.08% (59)
Analytical Precision, SCF Variability (SD)	0.250 (234)
Analytical Bias, Mean Surrogate Recovery (%)	91.3% (234)
Analytical Sensitivity , Samples reported as < MDL (%)	0%

[a] RPD = Relative percent difference.
MDL = Method detection limit.
SCF = Surrogate correction factor.
[b] Number of sample/duplicate pairs used in the assessment is provided in parentheses.

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