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Results of the Lake Michigan Mass Balance Project: Atrazine Modeling Report

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Notice

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Foreword

The Lake Michigan Mass Balance Project (LMMBP) was initiated by the United States Environmental Protection Agency (USEPA), Great Lakes National Program Office (GLNPO) to determine strategies for managing and remediating toxic chemicals in the lake basin. Within the ecosystem approach, the mass balance framework is considered the best means of accomplishing this objective, and GLNPO requested the assistance of the USEPA Office of Research and Development (ORD) to facilitate and produce mathematical models that account for the sources, sinks, transport, fate, and food chain bioaccumulation of certain chemicals. This approach has been used in the past and builds upon the modeling efforts that have occurred in the Assessment and Remediation of Contaminated Sediments (ARCS) Program and the lower Fox River/Green Bay Mass Balance Project. The feasibility of such studies and resultant alternative management options for contaminants in large rivers and a large embayment were demonstrated, and a logical extension to the entire Lake Michigan receiving water body and major tributaries was warranted. There were a large number of cooperators in this project, and by focusing federal, state, local, private, and academic efforts and resources on a common goal, much more was accomplished than if these entities acted independently.

The project was conducted in conjunction with the Enhanced Monitoring Program, and the approach required that all monitoring and field research be coordinated and common methodologies used. Mathematical modelers were consulted during planning for sample design, parameters, and temporal and spatial sampling considerations. This yielded a consistent and reliable database of information that was accessible by project participants and the public. Data for the LMMBP were collected during 1994 and 1995 and have been compiled according to specified quality assurance/quality control (QA/QC) requirements, and other data assessments have been made for modeling purposes.

The need to consider the environmental benefits and consequences of alternative remediation choices to protect and improve our environment continues to intensify as: 1) environmental problems become more complex; 2) the means to address and investigate problems become more technical, time-consuming, and expensive; and 3) the actual cost to implement action strategies has escalated. The integrated atrazine mass balance modeling results are presented in this document and can aid managers in establishing priorities for both lake-wide and local improvements. Primary goals of the modeling effort were to determine the persistence of atrazine and to forecast concentrations in Lake Michigan water. The capability of forecast modeling presented here is a salient feature of this approach directed toward providing multiple alternatives, which then can be examined through benefit-cost analyses.

This report presents the current status and results of the atrazine modeling effort through 2005, and it fulfills documentation requirements as described in the Quality Assurance Plan for Modeling: The Lake Michigan Mass Balance Project. Of course, a model and modeling applications are never complete, and it is expected that further efforts will change some results, insights, and our understanding of Lake Michigan. These efforts require an investment of resources and time, and improvements with additional model run executions are measured in years. In the larger picture, the need for Agency modeling technologies continues to intensify, and the requirement for reduced uncertainty will lead to future improved generations of models. We have

placed great emphasis on following guidance provided by the USEPA and other agencies in assuring that the scientific theory is implemented accurately and completely by model computer code and that best modeling practices have been instituted. The fundamental principles driving the atrazine models presented in this report have received scientific peer review using an interdisciplinary panel of scientists and experts. The purpose of the reviews was to ensure that decisions based on the modeling efforts are reliable and scientifically credible.

This document is not intended to include all of the details and background required to understand the entire LMMBP. Rather, the reader should refer to the LMMBP Work Plan and other materials on the GLNPO web site and the Lake Michigan Mass Balance Modeling Quality Assurance Plan on the ORD-Grosse Ile web site for further information.

Abstract

The Lake Michigan Mass Balance Project (LMMBP) was conducted to measure and model nutrients, atrazine, polychlorinated biphenyls (PCBs), *trans*-nonachlor, and mercury to gain a better understanding of the sources, sinks, transport, fate, and effects of these substances within the system and to aid managers in the environmental decision-making process for the Lake Michigan basin. The United States Environmental Protection Agency (USEPA) Office of Research and Development (ORD) was requested to conduct and facilitate modeling in cooperation with the USEPA Great Lakes National Program Office (GLNPO); the USEPA Region V; other federal agencies; the states of Michigan, Wisconsin, Illinois, and Indiana; the tribes; and the public and private sectors.

This report focuses on the load sources and fate and transport modeling of atrazine only. In the Lake Michigan basin, atrazine is used primarily as a herbicide on corn crops. With the recent increase in corn acreage in the United States associated with biofuel (ethanol) production, increased loadings of atrazine to lakes and streams are expected.

The atrazine modeling effort described in this report was supported by intensive sampling of the atmosphere, major tributaries, and water column during the 1994-1995 field years as well as by extensive quality assurance and database development. Using these data and historical data, loadings of atrazine to the lake were estimated for the tributaries and atmosphere. Multimedia, mass balance modeling frameworks were applied to examine primary source and loss categories and make various model forecasts for a variety of loading scenarios. A literature search revealed that atrazine sorption to particles is negligible. Hence, atrazine transport associated with settling, resuspension, and burial were determined to be negligible. This report focuses on the modeling practices applied and results for atrazine from the MICHTOX screening-level model and the higher-resolution LM2-Toxic and LM3-Atrazine models.

The results of the LM2-Toxic system mass balance model show that the largest atrazine load to the lake is from the watershed. For the year 1994, it was estimated that 5,264 kg of atrazine were discharged to the lake *via* the tributaries. The second major load to the lake was from atmospheric wet deposition with a loading estimate of 2,493 kg. The greatest loss of atrazine from the lake was through transport to Lake Huron (2,546 kg) *via* the Straits of Mackinac. Loss due to internal decay (1,662 kg) was the second largest loss mechanism. The total inventory of atrazine in the lake was determined to be 184,310 kg in 1994. In this large, cold northern lake, the model suggests that *in situ* atrazine decay is very slow (0.009/year). This translates into an estimated atrazine half-life of 77 years. Using the model to forecast alternative futures, a 35% load reduction, if implemented in January 1, 2005, would have been needed in order to prevent atrazine concentrations from increasing further in the lake. If loadings and boundary conditions are assumed to be constant in the future, the model predicts that the lake will eventually reach a steady-state concentration of 66 ng/L in the year 2194.

Our high-resolution model, LM3-Atrazine, was primarily used to evaluate environmental exposure concentrations of atrazine in 5 km x 5 km model cells receiving loadings from the major tributaries to the lake.

The model segment receiving loads from the St. Joseph River, associated with the largest tributary load of atrazine to the lake, ranged from winter concentrations of 37 ng/L to spring peaks of 100-350 ng/L. These predicted exposure concentrations in the lake are all below selected toxicological endpoints, including the most sensitive, phytoplankton primary production reduction.

This synthetic lake-wide perspective is anticipated to aid lake managers in moving forward on prevention, remedial actions, and legislative priorities associated with Lake Michigan Lake-wide Management Plans. The models developed provide an in-depth understanding of atrazine transport and fate processes in this valuable freshwater resource. *This abstract does not necessarily reflect USEPA policy.*

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Abbreviations

AOCs	Areas of Concern
AREAL	Atmospheric Research and Exposure Assessment Laboratory
CMAQ	Community Multiscale Air Quality
CMC	Criterion maximum concentration
CO_2	Carbon dioxide
DAR	Deethylatrazine/atrazine ratio
DEA	Deethylatrazine
DIA	Deisopropylatrazine
DOC	Dissolved organic carbon
DQOs	Data quality objectives
EMPs	Enhanced Monitoring Plans
ERS	Economic Research Service
EU	European Union
FIFRA	Federal Insecticide, Fungicide, and Rodenticide Act
FQPA	Food Quality Protection Act
GBMBP	Green Bay Mass Balance Project
GIS	Geographical Information System
GLENDA	Great Lakes Environmental Monitoring Database
GLERL	Great Lakes Environmental Research Laboratory
GLNPO	Great Lakes National Program Office
GLWQA	Great Lakes Water Quality Agreement
GWP	Great Waters Program
HUC	Hydrological Unit Code
IDLs	Instrument detection limits
IJC	International Joint Commission
IRED	Interim Reregistration Eligibility Decision
LaMP	Lake-wide Management Plan
LAPU	Load as a percentage of use
LLRFRB	Large Lakes and Rivers Forecasting Research Branch
LLRS	Large Lakes Research Station
LMMBP	Lake Michigan Mass Balance Project
MCL	Maximum Contaminant Level
MDEQ	Michigan Department of Environmental Quality
MDLs	Method detection limits
MED	Mid-Continent Ecology Division
MQOs	Measurement quality objectives
NDBC	National Data Buoy Center
NHEERL	National Health and Environmental Effects Research Laboratory
NOAA	National Oceanic and Atmospheric Administration

ORD	Office of Research and Development
PCB	Polychlorinated biphenyl
PEM	Pesticide Emissions Model
PIs	Principal Investigators
POM	Princeton Ocean Model
QA	Quality assurance
QAPPs	Quality Assurance Project Plans
QC	Quality control
RAP	Remedial Action Plan
RDMQ	Research Data Management and Quality Control System
RED	Reregistration Eligibility Decision
RMSD	Root mean square difference
RPD	Relative percent difference
SAP	Scientific Advisory Panel
SBRE	Stratified Beale Ratio Estimator
SCFAH	Standing Committee on the Food Chain and Animal Health
SDLs	System detection limits
TiO_2	Titanium dioxide
TMDL	Total Maximum Daily Load
USDA	United States Department of Agriculture
USDOI	United States Department of Interior
USEPA	United States Environmental Protection Agency
USFWS	United States Fish and Wildlife Service
USGAO	United States General Accounting Office
USGS	United States Geological Survey
VWA	Volume-weighted averages
WEP	Watershed export percentage

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Executive Summary

The Lake Michigan Mass Balance Project (LMMBP) provided an opportunity to improve our understanding of atrazine transport and fate in a large freshwater lake, Lake Michigan. A rigorous, quality-assured large supporting data set derived from samples collected in 1994-1995 was used to establish atmospheric and tributary loads, estimate initial conditions, and perform model calibration and confirmation exercises. Historical data collected outside of the LMMBP were also used to support the modeling effort.

Models developed at the United States Environmental Protection Agency's Large Lakes Research Station, to assess atrazine transport and fate in Lake Michigan included MICHTOX, LM2-Toxic, and LM3-Atrazine. Both LM2-Toxic and LM3-Atrazine utilized results from a hydrodynamic model to describe the lake's physics. Results from air and tributary models were used to provide atrazine loadings to the lake.

Lake Michigan is acted upon by a number of physical parameters that impact the hydrology, chemistry, and biology of the lake. For a lake the size of Lake Michigan, changes in these parameters can lead to significant changes, especially when models are used in long-term predictions to predict the outcome of various scenarios. The primary driving forces are wind, air temperature, and precipitation. These impact tributary flows, lake levels, waves, water circulation, water temperature, and ice cover. For the period of record, these driving forces vary from year-to-year. The period of 1982 to 1983 was used to calibrate the hydrodynamic models. For this period of time, hydrodynamic conditions were not at any extreme. This is also true for the period of 1994 and 1995 when the models were applied.

Temperature will impact contaminant modeling. Air temperature impacts how quickly the lake warms in any one year. Water temperature impacts the volatilization of contaminants. There appears to be a four-year cycle of quicker warming which exists within a trend of general warming of the lake. The trend of warming may be part of a longer term, undocumented cycle, or may be related to climate change.

MICHTOX is a toxic chemical mass balance and food chain bioaccumulation model developed in the early 1990s. The model has nine water segments encompassing both Lake Michigan and Green Bay and is derived from the general water quality model WASP4. Before the onset of the LMMBP, MICHTOX was applied to Lake Michigan in a hindcast mode to gain an initial understanding of key atrazine processes in the lake and controlling loads. Tributary loadings of atrazine to the lake were determined based on historical usage of the chemical in the basin and a literature-derived Watershed Export Percentage (WEP) of 0.6%. The processes modeled included advection, dispersion, and reaction (decay). MICHTOX was used to provide a screening-level analysis of the potential future trends in atrazine concentrations in lake water under a variety of contaminant load scenarios. MICHTOX was run for seven scenarios to help evaluate the impacts on atrazine trends caused by various loading sources and boundary conditions. Results using the assumption of average boundary conditions indicate that atrazine decays at a rate of approximately 0.01/yr. This represents a half-life of atrazine in the lake due to decay of 69.3 years. MICHTOX modeling indicates that a total loading reduction of approximately 37%, if implemented on January 1, 2005, would be needed to keep concentrations in the lake near steady-state.

LM2-Toxic is a sophisticated and state-of-the-art toxic chemical fate and transport model for Lake Michigan. LM2-Toxic is also a revision of the USEPA-supported WASP4 water quality modeling framework. The processes modeled included advection, dispersion, decay, absorption, and volatilization. The transport fields that were output from the 19-layered 5 km x 5 km gridded Princeton Ocean Model for the Great Lakes (POMGL) were aggregated and used by LM2-Toxic. The results of the LM2-Toxic system mass balance model show that the largest atrazine load to the lake is from the watershed. For the year 1994, it was estimated that 5,264 kg of atrazine were discharged to the lake *via* the tributaries. The second major load to the lake was from atmospheric wet deposition with a loading estimate of 2,493 kg. The greatest loss of atrazine from the lake was through transport to Lake Huron (2,546 kg) *via* the Straits of Mackinac. Loss due to internal decay (1,662 kg) was the second largest loss mechanism. The total inventory of atrazine in the lake was determined to be 184,310 kg in 1994. In this large, cold northern lake, the model suggests that *in situ* atrazine decay is very slow (0.009/year). This translates into an estimated atrazine half-life of 77 years. Using the model to forecast alternative futures, a 35% load reduction, if implemented in January 1, 2005, would have been needed in order to prevent atrazine concentrations from increasing further in the lake. If loadings and boundary conditions are assumed to be constant in the future, the model predicts that the lake will eventually reach a steady-state concentration of 66 ng/L in the year 2194.

LM3-Atrazine is a high-resolution (44,042 cells and 19 sigma layers) model that provides a better description of areas such as near and offshore zones, bays, river confluences, and the thermocline. The transport fields are provided by output from the Princeton Ocean hydrodynamics Model. Our high-resolution model, LM3-Atrazine, was primarily used to evaluate environmental exposure concentrations of atrazine in 5km x 5km model cells receiving loadings from the major tributaries to the lake. The modeled processes included advection, dispersion, decay, absorption, and volatilization. The atrazine decay (0.009/year) used in LM3-Atrazine was taken from the results derived from the hindcast run using LM2-Toxic.

The model segment receiving loads from the St. Joseph River, associated with the largest tributary load of atrazine to the lake, ranged from winter concentrations of 37 ng/L to spring peaks of 100-350 ng/L. These predicted exposure concentrations in the lake are all below selected toxicological endpoints, including the most sensitive, phytoplankton primary production reduction.

In comparing the results from the three LMMBP atrazine models to other models in the literature, it is apparent that atrazine decays very slowly in large lakes that stratify in the summer months. The literature suggests that degradation of atrazine in small lakes and streams that are well-mixed can be significant. A hypothesis can be formulated that the decay in surface water is likely to be dominated by photolytic processes, either directly or indirectly. In lakes that stratify in the summer, atrazine in the hypolimnion is isolated from the intense solar radiation during the peak time of the year. Hence, atrazine in this layer of the lake receives little degradation.

The LMMBP atrazine models differ from two other atrazine models recently applied to Lake Michigan. The main reason for the differences appears to be based on how they estimated tributary loadings – both used higher estimates of tributary loadings. Consequently, these other models predicted much faster *in situ* decay. Since tributary loadings are the major source atrazine to the lake, detailed assessments of these loads is very important.

PART 1

INTRODUCTION

Chapter 1. Project Overview

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The United States Environmental Protection Agency's (USEPA) Great Lakes National Program Office (GLNPO) instituted the Lake Michigan Mass Balance Project (LMMBP) to measure and model the concentrations of representative pollutants within important compartments of the Lake Michigan ecosystem. For the LMMBP, concentrations of polychlorinated biphenyls (PCBs), *trans*-nonachlor, and mercury were measured in tributaries, lake water, sediments, food webs, and the atmosphere surrounding Lake Michigan. Atrazine was measured only in the tributaries, lake water, and atmospheric components. This chapter provides an overview of the entire LMMBP. It includes a summary of the parameters measured and identifies the participants. Some of the data handling procedures are covered, as well as a listing of various project reports.

1.1.1 Background

The Great Lakes, which contain 20% of the world's freshwater, are a globally important natural resource 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 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, require the development of a Lake-wide Management Plan (LaMP) for each Great Lake. The purpose of these LaMPs is to document an approach to reduce inputs of critical pollutants to the Great Lakes and restore and maintain 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 (EMPs). 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 LMMBP is a part of the EMPs for Lake Michigan. The LMMBP 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 fate 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.

1.1.2 Description

The LMMBP 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 entering a system is equal to the amount of that pollutant leaving, trapped in, and chemically changed in the system (Figure 1.1.1). In the Lake Michigan system, pollutant inputs may come from atmospheric sources, adjacent lakes, or tributary loads.

Pollutants may leave the system through burial in bottom sediments, volatilization to the atmosphere, or discharge into Lake Huron through the Straits of

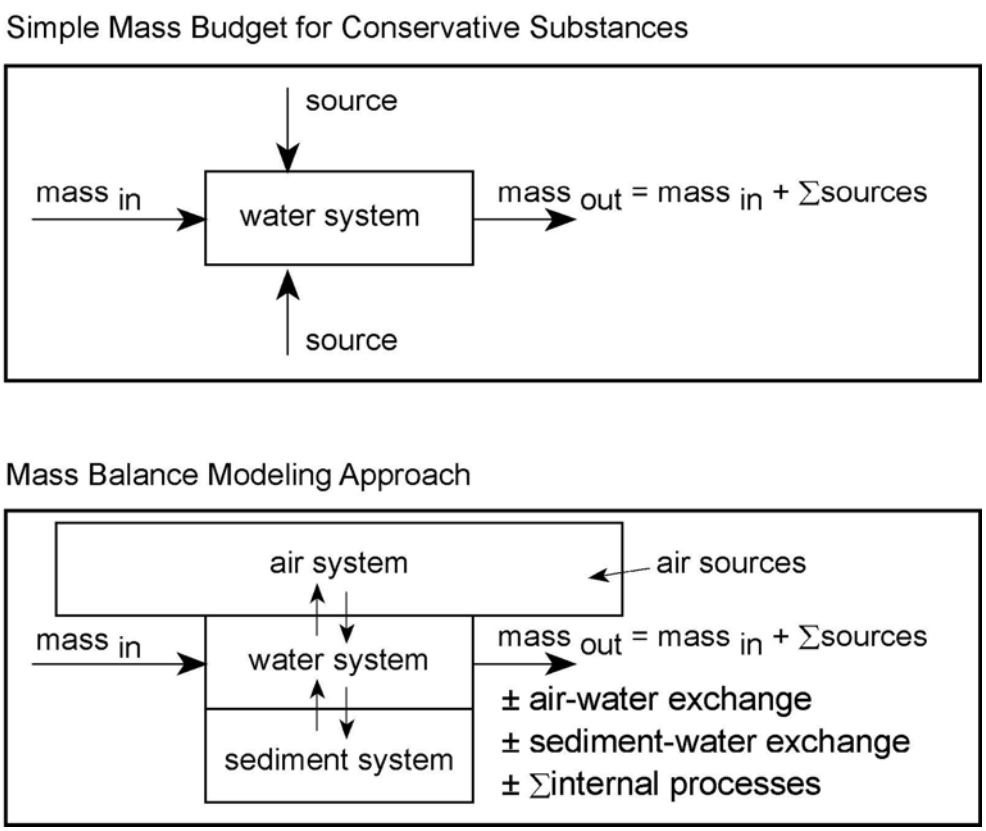

Figure 1.1.1. Simplified mass balance approach.

Mackinac. The relative magnitude of these loss mechanisms is, in part, due to the physical and chemical properties of the chemicals being modeled. Pollutants within the system may be transformed through degradation or stored in ecosystem compartments such as the water column, sediments, or biota.

For the LMMBP, contaminant concentrations in various inputs and ecosystem compartments over spatial and temporal scales were measured. Mathematical models that track the transport and fate of contaminants within Lake Michigan were developed and calibrated using these field data. The LMMBP models will serve as a basis for future mass budget/mass balance efforts for the LMMBP contaminants and other chemicals of interest.

1.1.3 Scope

1.1.3.1 Modeled Pollutants

When the USEPA published the Water Quality Guidance for the Great Lakes System (58 FR 20802), the Agency established water quality criteria for 29 pollutants. Those criteria were 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 LMMBP focused on constructing mass balance models for a limited group of pollutants. PCBs, *trans*-nonachlor, atrazine, and mercury were selected for inclusion in the LMMBP because these pollutants currently or potentially pose a risk to aquatic and terrestrial organisms (including humans) in the Lake Michigan ecosystem (Table 1.1.1). 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 calibrated, additional contaminants can be modeled with limited data and future resources can be devoted to activities such as emission inventories and dispersion modeling.

1.1.3.1.1 PCBs

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 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 the USEPA 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.

Because they were found by the USEPA in the effluents from one or more wastewater treatment facilities, seven Aroclor formulations were included in the Priority Pollutant List developed by the USEPA Office of Water under the auspices of the Clean Water Act. 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 build up, in living tissues. Levels of PCBs in some fish from Lake Michigan exceed

Table 1.1.1. Characteristics of the LMMBP Modeled Pollutants

Pollutant	Sources	Uses	Toxic Effects	Biocon-centration Factor[1]	USEPA Regulatory Standards[2]
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-Non-achlor[3]	• 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[4] = 350 µg/L CCC[4] = 12 µg/L
Mercury	• Waste disposal • Manufacturing processes • Energy production • Ore processing • Municipal & 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[5] = 2.4 µg/L FWC[5] = 12 ng/L Wildlife[6] = 1.3 ng/L

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

[2]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: U.S. Environmental Protection Agency, 1999, National Recommended Water Quality Criteria-Correction, EPA 822/Z-99/001, USEPA, Office of Water, Washington, D.C.

[3]Characteristics presented are for chlordane. *trans*-Nonachlor is a principal component of the pesticide chlordane.

[4]Draft water quality criteria for protection of aquatic life. From: U.S. Environmental Protection Agency, 2001b, Ambient Aquatic Life Water Quality Criteria for Atrazine, USEPA, Office of Water, Washington, D.C.

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

[6]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).

the 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.

1.1.3.1.2 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 United States. In 1988, the USEPA banned all production and use of chlordane in the United States.

Like PCBs, chlordane is relatively persistent and bioaccumulative. *trans*-Nonachlor is the most bioaccumulative of the chlordanes and 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 soil washing into the watershed. In the LMMBP, *trans*-nonachlor served as a model for the cyclodiene pesticides.

1.1.3.1.3 Atrazine

Atrazine is a triazine herbicide based on a ring structure with three carbon atoms alternating with three nitrogen atoms. Atrazine is the most widely used herbicide in the United States 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 United States. 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 bioaccumulative. It can be persistent in water; however, it is moderately susceptible to biodegradation in soils with a half-life of about 60-150 days. Atrazine rarely exceeds the 3 ppb maximum contaminant level (MCL) set by the USEPA as a drinking water standard, but localized peak values can exceed the MCL following rainfall events after atrazine application.

On January 31, 2003, the USEPA issued an Interim Reregistration Eligibility Decision (IRED) for atrazine. In an October 2003 addendum to the IRED, the Agency concluded that there is sufficient evidence to formulate a hypothesis that atrazine exposure may impact gonadal development in amphibians, but there are currently insufficient data to either confirm or refute the hypothesis. However, in an October 2007 report to the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Board, the Agency's review concluded that the weight-of-evidence from a literature review does not show that atrazine produces consistent, reproducible effects across the range of exposure concentrations and amphibian species tested. Based on available test data, atrazine is not likely to be a human carcinogen. The Agency does have concern in regards to the potential hormonal effects observed in laboratory animals exposed to atrazine. Above certain concentration thresholds, atrazine is toxic to aquatic plants. In the LMMBP, atrazine served as a model to describe the transport and fate of a water soluble pesticide in current use.

1.1.3.1.4 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 11,000 metric tons of mercury

are released annually to the air, soil, and water from anthropogenic sources. These sources include combustion of various fuels such as coal; mining, smelting, and manufacturing activities; wastewater; and 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 fetal damage. In the LMMBP, mercury served as a model for bioaccumulative metals.

1.1.3.2 Other Measured Parameters

In addition to the four chemicals modeled in the LMMBP, many other chemicals and parameters were measured in the LMMBP as part of the EMPs. A survey of these chemicals and parameters aids in the understanding of 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. Many of the parameters included in this study are provided in Table 1.1.2.

Table 1.1.2. The LMMBP 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	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

Organics (Continued)	
benzo[*a*]pyrene	*trans*-nonachlor
α-chlordane	oxychlordane
γ-chlordane	PCBs 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

Conventionals	
alkalinity	particulate organic carbon
ammonia	percent moisture
bromine	pH
chloride	phosphorus
chlorine	silica
sulfate	silicon
conductivity	temperature
dissolved organic carbon	total Kjeldahl nitrogen
	total organic carbon
dissolved oxygen	total phosphorus
dissolved phosphorus	total suspended particulates
dissolved reactive silica	*ortho*-phosphorus
dry weight fraction	total hardness
element carbon	turbidity
nitrate	

Biologicals	
fish species	fish weight
fish age	fish length
fish maturity	fish taxonomy
chlorophyll *a*	fish diet analysis
fish lipid amount	primary productivity
zooplankton	

Meteorological	
air temperature	wind direction
relative humidity	wind speed
barometric pressure	visibility
weather conditions	wave height and direction

1.1.3.3 Measured Compartments

In the LMMBP, 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:** Major tributaries 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.

- **Lower Pelagic Food Chain:** Phytoplankton and zooplankton were sampled and analyzed for species diversity, taxonomy, and contaminant burden.

- **Sediments**: Cores were collected and trap devices were used to collect sediment for determination of contaminants and sedimentation rates.

- **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 at more than 300 sampling locations and analyzed, including more than 9,000 quality control (QC) samples (Figure 1.1.2). 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

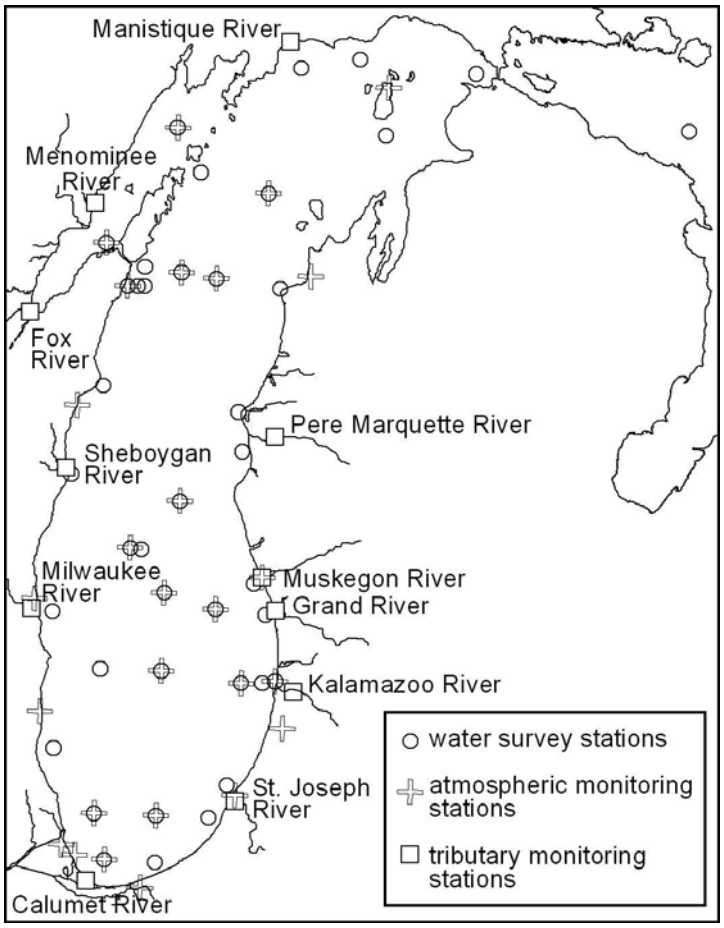

Figure 1.1.2. The LMMBP sampling locations.

information on contaminant loads and ambient concentrations for modeling purposes. Therefore, field sampling occurred from April 1994 to October 1995.

1.1.4 Objectives

The goal of the LMMBP 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 LMMBP 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 LMMBP monitoring and modeling efforts will improve our scientific understanding of the environmental processes governing contaminant cycling and availability within relatively closed ecosystems.

1.1.5 Design

1.1.5.1 Organization

The GLNPO proposed a mass balance approach to provide coherent, ecosystem-based evaluation of toxics in Lake Michigan. GLNPO served as the program sponsor for the LMMBP. GLNPO formed two committees to coordinate study planning, the Program Steering Committee and the Technical Coordinating Committee. These committees were comprised of federal, state, and academic laboratories as well as commercial laboratories (see Section 1.1.5.2, 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 Mid-Continent Ecology Division (MED) at Duluth, in cooperation with the National Oceanic and Atmospheric Administration (NOAA) Great Lakes Environmental Research Laboratory (GLERL) and the Atmospheric Sciences Modeling Division, supported 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.

1.1.5.2 Study Participants

The LMMBP was a coordinated effort among federal, state, and academic scientists; and commercial laboratories. The following agencies and organizations have all played roles in ensuring the success of the LMMBP. Except for the three organizations indicated with an asterisk (*), all of the participants were members of the LMMBP Steering Committee.

Federal and International

- USEPA/GLNPO (*Program Sponsor*)
- USEPA/Region V Water Division (WD)
- USEPA/Region V Air Division
- USEPA/ORD/NHEERL/MED/LLRFRB
- ORD/National Exposure Research Laboratory
- U.S. Department of the Interior (USDOI) U.S. Geological Survey (USGS) Water Resources Division (WRD)
- USDOI/USGS Biological Resources Division Great Lakes Science Center (GLSC)
- U.S. Fish and Wildlife Service (USFWS)
- U.S. Department of Energy
- U.S. Department of Commerce NOAA/GLERL
- USEPA/Office of Air and Radiation*
- USEPA/Office of Water*
- Environment Canada*
- U.S. Department of Energy Battelle NW

State

- Illinois Department of Natural Resources
- Illinois Water Survey
- Indiana Department of Environmental Management
- Michigan Department of Natural Resources
- Michigan Department of Environmental Quality (MDEQ)
- 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
- Grace Analytical

1.1.5.3 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 (USEPA/GLNPO)
- Technical Coordinating Committee – Paul Horvatin (USEPA/GLNPO)
- Modeling Workgroup – William Richardson (USEPA/ORD/NHEERL/MED/LLRFRB)
- Air Monitoring Workgroup – Jackie Bode (USEPA/GLNPO)
- Biota Workgroup – Paul Bertram (USEPA/GLNPO) and John Gannon (USDOI/USGS/GLSC)
- Chemistry Workgroup – David Anderson (USEPA/GLNPO)
- Data Management Workgroup – Kenneth Klewin and Philip Strobel (USEPA/GLNPO)
- Lake Monitoring Workgroup – Glenn Warren (USEPA/GLNPO)
- Tributary Monitoring Workgroup – Gary Kohlhepp (USEPA/Region V/WD) and Robert Day (MDEQ)
- Quality Assurance Workgroup – Louis Blume and Michael Papp (USEPA/GLNPO)
- Sediment Monitoring Workgroup – Brian Eadie (NOAA/GLERL)

1.1.5.4 Information Management

As program sponsor, GLNPO managed information collected during the LMMBP. 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 was also 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 1.1.3.

1.1.5.4.1 Data Reporting

Over 20 organizations produced LMMBP 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 the LMMBP 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 minimize the number of data elements reported from the field crews and laboratory analysis. Data reporting formats and the resulting Great Lakes Environmental Monitoring Database (GLENDA, see Section1.1.5.4.2) were designed to be applicable to projects outside the LMMBP as well.

Principal Investigators (PIs) (including sampling crews and the analytical laboratories) supplied sample collection and analysis data following the standardized reporting formats, if possible. The LMMBP data were then processed through an automated SAS-based data verification system, Research Data Management and Quality Control System (RDMQ), for quality assurance (QA)/QC

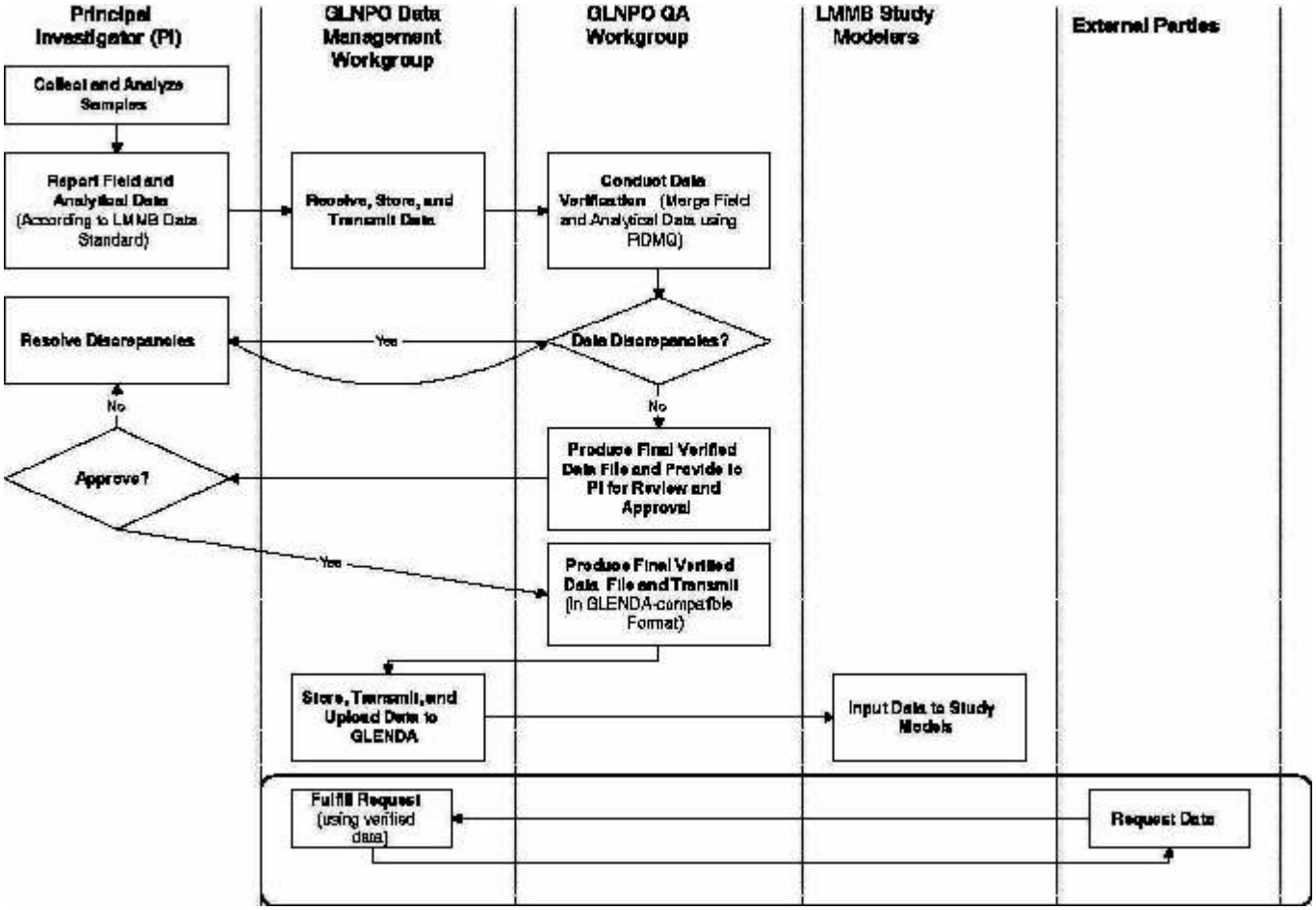

Figure 1.1.3. Flow of information in the LMMBP.

checking. After verification and validation by the PIs, the data sets were output in a form specific for upload to GLENDA. Finally, these data sets were uploaded to GLENDA.

1.1.5.4.2 Great Lakes Environmental Monitoring Database

Central to the data management effort is a computerized database system to house LMMBP and other project results. That system, 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:** Ensure data longevity by including enough information to allow future or secondary users to make use of the data.

- **Flexible and expandable:** 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.

1.1.5.4.3 Public Access to LMMBP Data

All LMMBP 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 the LMMBP data. The data sets are available in several formats including WK1, DBF, and SD2. More information about the data sets is available on the LMMBP web site at: http://www.epa.gov/glnpo/lmmb/database.html.

The primary reason for requiring an official request form for the LMMBP 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 the LMMBP data have been made: eight from USEPA, five from other federal agencies, five from state agencies, five from universities, ten from consultants, three from international agencies, and two from non-profit or other groups. In the future, after all data are verified and validated, GLNPO intends to make condensed versions of the data sets available on the LMMBP web site for downloading. This will allow easy public access to the LMMBP data.

Further information on the information management for the LMMBP can be found in The Lake Michigan Mass Balance Study Quality Assurance Report (U.S. Environmental Protection Agency, 2001a).

1.1.5.5 Quality Assurance Program

At the outset of the LMMBP, 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, the LMMBP managers established a QA program goal of ensuring that data produced under the LMMBP 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:** USEPA established a QA Workgroup whose primary function was to ensure that the overall QA goals of the study were met.

- **QA Project Plans (QAPPs):** USEPA worked with PIs to define program objectives, data quality objectives (DQOs), and measurement quality objectives (MQOs) for use in preparing Quality Assurance Project Plans (QAPPs). PIs submitted QAPPs to the USEPA for review and approval. USEPA reviewed each QAPP for required QA elements and soundness of planned QA activities.

- **Training:** Before beginning data collection activities, PIs conducted training sessions to ensure that individuals working on the project were capable of properly performing data collection activities for the LMMBP.

- **Monthly Conference Calls and Annual Meetings:** USEPA, 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:** PIs 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:** USEPA 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, USEPA 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 the USEPA 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:** USEPA made statistical assessments of the LMMBP data to estimate elements of precision, bias, and uncertainty.

- **Data Validation:** USEPA and modelers evaluated the data against the model objectives.

Comparability of data among PIs participating in the LMMBP was deemed to be important for successful completion of the study. Therefore, 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 LMMBP QA Workgroup. The workgroup was chaired by GLNPO's QA Manager and consisted of QC 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 LMMBP 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 LMMBP data set for a subset of the attributes listed above, specifically sensitivity, precision, and bias. The LMMBP modelers and the LLRS Database Manager also performed data quality assessments prior to inputting data into study models. Such activities included verifying the readability of electronic files, identifying missing data, checking units, and identifying outliers. A detailed description of the QA program is included in The Lake Michigan Mass Balance Project Quality Assurance Report (U.S. Environmental Protection Agency, 2001a). A brief summary of quality implementation and assessment is provided in each of the following parts.

1.1.6 Project Documents and Products

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

The LMMBP Work Plan

Designers of the LMMBP have documented their approach in a report entitled Lake Michigan Mass Budget/Mass Balance Work Plan (U.S. Environmental Protection Agency, 1997a). The essential elements of a mass balance study and the approach used to measure and model these elements in the Lake Michigan system are described in the work plan. 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.

QA Program/Project Plans

The Lake Michigan Mass Balance Project: Quality Assurance Plan for Mathematical Modeling, Version 3.0 (Richardson *et al*., 2004) documents the QA process for the development and application of LMMBP models, including hydrodynamic, sediment transport, eutrophication, transport chemical fate, and food chain bioaccumulation models.

The Enhanced Monitoring Program QA Program Plan

The Enhanced Monitoring Program Quality Assurance Program Plan (U.S. Environmental Protection Agency, 1997b) was developed in 1993 to ensure that data generated from the LMMBP supported its intended use.

The LMMBP Methods Compendium

The Lake Michigan Mass Balance Project Methods Compendium (U.S. Environmental Protection Agency, 1997c, 1997d) describes the sampling and analytical methods used in the LMMBP. The entire three volumes are available on GLNPO's website mentioned above.

The LMMBP Data Reporting Formats and Data Administration Plan

Data management for the LMMBP 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 LMMBP 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 a Lake-wide Area Management Plan (LaMP) 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 LMMBP 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.

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PART 1

INTRODUCTION

Chapter 2. General Information on the Herbicide Atrazine and Its Degradation Products

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1.2.1 Background

Atrazine is a triazine herbicide registered to control broadleaf weeds and some grassy weeds by inhibiting photosynthesis. Its primary use in the Lake Michigan basin is for the control of weeds in corn crops. It is estimated to be the most heavily used herbicide in the United States. Usage on corn accounts for approximately 86% of total United States domestic usage, followed by sorghum at 10%, and sugarcane at 3% (all other uses make up the remaining 1%). For corn crops, it is usually applied in the spring prior to, during, or after planting a crop or after crop emergence. The product is formulated as an emulsifiable concentrate, flowable concentrate, water dispersible granular (dry flowable), soluble concentrate, wettable powder, granular, and as a ready-to-use formulation. It may be applied to the field with a groundboom sprayer, aircraft, or by means of a tractor-drawn spreader (U.S. Environmental Protection Agency, 2003a). In a 1990-1991 period, atrazine was the single highest-use pesticide in the Great Lakes basin (United States only) and represented 19.4% of all pesticides used on agricultural crops (U.S. General Accounting Office, 1993).

Atrazine was registered in 1958 (U.S. Environmental Protection Agency, 2003a), and is currently undergoing a reregistration review. Syngenta is the primary atrazine registrant. Pesticides registered prior to November 1984 are subject to the reregistration process. On January 31, 2003, the U.S. Environmental Protection Agency (USEPA) issued an Interim Reregistration Eligibility Decision (IRED) for atrazine (U.S. Environmental Protection Agency, 2003b). In October 2003, the USEPA issued an addendum that updates the January 31, 2003 IRED (U.S. Environmental Protection Agency, 2003c). The Agency expects the registrants to adopt the risk management measures presented in the IRED. Among other requirements, the IRED mandates the monitoring of 40 representative watersheds in the United States to determine if specific atrazine levels of concern are exceeded, a testing program to better evaluate potential risk to amphibians, and measures to mitigate exposure risk to applicators in both residential and agricultural settings. Watersheds exceeding levels of concern criteria will be subject to remedies under the USEPA's Total Maximum Daily Load (TMDL) program requirements. In the October 2003 addendum to the IRED, the Agency concluded that there is sufficient evidence to formulate a hypothesis that atrazine exposure may impact gonadal

development in amphibians, but there are currently insufficient data to confirm or refute the hypothesis. On October 9-12, 2007, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) Scientific Advisory Panel (SAP) met with the Agency to evaluate the potential for atrazine to affect the development of amphibian species. However, in an October 2007 report to the FIFRA Scientific Advisory Panel, the Agency's review of the literature indicated that studies do not show that atrazine produces consistent, reproducible effects across the range of exposure concentrations and amphibian species tested. Based on available test data, atrazine is not likely to be a human carcinogen. The Agency does have concern in regards to the potential hormonal effects observed in laboratory animals exposed to atrazine. A Reregistration Eligibility Decision (RED) was issued for atrazine, a triazine pesticide, in April 2006. In that RED, an evaluation was performed to determine if the cumulative effect from the triazine pesticides (atrazine, simazine, propazine, and their chlorinated degradates) that share a common mechanism of toxicity are below the Food Quality Protection Act (FQPA) regulatory level – that the risks associated with the pesticide residues pose a reasonable certainty of no harm.

A comprehensive review of atrazine toxicity to various freshwater trophic groups was conducted by Solomon *et al.* (1996). A total of 85 species were tested, and the order of sensitivity from most to least sensitive trophic groups was as follows: phytoplankton > aquatic macrophytes > benthos > zooplankton > fish. Due to limited data, amphibians were not included in this sensitivity review. Atrazine was found to be more inhibitory to photosynthesis than were its transformation products. Atrazine was seven to 10 times more inhibitory to blue-green algae and four to six times more inhibitory to green algae than the most potent transformation product, deethylatrazine (DEA). Young fish survival may be at risk if the atrazine exposure concentrations are significant enough to impact phytoplankton populations and macrophytes. Zooplankton, an important food source for juvenile fish, may be depleted if the phytoplankton are reduced, and the juvenile fish may become easier prey if they lose the protective cover of macrophytes.

Atrazine is often found in surface water and is regulated under the Safe Drinking Water Act. A Maximum Contaminant Level (MCL) of 3 ppb was established in 1991 by the USEPA's Office of Water (U.S. Environmental Protection Agency, 1995). Loadings associated with run-off from farm fields are often seasonal with the spring and early summer-time periods being the highest. For municipalities dependent upon drinking water supplies from rivers, potential exceedences of the MCL are most likely to occur from mid-April through mid-July in the Lake Michigan basin when atrazine concentrations are most likely to be high. Using a variety of bench-scale water treatment processes such as coagulation, softening, ozonation, chlorination, and powdered activated charcoal, researchers had difficulty adequately removing atrazine from the water and recommended that other removal processes should be investigated (Westerhoff *et al.*, 2005).

Atrazine has been banned in the European Union (EU) since October 4, 2003 when the herbicide was not granted re-registration. This decision was taken by the Standing Committee on the Food Chain and Animal Health (SCFAH), the EU regulatory body.

Additional background information on atrazine and access to the documents cited in this section can be downloaded at http://www.epa.gov/pesticides/.

1.2.2 Physical-Chemical Properties of Atrazine

Physical and chemical properties of atrazine are given in Table 1.2.1. With a low Henry's law constant, atrazine volatilization from the lake is low. Also, with a moderate solubility in water, run-off from farm fields can occur, especially in the spring after significant rainfall and when soil moisture content is high. With a low octanol-water partition coefficient (K_{ow}), atrazine is not strongly sorbed to particles in the water, and it is not bioaccumulated to any extent. Frank *et al*. (1979) analyzed suspended solids from 12 streams (45 samples) in 1974 and 1976 flowing into the Great Lakes from the Canadian side (Ontario) and were unable to detect atrazine in these particulates (detection limit of 0.05 µg/g). However, of the 92 streams sampled in 1977, they detected atrazine in the water approximately 80% of the time. From that study, they concluded that atrazine was in

Table 1.2.1. Physical and Chemical Properties of Atrazine

Empirical Formula	$C_8H_{14}ClN_5$
Chemical Name	2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine
Chemical Family	Triazine

Structural Formula:

```
                        Cl
                        I
                        C
                      //   \
        (CH3)         N    N
          |           |    ||
(CH3)—(CH)—(NH)—C    C—(NH)—(CH2)—(CH3)
                      \\   /
                        N
```

Molecular Weight	215.7 g/mol
Melting Point	173°C to 175°C
Vapor Pressure	40 µPa at 20°C
Solubility in Water	33 PPM at 25°C
Density	0.35 g/ml
Henry's Law Constant	8.1×10^{-8} (dimensionless) at 25°C (U.S. Department of Agriculture, 2001)
Physical state	White crystalline solid
log K_{ow}	2.7645

the dissolved phase, rather than attached to particles. Laboratory measurements of the partition coefficients for atrazine, DEA, and deisopropylatrazine (DIA) resulted in the following: 1.1, 0.4, and 0.3 (ng/g)/(ng/ml), respectively. The particulate substrate was Eudora Silt Loam with a 1.0% carbon content. These results indicated that the two degradation products are even more soluble than the parent compound, atrazine (Mills and Thurman, 1994). So, models often omit the interaction of atrazine with solids (both suspended solids and sediment) and do not include bioaccumulation components. Because atrazine is primarily transported in a dissolved phase, groundwater is vulnerable to contamination as it can receive a load associated with infiltration.

Other chemical compounds, such as cyanazine and simazine, with the same triazine ring structure as atrazine have been used in the Great Lakes watershed. Cyanazine usage in the basin in the early 1990s was about 40% that of atrazine, and simazine was approximately 1% that of atrazine (U.S. General Accounting Office, 1993). Both cyanazine and simazine were used as herbicides.

Unless otherwise specified, the information in Table 1.2.1 was obtained from USEPA's Office of Pesticides (January 2003a).

1.2.3 Atrazine Degradation

Atrazine is known to degrade in the environment through either biotic or abiotic processes. The specific bacteria strain and population, physical and chemical conditions present, and media type all contribute to determining the degradation fate of atrazine in the environment.

1.2.3.1 Biotic Degradation in Surface Water

Bacterial processes are known to convert atrazine to DEA and DIA; however, this degradation is not likely occurring in the surface water. Abiotic processes often convert atrazine to hydroxyatrazine. See Figure 1.2.1 for the chemical structures of these major degradation products. Biodegradation assays of 14- to 32-days of unfiltered water from the River Po, Italy, spiked with various concentrations of atrazine, yielded no degradation products (Brambilla *et al.*, 1993). Ingerslev and Nyholm (2000) tested natural water samples from an unpolluted forest stream using ^{14}C-labeled atrazine. Microbial degradation of atrazine was evaluated by measuring the evolution of ^{14}C in carbon dioxide (CO_2). Testing these samples with a wide range of atrazine concentrations typically found in streams showed that the natural population of microbes did not degrade the labeled atrazine. Biodegradation of atrazine was not found in two shallow impounded small lakes in Nebraska that receive agricultural inputs of atrazine from run-off (Spalding *et al.*, 1994). Half-lives of atrazine in these lakes were estimated to range from 193 to 124 days. The biodegradation product, DEA, was not increasing relative to atrazine in the lake, therefore suggesting that the degradation observed was not biotic. They surmised that degradation was

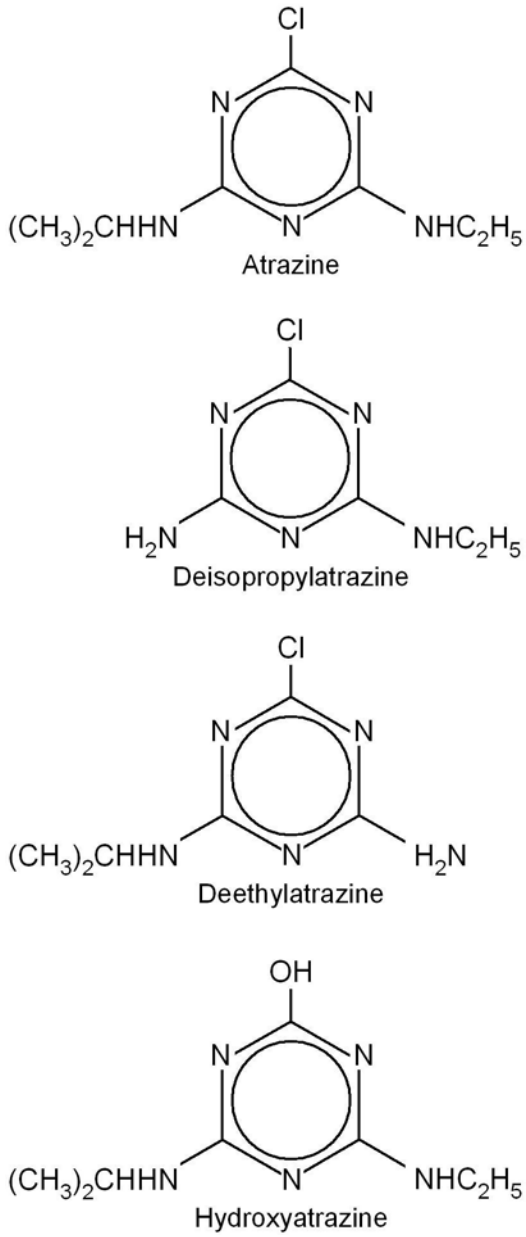

Figure 1.2.1. Chemical structures of atrazine and its major degradation products.

due to abiotic processes. Evidence of biodegradation was not found in a study of a lake in Nebraska (Ma and Spalding, 1997). However, these researchers did suggest that abiotic degradation was the likely mechanism for degradation. A study of atrazine degradation in an Iowa stream determined that atrazine biodegradation was not occurring in the river (Kolpin and Kalkhoff, 1993). Modeling analysis of a small Swiss lake (hydraulic detention time of 1.2 years) found that atrazine is rather stable in the lake water with removal primarily due to export with water flowing out of the lake (Buser, 1990; Ulrich *et al.*, 1994; Müller *et al.,* 1997). Atrazine degradation *via* biotic and/or abiotic processes in Lake Michigan was found to be negligible using a mass balance model (Rygwelski *et al.*, 1999). Biodegradation products of atrazine are commonly found in surface waters, but their origin is likely from agricultural soils where biodegradation is known to occur to a significant extent.

There are various hypotheses why researchers cannot find evidence of atrazine biodegradation in surface water. In systems such as Lake Michigan, this potential biotic "food" source (atrazine) is very dilute, and therefore, it is hypothesized that bacteria specific to atrazine degradation do not thrive. If atrazine were to substantially partition to particles in the water, then perhaps atrazine would be in a more concentrated form that could sustain the specific strain of atrazine-degrading bacteria. Using granular activated charcoal to enhance atrazine adsorption and the inclusion of atrazine-specific bacterial degraders in a laboratory batch reactor, significant reductions (45% to 86%) in atrazine concentrations were achieved after a 15-day incubation period at 10°C (Feakin *et al.*, 1994). Also, if present in sufficient quantities, more readily available sources of nitrogen other than that provided by the 1,3,5-triazine structure may be preferentially used by the atrazine-degrading bacteria. Therefore, the atrazine triazine structure would be left intact (Feakin *et al.*, 1994). Typically, the first stage in the biodegradation of the 1,3,5-triazines is deisopropylation and deethylation leading to the removal of nitrogen from positions four and six of the 1,3,5-triazine ring. Feakin *et al.* (1994) also showed that degradation in water without sufficient assimilable organic carbon did not support biodegradation. They theorized that the bacteria needed a certain minimum level of carbon for maintenance energy and growth.

While atrazine biodegradation is not likely to occur naturally in surface waters, efforts have been made to find ways to create better conditions for biotic degradation in water in laboratory operations, with the intent of applying the methodology to water treatment facilities. A pilot plant operation studying the potential to degrade atrazine in water found that

an atrazine-specific degrading bacterium, *Rhodococcus rhodochrous* strain SL1, was effective in degrading the herbicide after the atrazine was adsorbed to granular activated carbon packed in columns (Jones *et al.*, 1998). However, periodic reinoculation onto the columns was required to maintain adequate numbers of SL1. Conventional water treatment facilities are not effective in reducing atrazine concentrations. Conventional activated sludge wastewater treatment plants are also ineffective at removing atrazine from the waste stream (Monteith *et al.,* 1995).

1.2.3.2 Abiotic Degradation in Surface Water

1.2.3.2.1 Hydrolysis

Degradation by hydrolysis is likely in water if the environmental conditions are favorable. Hydrolysis was not found to occur at pH greater than 4 at 15°C in buffered distilled water or natural river water (Comber, 1999). Furthermore, the addition of iron hydroxide and aluminum silicate did not promote degradation *via* catalysis as some researchers have hypothesized. The pH of Lake Michigan is relatively high (8.2) and, therefore unlikely to support hydrolysis. However, at temperatures of 35°C, atrazine was found to slowly degrade *via* hydrolysis at a range of pHs from 3 to 8 in distilled water (Lei *et al.*, 2001). Hydrolysis rate constants were increased (half-lives shortened) with the addition of humic acids and nitrate ions. An evaluation of atrazine hydrolysis in groundwater samples at a pH of 7.8 and temperatures of 4°C and 30°C showed no significant loss (Widmer *et al.*, 1993). Also, when hydrolysis experiments were conducted at room temperature and a pH of 6.5, dissolved organic carbon (DOC) additions with and without nitrate did not cause any degradation (Hapeman *et al.*, 1998). Spalding *et al.* (1994) theorized that surface catalyzed hydrolysis was a possible mechanism for degrading atrazine in two small lakes located in Iowa. These shallow lakes had high turbidity with high DOC (5.1 to 8.4 mg/l).

1.2.3.2.2 Photolysis

Photolysis is enhanced when nitrate ions are present to facilitate indirect photolysis by acting as a catalyst. It is hypothesized that in the presence of the nitrate ion, hydroxy radicals are produced resulting in oxidation and/or removal of the alkyl groups. In a small stream in Iowa, isolated from groundwater intrusion, Kolpin and Kalkhoff (1993) found that the atrazine half-life had a significant inverse relationship with sunlight, suggesting that photolysis was responsible. This same inverse relationship was noted in a reservoir in Iowa (Chung and Gu, 2003). However, in both of these studies a correlation between atrazine half-lives and concentrations of nitrate ions was poor. The relationship between half-lives and nitrate concentrations may be masked in the natural environment because of the strong seasonality of photodegradation with sunlight. Using titanium dioxide (TiO_2) as a photocatalyst and simulated solar light in a laboratory setting, researchers have found that atrazine can be degraded very rapidly (Pelizzetti *et al.,* 1990) with a half-life estimated at 19 minutes (Konstantinou *et al.,* 2001a). Some DOC mimics can significantly increase photodegradation of atrazine, while others do not, leading researchers to believe that both the structural properties and concentration of DOC in water are important factors to consider when assessing potential photodegradation impact (Hapeman *et al.*, 1998). Using natural light sources, some studies have found that structural properties of some types of natural DOC present in surface water will actually reduce photodegradation rates (Konstantinou *et al.,* 2001b). The degradation products found in the Konstantinou study using natural water samples were the hydroxy and dealkylated derivatives of atrazine. It appears that light energy at wavelengths less than 300 nm is necessary to initiate direct photolysis where photolysis occurs without the need of an intermediary (Comber, 1999). However, natural sunlight provides very little of this light energy. Direct photodegradation produces primarily hydroxyatrazine (Konstantinou *et al.*, 2001b).

Even though Lake Michigan has very low nitrate (1994-1995 median 0.28 mg/L) and DOC concentrations (1994-1995 median 1.5 mg/L), it is possible that some degradation is occurring *via* various photolysis processes. However, it is believed that the impact on the lake is small because the depth of the lake limits light penetration through the water column and isolates the hypolimnion during the high solar radiation period. Studies of atrazine transport, atmospheric deposition, and fate in Isle

Royale National Park have shown that the shallow lakes have lower atrazine concentrations than the deeper lakes on this island in Lake Superior (Thurman and Cromwell, 2000). These island lakes are in a pristine area and receive their atrazine input from the atmosphere. If atrazine were highly persistent in water, then one would expect that the shallow lakes would have higher concentrations than the deeper lakes because the shallow lakes have a higher surface area to depth ratio. However, Thurman and Cromwell's findings are just the opposite, and a possible explanation for this is that photolysis in the shallow lakes occurs throughout the water column, but in the deeper lakes it may be limited to the upper water column only.

1.2.3.3 Atrazine Degradation in Soil

The degradation of atrazine in soils is much faster than in water. Durand and Barcelo (1992) presented half-life values for atrazine in soil from six studies. All of the studies found half-lives of 125 days or less. Nair and Schnoor (1994) found that degradation rates in soil depend strongly on soil environmental conditions. Degradation increased with increasing soil water and organic carbon content; however, degradation rates decreased in low oxygenated soils. Mirgain *et al.* (1993) found that bacteria degrade atrazine in soils where the organic carbon content is greater than 2%. Degradation increased with increasing carbon content. They also noted that repeated applications of atrazine on the same soil sample results in the enhancement of degradation with each successive application. They found that the reason for this is that bacteria populations specific to degrading atrazine increased with each application and the number of bacteria strains decreased. Compared to water, soil is better in facilitating degradation of atrazine because the "food" source (atrazine) is readily available to support bacterial strains that are efficient in degrading the herbicide.

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PART 1

INTRODUCTION

Chapter 3. Atrazine Field Data Observations

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1.3.1 Background

In this chapter, a summary of the Lake Michigan Mass Balance Project (LMMBP) atrazine data and historical data are presented along with a brief description of sampling and analytical methodology. A LMMBP atrazine data report by DynCorp Science and Engineering Group was prepared that provides more details regarding concentrations of atrazine and its degradation products related to sampling atmospheric components, tributaries, and the open-lake water column (Brent *et al.*, 2001). The DynCorp data report also provides an in-depth discussion on data quality implementation and assessment. Also, see Part 1, Chapter 1, Section 1.1.6 in this report for references to additional documents, such as the LLMBP Methods Compendium and quality assurance plans, that provide additional details on the project. Project data reside in a Great Lakes National Program Office (GLNPO)-managed Great Lakes Environmental Monitoring Database (GLENDA). The data were collected for use in the mass balance models.

For the LMMBP, measurements of atrazine, along with two degradation products deisopropylatrazine (DIA) and deethylatrazine (DEA), were attempted for all media. However, for some media, the detection of the degradation products was difficult because atrazine concentrations were very low. Whenever possible, Principal Investigators (PIs) were requested to report analytical results as measured, even if the value was lower than the method detection limit. This modeling report focuses on modeling atrazine and not the degradation products because of the sparsity of degradation data for some media. Also, triazines other than atrazine can degrade into DEA and DIA (Thurman *et al.,* 1994). So, if all of the parent compounds are not modeled, the degradation products cannot be modeled. In a summary report (U.S. General Accounting Office [USGAO], 1993) for pesticide usage in the basin for 1990 and 1991, two other triazines used as herbicides in the Lake Michigan basin (simazine and cyanazine) can degrade into DIA. Simazine usage in the basin was extremely low compared to atrazine usage so degradation products from simazine would be insignificant. Cyanazine usage, however, was about 37% of the atrazine usage estimates. Propazine can degrade into DEA, but this chemical was not listed in the usage tables of the USGAO report. It has

been estimated that atrazine is the major source for DEA (98%) in the Corn Belt (Thurman *et al.*, 1994).

Hydroxylated atrazine degradation products are also found in the environment (Lerch *et al.*, 1998) and are formed by substitution of the chlorine atom with a hydroxyl group in the parent atrazine compound. In a survey of Midwestern streams, they found that these hydroxylated atrazine degradation products were less abundant than DEA and DIA. Hydroxyatrazine is the primary hydroxylated atrazine degradation product but was not measured in the LMMBP.

1.3.2 Atmospheric Components

Atrazine enters the atmosphere by volatilization from either agricultural land (soil and plant) or water, by wind erosion from fields where the chemical is either sorbed onto soil particles or as a pure pesticide particle from plant or soil surfaces, and by physical drift of spray during application (Banks and Tierney, 1993). Once the chemical is airborne, a variety of physical and/or chemical processes can cause degradation, and various physical processes can cause deposition back to land or water. In addition to the atrazine data report by DynCorp and the LMMBP Methods Compendium, information on atmospheric media sampled can be found in a master's thesis by Sondra Miller (Miller, 1999).

1.3.2.1 Sampling and Analytical Methodology

Primary atmospheric sampling occurred at eight shoreline stations. Sampling locations are identified in Figure 1.1.2. Some limited atmospheric sampling also occurred at selected open-lake stations aboard the research vessel, *Lake Guardian*. Also, three stations (Eagle Harbor, Michigan; Brule River, Wisconsin on the southern shore of Lake Superior; and Bondville, Illinois) were located outside of the basin and were established to characterize air masses from the southwest or northwest directions. Vapor, particulate, and wet deposition were sampled and analyzed. Atmospheric sampling occurred from March 15, 1994 to October 20, 1995. A total of 294 vapor phase samples, 226 particulate samples, and 207 precipitation samples were collected. All samples were analyzed for atrazine and primary degradation products DEA and DIA except for the Sleeping Bear Dunes site where only atrazine was analyzed. From April 1994 through July 1994, samples from the Sleeping Bear Dunes site were collected and analyzed at the Illinois State Water Survey (Clyde Sweet). For the remaining period at the same site, August 1994 through October 1995, atmospheric samples were both collected and analyzed by Indiana University (Ronald Hites). Samples from all other atmospheric stations were collected and analyzed by the Illinois State Water Survey.

Wet deposition composite samples were collected over a 28-day period at the shore-based stations using a Meteorological Instruments of Canada (MIC-B) sampler modified with a heater for all-weather sampling. Equipped with a precipitation sensor, the sampler was open to the atmosphere only during wet events. Rain and snow that was collected flowed through a 30 cm XAD-2 resin column that absorbed the atrazine and degradation products from the sample. Glass wool plugs, before and after the column, prevented particles from entering the column. After the required collection period, the collection funnel was rinsed with water and wiped with clean quartz fiber filter paper to remove any adhering particles. Both the filter paper and the rinsing became part of the sample. Five percent of Illinois State Water Survey wet deposition samples were field duplicates with a system precision of 115% for samples above the method detection limit. The mean laboratory matrix spike recovery was reported at 82%. Indiana University analyzed only 14 routine samples and 12 field duplicates. Their system precision of the duplicates was 28.1% for samples above the method detection limit. They achieved laboratory matrix spike recovery of 110%.

Composite atmospheric vapor and particulate samples were collected over a period of 24 hours every 12 days using a high-volume air sampler. Air was passed through a XAD-2 resin to collect the atrazine and degradation products. Air flow was maintained at approximately 34 m^3/hour during sampling. Resin traps were wrapped in aluminum foil and sealed in tin cans and held at -18°C until analysis. Particulate phase atmospheric samples were collected on pre-fired quartz fiber filters. Filters were wrapped in aluminum foil and sealed in tin cans and stored at -18°C until analysis. Multiple 24-hour

samples were often composited to yield a monthly sample composite. At the Sleeping Bear Dunes site, and occasionally some other sites, 24-hour samples were analyzed individually and then mathematically composited to yield a monthly average.

The XAD-2 resin or filter samples were extracted by Soxhlet extraction with 300 ml of a 1:1 hexane and acetone mixture. The extract was concentrated by rotary evaporation and then cleaned-up with 3% deactivated silica with a sodium sulfate cap to remove non-target interfering compounds. Samples were analyzed using gas chromatography coupled to a mass spectrometer detector.

1.3.2.2 Results

1.3.2.2.1 Atrazine in the Gas Phase Fraction

Gas phase samples were extremely low; therefore, quantifying over-the-lake concentrations used in the volatilization and absorption mass balance algorithms was difficult. Only 11 samples were above the detection limits. And of these samples, four were flagged by the analysts as possibly contaminated due to field or laboratory blanks, and four others were from a station outside the Lake Michigan basin located in Bondville, Illinois. This leaves three samples collected in the basin with measurements of atrazine above the detection limit–one sample from South Haven collected July 7, 1994 through July 8, 1994 at 70 pg/m^3 and the rest at Sleeping Bear Dunes collected November 16, 1994 - November 17, 1994 at 22.1 pg/m^3 and September 9, 1995-September 14, 1995 at 31.5 pg/m^3. The sampling stations at both the Bondville and South Haven sites are located where local agricultural influences on the gas phase concentrations are likely. Therefore, these concentrations may not be representative of gas phase concentrations over-the-lake. Peck and Hornbuckle (2005) measured gas phase concentrations of atrazine in the intensively farmed state of Iowa. They found that gas phase atrazine concentrations showed a seasonal pattern with highest concentrations evident during the spring and early summer. In their study, the average concentration of atrazine in the air was 1,200 pg/m^3. In the LMMBP study, DEA and DIA were not detected in the gas phase.

Because gas phase measurements did not provide a reliable over-the-lake estimate in the LMMBP, we made assumptions about this value based on detection limits. In Miller (1999), the method detection limit (MDL) for atrazine for the shore-based and open-water sites gas phase concentration was 21.3 ng. Knowing the average flow rate of air through the sampler and assuming a 24-hour collection period, Miller estimated a MDL of 9.26 pg/m^3. Modeling scenarios presented in this report utilized this method detection limit to place an upper expected limit on this boundary condition.

1.3.2.2.2 Atrazine in the Particulate Fraction

Atrazine in the particulate fraction in air was low and often difficult to detect. This finding is also supported by other studies, such as in rural Iowa – a state with the highest pesticide applications in the United States and where 94% of the state is farmland and 60% of that area is planted with corn (Nations and Hallberg, 1992). Only 23% of the particulate samples taken for the LMMBP had atrazine concentrations above the sample-specific detection limit. Also, the chemical was primarily observed in the months of April, May, June, and July. Only one particulate sample collected from August through March contained levels above the MDL. Maximum monthly average atrazine concentrations ranged from a low of 160 pg/m^3 at Sleeping Bear Dunes in northern Lake Michigan to a high of 1,400 pg/m^3 at the Bondville site. The elevated concentration at the Bondville site is most likely related to the fact that it is in the middle of an intensive corn-growing region. A summary of spring/summer atrazine concentrations measured in the particulate phase can be found in the atrazine data report (Brent *et al.*, 2001). Particle size distribution analyses were not conducted on particulates collected in the air samples. Sweet and Harlin (1998) estimated that approximately 1% of the total atrazine load associated with wet and dry particle deposition to Lake Michigan is due to atrazine associated with particulates.

Of the over-water sampling stations, only two samples had detectable atrazine in the particulate fraction, and both of these samples were collected close to land in the southern part of the lake (near Chicago and Indiana Dunes). An atrazine concentration of 560 pg/m^3 was measured at station

1 in May 1994, and a concentration of 280 pg/m^3 was measured at station 5. Station 1 is shown on Figure 1.1.2 as the southern-most over-water atmospheric monitoring station, and station 5 is located immediately north and slightly west of station 1.

In the spring/summer of 1994, the LMMBP project detected atrazine but not the degradation products at the Eagle Harbor site, which is located in Michigan's Upper Peninsula near Lake Superior. From a period of early April to mid-September 1995, atrazine sampled at Eagle Harbor was detected approximately 34% of the time in the particulate fraction but not in the vapor phase at this remote site (Foreman *et al.*, 2000). In addition, both DIA and DEA were detected in the particulate phase. This suggests that long range transport is possible for both atrazine and the two degradation products *via* particles.

Having a higher detection limit than the Foreman *et al*. (2000) study may be one reason why atrazine was difficult to detect over Lake Michigan in the LMMBP study. Foreman's detection limit was 6 pg/m^3. For the LMMBP, the detection limit ranged from 3.0 to 68 pg/m^3 (average of 17 pg/m^3) for particulate phase samples analyzed at the Illinois Water Survey, and from 26.8 to 284 pg/m^3 (average of 70.7 pg/m^3) for samples analyzed at Indiana University. Another possible reason for the lack of particulate atrazine data over-the-lake is that the type of particulate matter carrying atrazine may not be transported very far from the source. As a consequence of the low number of detects at land-based collection sites, and the lack of evidence of atrazine-associated particulate fluxes over-the-lake, these fluxes were not estimated for modeling purposes.

1.3.2.2.3 Atrazine and Degradation Products in Wet Deposition

Atrazine in wet deposition was primarily detected in the spring and summer months. This seasonality was also reported by Nations and Hallberg (1992) and Goolsby *et al.* (1993). All LMMBP samples collected in April and May had detectable levels of atrazine. Atrazine was not detected in samples from November through February. DEA and DIA were also primarily detected in the spring and summer months. DEA was detected in samples collected from March through August, and DIA was only detected in samples collected from April through June. DEA had a higher frequency of being detected and also had a higher concentration on average than DIA. Twenty-eight day maximum atrazine concentrations measured over 1994 and 1995 ranged from 100 ng/L at Eagle Harbor to 2,800 ng/L at the Indiana Dunes site. The high Indiana Dunes value was associated with a low volume sample collected over a 28-day sampling period and may have been influenced by emissions from nearby agricultural fields. During a rain event, atrazine concentrations are often much higher at the beginning of the event compared to concentrations measured at the end of the event (Nations and Hallberg, 1992; Goolsby *et al*., 1993). Nations and Hallberg (1992) also found that a rain event closely following an earlier rain event by a day or two had much lower concentrations (and often non-detectable) levels of atrazine in the wet deposition sample. Presumably the first event scavenges the available pesticide in the atmosphere. Without a detailed record of the number and duration of rain events in the Indiana Dunes sample, it is difficult to conclude if any of the scavenging circumstances occurring early in a rain event(s) comprised a major volumetric proportion of the sample collected. Nations and Hallberg (1992) also found that atrazine concentrations in wet deposition tend to be higher in regions that have higher usage of atrazine. They found consistent, striking differences between two stations only 11 km apart. One station located adjacent to a row-cropped field had a much higher reported value compared to a station located in a forested region. Volume-weighted mean LMMBP spring/summer atrazine levels for the two-year sampling period (1994-1995) ranged from 19 ng/L at Eagle Harbor to 120 ng/L at Indiana Dunes. Due to the high variability of wet deposition concentrations of atrazine at sites, stations around the lake were not statistically different based on the Kruskal-Wallis test. Sampling at over-water stations was limited. A southern central lake station contained 7.5 ng/L on August 20, 1994 and a station in Green Bay contained 29 ng/L on April 12, 1995.

Concentrations of atrazine and DEA in wet deposition in 1995 were much lower than observations in 1990, 1991, and 1994. The concentrations of atrazine collected in the Lake Michigan basin, as reported in

Table 1.3.1 for 1990 and 1991, compare very well to other data collected by Goolsby *et al*. (1997) across the Midwestern and Northeastern United States. They found a range of 200 to 400 ng/L for 1990-1991. In 1994, atrazine was found in LMMBP rain samples collected between mid-March and mid-April, even though corn planting had not yet begun in southern Wisconsin. This suggests that atrazine was being transported long range, originating from farm fields in more southerly states that had been planted earlier in the season. In 1995, however, the occurrence of atrazine in wet deposition more closely coincided with application in the region (Sweet and Harlin, 1998). Further evidence that long range transport of atrazine to Lake Michigan was minimal in 1995 is reflected in a low deethylatrazine/atrazine ratio (DAR) (0.145) for 1995 (Table 1.3.1). The DAR was calculated using the volume-weighted means for DEA and atrazine. Generally, higher DAR ratios represent higher levels of degradation of atrazine to DEA. Long range transport allows more time for degradation of atrazine to occur in the air mass. DAR ratios were calculated for Isle Royale, a wilderness national park in Lake Superior, and the ratio at the park was calculated to be approximately 0.4 (Thurman and Cromwell, 2000) for the study period 1991-1994. So in regards to DAR and except for 1995, the two areas (Isle Royale and Lake Michigan) appear to compare very well, suggesting that under normal circumstances, transport of atrazine from distant sources does occur in the wet deposition phase.

A possible explanation of the low atrazine concentrations for 1995 is that the spring of 1995 was cold and wet in major corn-growing areas south and west of the Lake Michigan basin compared to 1991 and 1994. This may have limited long range transport to the Lake Michigan basin. Omaha, Nebraska and Peoria, Illinois were selected as being representative of that area south and west because they are located in geographic areas where the

Table 1.3.1. Summary of Wet Deposition Annual Volume-Weighted Mean Deethylatrazine (DEA) Concentrations, Atrazine Concentrations, and Deethylatrazine/Atrazine Ratios (DAR) for All Stations in the Lake Michigan Basin

Year	Deethylatrazine ng/L	Atrazine ng/L	Deethylatrazine/Atrazine Ratios (DAR)	Sampling Data Range
1990[1]	101.0	259.0	0.402	3/27/1990 - 8/14/1990
1991[1]	233.0	432.0	0.540	4/2/1991 - 7/9/1991
1994[2]	32.4	80.6	0.422	3/15/1994 - 7/5/1994
1995[2]	4.02	30.0	0.145	3/14/1995 - 8/31/1995
Mean	92.6	200	0.377	
Mean (Year 1995 Excluded)	122	257	0.455	

[1]Data from Goolsby *et al*., 1995. All data were used in calculating the volume-weighted mean concentrations. Data reported with the detection limit were converted to half the detection limit. DAR represents only situations where both the reported DEA and atrazine concentrations were above the detection limit.

[2]Data from the LMMBP. All data, including zeros, were used in calculating the volume-weighted mean concentrations. DAR represents only situations where both reported DEA and atrazine concentrations were above the detection limit.

greatest spring atrazine emissions were estimated (Scholtz *et al.*, 1997). Figure 1.3.1 shows the monthly precipitation at these cities for the important months when wet deposition fluxes are normally high (National Climatic Data Center, 2000). For both Peoria and Omaha, 1991 and 1994 were similar in rainfall events; however, for 1995, the months of April and May were wetter than the other two years. Figure 1.3.2 shows the monthly average temperatures for the same two cities. For both Peoria and Omaha, 1991 and 1994 were similar in average temperatures; however, for 1995 the months of April and May were colder than the two other years. Not only were the LMMBP atrazine concentrations in precipitation low for 1995, but the total atrazine deposition for 1995 was approximately half of what it was in 1994. This cannot be explained by very low precipitation in the Lake Michigan basin for 1995. Table 1.3.2 displays the combined mean precipitation amounts from Chicago, Illinois; South Bend, Indiana; Muskegon, Michigan; Grand Rapids, Michigan; Green Bay, Wisconsin; and Milwaukee, Wisconsin for 1994 and 1995 (34.26 and 33.73 inches, respectively) and they are close to the 30-year mean of all these sites (34.22 inches). Comparisons to a 50-year mean for over-lake precipitation to Lake Michigan can be found in Figures 1.4.11 and 1.4.12 in Part 1, Chapter 4 of this report and show similar results. Also, the differences between 1994 and 1995 cannot be explained by differences in amounts of atrazine applied in the basin between the two years, because these amounts are nearly the same (see the atrazine loading chapter for more information). The differences may be explained by the cold and wet spring in the south and west corn-growing regions relative to the Lake Michigan basin. In a cold and wet spring, less atrazine emission would be expected to occur because temperature is a driving force of atrazine volatilization from the soil to the air. In the wet spring of 1995, among both the Peoria and Omaha stations, there was one rain event in April over one inch and seven events in May where rainfall was over one inch (and as high as 2.5 inches on May 8 at one of the stations). For spring 1994, there was only one rainfall event among the two stations

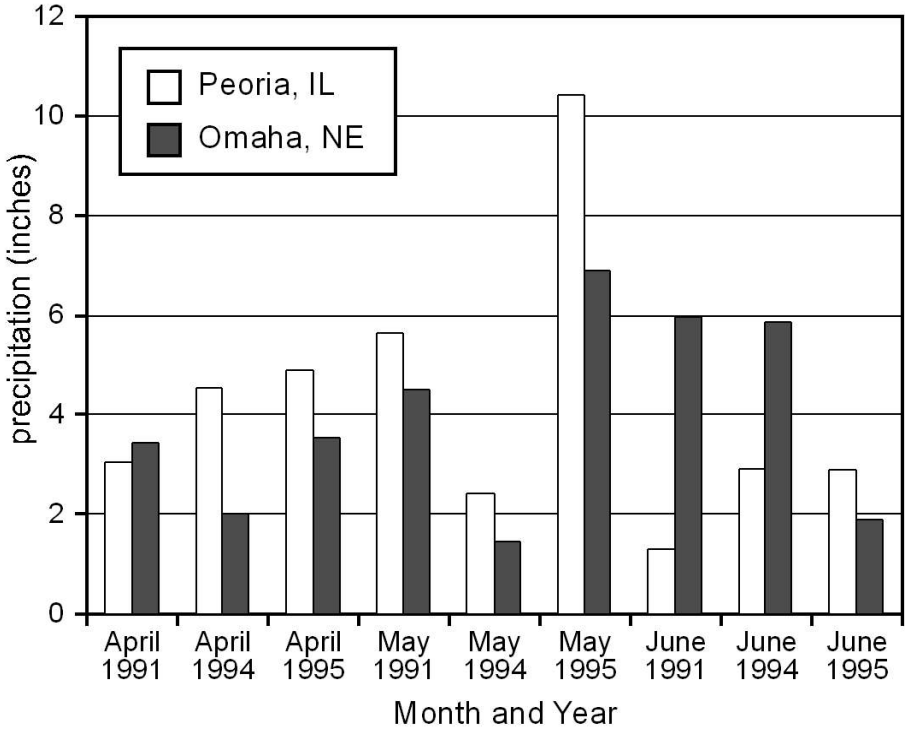

Figure 1.3.1. Monthly precipitation amounts at cities in two large corn-growing regions. Data are from Peoria, Illinois and Omaha, Nebraska.

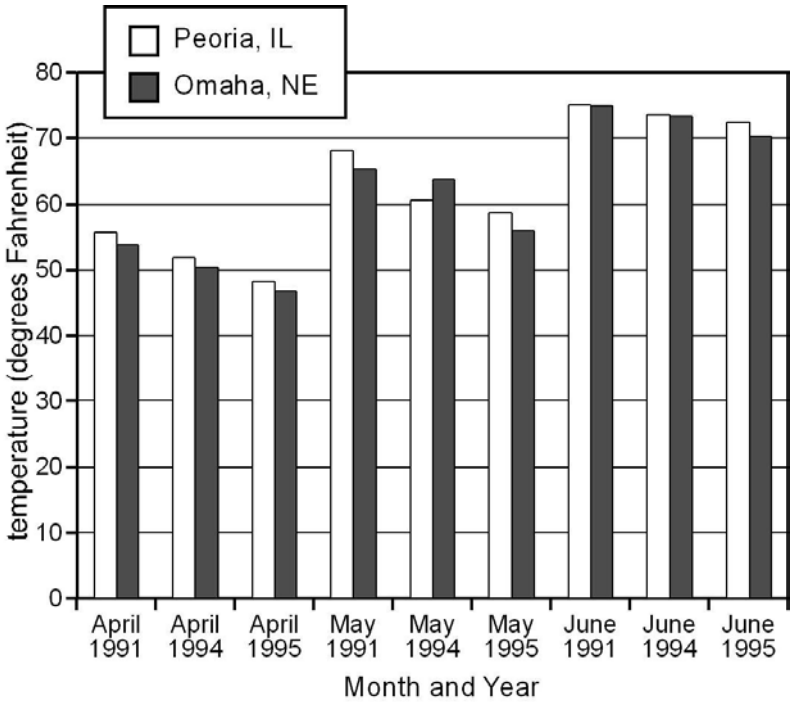

Figure 1.3.2. Monthly average temperatures at cities in two large corn-growing regions. Data are from Peoria, Illinois and Omaha, Nebraska.

Table 1.3.2. Annual Mean Precipitation Amounts Measured at Chicago, Illinois; Fort Wayne, Indiana; South Bend, Indiana; Muskegon, Michigan; Grand Rapids, Michigan; and Milwaukee, Wisconsin

Time Period	Total Inches (Mean at All Sites)	Standard Deviation
30 Years	34.22	3.57
1994	34.26	6.94
1995	33.73	4.61

over one inch and that was on June 22, 1994. Perhaps the frequent rainfall events in 1995 washed significant quantities of atrazine from the fields into streams, rivers, reservoirs, and groundwater *via* infiltration which allowed less of the atrazine to volatilize from the farm fields. Atrazine that is diluted in reservoirs, lakes, and rivers would have a lower volatilization flux than if it were in a concentrated form on farm soil. Also, heavier rainfall in the corn-growing region could increase scavenging of the chemical from the atmosphere, thereby leaving less available for long-range transport.

1.3.3 Atrazine in Tributaries

Eleven tributaries to Lake Michigan were sampled from April 4, 1995 through October 31, 1995. A total of 108 filtered samples were collected. Most tributary samples contained detectable levels of atrazine, DEA, and DIA. The tributary samples were collected for purposes of estimating loadings of atrazine to the lake. However, the load estimates are believed to be low, and consequently, alternative tributary loadings were estimated based on watershed run-off algorithms using the amount of atrazine applied and a watershed export factor of 0.6% for the MICHTOX

and LM2-Atrazine models. For LM3, the United States Geological Survey (USGS) provided loadings that they calculated from flow and concentration data. However, for a 90-day period in the spring months, loadings were enhanced to make up for a "lost" load (please see section 5.3.3.3.1 in Part 5 for more information). Because the concentration data were not directly used in the models, only a brief description of the data will be presented here. For a more complete description of these data, please refer to Brent *et al.* (2001).

1.3.3.1 Sampling and Analytical Methodology

Samples were collected as near to river mouths as possible without being subject to flow reversals where lake water moves up the river. Composites were collected using the USGS quarter-point sampling procedure. In this procedure, the river is visually divided into three equal flow areas. The midpoint of each flow panel is sampled at 0.2 and 0.8 times the depth. All samples were pumped and composited using a peristaltic pump through a 0.7 µm glass fiber filter. The filtrate was passed through a 250 g, XAD-2 resin to trap the dissolved atrazine. Chilled samples were then taken to the analytical lab. Analyses were conducted using gas chromatography coupled to a mass spectrometer. Full details of the analytical methods have been published in the Methods Compendium (U.S. Environmental Protection Agency, 1997a; 1997b).

1.3.3.2 Results

Since tributary samples were only collected over a seven-month period, full seasonal trends could not be assessed. For the three tributaries with the highest mean concentrations of atrazine (St. Joseph River, Kalamazoo River, and the Grand River), peaks in atrazine concentrations occurred in mid- to late-May. Spring peaks were also observed for the degradation products DIA and DEA.

Individual atrazine concentrations measured in the streams ranged from a low of 0.5 ng/L in the Pere Marquette River to 2,700 ng/L in the St. Joseph River. Mean concentrations of atrazine in the tributaries ranged from 3.7 in the Manistique River to 350 ng/L in the St. Joseph River. Per Brent *et al.* (2001), these concentrations are comparable to concentrations measured elsewhere in the Great Lakes region. Eighty-six percent of the tributary samples contained less than 100 ng/L of atrazine, and all samples above 100 ng/L were in the St. Joseph, Kalamazoo, or Grand Rivers. Tributaries with the lowest mean atrazine levels were located in the northern portions of the lake, where land use is less dominated by agriculture.

Atrazine degradation in the watershed can be assessed by looking at the degradation products. DEA and DIA concentrations correlated well with atrazine concentrations in tributary water samples (Brent *et al.*, 2001). As atrazine concentrations increased, both the DEA and DIA increased. The ratio of concentrations of [DEA]/[atrazine] or DAR is often used to assess the extent of atrazine degradation in a sample. Ratios on individual measurement pairs ranged from 0.08 to 3.7, and the median was 0.77. Mean DARs were above 1.0 at the Pere Marquette, Sheboygan, and Milwaukee Rivers, and were significantly higher than the mean ratios at the Kalamazoo, Manistique, Grand, and St. Joseph Rivers. For all samples, the mean DAR of 1.4 measured in October was significantly greater than the mean ratios in April (0.75), May (0.63), and June (0.87). It is common to find that the ratios increase for a given tributary as the time since application of atrazine increases. Thurman *et al.* (1994) also found an increase in DAR from <0.1 shortly after atrazine application to 0.4 measured later in the year. As the atrazine resides in the soil, processes (both biotic and abiotic) are operative that degrade the chemical. Run-off from these fields will reflect the composition of DAR in the soil. Furthermore, during dry spells in the late summer, groundwater can make up a significant percentage of the total flow of a river. Groundwater is often associated with high DARs. In July-August 1991, Pereira and Hostettler (1993) found that the DAR for Mississippi River water was relatively constant at 0.2 for the entire river. This suggests that during the travel time from Minneapolis to New Orleans (45-65 days), the DAR showed no evidence of degradation. However, in October-November, 1991, they found that the DAR in the river was 0.6 in the upper reaches of the river. The low DAR is believed to be associated with more run-off in July and August. During the fall period, the river was near base flow in the upper river. During base flow, most of the river flow is due to groundwater. DARs

measured in groundwater impacted by infiltration through an agricultural soil matrix are often high, and exceed or are close to unity (Ma and Spalding, 1997).

1.3.4 Atrazine in Lake Water

1.3.4.1 Sampling and Analytical Methodology

Open-lake water column samples were collected during six cruises from April 25, 1994 to April 17, 1995. Open-lake samples were collected from 35 sampling locations on Lake Michigan, two sampling locations in Green Bay, and one sampling location on Lake Huron (see Figure 1.1.2). The Lake Huron samples were collected to characterize a model boundary condition. Samples were collected at depths ranging from 1 to 257 m. During stratification, samples were collected at mid-epilimnion and mid-hypolimnion, and master stations were sampled at one meter below the surface and two meters off the bottom. During non-stratification, samples were collected at mid-water column depths, one meter below the surface, and two meters off the bottom.

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

Atrazine, DEA, and DIA were isolated from filtered water samples using 250 mg Carbopack (Supelco Corporation) solid phase extraction (SPE) cartridges. Analytes were eluted from the SPE using 7 ml of a 90% dichloromethane and 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. Further details of the analytical methods can be found in the methods compendium (U.S. Environmental Protection Agency, 1997a; 1997b).

1.3.4.2 Results

1.3.4.2.1 Spatial Variation

A total of 234 samples (including Green Bay and the northern Lake Huron boundary condition samples) were collected and analyzed for atrazine, DEA, and DIA. All lake samples contained levels of atrazine and DEA above the MDL. All but 12 samples contained DIA above the MDL for that parameter. MDLs computed were 1.25 ng/L for atrazine, 2.46 ng/L for DEA, and 8.27 ng/L for DIA. Skewness characterizes the degree of asymmetry of a distribution. Positive skewness indicates a distribution with an asymmetric tail extending towards more positive values. In a normal distribution, skewness is approximately zero. A statistical analysis of all lake data indicated that atrazine skewness equaled 0.145. To further evaluate the skewness for atrazine, the following analysis was performed (Tabachnick and Fidell, 1996).

Skewness values of two standard errors of skewness (***ses***) or more (regardless of the sign) are probably skewed to a significant degree. The ***ses*** for atrazine can be estimated by:

$$ses = \sqrt{6/n} = 0.144$$

where, n = total number of open Lake Michigan values including duplicates and triplicates (excludes Green Bay and the northern Lake Huron stations) = 288

2(***ses***) = 0.2886

Since the skewness for the atrazine lake data, 0.145, is less than 2 x ***ses***, the distribution can be assumed to be normal. The deviation from zero can be assumed to be to chance fluctuation.

Within Lake Michigan (excluding Green Bay and northern Lake Huron stations), lateral and vertical atrazine concentrations were relatively consistent during the LMMBP (Brent *et al*., 2001). 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. Similar patterns of consistency among sampling stations were observed

for DEA and DIA concentrations. Atrazine concentrations in southern Green Bay were significantly higher than atrazine concentrations at 18 Lake Michigan sampling stations. Due to the spatial consistency of atrazine, DEA, and DIA concentrations within Lake Michigan, lake-wide mean concentrations can be calculated to reliably represent the lake. Schottler and Eisenreich (1994) also found Lake Michigan (excluding Green Bay) to lack vertical and lateral gradients in the 1991 and 1992 data. It is not surprising that no vertical gradients were found, because most of the samples collected for the LMMBP were collected during times of non-stratification of the lake. Lake-wide concentrations from the LMMBP study (April 1994-April 1995) and previous studies are summarized in Table 1.3.3. A graphical representation of concentrations observed in 1994 is depicted in Figure 1.3.3.

1.3.4.2.2 Seasonal Variation

Open-lake atrazine concentrations were measured during six sampling cruises. Brent *et al*. (2001) concluded that statistically significant mean open-lake concentrations of atrazine, DEA, and DIA increased during the one-year LMMBP sampling campaign (1994-1995). Schottler and Eisenreich (1997) found that 1992 atrazine concentrations in the lake were statistically higher than the mean lake concentration measured in 1991. Based on these field measurements, it appears that the lake is accumulating atrazine over time. More information on this accumulation will be discussed in the modeling chapters.

Table 1.3.3. Summary of Historical Atrazine, DEA, and DIA Concentrations in Lake Michigan

Year	Atrazine (ng/L)	DEA (ng/L)	DIA (ng/L)
1991	35 (2.0)[1*]	16[3]	Not Available
1992	37 (1.8)[1]	24[3]	Not Available
4/1994-4/1995[2]	38.1	25.8	14.9

[1]Schottler and Eisenreich, 1997
[2]Brent *et al.*, 2001
[3]Schottler and Eisenreich, 1994
*Values are means with the standard deviation in parenthesis.

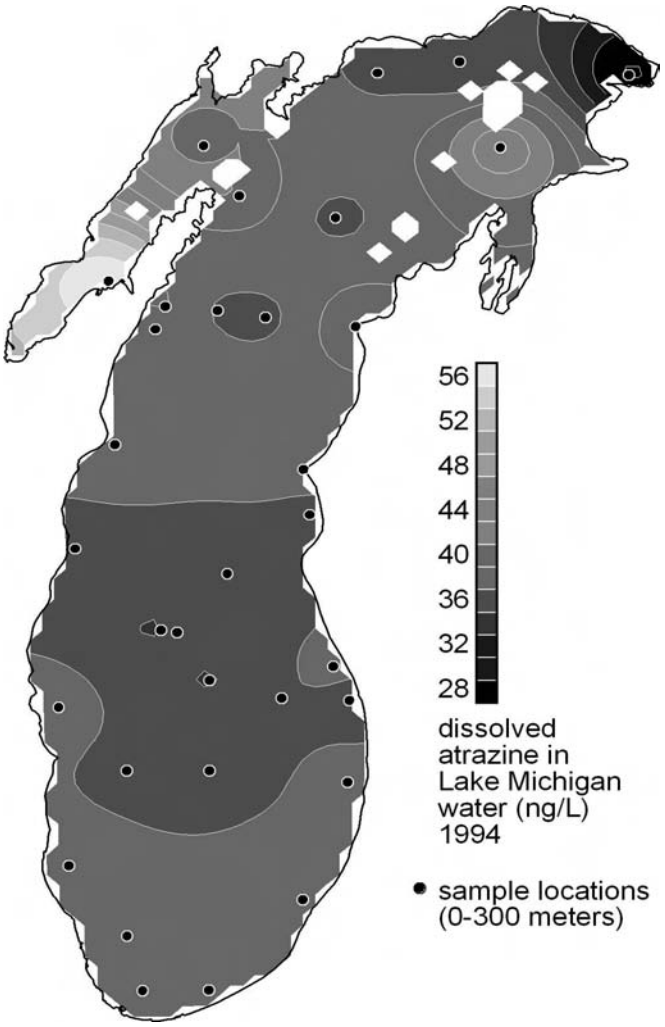

Figure 1.3.3. Atrazine concentrations in Lake Michigan, 1994.

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PART 1

INTRODUCTION

Appendix 1.3.1 Information Management

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To support the modeling efforts of the Lake Michigan Mass Balance Project (LMMBP), samples were collected and analyzed by the United States Geological Survey (USGS) and several universities (Table A1.3.1). The focus group acronyms in the table provide a unique identifier of data sets. The first two letters stand for the organization, the third letter represents the media sampled (air, lake, or tributary), and the fourth letter identifies the chemical (atrazine) analyzed. Project data were sent to the United States Environmental Protection Agency (USEPA) Great Lakes National Program Office (GLNPO) in Chicago, Illinois. GLNPO staff, under the direction of Louis Blume, were responsible for quality assurance (QA) assessment, organization, and consolidation of all data. To facilitate the QA assessment process, a SAS application, the Research Data Management and Quality Assurance System (RDMQ), developed by Syd Allen, a private contractor, was used to automate the QA process (Sukloff *et al.*, 1995). RDMQ is a menu-driven SAS program. It has capabilities for loading data, applying quality control (QC) checks, adding validity flags, viewing and editing data, producing user-defined tables and graphs, and exporting data in ASCII files. These tasks are performed through a set of menu-driven SAS programs and macros. Data which had been put through the assessment process and approved for release by both GLNPO and the Principal Investigator (PI) were then sent to USEPA, Office of Research and Development (ORD)/National Health and Environmental Effects Research Laboratory (NHEERL)/Large Lakes and Rivers Forecasting Research Branch (LLRFRB)/Large Lakes Research Station (LLRS) for use by the modeling staff.

A1.3.1.1 Overview of Information Management at the LLRS

Data received from GLNPO were usually in the form of electronic media. Data were typically E-mailed, but sometimes they were downloaded from GLNPO databases or received on CD-ROM. Data were reformatted by GLNPO into a form facilitating entry into database programs at the LLRS. Upon arrival, raw data were copied to the “lmmb” folder on David Griesmer’s personal network space (“M:\” drive). In addition, data were imported into one of several Microsoft Access databases in the “\Access\lmmb” folder on Mr. Griesmer’s “M:\” drive. The “M:\” drive was used to facilitate data security because this file

Table A1.3.1 List of Parameters Analyzed and Principal Investigators for the LMMBP Atrazine Modeling

Parameter	Focus Group	Media	Notes	Principal Investigator
Atrazine, Deethylatrazine (DEA), Deisopropylatrazine (DIA), Terbuthylazine	IUAA	Atmospheric Vapor and Particulate Phase, Precipitation	Sleeping Bear Dunes site only. Keri Hornbuckle, U. of Iowa, used these data to calculate loadings	Ronald Hites, Indiana University
Atrazine, DEA, DIA, d5-Atrazine	WSAA	Atmospheric Vapor and Particulate Phase, Precipitation	All stations except Sleeping Bear Dunes site. Keri Hornbuckle, U. of Iowa, used these data to calculate loadings	Clyde Sweet, Illinois State Water Survey
Atrazine	RULA	Open-lake		Steven Eisenreich, Rutgers University
Atrazine	RUTA	Tributary	David Hall, USGS, used these data to calculate loadings	Steven Eisenreich, Rutgers University
Flow	N/A	Tributary		David Hall, USGS

space is backed up regularly and is available only to Mr. Griesmer. At some point in the future, the location of these data may change; however, limited access and backups of the data will be maintained. Data were placed in the Microsoft Access databases to facilitate data review/assessment and later retrieval for the modeling team.

Prior to use, several reviews were done of the data received to look for errors in the data sets. At the LLRS, this review was broken up into two parts. First, an initial review was made to check for completeness of information; to look for transcription, programming, and formatting errors; and to review comments added by collection and analysis personnel. Second, a review was done by the data users to determine if the data made environmental sense. This type of review was conducted for the open-lake data. Tributary atrazine loadings and atmospheric atrazine fluxes/loadings did not go through this review process at the LLRS, but they were assessed by study members assigned with providing these loading values. Tributary atrazine, deisopropylatrazine (DIA), and deethylatrazine (DEA) loading assessments were done by David Hall, (USGS). All atmospheric atrazine loading/-

concentration data were assessed by Keri Hornbuckle, University of Iowa.

Samples that GLNPO determined had failed the RDMQ QA process were flagged with the value of -9999 in the Grosse Ile database. GLNPO preserved all of the values in the data sets that were received and flagged the analytical remark field for that parameter. Flagging these values as -9999 facilitated processing by analytical software such as IDL. In addition, parameter values with analytical remark flags of "INV" (invalid data, as determined by the GLNPO QA evaluation), and "NAI" (no result reported – interference) were changed to -9999. Samples with the analytical remark flag of "LAC" (no results reported, laboratory accident) were removed.

Documentation associated with the data was reviewed. RDMQ data warning fields (RS_NMAND,RS_WARN, RS_UPDAT) were checked to verify that there were no problems flagged by RDMQ which were inadvertently included in the database. Every routine field sample (RFS) and field duplicate (FD#) was checked to verify that a valid station name, sampling date, and depth collection information were included. The value ranges (minimum, maximum, average) for atrazine and its degradation products (DEA and DIA) were checked to look for any obvious errors. Data ranges of all data were also checked for obvious errors. Data were checked to verify units and to confirm whether blank, dilution, or surrogate correction were done. Sample QC and station comment fields (RECSTAT, RECSTATF, and STNNOTES) were checked for any comments associated with a sample. All of this information was recorded on a Data Verification Checklist (Table A1.3.2). If questions or errors were found, they were referred back to GLNPO for resolution.

Upon completion of this initial data check, readme files were created to describe the data, and the raw data set(s) and readme files were copied to a data archive on the LLRS Unix systems. This archive is located at \usr\lmmbdata on the Unix servers and is available to modeling staff at the LLRS. Each study has its own directory (LMI0001-LMI0028) within the lmmbdata archive. The directories related to the atrazine modeling can be found in Table A1.3.3. Information on other LMMBP directories can be found in the LMMBP PCB report (Rossmann, 2006).

At the same time, information about data received (metadata) was stored in a searchable Microsoft Access database. The database is found on the LLRS common drive "\\giord2\grlcommon", which is also known as the "L:\" drive. This database is named "lmtrack2000.mdb" and is found in the L:\Public\Access\lmmb folder. This database is available to all staff. This database can be searched by library number (consecutive number assigned when data are logged in, corresponds to LMI folder name in lmmbdata archive), PI, parameter, PI and parameter, or library number and parameter (Table A1.3.3).

After initial review of a data set was completed, data were retrieved from the Microsoft Access databases and exported into files (usually Microsoft Excel) for assessment by the modeler who would be using the data set. Atrazine data were assessed by William Richardson. Initially, only routine field samples and field duplicates were given to the data assessors. If issues or problems were found, the person assessing the data would then request additional QA data. If questions/problems could not be resolved by looking at QA data, they were referred back to GLNPO for resolution. GLNPO was informed whenever we rejected data.

After the assessment process was completed, files were created which could be used in IDL, which is a software package used for visualization and analysis of LMMBP data. A standard format was developed for water data (Table A1.3.4). All files were fixed format ASCII text files. One of the principal uses of IDL was to develop volume-weighted averages (VWA) estimates of parameter concentrations for each cell in the modeling grid. These VWA estimates could then be compared to model results.

A1.3.1.2 Summary

The LMMBP data received at the LLRS were carefully evaluated prior to use to ensure that the field data being used by the modelers were as accurate as possible. In addition, data were archived and cataloged to protect these valuable data sets

Table A1.3.2. Example of Data Verification Checklist Used for the LMMBP

Data Verification Checklist

FOCUS _____ Version Number _____ Date Received _____

Description: _____

1. Read any documentation which came with data files: _____

2. Make sure I understand field names in RDMQ files: _____

3. Check fields which according to RDMQ should not be flagged/or indicate some question, with data (e.g. RS_NMAND, RS_WARN, RS_UPDAT).

   RS_NMAND _____

   RS_WARN _____

   RS_UPDAT _____

4. Make sure every RFS and field duplicate has station, date, depth collected information.

_____

_____

5. Check to make sure every sample has station name that is valid.

_____

_____

6. Check number of RFS and field duplicates for every analyte. Total Samples _____

   Analyte _____ RFS _____ FDn _____

   Analyte _____ RFS _____ FDn _____

   Analyte _____ RFS _____ FDn _____

   Analyte _____ RFS _____ FDn _____

   Analyte _____ RFS _____ FDn _____

   Analyte _____ RFS _____ FDn _____

7. Analysis Results for RFS and field duplicates for every analyte.

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

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Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

Analyte _____ Avg _____ Min _____ Max _____ Count _____

8. Check date ranges of data to see if they are reasonable.

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

Analyte _____ Min _____ Max _____

9. Check to verify units information looks alright.

_____

_____

10. Number of significant digits for each analyte.

_____

_____

11. Number of negative values for each analyte.

_____

_____

12. Check flags on RFS and field duplicates.

_____

_____

13. Core slice range (sediment)/species, age, length, weight (fish).

14. Check blank correction, dilution, and surrogate correction fields.

15. Questions about QC Coordinator remarks (RECSTAT). Check flags for whole record (RECSTATF). Questions about Station Notes (STNNOTES), Field Remarks (FREMARK), and Sample Description (SAMPDESC).

16. Additional Questions.

Table A1.3.3. Printout of Information Stored in the LMMBP Tracking Database Related to Atrazine Modeling (L:\Public\Access\lmmb\lmtrack2000.mdb)

LMMBP DATA ARCHIVE - QUICK REPORT. Note: All Data Archived on superior.grl.epa.gov in /usr/lmmbdata.

Library No.	LM10001	PI:	David Schwab
Description	Hourly Lake Michigan wind, wave, and atmospheric data (5 km grid) for 1982, 1983, 1994, 1995. Original data files were converted to SEDZL and POM formerly by M. Settles. Also, bathymetric data for Lake Michigan.		
Library No.	LM10002	PI:	William Richardson
Description	STORET conventional and general chemistry data for Lake Michigan, April 1962-August 1993. Note: Date range varies by parameter, includes original file, reformatted spreadsheet, and MS Access file.		
Library No.	LM10003	PI:	David Schwab
Description	Two-dimensional and three-dimensional GLERL hydrodynamics data for the Lake Michigan 5 km grid. 2D data: January 1982-September 1983; 3D: covers January-July 1982. Program//llrssrv2 /~model/dev/PATRIC2D/RCS is for 2D processing, no three-dimensional programming yet.		
Library No.	LM10004	PI:	Steven Eisenreich
Description	Open-lake (RULA) and tributary (RUTA), atrazine, DEA, DIA data for the LMMBP. Open-lake 325 samples (1/17/94-4/17/95). Tributary: 126 samples (4/4/95-5/15/96). Revised version of data sent 2/19/98.		
Library No.	LM10005	PI:	Angela Bandemehr
Description	Hourly meteorological data (air temperature, solar radiation, relative humidity, wind speed and direction, and precipitation) from 13 air sampling sites both in and outside of the Lake Michigan basin. 11/30/90-12/31/96 (Dates vary by site).		
Library No.	LM10006	PI:	Glenn Warren
Description	Seabird water temperature data for seven LMMBP surveys, April 1994-October 1995. Data collected at 0.5 m intervals. Does not include January 1994 survey. Note: Data received was extensively revised from original version.		
Library No.	LM10007	PI:	David Hall
Description	Tributary flow data for 11 tributaries to Lake Michigan (Fox, Grand, Indiana Harbor, Kalamazoo, Manistique, Menominee, Milwaukee, Muskegon, Pere Marquette, Sheboygan, St. Joseph), 1/1/94-12/31/95. Some data estimated.		
Library No.	LM10011	PI:	David Schwab
Description	Lake Michigan final report, hourly circulation, meteorology, and wave data (5 km grid) for 1982, 1983, 1994, 1995. Includes intake, cruise, mooring, water level data. Also, HTML files and images, model results (XDR format), Fortran and IDL programs.		
Library No.	LM10020	PI:	Keri Hornbuckle
Description	Atmospheric atrazine and nutrient (NO_3, total phosphorus, TKN) wet deposition loading data for Lake Michigan 5 km grid cells used in hydrodynamic model. Atrazine wet deposition and particulate monthly concentration data. Data for 10/94-10/95 (nutrient) and 5/94-10/95 (atrazine).		

Table A1.3.3. Printout of Information Stored in the LMMBP Tracking Database Related to Atrazine Modeling (L:\Public\Access\lmmb\lmtrack2000.mdb) (Continued)

Library No.	LM10022	PI:	David Hall
Description	Atrazine, DEA, DIA tributary loading data for 11 monitored tributaries and atrazine data for unmonitored tributaries to Lake Michigan. Data covers the time period: 1/1/94-12/31/95.		
Library No.	LM10026	PI:	Nathan Hawley
Description	Current velocity, water transparency, temperature from three stations, 10/31/94-10/11/95. *In situ* sediment resuspension from sediment flume experiments (8/12/95-9/23/98). Also profile data – temperature, dissolved oxygen, conductivity, BAT, pH, fluorescence, TSM data from six stations in Lake Michigan (1/4/95-11/29/95).		
Library No.	LM10027	PI:	Barry Lesht
Description	Current velocity and direction, bottom wave orbital velocity, temperature, beam attenuation, and TSM data collected from Tripod Station 98 (latitude 42 52.18, longitude 87 42.41), during the EEGLE project, 4/2/98-12/1/98. Data collected every 30 minutes.		
Library No.	LM10028	PI:	Michael Settles
Description	NEMA and NOAA wind speed and direction, wave height and period data for six stations in Lake Michigan, retrieved from USACOE Web Site (http://bigfoot.wes.army.mil/c300.html). 1980-1998 (not all stations cover entire date range). NEMO-Daily data, NOAA-Hourly data.		

Table A1.3.4. Generalized Format for the LMMBP Water Data to be Analyzed With IDL Programs

Beginning - Ending Columns	Variable Description	Format (A = Alpha, F = Floating Point No., I = Integer, X = Skip)	Sort Order (A = Ascending, D = Descending, Blank = None)	Missing Data Code
1 - 7	Cruise Name	A7	A	Blank
8 - 8	Blank Space	1X	N/A	N/A
9 - 14	Latitude (ddd.ddd)	F6.3		Blank
15 - 15	Blank Space	1X	N/A	N/A
16 - 22	Longitude (-ddd.ddd)	F7.3		Blank
23 - 23	Blank Space	1X	N/A	N/A
24 - 35	Station Name	A12	A	Blank
36 - 36	Blank Space	1X	N/A	N/A
37 - 44	Depth Sampled	F8.0	A	Blank
45 - 45	Blank Space	1X	N/A	N/A

Table A1.3.4. Generalized Format for the LMMBP Water Data to be Analyzed With IDL Programs (Continued)

Beginning - Ending Columns	Variable Description	Format (A = Alpha, F = Floating Point No., I = Integer, X = Skip)	Sort Order (A = Ascending, D = Descending, Blank = None)	Missing Data Code
46 - 53	Sampling Start Date (mm/dd/yy)	A8	A	Blank
54 - 54	Blank Space	1X	N/A	N/A
55 - 58	Sampling Start Time (24 hour clock)	A4		Blank
59 - 59	Blank Space	1X	N/A	N/A
60 - 67	Sampling End Date (mm/dd/yy)	A8	A	Blank
68 - 68	Blank Space	1X	N/A	N/A
69 - 72	Sampling End Time (24 hour clock)	A4		Blank
73 - 73	Blank Space	1X	N/A	N/A
74 - 75	Filter Fraction	A2	A	Blank
76 - 76	Blank Space	1X	N/A	N/A
77 - 79	Sample Type	A3	D	Blank
80 - 80	Blank Space	1X	N/A	N/A
81 - 88	Value Parameter 1	F8.0		-9999
89 - 103	Parameter 1 Flags	A15		Blank
104 - 111	Value Parameter 2	F8.0		-9999
112 - 126	Parameter 1 Flags	A15		Blank
	Value Parameter n	F8.0		-9999
	Parameter n Flags	A15		Blank

and make it easier for users to find the information. Incorporation of this information into LLRS Microsoft Access databases has given us flexibility in retrieving the information needed by the modeling staff at the LLRS.

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Rossmann, R. (Editor). 2006. Results of the Lake Michigan Mass Balance Project: Polychlorinated Biphenyl Modeling Report. U.S. Environmental Protection Agency, Office of Research and Development, National Health and Environmental Effects Research Laboratory, Mid-Continent Ecology Division-Duluth, Large Lakes Research Station, Grosse Ile, Michigan. EPA/600/R-04/167, 579 pp.

Sukloff, W.B., S. Allan, and K. Ward. 1995. RDMQ User Manual. Environment Canada, Atmospheric Environment Service, North York, Ontario, Canada. 91 pp.

PART 1

INTRODUCTION

Chapter 4. Representativeness of the Lake Michigan Mass Balance Project (LMMBP) Years Relative to Lake Michigan's Historic Record

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1.4.1 Introduction

A major concern related to modeling contaminants in the lake was the representativeness of the years of sampling (1994-1995) relative to the historical record. This was particularly important when using the models to predict future conditions in the lake. The LM2-Atrazine and LM3-Atrazine models used hydrodynamic model output from 1994-1995 in their construct (see Parts 4 and 5 of this report, respectively, for more information). In addition, atrazine loading estimates for any given year can be affected by various meteorological conditions (see Part 2, Chapters 2 and 3 of this report). If these data did not represent something close to average conditions, the resulting predictions could be biased. Parameters considered most important to the performance of the atrazine models included ice cover, air temperature, water temperature, lake water levels, precipitation, tributary flows, wind, and waves. Potential impacts on the various models are discussed below. Each of these were investigated for the representativeness of the 1994-1995 project data relative to the available historical data record.

1.4.2 Ice Cover

Ice cover impacts the volatilization, absorption, and physical mixing of the lake during the winter months. In locations where there is ice cover, gas exchange between the water and atmosphere is prevented by the physical barrier. Physical mixing includes not only the mixing of the water column, but also the interaction of waves with the lake bottom to resuspend sediments. Winters having extensive ice cover yield a more poorly mixed water column, and a large region of the lake becomes depositional due to the lack of wave resuspension of sediments. Once ice retreats in the spring, sediments accumulated during ice cover will be resuspended as a pulse. Ice cover can cause significant changes in winter circulation patterns in a large lake (Campbell *et al*., 1987). The years of interest were 1982, 1983, 1994, and 1995. The hydrodynamic modeling included three-dimensional lake circulation, surface flux for atmospheric input, and wind-wave models (Schwab

and Beletsky, 1998). These were calibrated for the period of 1982-1983 using temperature, current, water level, and wind-wave measurements. The calibrated model was applied to 1994-1995 and verified. There was no ice modeling component for the version of the hydrodynamic model applied. Thus ice cover was important for understanding any potential weaknesses associated with the hydrodynamic results as well as the dynamics of exchanges between the water and the atmosphere.

Ice cover data were available from the National Oceanic and Atmospheric Administration (NOAA)/ Great Lakes Environmental Research Laboratory (GLERL) (Assel, 2003). This data set is partially described in Assel *et al*. (2002). Tabular information presented in Assel (2003) were summarized in a manner that seemed appropriate for this discussion (Table 1.4.1). For the period when ice was recorded on Lake Michigan, the mean and median daily ice cover were 16.7% and 14.7%, respectively. An ice year began with the first ice. For example, 1982 may include December of 1981. Both 1982 and 1994 were greater than the mean and median; whereas 1983 and 1995 were less than the mean and median. None of the four years represented an extreme of mean daily ice cover. The lowest mean daily ice cover was observed in 2002, and the highest was observed in 1977. Results for each winter's maximum daily ice cover were similar to mean daily ice cover. Ice cover is extremely variable from year-to-year. The impact upon hydrodynamics as modeled was believed to be minimal with respect to 1983 and 1995 when ice cover was quite low. Though high ice cover occurred during the winters of 1982 and 1994, these periods were not a part of the hydrodynamic model period. Using the hydrodynamic model information for models used to predict future conditions could lead to potential errors. Modeled circulation patterns could be in error and impact a high bias to modeled current velocities during the winters of high ice cover years due to the lack of an ice model within the hydrodynamics model.

1.4.3 Water and Air Temperatures

Water and air temperature data were retrieved from the National Data Buoy Center (U.S. Department of Commerce, 2002). Data from buoy numbers 45002 (north buoy) and 45007 (south buoy) were reviewed (Figure 1.4.1). Water temperature sensors were located 1 m below the water surface, and air temperature sensors were located 4 m above the surface. Water and air temperature data were available 1979 through 2002 for the north buoy and 1981 through 2002 for the south buoy.

Water temperature is highly variable from year-to-year. The data had been stratified in two ways for presentation. First, monthly mean temperatures were calculated and plotted for the south (Figure 1.4.2) and north (Figure 1.4.3) buoys. Years of importance to the hydrodynamic model were highlighted. It was interesting to note that 1983 and 1995 had higher monthly mean temperatures than 1982 or 1994. Both 1983 and 1995 had above normal maximum mean monthly temperature; whereas, 1982 had a typical maximum and 1995 had a very low maximum. This was reflected in the previously discussed ice cover for the four years. Water temperatures tended to be higher at the southern buoy than at the northern buoy, reflecting its more southerly latitude.

One way to identify the relative lake warming rate among years was to look at the mean June water temperature for the period of observation available from the NOAA buoys. Mean June temperatures at the south (Figure 1.4.4) and north (Figure 1.4.5) showed similar patterns that were quite interesting. Beginning in 1983, relatively high mean June temperatures were observed every four years (1983, 1987, 1991, 1995, 1999). This cycling, as well as the apparent increasing mean June water temperature for the period of record, should be further investigated. Both of these trends can impact long-term model forecasts. The years of the Lake Michigan Mass Balance Project (LMMBP) (1994 and 1995) represented a fairly average mean June temperature and one of the relatively high means, respectively.

The exchange of atrazine between the air and water are dependent on both water and air temperatures. Air temperature varied from year-to-year at the south and north buoys (Figures 1.4.6 and 1.4.7). Because air temperature drives observed water temperatures, it was not surprising that patterns observed and

Table 1.4.1. Summary of Lake Michigan Ice Cover Based Upon Assel (2003)

Year	Mean Daily Percent Ice Cover During Ice Period	Days of Observed Ice	Maximum Daily Percent Ice Cover
1973	13.3	104	33.0
1974	16.9	122	39.4
1975	13.9	113	28.1
1976	15.5	119	29.5
1977	46.5	132	93.1
1978	26.6	132	66.6
1979	35.2	132	92.3
1980	18.2	106	38.6
1981	24.6	112	53.8
1982	24.0	135	60.2
1983	8.2	118	23.6
1984	15.6	127	43.3
1985	20.1	119	41.3
1986	25.3	126	66.8
1987	9.1	100	19.3
1988	16.6	104	32.7
1989	13.1	140	30.9
1990	17.5	132	32.4
1991	10.0	120	21.5
1992	8.3	149	32.8
1993	11.0	126	32.2
1994	27.3	134	82.7
1995	7.2	120	21.6
1996	19.4	161	75.0
1997	13.4	156	37.8
1998	6.1	109	15.1
1999	8.7	111	23.0
2000	9.2	103	27.2
2001	13.4	134	29.5
2002	6.0	116	12.4
Mean	16.7	124	41.2
Median	14.7	121	32.8
Minimum	6.0	100	12.4
Maximum	46.5	161	93.1

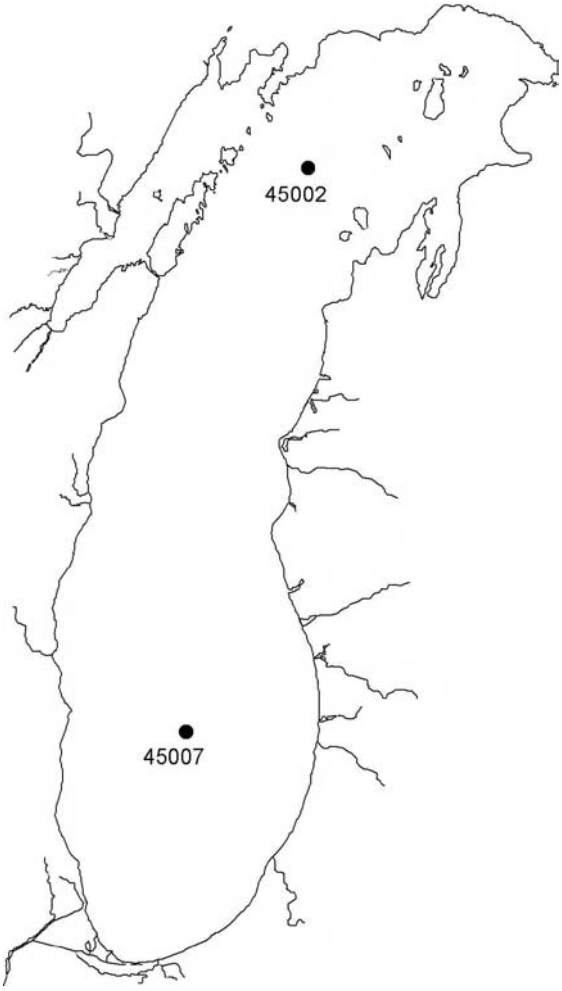

Figure 1.4.1. Location of the NOAA buoys in Lake Michigan.

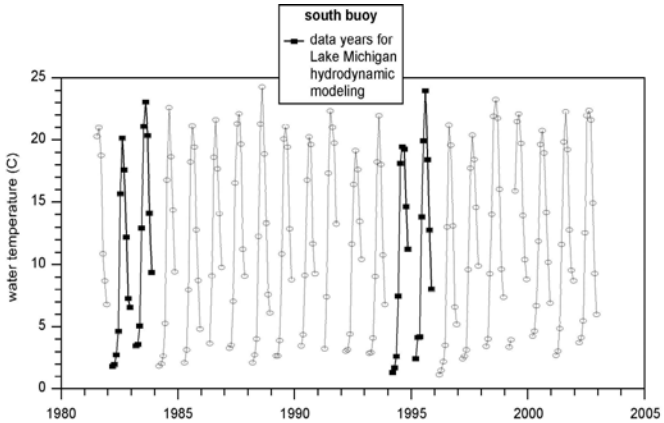

Figure 1.4.2. Monthly mean water temperatures in southern Lake Michigan.

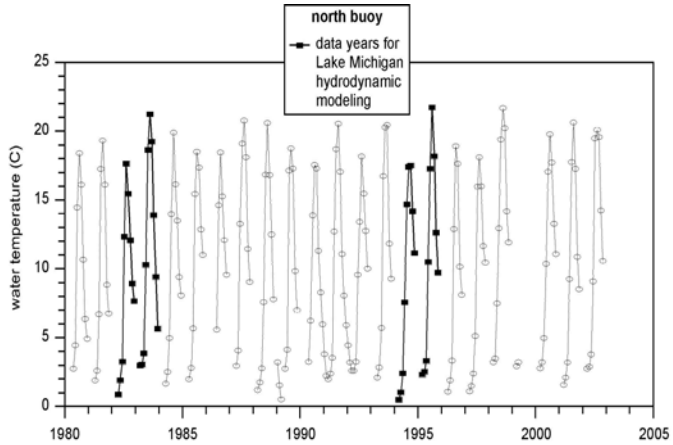

Figure 1.4.3. Monthly mean water temperatures in northern Lake Michigan.

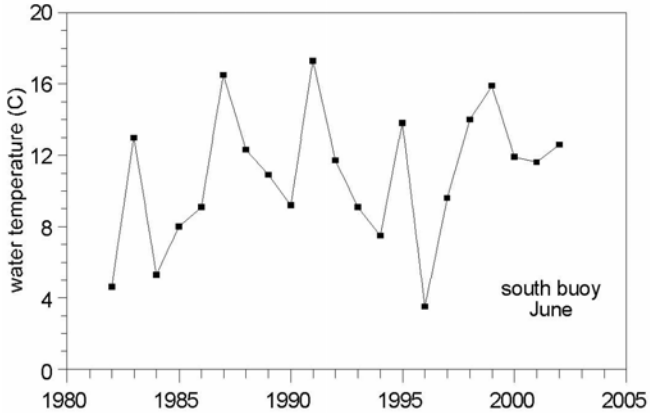

Figure 1.4.4. Mean June water temperatures in southern Lake Michigan.

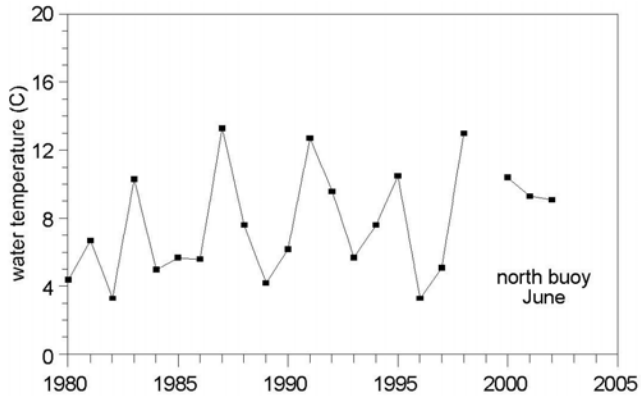

Figure 1.4.5. Mean June water temperatures in northern Lake Michigan.

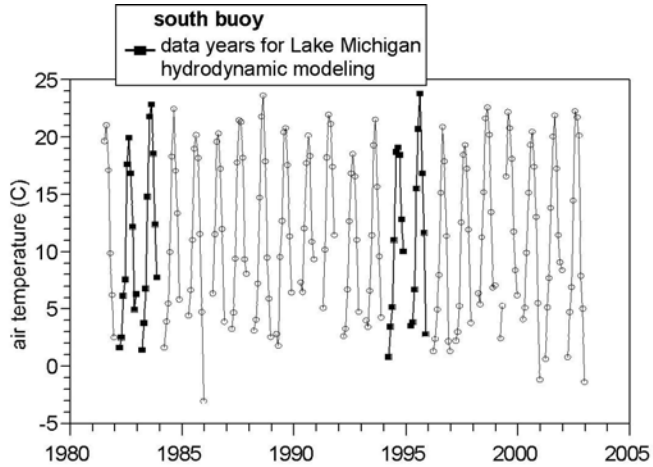

Figure 1.4.6. Monthly mean air temperatures in southern Lake Michigan.

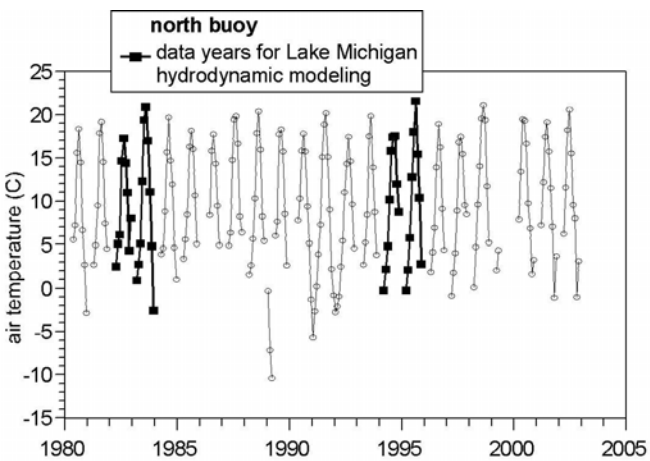

Figure 1.4.7. Monthly mean air temperatures in northern Lake Michigan.

conclusions made for water temperature are the same for air temperature. The cyclic pattern of June mean water temperatures was also found for the air temperatures (Figure 1.4.8 and 1.4.9). As additional data become available, future modeling efforts will need to address these cyclic patterns and long-term temperature trends for water and air temperatures.

1.4.4 Lake Water Levels

Lake levels can affect model geometry. If segment volume deviates significantly from the volumes used at the time of calibration, model results can be impacted. On a percentage basis, the impact will be

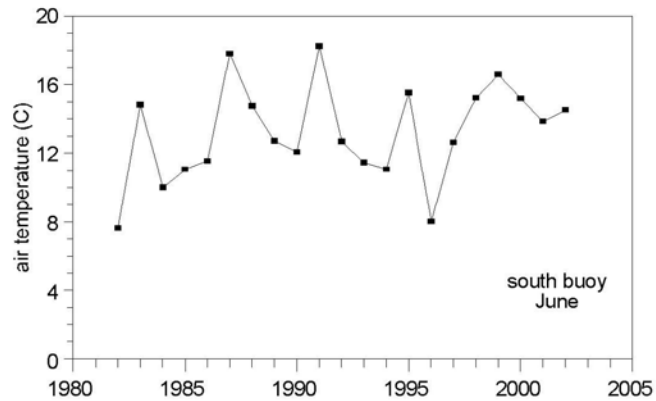

Figure 1.4.8. Mean June air temperatures in southern Lake Michigan.

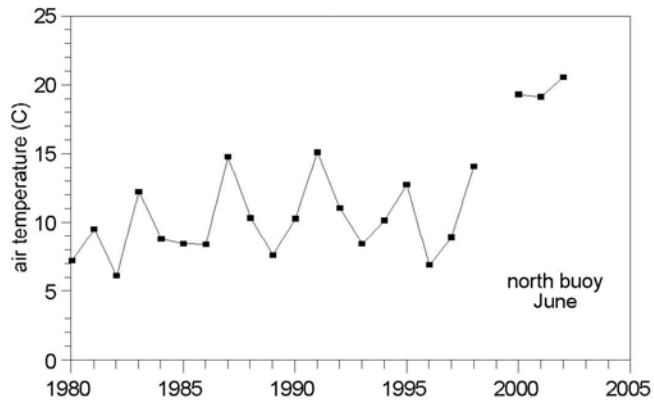

Figure 1.4.9. Mean June air temperatures in northern Lake Michigan.

most noticeable for shallow water segments and predictions from the hydrodynamic model and surface water model could be affected. Monthly mean lake water levels varied between 175.5 and 177.5 m for the period of record (1918-1997). Lake levels during 1994 and 1995 were near the average for the period of record (Figure 1.4.10).

1.4.5 Precipitation

Precipitation influences the flux of airborne contaminants to the lake, impacts tributary loading rates, and controls water levels. The 1982 and 1983 hydrodynamic years, and the 1994 and 1995 project years were compared to the previous 50 years of data (Croley and Hunter, 1994).

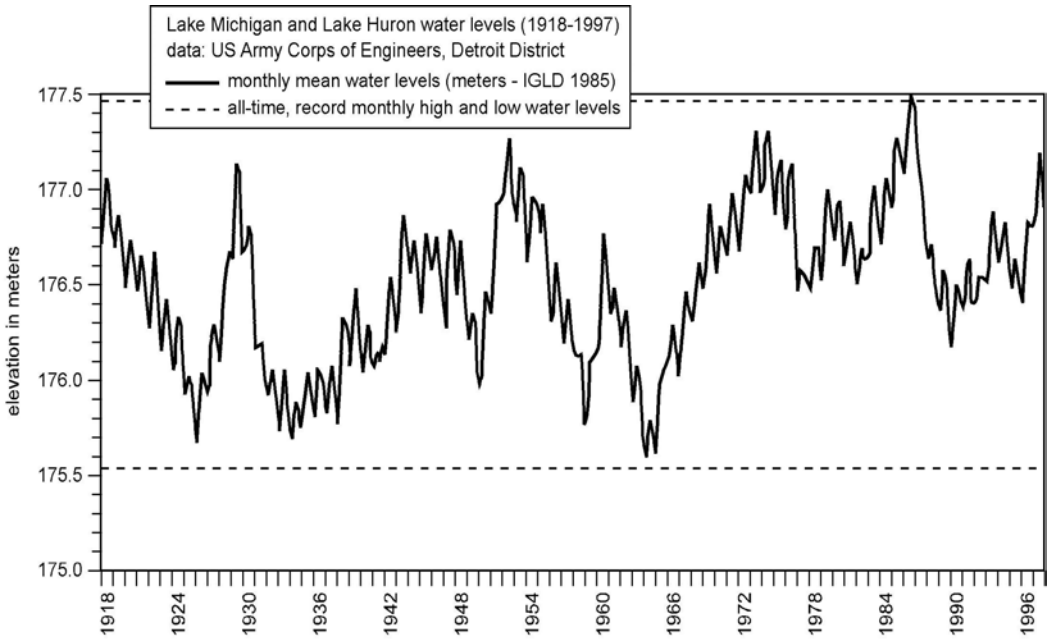

Figure 1.4.10. Record of mean monthly water levels for Lake Michigan.

1.4.5.1 Annual Comparisons

Precipitation to Lake Michigan for 1982, 1983, 1994, and 1995 were close to the 50-year mean for the lake (Figure 1.4.11). 1982 and 1983 were slightly above the mean and 1994 and 1995 were slightly below the mean. 1995 total annual precipitation was very close to the 50-year mean for over-lake precipitation. No visual trend was apparent in the total annual amounts of precipitation over the 50-year period.

1.4.5.2 Monthly Comparisons

The monthly mean precipitation for 1982, 1983, 1994, and 1995 were compared to the 50-year mean for the period of 1949 through 1998 (Figure 1.4.12). For the years of interest, January, July, November, and December of 1982; May of 1983; and October of 1995 had relatively high amounts of precipitation, exceeding one standard deviation of the 50-year mean. For the four years of interest, February of 1982; June of 1983; March, May, and December of 1994; and June of 1995 had relatively low amounts of precipitation. This illustrates that, in any one year, precipitation varies from month-to-month while the precipitation for the year can be at or near the average expected.

1.4.6 Tributary Flows

Tributary flows impact the delivery of materials to the lake, including nutrients and contaminants. During high flow events triggered by spring snow melt or rain events, tributary flows increase and materials can be carried from the watersheds to the tributaries. Within the tributary, sediments containing contaminants may resuspend. Thus the fluxes of solids, nutrients, and contaminants to the lake have the potential to increase during high flow events. Tributary flows were obtained from the United States Geological Survey (USGS) website (www.usgs.gov). A historical average and median daily flow were calculated for each tributary for the period of record, as well as for the 1994-1995 and 1982-1983 time periods. During 1982 and 1983, tributary flows were approximately 20% greater than the average flow (Figure 1.4.13). The 1994-1995 time period had relatively ordinary tributary flows (Figure 1.4.14).

1.4.7 Summary

Lake Michigan is acted upon by a number of physical parameters that impact the physics, chemistry, and biology of the lake. For a lake the size of Lake Michigan, changes in these parameters can be

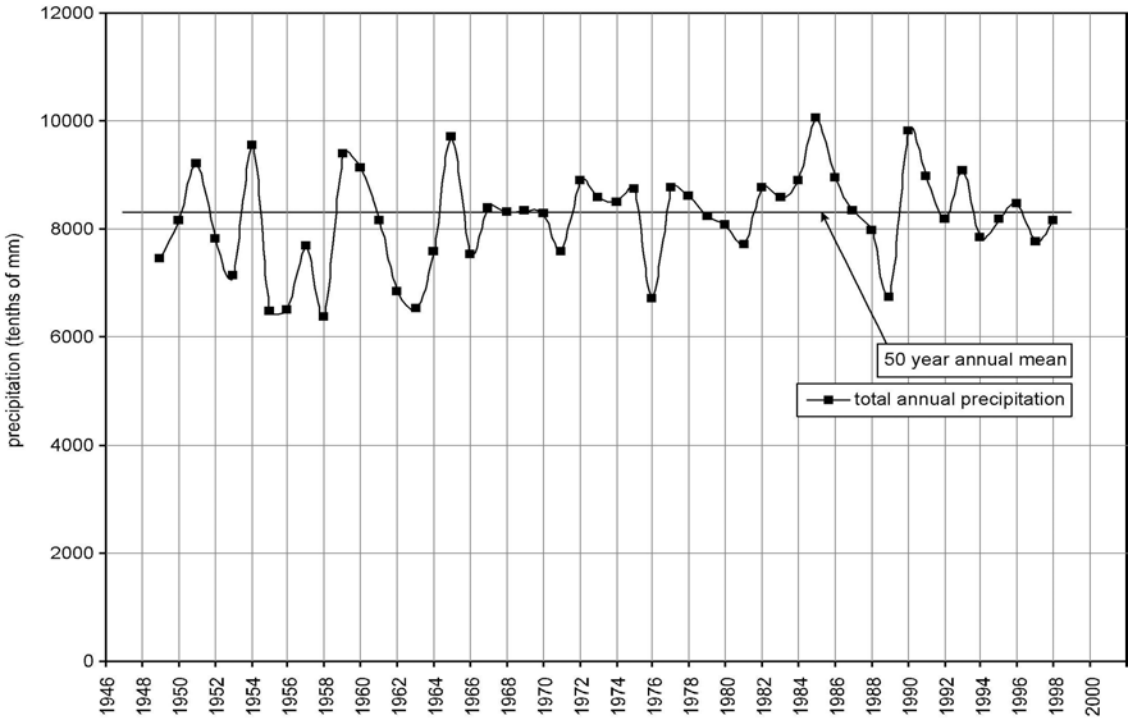

Figure 1.4.11. Annual precipitation to Lake Michigan between 1949 and 1998.

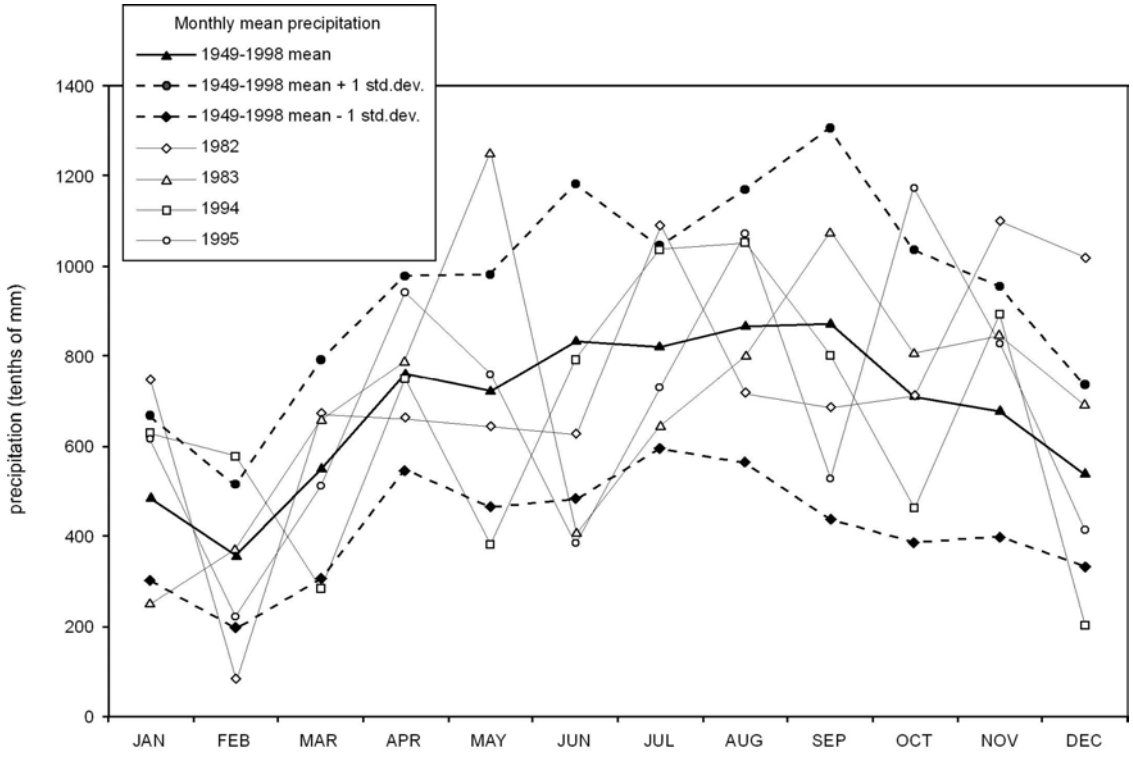

Figure 1.4.12. Comparison of 1982, 1983, 1994, and 1995 monthly mean precipitation to the mean for the period of 1949 through 1998.

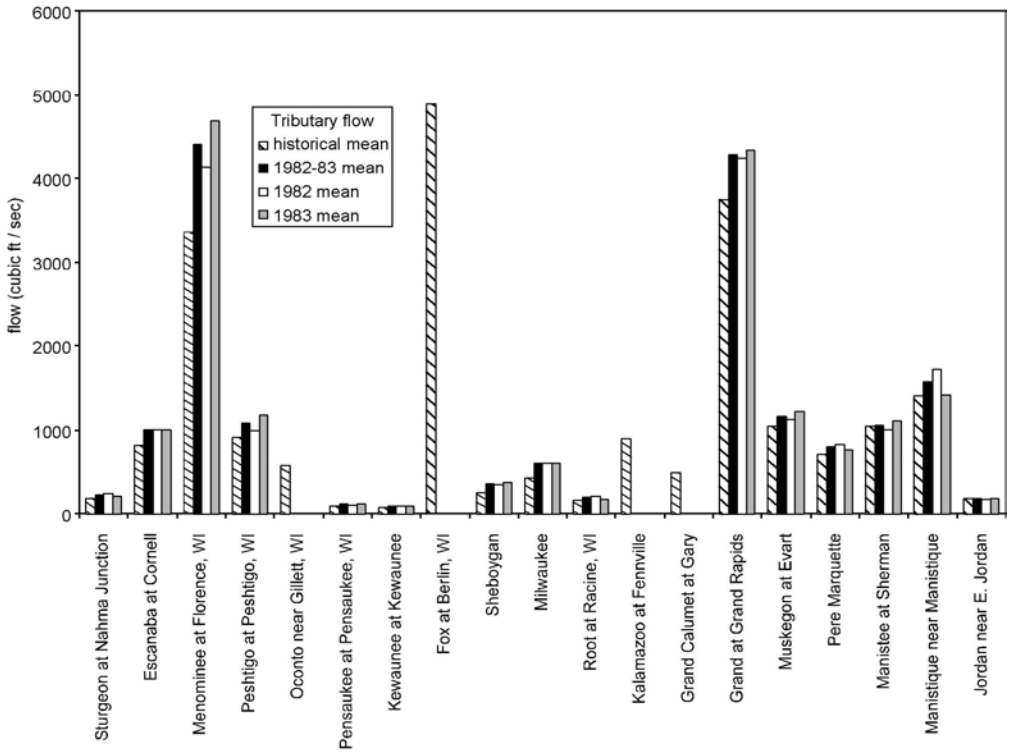

Figure 1.4.13. Comparison of tributary flow for hydrodynamic model calibration (1982-1983) to the historic means.

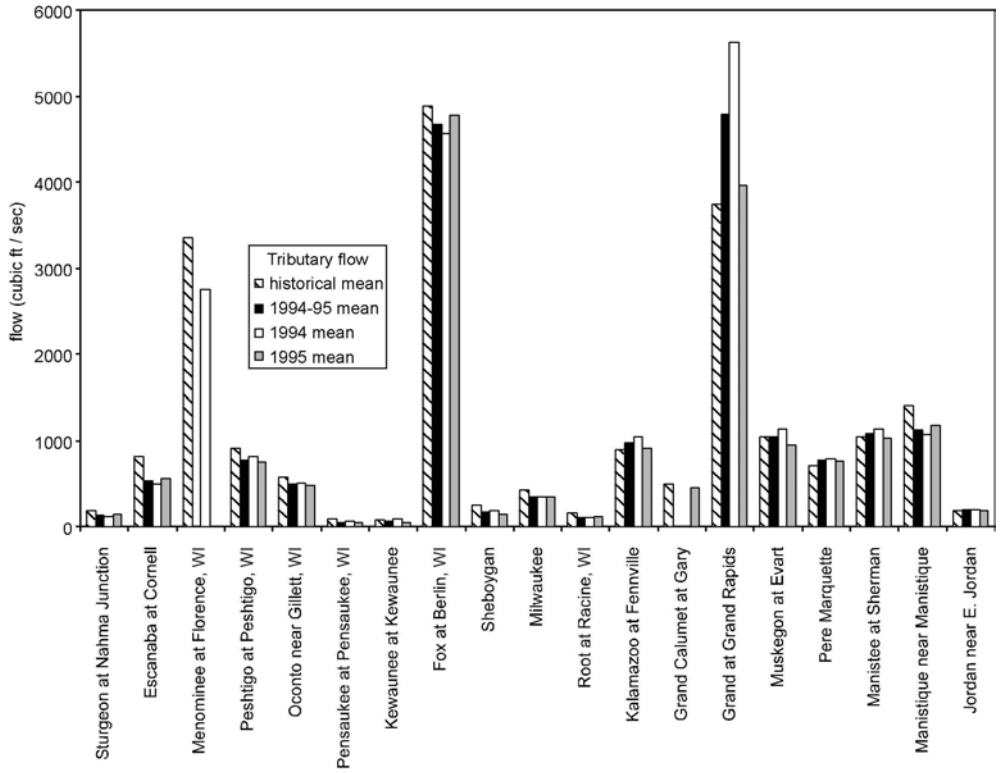

Figure 1.4.14. Comparison of tributary flow for the study period (1994-1995) to the historic means.

significant, especially when models are used in long-term predictions to predict the outcome of various scenarios. The primary driving forces are wind, air temperature, and precipitation. These impact tributary flows, lake levels, waves, water circulation, water temperature, and ice cover. For the period of record, these driving forces varied from year-to-year. The period of 1982 to 1983 was used to calibrate the hydrodynamic models. Fortunately for the period of time the models were calibrated, conditions were not at any extreme. This was also true for the period of 1994 and 1995 when the models were applied. However, the impact of ice cover remains a concern and will have to be dealt with in the future.

Temperature can impact atrazine contaminant modeling. Air temperature impacts how quickly the lake warms in any one year. Water temperature impacts the volatilization of atrazine. There appears to be a four-year cycle of quicker warming which exists within a trend of general warming of the lake. The trend of warming may be part of a longer-term undocumented cycle or may be related to climate change. For future modeling, these cycles and trends will have to be considered to improve long-term predictions.

Precipitation will impact both lake levels and tributary flows. In wet years, more atrazine may be delivered to the lake (see Part 2, Chapter 2). Precipitation was within the normal range for all years of modeling interest, resulting in lake levels and tributary flows that were within normal bounds. Changes in lake levels as well as the response of tributaries to precipitation events will need to be considered for future modeling used to predict changes of contaminants within the lake.

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PART 1

INTRODUCTION

Chapter 5. Atrazine Modeling Overview

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1.5.1 Background

The atrazine mass balance project was based upon the Enhanced Monitoring Program (EMP), a comprehensive, two-year synoptic survey for selected toxic chemicals in the Lake Michigan ecosystem. The atrazine EMP included tributary load and atmospheric deposition monitoring; ambient water column; and additional measurements to define and confirm transport and fate processes. The project was led by the United States Environmental Protection Agency (USEPA)/Great Lakes National Program Office (GLNPO). Modeling support to the project was provided by the USEPA/Mid-Continent Ecology Division (MED)/Office of Research and Development (ORD)/Large Lakes Research Station (LLRS) in cooperation with the Atmospheric Research and Exposure Assessment Laboratory (AREAL); the National Oceanic and Atmospheric Administration (NOAA)/Great Lakes Environmental Research Laboratory (GLERL); and other cooperators. The research developed a suite of integrated mass balance models to simulate the transport and fate of atrazine in Lake Michigan.

The project directly supports the development of a Lake-wide Management Plan (LaMP) for Lake Michigan that is mandated under Section 118 of the 1992 Clean Water Act. Atrazine and degradation products are on the Lake Michigan LaMP 2008 Watch List. Chemicals on the Watch List include those chemicals that have the potential to impact the Lake Michigan ecosystem; is present in the Lake Michigan watershed; and has the potential for bioaccumulation, persistence in water or sediment, or toxicity singly or through synergistic effects. In a June 1993 response to an inquiry by U.S. Senator Carl Levin, the United States General Accounting Office (now called the United States Government Accountability Office [USGAO]) recommended that the USEPA assess the persistence of pesticides, such as atrazine, in the Great Lakes and to report their findings to the pesticides reregistration program (U.S. General Accounting Office, 1993). The results of the Lake Michigan Mass Balance Project (LMMBP) atrazine modeling have been forwarded to the reregistration program for consideration.

1.5.2 LMMBP Modeling Objectives

Development of effective strategies for atrazine management requires a quantitative understanding of the relationships between sources, inventories,

concentrations, and effects of atrazine in the ecosystem. This approach integrated load estimation, ambient monitoring, and research efforts within a modeling framework that was compatible with both scientific as well as ecosystem management objectives. The mass balance approach estimated the magnitude of mass fluxes that constitute the pathways for atrazine transport into and out of the lake and processes that distribute toxics within the lake water column. Based upon these estimates, the mass balance was used to determine the rate of change in concentrations and inventories of atrazine as inputs such as atmospheric and tributary loadings changes. Thus the mass balance can serve as a useful tool to estimate or predict the outcome of alternatives under consideration for toxics management.

In general, atrazine modeling efforts associated with the LMMBP had the following objectives:

1. Provide a consistent framework for integrating load estimates, ambient monitoring data, and research efforts, leading to a better understanding of atrazine chemical sources, transport, and fate in Lake Michigan.

2. Using flow and concentration measurements, estimate the loading of atrazine from all major tributaries to Lake Michigan for the duration of the study.

3. Based on county-level usage of atrazine within the basin, make independent estimates of atrazine loading to the lake *via* tributaries.

4. Estimate the atmospheric deposition and air-water exchange of atrazine, including spatial and temporal variability over Lake Michigan.

5. Calibrate and confirm mass balance models for atrazine using project data based upon models for hydrodynamic and atrazine transport and fate.

6. Based upon the mass balance models, evaluate the magnitude and variability of toxic chemical fluxes within and between lake compartments, especially between the water column and the atmosphere.

7. Apply the calibrated mass balance models to forecast atrazine concentrations in water throughout Lake Michigan based upon meteorological forcing functions and future loadings based upon load reduction alternatives.

8. Predict the water concentration of atrazine in lake model cells receiving loads from tributaries contributing a relatively high percentage of the total tributary load to the lake. Compare these predictions to water quality standards.

9. Estimate (quantify) the uncertainty associated with estimates of tributary and atmospheric loads of atrazine and model predictions of contaminant concentrations.

10. Identify and prioritize further monitoring, modeling, and research efforts to (1) further reduce uncertainty and improve accuracy of predictions; (2) establish additional cause-effect linkages, such as ecological risk endpoints and feedbacks; and (3) evaluate additional source categories, such as non-point sources in the watershed.

Unlike the other LMMBP-modeled toxics (polychlorinated biphenyls (PCBs), mercury, and *trans*-nonachlor), atrazine does not sorb to solids to any great extent, and it does not bioaccumulate. It is soluble in water and can migrate from farm fields to Lake Michigan *via* run-off events. The herbicide is also transported to Lake Michigan *via* atmospheric pathways.

1.5.3 Historical Modeling

The modeling design and approach for the LMMBP reflects a progression of prior modeling efforts in Lake Michigan and throughout the Great Lakes. These include eutrophication and toxic substance mass balance models, food web bioaccumulation models, and predictive hydrodynamic and sediment transport models. Although not a comprehensive review, several of these prior modeling efforts are discussed below.

1.5.3.1 Completely-Mixed Lakes-In-Series Model

A lakes-in-series model for conservative substances was developed by Sonzogni *et al*. (1983) and applied to forecast chloride concentrations in each of the Great Lakes as a function of expected future loadings. This model demonstrated that concentrations of non-reactive substances would substantially "lag" the history of their input. This was especially the case for Lake Michigan, where maximum chloride concentrations were not predicted to occur until the 22nd Century despite declining loads after the 1970s. Similarly strong, non-steady-state behavior may be expected for other chemicals which are non-reactive and weakly associated to particles.

1.5.3.2 MICHTOX

MICHTOX was adapted from the general model, WASP4 (Ambrose *et al.,* 1988), and has served well as a screening-level model for Lake Michigan over the past several decades. An integrated mass balance and bioaccumulation model for PCBs (modeled as two homologs) and 10 other toxic chemicals was developed as a planning tool for the LMMBP (Endicott *et al.*, 2005). The MICHTOX mass balance model was calibrated to suspended solids and plutonium data for the southern lake basin, while the bioaccumulation model combined Thomann and Connolly's (1984) effort with chemical-specific parameterization from Lake Ontario. MICHTOX demonstrated that reasonable predictions of PCB concentration trends in water, sediment, and biota could be developed although significant uncertainties regarding sediment-water and air-water contaminant transport remained. These are the most significant transport fluxes for PCBs and presumably other hydrophobic contaminants. Major data gaps for other priority toxics allowed only order-of-magnitude estimates of load-concentration relationships. When this model was developed and run, available monitoring data for toxic chemical concentration in tributaries, air, lake water, sediment, and biota were not adequate to define loading trends or to relate the distribution of loadings to contaminant gradients observed for sediment and biota. Credible model predictions of toxic chemical transport, fate, and bioaccumulation would depend upon developing a comprehensive data set quantifying loadings, sediment inventories, concentrations, and transport fluxes on a spatially-resolved basis and localized descriptions of food web structures.

MICHTOX was also applied to model atrazine in Lake Michigan and Green Bay. It was first applied prior to the release of LMMBP data using only historical data (Rygwelski *et al.*, 1999), and it was also applied again after LMMBP data became available. MICHTOX served as a low-resolution model and the application is discussed in this report.

1.5.3.3 Green Bay Mass Balance Project

The Green Bay Mass Balance Project (GBMBP) demonstrated the feasibility of applying mass balance principles to manage toxic chemicals in the Great Lakes ecosystem. A two-year (1989-1990) synoptic sampling program was designed to collect appropriate and complete data for the mass balance study. A suite of integrated mass balance and bioaccumulation models were developed which, together, provided an ecosystem-level simulation of sources, transport, fate, and bioaccumulation of PCBs throughout the Fox River and Green Bay. These mass balance models were also based on the general WASP4 model construct. This study advanced the state-of-the-art of mass balance modeling, particularly the ability to construct a fairly complete and accurate description of contaminant mass transport.

Several aspects of the Green Bay modeling effort were noteworthy. Particle transport and sorption processes were found to be of fundamental importance as bases for contaminant modeling. Resuspension of contaminated sediments in the Fox River constituted the major source of PCBs to the river as well as the bay. In the bay, particle sorbent dynamics were strongly affected by phytoplankton production and decay. The relative significance of hydraulic transport, sediment transport, burial, volatilization, and open-lake boundary exchange processes upon the PCBs mass balance varied considerably with location in Green Bay. Radionuclide tracers were again essential for calibration of particle fluxes and confirmation of long-term contaminant transport predictions. The significance of contaminant accumulation at the base of the food web and fish movement in relation to

exposure gradients were demonstrated in the bioaccumulation model. The LMMBP demonstrated the linked submodel approach to ecosystem model development and application, and the feasibility of using such a model for assessing the effectiveness of toxics management control alternatives.

The GBMBP models were a precursor to our LM2-Atrazine model. LM2-Atrazine served as our mid-level spatial resolution atrazine model, and the application is discussed in this report.

1.5.4 Resolution for the LMMBP Models

Model resolution is the spatial and temporal scale of predictions, as well as the definitions of model state variables. While factors such as data availability, model sophistication, and computer resources constrain resolution to a degree, different levels of model resolution are possible and are, in fact, necessary. Three "levels" of spatial resolution, indicated by the segmentation grid of the lake surface, are illustrated in Figure 1.5.1. Level 1 was resolved at the scale of lake basins (characteristic length, L = 150 km) with an associated seasonal temporal resolution. This was a screening-level model resolution used in MICHTOX. Level 2 was resolved at a regional scale defined by food webs (L = 40 km); temporal resolution was weekly-to-monthly. This resolution was roughly comparable to that achieved by models developed in the GBMBP. Level 3 was a hydrodynamic scale resolution (L = 5 km), with associated daily temporal resolution. Both near-shore and offshore regions can be distinguished with the Level 3 resolution. Level 3 was scaled to resolve to predict hydrodynamic transport.

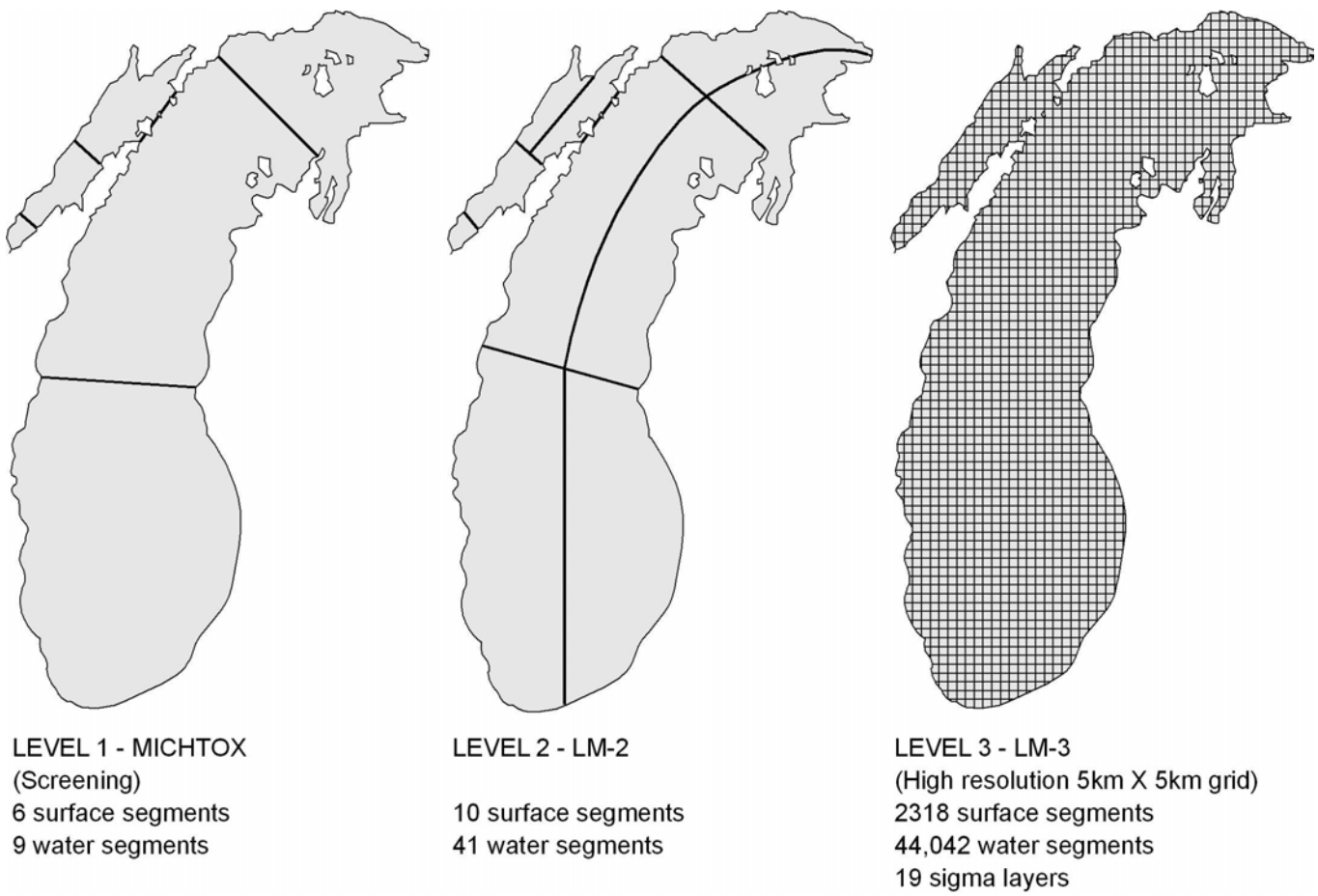

Figure 1.5.1. Surface water segmentation for alternative Lake Michigan mass balance model levels.

Although the LaMP and the Great Waters Program (GWP) objectives are "lake-wide," both of these emphasize biotic impairments occurring primarily in localized, near-shore regions. LaMP objectives also require that the transport of contaminants from tributaries and other near-shore sources to the open-lake be resolved. Therefore, the Level 1 model was not adequate for the study objectives. Level 2 resolution was adequate for most modeling objectives but not for resolution of significant hydrodynamic impact or near-shore influence of atrazine from tributaries. Level 3 resolution was required for accurate hydrodynamic modeling and was desirable for predicting near-shore gradients, especially those formed by transients such as thermal bars and upwelling; as well as more persistent features such as tributary plumes and thermal stratification. Level 3 transport resolution also has the potential in relating toxics loading from the 10 Areas of Concern (AOCs) adjoining Lake Michigan which must be addressed by the Remedial Action Plan (RAP) process to the LaMP *via* the LMMBP.

The modeling design for the LMMBP was based on the development of a number of models at three levels of resolution. For the atrazine contaminant transport and fate models, MICHTOX was resolved at Level 1; LM2-Atrazine was resolved at Level 2; and LM3-Atrazine was resolved at Level 3. The Princeton Ocean Model (POM) and atmospheric loading models were resolved at Level 3. Results of the hydrodynamic model were spatially and temporally averaged prior to coupling to the Level 2 model. The rationale for specifying different resolutions was the hydrodynamic models require a Level 3 resolution to offer the best capability for transport simulation and forecasting. A lower resolution was specified for LM2-Atrazine because this model had been demonstrated at this resolution.

1.5.5 Models Developed and Applied

The transport and fate atrazine models developed, refined, and applied by the Large Lakes and Rivers Forecasting Research Branch (LLRFRB) included MICHTOX, LM2-Atrazine, and LM3-Atrazine (Figure 1.5.2). Models developed and run elsewhere included a hydrodynamics model (POM) (Schwab and Beletsky, 1998), an atmospheric loading model based on local observations (Green *et al*., 2000; Miller *et al*., 2001), a tributary loading model (Hall and Robertson, 1998), and the Community Multiscale Air Quality (CMAQ) model. CMAQ was adapted to simulate the regional atmospheric fate and transport of atrazine (Cooter *et al*., 2002; Cooter and Hutzell,

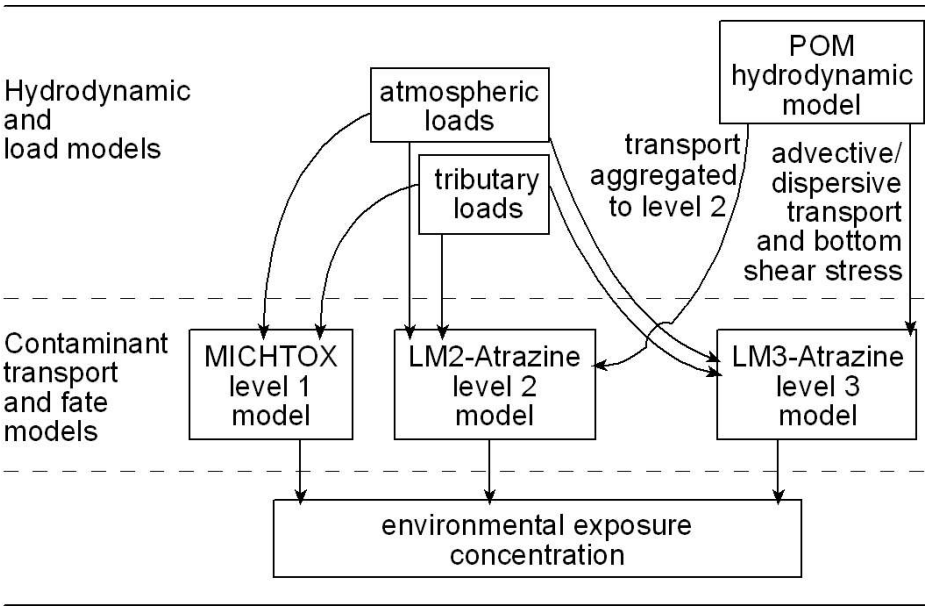

Figure 1.5.2. Model construct used for the LMMBP to model atrazine.

2002). This atmospheric model utilized atrazine emissions from agricultural soils provided by the Pesticide Emissions Model (PEM) (Scholtz *et al*., 1999; and Scholtz *et al*., 2002). The CMAQ predictions of atrazine in air and rainfall compared well with some field observations taken along the Lake Michigan shoreline in 1995. Although the results from the CMAQ were not used directly in the any of the LMMBP atrazine models, the model demonstrated a potential for this purpose in future modeling efforts. Only the models developed, refined, and applied at LLRFRB will be discussed in detail within this document.

1.5.5.1 Lake Process Models

The mass balance models for atrazine in Lake Michigan were comprised of linked hydrodynamic (POM) with LM2-Atrazine and LM3-Atrazine. The hydrodynamic model-predicted water movements necessary to describe the three-dimensional transport of dissolved constituents in the water column, and these transport parameters were incorporated into the water quality models. The benefit of using hydrodynamic model output in this way relieves the modeler from having to use a tracer in the water, such as chloride, to calibrate advective and dispersive transport functions. More discussion can be found on this topic in Part 4 (LM2-Atrazine) and Part 5 (LM3-Atrazine).

MICHTOX was not linked in any way with the POM hydrodynamic model. In MICHTOX, circulation is specified as advective and dispersive transport functions. This approach suffers the disadvantages in that calibration of the transport functions requires extensive tracer data (chloride), circulation is not predicted by meteorologic forcing functions, and the model loses resolution because of the difficulty in measuring/calibrating fine-scale transport variability. In Green Bay, chloride data was used to calibrate the transport functions. However, in the main lake, the chloride gradients were not evident, and therefore, were of no value for the purpose of calibrating the transport functions. MICHTOX vertical and horizontal exchange coefficients were obtained from previous Great Lakes modeling studies. See Section 3.3.2 in the MICHTOX chapter for more discussion on this topic.

The models described the contaminant transport and fate within the water column, mass transfer between media (air and water), and atrazine degradation *via* total kinetic decay processes. Together, these models formed an integrated description of atrazine chemical cycling in the aquatic ecosystem with which to predict the relationship between loadings and concentrations of atrazine in the lake.

1.5.5.2 Hydrodynamics (POM)

The Princeton Ocean Model (POM) (Blumberg and Mellor, 1980, 1987) was used to compute three-dimensional current fields in the lake. The POM simulated large- and medium-scale (km) circulation patterns, vertical stratification, velocity distribution, seiche, and surface waves. This model was also used to simulate a thermal balance for the lake. The POM is a primitive equation, numerical hydrodynamic circulation model that predicts three-dimensional water column transport in response to wind stress, temperature, barometric pressure, and Coriolis force. The POM has been demonstrated to accurately simulate the predominant physics of large water bodies (Blumberg and Mellor, 1983, 1985; Blumberg and Goodrich, 1990). This model was used to develop year-long simulations on a 5 km horizontal grid with 19 sigma-coordinate vertical layers at one-hour intervals for Lake Michigan (Schwab and Beletsky, 1998). Observed and simulated meteorological data were used to define model forcing functions. Extensive measurements of temperature and current distributions collected in Lake Michigan during 1982-1983 were used to provide the necessary data for model calibration; measurements of water temperature and current distributions were used to confirm hydrodynamic simulations for 1994-1995.

1.5.6 Model Quality Assurance

A Quality Assurance Project Plan (QAPP) was prepared and implemented for the atrazine modeling (Richardson *et al*., 2004). The QAPP specified procedures for code development; testing; modification; documentation; as well as methods and measures applied in model calibration, confirmation, and uncertainty analysis.

1.5.7 Model Application and Computational Aspects

1.5.7.1 Annual Simulations

Annual forecast simulations were run with the LM3-Atrazine model. Model input reflected seasonal, regional, and lake-wide contaminant loads. Model output was analyzed within the high-resolution of spatial and temporal gradients of contaminant concentrations.

1.5.7.2 Long-Term Simulations

MICHTOX and LM2-Atrazine long-term simulations were used to forecast the lake-wide impact of various management scenarios. Forecasts were performed to determine time to near steady-state conditions for both continuing and discontinued loads. Forecasts were also run to evaluate reductions in exposure concentrations resulting from elimination of tributary and/or atmospheric loading.

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PART 2

LAKE MICHIGAN MASS BALANCE PROJECT ATRAZINE LOADINGS TO LAKE MICHIGAN

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Chapter 1. Historical Atrazine Usage in the United States

2.1.1 Background

The company, J.R. Geigy A.G., of Basel Switzerland applied for a patent with the United States Patent Office on January 12, 1955 that described a method for making atrazine and listed various mixtures with the active ingredient that could be used to kill weeds (U.S. Patent Office, 1959). Atrazine was registered with the United States Department of Agriculture (USDA) in 1958 (U.S. Environmental Protection Agency, 2003). On June 23, 1959, the atrazine patent (Number 2891855) was issued. By the mid-1960s, widespread use of atrazine was observed (Duke, Ciba Geigy Patent Office, personal communication, 1994; Kells, Michigan State University, personal communication, 1994).

In the Lake Michigan basin, atrazine is primarily used on corn crops to control broadleaf and some grassy weeds by inhibiting photosynthesis. For corn crops, it is usually applied to the fields in the spring, prior to, during, or after planting a crop or after emergence of the corn seedlings. Atrazine is usually mixed in a water solution along with other herbicides. Estimates by Nako and Keitt (1994) indicate that atrazine is relatively inexpensive compared to other herbicides. Cost for chemically treating one acre in 1992 was about three dollars (estimate does not include costs for fuel and labor). During 1994-1995, atrazine use as a percentage of total pesticide use in the basin was 13.8% (Brody *et al.*, 1998). During the same time frame, corn represented 38.8% of planted acreage. For the period 1964 through 1993, atrazine was the leading herbicide used in the United States (U.S. Department of Agriculture, 1994; Lin *et al.*, 1995). Atrazine trade names/synonyms include: Aatrex, Actinite PK, Akticon, Argezin, Atazinax, Atranex, Atrataf, Atred, Candex, Cekuzina-T, Chromozin, Crisatrina, Cyazin, Fenamin, Fenatrol, Gesaprim, Griffex, Hungazin, Inakor, Pitezin, Primatol, Radazin, Strazine, Vectal, Weedex A, Wonuk, and Zeapos (U.S. Environmental Protection Agency, 2006).

Application rates of atrazine to farm fields have decreased over time. In 1990, a label change initiated by the manufacturers of atrazine set the maximum recommended application rate for atrazine to three pounds active ingredient per acre. Prior to this, four pounds active ingredient per acre was recommended (Scribner *et al.*, 2000). In 1992, the manufacturers again voluntarily reduced the maximum recommended application rate of atrazine on corn and sorghum to a range of 1.6-2.5 pounds active ingredient per acre depending on soil organic residue and erosion potential. The 1992 label changes also included atrazine mixing/loading and application setbacks to protect various water sources including wells, streams, lakes, and reservoirs (Pearson and Giles, 1993). The lower 1992 application rate was recommended for fields with less than 30% plant residues on the surface. The label changes reduced recommended application rates by nearly 50%, however, actual application rates used by farmers decreased by only about 11% from an average 1.1 pounds per acre in 1991 to 0.97-0.98 pounds per acre in 1994-1995. (U.S. Department of Agriculture, 2006). Evidently, farmers were satisfied with the results from lower than recommended application rates set by the manufacturers of the herbicide. The reduced application rates in 1994-1995 and 1998 compared to 1989-1990 were reflected in reduced concentrations observed in several Midwestern streams during post-application run-off (Scribner *et al*., 2000).

2.1.2 Total Annual Usage Estimates

Usage of atrazine is predominant in the eastern half of the United States (see Figure 2.1.1). As depicted in the figure, usage is heavy south of the Lake Michigan basin in the states of Illinois and Indiana. However, except for the northwestern part of Indiana, most of the drainage and associated load from these two states discharge into the Mississippi River watershed. But, the proximity of these high-use areas to Lake Michigan does impact the atmospheric loading of atrazine to the southern area of the lake.

In Table 2.1.1, some statistics are presented on the usage of atrazine on corn crops in the United States for crop years 1991, 1994, and 1995 (U.S. Department of Agriculture, 2006). For all three years, atrazine was the most used herbicide on corn crops. In the survey year 1994, the ranking of the top 10 states in order of highest corn acreage to lowest was Iowa, Illinois, Nebraska, Minnesota, Indiana, South Dakota, Wisconsin, Ohio, Michigan, and Montana.

Figure 2.1.2 depicts county usage of atrazine during the Lake Michigan Mass Balance Project (LMMBP). Note the highest use region is in the southwestern part of Michigan and northern Indiana. Little atrazine is used in the northern parts of the basin. The data for 1994 were provided by Kirschner (International Joint Commission, personal communication, 1997) and the data from 1995 were provided by Macarus (U.S. Environmental Protection Agency, personal communication, 1999).

Historical total annual atrazine usage estimates in the United States are depicted in Figure 2.1.3 for years where data were available. The data used in the graphic are presented in Table 2.1.2. The atrazine data (zero usage) for 1963 (Duke, Ciba Geigy Patent Office, personal communication, 1994) matches estimates made by Scribner *et al.* (2000). Robert Torla's (United States Environmental Protection Agency (USEPA), personal communication, 1994) data (1964, 1966, and 1971) are from USDA/Economic Research Service (ERS) published estimates (U.S. Department of Agriculture, 2003), and the rest of the data are from Aspelin and Nako (USEPA, personal communication, 1997). The data represent total annual usage (both agricultural and non-agricultural). However in the 1990s, it was estimated that approximately 95% was used for agricultural purposes. For some of the years (such as 1993 and 1995), a range of values was reported. When this occurred, a mean of the range was used. Also plotted on Figure 2.1.3 are historical (1964-2002) total United States acreage for corn and another for the sum acreage of corn, sorghum, and sugarcane – all crops that use atrazine to suppress weeds. Notice that the pattern of atrazine use, except for the earliest years, follows the pattern of corn acreage planted in the United States. The low corn acreage in 1983 and 1988 were due to drought conditions (Shapouri *et al.*, 1995).

2.1.3 Future Atrazine Use Estimates

Atrazine currently holds its large market share because it is a pre-emergent herbicide active against most of the serious broadleaf weeds in corn, and it is

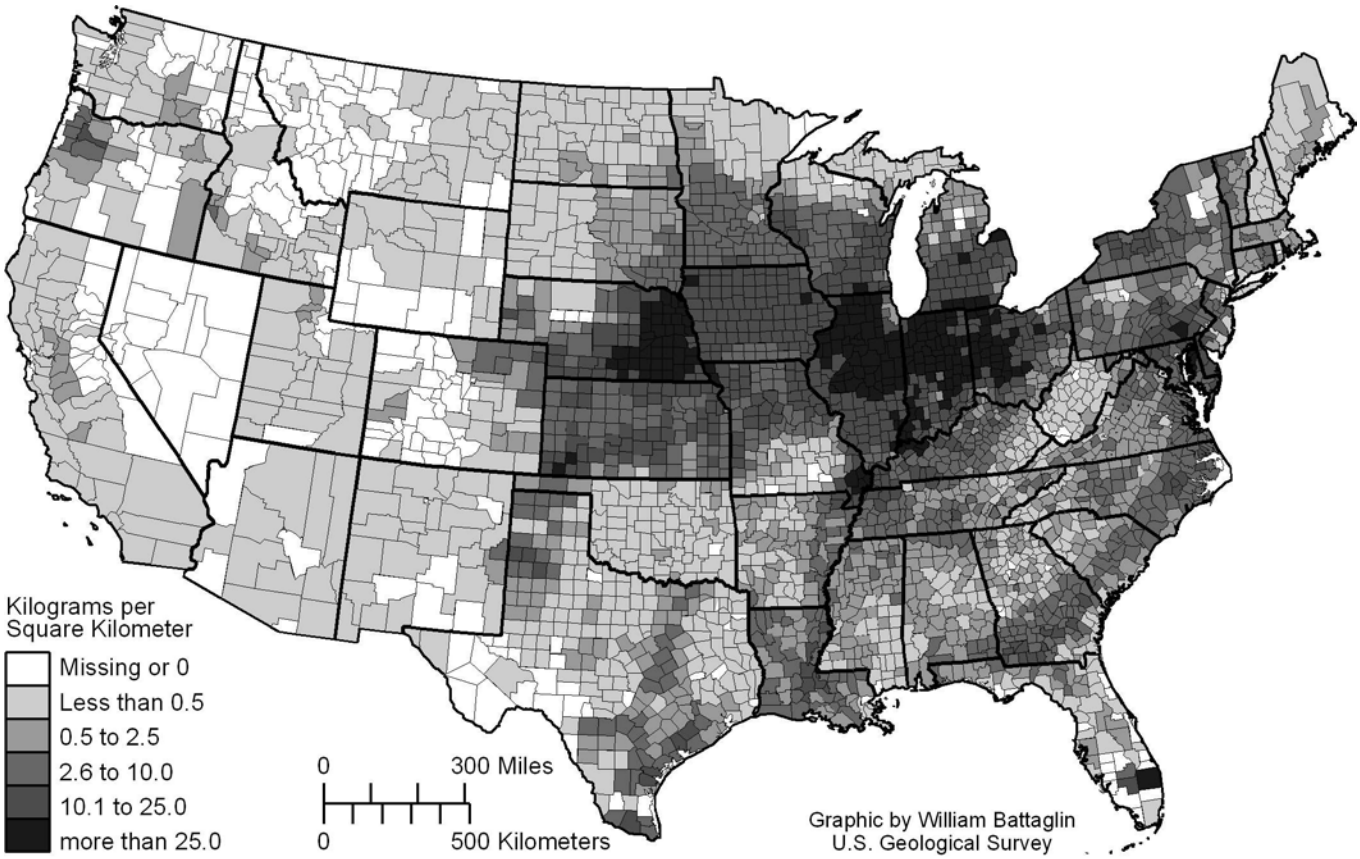

Figure 2.1.1. Atrazine usage in the United States for 1991.

Table 2.1.1. U.S. Department of Agriculture Corn Crop Summaries of Atrazine Usage in the United States for 1991, 1994, and 1995

Year	Number of States Surveyed	% of Total Corn Crop Surveyed	% of Corn Crop Treated With Herbicides	% of Corn Crop Treated With Atrazine	Average Application Rate of Atrazine (lbs/acre)	Total Amount of Atrazine Applied (millions of kg)
1991	17	90	94	66	1.1	23.61
1994	10	79	98	68	0.97	20.59
1995	15	90	96	65	0.98	20.74

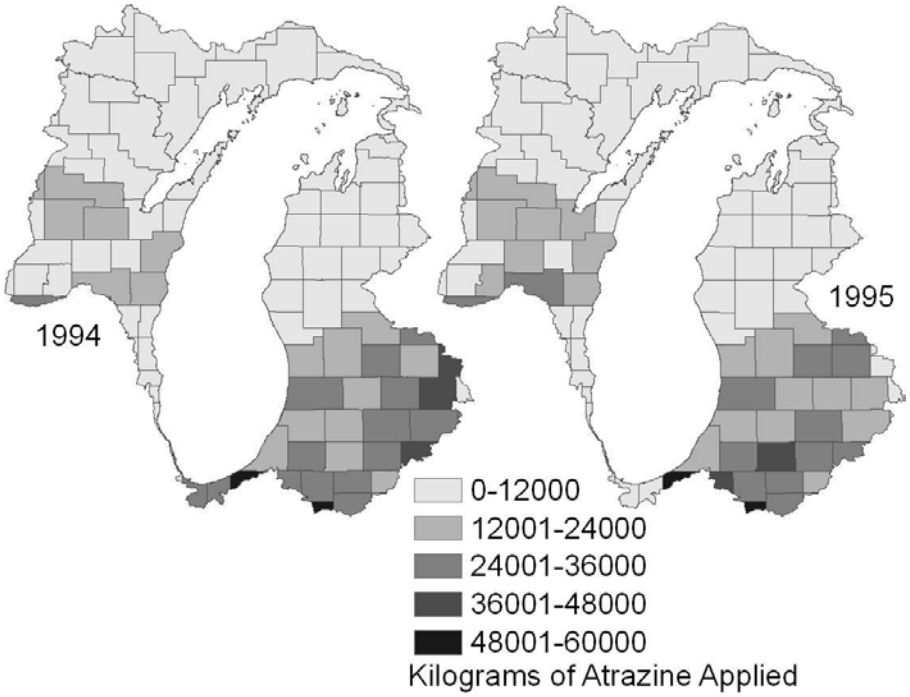

Figure 2.1.2. Estimates of atrazine usage in the Lake Michigan basin for 1994 and 1995.

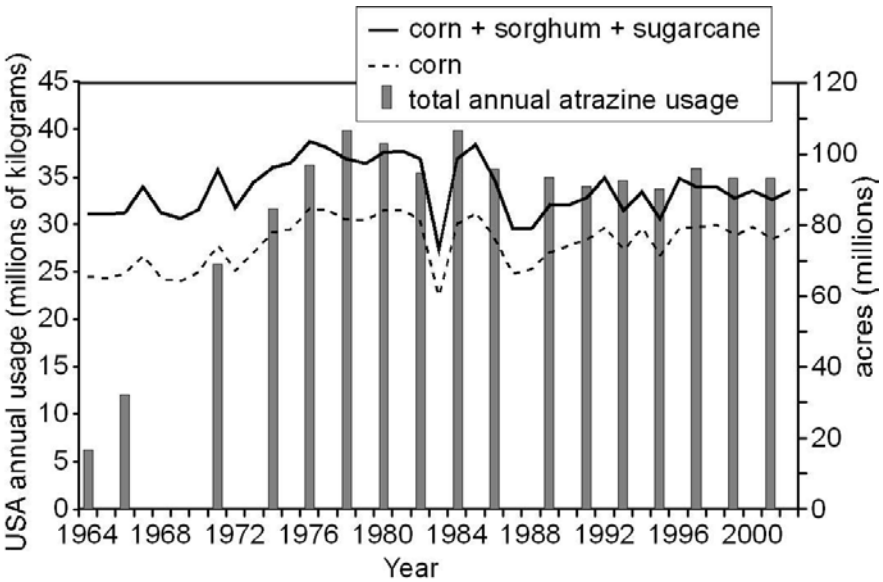

Figure 2.1.3. Historical trend of total annual usage of atrazine in the United States with acreage planted in corn, sorghum, and sugarcane.

Table 2.1.2. Total Annual Usage of Atrazine in the United States (Aspelin and Nako, U.S. Environmental Protection Agency, Personal Communication, 1997; Torla, U.S. Environmental Protection Agency, Personal Communication, 1994)

Year	Millions of kg Atrazine Used in the United States
1963	0.0
1964	6.3
1966	12.0
1971	25.8
1974	31.8
1976	36.3
1978	39.9
1980	38.6
1982	35.4
1984	39.9
1986	35.8
1989	34.9
1991	34.0
1993	34.7
1995	33.8

inexpensive (Nako and Keitt, 1994). Any replacements must be equally as effective in controlling weeds and matching or beating costs. Due to repeated annual usage, some weeds, such as pigweed, are showing resistance to triazine herbicides. Blending other herbicides with atrazine may help to eliminate some of these resistant plants.

If the resistant plants do not have an efficient seed dispersal mechanism, then these problem plants become a local problem. However, if the resistant plant shows resistance to other herbicides and has an effective seed dispersal mechanism, then usage of atrazine may decline. Another factor to consider in projecting future usage is possible regulatory action that could restrict usage in some manner. With growing ethanol demand and strong export sales of corn, U.S. farmers planted 92.9 million acres of corn in 2007. This exceeded the 2006 acreage by 19 percent (U.S. Department of Agriculture, 2007). The actual planted acreage is the highest since 1944.

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PART 2

LAKE MICHIGAN MASS BALANCE PROJECT ATRAZINE LOADINGS TO LAKE MICHIGAN

Chapter 2. Estimation of Atrazine Tributary Loadings

Tributary loadings for the Lake Michigan Mass Balance Project (LMMBP) atrazine models were estimated using an approach based on watershed export of the applied chemical from farm fields to the lake and another approach that utilized LMMBP measurements of atrazine concentration and flow in the 11 monitored streams within the construct of the Stratified Beale Ratio Estimator (SBRE) to calculate loadings. Watersheds that drained into a monitored tributary were identified as a monitored watershed. The other watersheds in the Lake Michigan basin were identified as unmonitored. Both methods made estimates of watershed loadings of atrazine to Lake Michigan for both the monitored and unmonitored watersheds. The MICHTOX and LM2-Atrazine models solely utilized estimates based on watershed export. The LM3-Atrazine model utilized load estimates based on the SBRE and on a hybrid of the two load estimates, whereby the SBRE loads were enhanced with additional loadings based on the annual watershed export estimates (see Part 5, Chapter 3, Section 5.3.3.3.1). Both the MICHTOX and LM2-Atrazine models utilized annualized loadings only and are useful for long-term simulations. LM3-Atrazine loadings were calculated on a daily basis so as to capture seasonal variations on a finer time and spatial resolution that were not available in either of the other two models.

Watershed loading estimates were made for all of the Lake Michigan sub-basins. A sub-basin may have an identifiable tributary that discharges this loading into the lake, or it may not. However they were calculated, both were collectively referred to as tributary loadings.

2.2.1 Atrazine Tributary Load Estimates Utilizing County-Level Atrazine Application Data

Literature values for estimates of the percentage of the amount of atrazine applied in a watershed that is delivered to a receiving body of water were used in the loading estimates. This percentage is identified as the Watershed Export Percentage (WEP), but it is also referred to in the literature as Load as a Percentage of Use (LAPU). The calculation of atrazine tributary loads (mass/time) to a MICHTOX or LM2-Atrazine segment for a given year when application rates and corn acreage are known were calculated as follows:

Watershed Export Load or Tributary Load =

$$\sum_{k=1}^{m}\left[\sum_{j=1}^{n}\left[A \times T \times C \times F \times L\right]_j\right]_k \qquad (2.2.1)$$

where

j = a county within a Hydrological Unit Code (HUC) draining into a given water segment

n = total number of counties in a HUC

k = the load from a given HUC in a sub-basin delivered to a model segment

m = total number of HUC loads in a sub-basin delivered to a model segment

A = atrazine application rate (mass/acre/time) for corn

T = fraction of corn acreage treated with atrazine

C = corn acreage in a given county

F = fraction of county within the HUC

L = (Watershed Export Percentage)/100

2.2.1.1 County-Level Atrazine Application Data

In this project, we received atrazine data in the form of county-level application estimates for a given year or the product of variables A, T, and C in Equation 2.2.1. Sources of these data are identified in Table 2.2.1. As is evident from the table, data were only available for six years. Additional data beyond 2002 are likely but were not included in this analysis. The atrazine data were reported as an active ingredient, so no conversion was required before model loadings were estimated.

The area fraction of a given county that lies within a HUC in the Lake Michigan basin was determined by Geographical Information System (GIS)-defined HUC boundaries and county boundaries. Within the basin, there are a number of HUCs that collectively form sub-basins. Some of these sub-basins defined watersheds of the 11 LMMBP major tributaries in the Lake Michigan basin. Other sub-basins were not readily identifiable with tributaries; however, load estimates, identified as unmonitored tributary loads, were made for these sub-basins and the discharge into the lake was associated with a model segment. The GIS was used to calculate what fraction of a county fell into a given HUC. Note that more than one county may fall within a given HUC.

2.2.1.2 The Watershed Export Percentage

The atrazine WEP (variable ***L*** in Equation 2.2.1) is known to be a function of soil type, population of atrazine-degrading bacteria in the soil, field topography, timing and amount of rainfall after application, and other explanatory variables. Seventy-six reservoir drainage basins in the Midwestern United States were studied using multiple linear regression and logistic regressions to

Table 2.2.1. Sources of County-Level Atrazine Application Data for the Lake Michigan Basin

Application Year	Data Source	Affiliation	Date Received
1989	W.A. Battaglin and D.A. Goolsby (see reference)	U.S. Geological Survey	1995 (Publication Date)
1992	B. Kirschner and R. Baksh (personal communication)	International Joint Commission (IJC), Windsor, Ontario, Canada	1994
1993	R. Baksh (personal communication)	IJC	1995
1994	B. Kirschner (personal communication)	IJC	1997
1995	D. Macarus (personal communication)	USEPA/Region V, Chicago, Illinois	1999
1998	D. Macarus (personal communication)	USEPA/Region V	2000

determine the significance of the explanatory variables in predicting concentrations of atrazine in the reservoirs (Battaglin and Goolsby, 1996). Both of the statistical tests used in the analysis found soil hydrologic group values to be a significant explanatory variable. This same conclusion was drawn from studies performed by Blanchard and Lerch (2000) in northern Missouri. Small hydrologic group values (1.75) are associated with well-drained soil (sand and gravel), whereas larger values (>3.25) are associated with poorly-drained soil (clays, wetlands, urban). Soil textures in Michigan, Wisconsin, Illinois, Indiana, and Ohio are shown in Figure 2.2.1. These data were obtained from the State Soil Geographic (STATSGO) database provided by the United States Department of Agriculture (USDA), Soil Conservation Service (SCS). A review of 1992 and 1993 atrazine field application data revealed that approximately 80% of the total atrazine application in the Lake Michigan basin is applied to crops in the sub-basins that drain into the southeastern part of the lake. These sub-basins include the southwestern quarter of the lower peninsula of Michigan including a small portion of northern Indiana that also resides in the Lake Michigan basin. Soils in that part of the basin can be identified as moderate to fine textures and have hydrologic group values ranging from 2.51 to 3.25.

At the start of a rain event, the rate of rainfall may equal the rate of infiltration into the soil. However, after some time, the infiltration rate will start to decrease asymptotically and reach some constant, but lower, infiltration rate. Run-off begins at the point the rainfall rate exceeds the infiltration rate.

A literature review of atrazine watershed export percentages is summarized in Table 2.2.2. The raw data used in this summary are presented in Table 2.2.3. Watershed export percentages for various watersheds are grouped by soil type. The data are from northern watershed systems (Ontario, Canada; northern Ohio; northern Iowa; and southern Minnesota). In addition, the data reflect watershed export percentages that were calculated for an entire year. Many published studies of WEP fall short of a full year of monitoring and this causes the estimate to be biased low for the annual estimate. Based on this literature review, a watershed export percentage of 0.6% was selected for the Lake Michigan and Green Bay watersheds to represent the predominant moderate texture soil hydrologic group in this area. Note that WEPs for clay soils (1.4) are much higher than for sandy soils (0.2). WEP differences between clay and sandy soils will yield large differences on loading estimates as Equation 2.2.1 indicates. In a rain event, run-off will occur sooner on non-saturated clay soils than non-saturated sandy soils, because sandy soils have a higher infiltration rate. So, it is important to carefully assess this parameter when estimating watershed export of atrazine. Climatic conditions for the 12 annual studies used in deriving this watershed export percentage for loam/fine-textured soils included a balance of five wet and five dry years. For the other two years, one was considered average in precipitation and conditions for the other year were not reported. Including both wet and dry years should help minimize bias in the estimate, since atrazine-associated run-off in drought years has been observed to be lower compared to wet years (Richards *et al.* 1996). A plot of WEPs versus watershed size indicated that there was no relationship, and this was also the conclusion by Capel and Larsen (2001). They evaluated data from 408 observations of WEPs across numerous types of soil textures. Their median WEP was calculated to be 0.66% for watersheds less than 100,000 ha. Although not calculated, a more rigorous derivation of the average watershed export percentage could be achieved if a detailed accounting of soil types was performed for corn croplands within the basin. With that detailed soil type information, a weighted-average WEP could be calculated for each sub-basin.

2.2.1.3 Calculating the Atrazine Tributary Load

County-level application data for a given year were multiplied by the fractional area of the county in a HUC (Equation 2.2.1). This load was further divided if a monitored river basin occupied a portion of that county. In that case, the atrazine load was further divided and apportioned by area to a monitored river load and the rest to unmonitored tributary load. This procedure was repeated for all counties that had overlap in any given HUC within the Lake Michigan basin. These fractional application loads (monitored and unmonitored) were summed separately for each HUC. The point of discharge of the monitored tributary into the lake was associated with a model segment and likewise for unmonitored tributary loads. Only those whole counties or fractional counties that

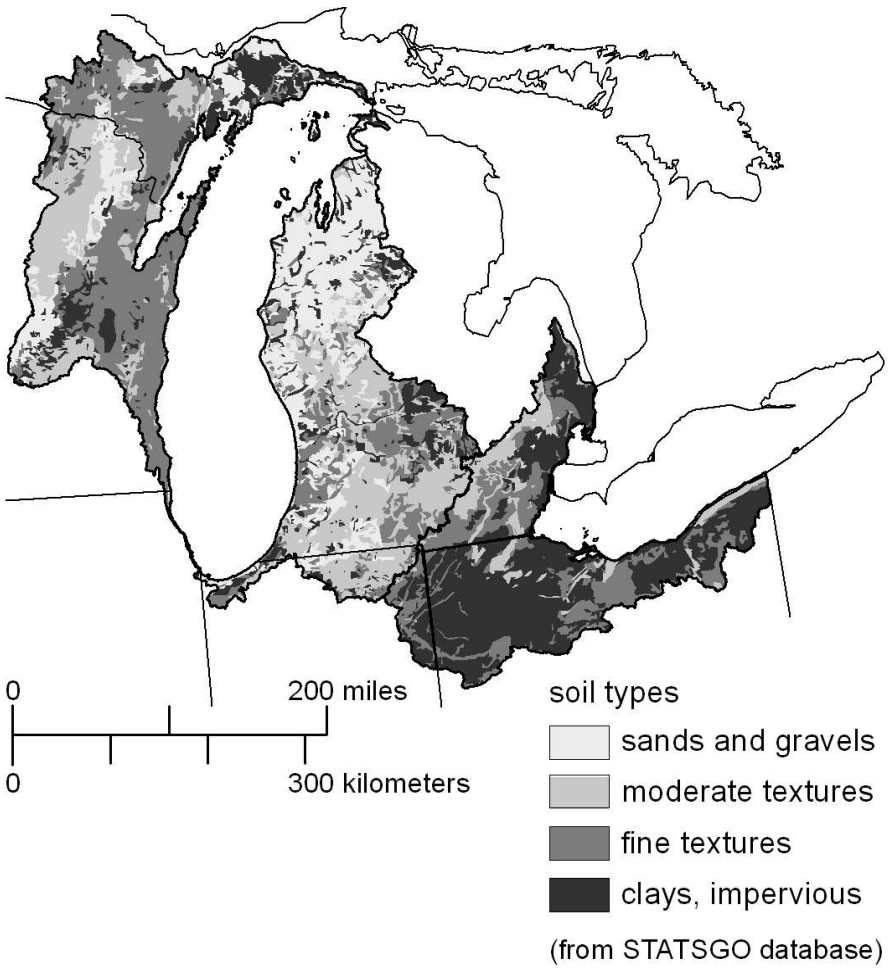

Figure 2.2.1. Soil textures typical for the Lake Michigan basin and part of the Lake Erie basin.

Table 2.2.2. Atrazine Watershed Export Data Summarized From the Literature. Raw Data Used to Create This Table Can be Found in Table 2.2.3

Soil Type	Watershed Export Percentage	Standard Deviation	95% Confidence Level	Range	Number of Studies
Clay	1.4	0.61	0.94-1.85	0.11-2.5	9
Loam/Fine Textured	0.61	0.38	0.37-0.85	0.21-1.5	12

Table 2.2.3. Atrazine Watershed Export Data From Various Northern Sites

Water-shed Size (sq km)	Location	Soil Type	Watershed Export Percentage	Year(s)	Watershed	Annual Precipita-tion	Reference	Adjusted % Loss to Represent Atrazine Only
23.83	Ontario	Clay	0.11	1976	Humber R.	Dry	Frank & Sirons, 1979	Y
30.25	Ontario	Clay	1.47	1975	Twenty Mile Cr	Wet	Frank & Sirons, 1979	Y
30.25	Ontario	Clay	1.35	1976	Twenty Mile Cr	Dry	Frank & Sirons, 1979	Y
50.8	Ontario	Clay	2.51	1975	Thames R.	Wet	Frank & Sirons, 1979	Y
50.8	Ontario	Clay	1.40	1976	Thames R.	Dry	Frank & Sirons, 1979	Y
62	Ontario	Clay	1.28	1975	Au Sable R.	Wet	Frank & Sirons, 1979	Y
62	Ontario	Clay	1.31	1976	Au Sable R.	Dry	Frank & Sirons, 1979	Y
6790	Ontario	Clay/Loam/Sand	1.49	1981,82,83,84,85	Grand R.	Average	Frank & Logan, 1988	Y
16395	Ohio	Clay	1.50	NA	Maumee R.	Average	Richards *et al*., 1996	N
18.6	Ontario	Loam	0.32	1975	Grand R.	Wet	Frank & Sirons, 1979	Y
18.6	Ontario	Loam	0.54	1976	Grand R.	Dry	Frank & Sirons, 1979	Y
30	Ontario	Loam	0.21	1975	Thames R.	Wet	Frank & Sirons, 1979	Y
30	Ontario	Loam	0.26	1976	Thames R.	Dry	Frank & Sirons, 1979	Y
54.72	Ontario	Loam	0.50	1975	Maitland R.	Wet	Frank & Sirons, 1979	Y
54.72	Ontario	Loam	0.35	1976	Maitland R.	Dry	Frank & Sirons, 1979	Y
45.04	Ontario	Loam	1.09	1975	Saugeen R.	Wet	Frank & Sirons, 1979	Y
45.04	Ontario	Loam	0.80	1976	Saugeen R.	Dry	Frank & Sirons, 1979	Y
3998	Ontario	Sandy/Loam	0.65	1981,82,83,84,85	Saugeen R.	Average	Frank & Logan, 1988	Y
17820	N. Iowa	Fine Textured	1.50	84	Cedar R. Basin	NA	Squillace&Thuman, 92	N
38585	S. Minnesota	Fine Textured	0.33	90	Minn. R. Basin	Dry	Schottler *et al*., 1994	N
38585	S. Minnesota	Fine Textured	0.62	90	Minn. R. Basin	Wet	Schottler *et al*., 1994	N
19.9	Ontario	Sandy	0.15	1975	Hillman Cr	Wet	Frank & Sirons, 1979	Y
19.9	Ontario	Sandy	0.20	1976	Hillman Cr	Dry	Frank & Sirons, 1979	Y
56.45	Ontario	Sandy	0.17	1975	Shelter Val. Cr	Wet	Frank & Sirons, 1979	Y
79.13	Ontario	Sandy	0.29	1975	Big Creek	Wet	Frank & Sirons, 1979	Y
79.13	Ontario	Sandy	0.18	1976	Big Creek	Dry	Frank & Sirons, 1979	Y

lie within the Lake Michigan basin boundaries were considered for tributary load estimation. When taking fractional areas of a county, we assumed that atrazine usage within the county was uniform. Tributary loading estimates were made for each of the years in Table 2.2.1 using this method.

2.2.2 Estimating Atrazine Tributary Loads for Years When County-Level Atrazine Application Data Was Not Available

For the six years where county-level application data were available, tributary loads were estimated using the approach identified in the previous section, 2.2.1; however, to make estimates for additional years, an approach was selected that utilized some of the results from Section 2.2.1 and estimates of total annual atrazine usage in the United States. The approach was to calculate a Tributary Load Ratio (TLR) of known application rates for a given year and divide this number by the total annual United States usage amount of atrazine for that same year. For years when application data are missing but total annual usage is known, the ratio multiplied by the total annual usage yields an estimate of tributary load. Seventeen years of total annual United States usage data are displayed in Figure 2.2.2. This approach was used for both MICHTOX and LM2-Atrazine model runs.

$$\textit{Tributary Load Ratio} = (\textit{Tributary Load to Model Segment})/(\textit{Total Annual USA Atrazine Usage}) \tag{2.2.2}$$

For any year (y), where only total annual United States usage is known, a tributary load was calculated utilizing a tributary load ratio:

$$\textit{Tributary Load} = (\textit{Tributary Load Ratio}) \times (\textit{Total Annual USA Usage for Any Year } (y)) \tag{2.2.3}$$

Due to label changes that lowered application amounts and established planting setbacks from water bodies in 1990 and 1992, a decision was made to use two TLRs in order to address atrazine application practices for pre- and post-label changes. For the pre-label change period, tributary load estimates for years 1964 through 1986 used the TLR calculated for 1989. We used 1989 because this was the only year during that pre-label change period where we had both county-level application data and total annual United States usage estimates. An average atrazine application rate of 1.54 pounds/acre on corn from a 1982 survey of 16 states with more than one million acres of corn compares well to an average application rate for Michigan and Wisconsin of 1.5 pounds/acre for the same year (Gianessi and Puffer, 1988). So for at least that year, the atrazine usage rate per acre in the Lake Michigan basin matches usage rates in the rest of the major United States corn-growing regions. For comparison purposes, atrazine tributary load estimates to MICHTOX segment 1 were made for the year 1984 using the TLR method based on total annual United States usage estimates for 1984 and also by using available atrazine use data (Gianessi and Puffer, 1988) that included application rate data by state, total corn crop acreage by state, and fraction of corn crop that was treated with atrazine. The TLR method yielded a total tributary load estimate of 15.4 kg/day of atrazine to segment one. The tributary load estimate based on Equation 2.2.1 and data from Gianessi and Puffer yielded a result of 17.7 kg/day. For this latter estimate, data on the percent of corn acreage treated with atrazine was from 1984 (Michigan), 1982 (Illinois), and early 1980s (Wisconsin and Indiana). Also, the application rate data are from 1984 for Michigan, Indiana, and Wisconsin and from 1982 for Illinois. Data on the percent of corn acreage treated with atrazine for Wisconsin and Indiana were based on expert opinion of the U.S. Department of Agriculture/Economics Research Service, rather than survey data. Total corn acreage in each county within the sub-basin draining into segment 1 was based on actual survey data for 1984 (Kevin Pautler, U.S. Department of Agriculture, personal communication, 1997). Given the uncertainties of both methods, the two numbers are reasonably close.

For the post-label change period, an average of the tributary ratios for 1992 and 1993 was used to calculate tributary loadings for 1991. For the rest of the post-label change years 1992, 1993, 1994, 1995, and 1998, loads were calculated based on county-level application data using Equation 2.2.1. In

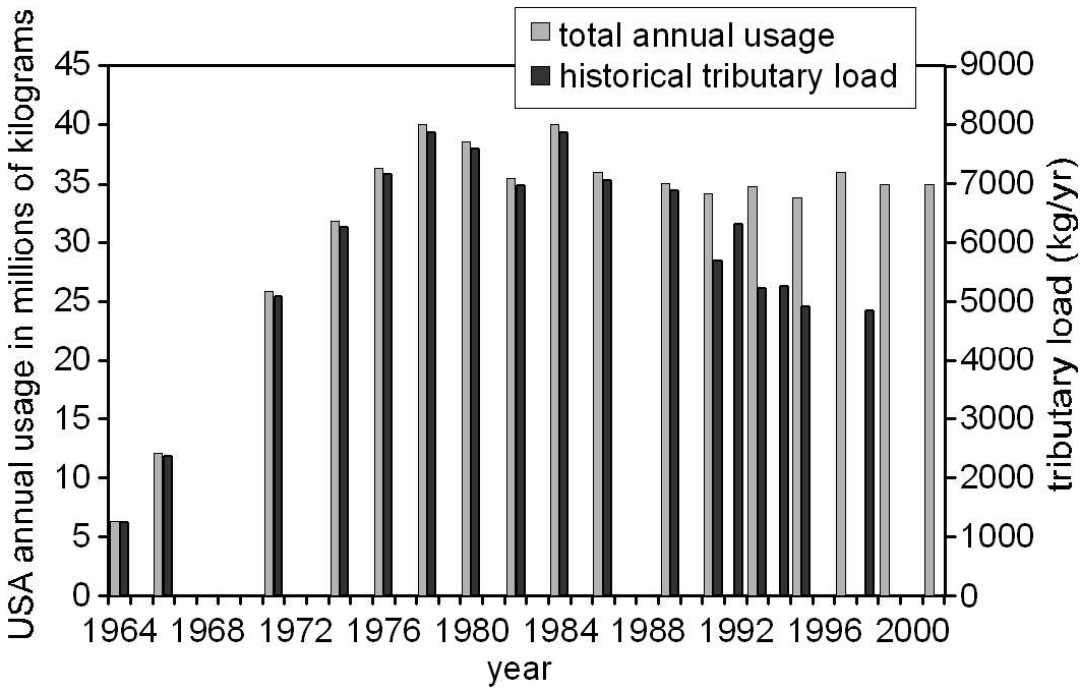

Figure 2.2.2. WEP-based total atrazine tributary loading estimates to Lake Michigan.

comparing tributary loading ratios for pre- and post-label change years 1989 and 1995, the TLR for 1995 (MICHTOX segment 1), which carries most of the atrazine tributary loading to Lake Michigan, was 26% lower than what it was in 1989. A similar trend was noted for the other segments.

Yet, total annual United States usage only dropped three percent from 1989 through 1995, and total corn crop acreage fell just 1.16 percent (Good and Irwin, 2007). This indicates that usage in the Lake Michigan basin dropped more relative to the rest of the United States during that period. The Lake Michigan basin has a number of rivers and lakes. Perhaps the label changes requiring setbacks from these water bodies reduced the corn acreage and hence usage dropped. The state of Wisconsin mandated atrazine usage changes that went beyond those related to the 1990 and 1992 label changes and includes establishment of statewide usage rates, application timing, record keeping (Wisconsin Register, 2004), and prohibited use areas (Wisconsin Register, 2005). Efforts to reduce atrazine usage in the state have been ongoing since 1991. Other possible reasons for the use reduction in the Lake Michigan basin include substitution of different herbicides, cropland taken out of corn production, changes in farming practices, increase of corn acreage outside the Lake Michigan basin that replaced lost acreage within the basin, etc. Regardless of the reason for the pre- and post-label changes reflected in the TLRs, use of two ratios seems to be warranted.

2.2.3 Atrazine Tributary Loads for MICHTOX and LM2-Atrazine

Based on methods described above, total tributary loadings to Lake Michigan are depicted in Figures 2.2.3 and 2.2.4. Since the mid-1980s, atrazine tributary loadings have been declining in the Lake Michigan basin; however, total annual usage in the United States has not changed much since approximately 1986. Tributary loadings for MICHTOX segments are shown in Figure 2.2.3. Note that the watershed delivering atrazine to model segment 1 delivers the highest load to the lake. See Figure 3.1 in Part 3 for a graphic showing MICHTOX segments. This watershed drains the southwestern part of the state of Michigan and a section of

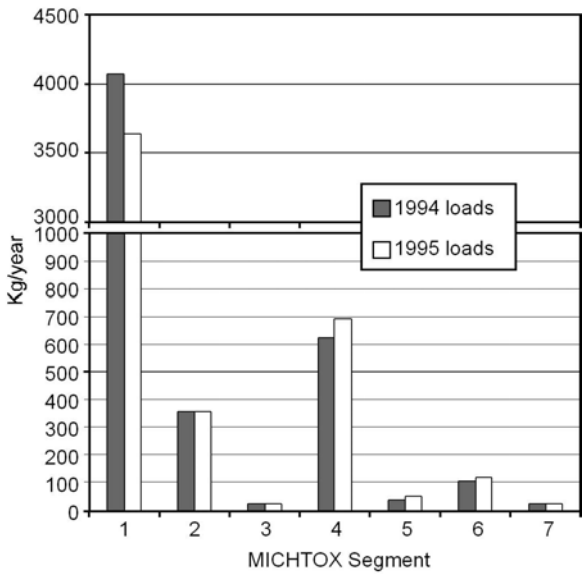

Figure 2.2.3. Tributary loadings to Lake Michigan MICHTOX model segments.

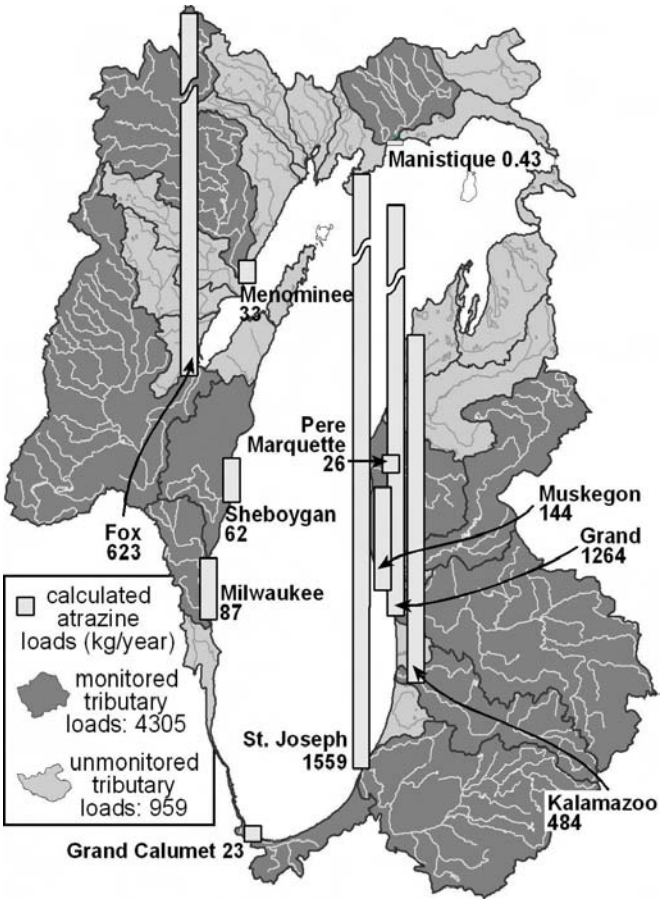

Figure 2.2.4. WEP-based Lake Michigan tributary loadings, 1994.

Northeastern Indiana. For the whole-lake, the total annual tributary load estimate is the same for both models. However, LM2-Atrazine had 10 receiving surface water segments and MICHTOX had seven (six primary segments and a small segment representing the lower Fox River). Each surface-water segment sharing a boundary with a sub-basin received that sub-basin load.

For years where atrazine application data or total annual USA usage are unknown, both MICHTOX and LM2-Atrazine calculate loads by assuming that the loads between the two years bracketing the missed annual loads are linear.

2.2.4 Atrazine Tributary Load Estimates for LM3-Atrazine

The LM3-Atrazine model was not used to conduct a hindcast simulation. This model used United States Geological Survey (USGS) loading estimates that were based on actual measurements of river flow and atrazine concentration. Because these load estimates were low compared to the WEP-based load estimates discussed in the previous section, the USGS loadings were adjusted upward in the spring/early summer period so that the total annual load was equal to the WEP-based annual loading. See Section 5.3.3.3.1 in the LM3-Atrazine modeling chapter for more information on LM3 tributary loadings.

2.2.4.1 Tributary Sampling Program

As part of the LMMBP, the USGS calculated loads for 11 monitored tributaries in the Lake Michigan basin (Hall *et al.*, 1998). Based on these load calculations and land use information, estimates of loadings from unmonitored areas were made. Loadings were calculated for atrazine, deethylatrazine (DEA), and deisopropylatrazine (DIA). Tributary data used in the load estimates were gathered from samples collected from April 4, 1995 through October 30, 1995 (U.S. Geological Survey and Eisenreich, 1997). Samples were collected far enough upstream to minimize mixing of lake and tributary water. The Grand Calumet, Kalamazoo, and Pere Marquette Rivers were generally well-mixed throughout the sampling period. The Sheboygan, Menominee, Manistique, Muskegon, Grand, and St.

Joseph Rivers were generally well-mixed during the winter months and stratified with respect to temperature and conductance in summer months. The Milwaukee River, and to a lesser extent the Fox River, were found to be poorly mixed at irregular intervals throughout the sampling period. The location and identification of the USGS stations sampled can be found in Hall *et al.* (1998). Sampling was conducted by the USGS in cooperation with the Wisconsin and Michigan Departments of Natural Resources, the Wisconsin State Laboratory of Hygiene, and the University of Wisconsin Water Chemistry Program. The primary objective of the contaminant-loading data was to provide a detailed space and time tributary loading history for input into the LMMBP LM3-Atrazine model.

To reduce errors associated with the load calculations, sampling was deliberately biased toward high-flow conditions where more than 20% of samples were collected at times of discharge above the 20% exceedance, (Dolan *et al.*, 1981; Hall *et al.*, 1998). The assumption is that during the high-flow periods, most of the load is transported. Sampling for atrazine was delayed for one year due to uncertainty in selection of methods and laboratory. As a consequence of having only seven months of load data to quantify atrazine loadings, the USGS believed that the atrazine load estimates based on actual concentration and flow measurements were not as good as estimates for the other mass balance contaminants of interest that were based on 19 months of measurements. Furthermore, load error estimates for atrazine were especially poor, again due to the short sampling period.

Three to four sampling crews in three states were on call to capture storm-induced flow events (Hall, U.S. Geological Survey, personal communication, 2001). Weather was monitored 24 hours per day. Equipment was used to trigger pagers upon the onset of rising hydrographs. Sampling occurred during rising, peak, and falling hydrographs. Except for the shallow Pere Marquette and Kalamazoo Rivers, rivers were sampled at 0.2 and 0.8 of the total depth. These samples were taken at the midpoints of river panels that divided the total river flow into three visually estimated equal flow panels that were determined during discharge calibration measurements (Hall *et al.*, 1998). These six samples were composited into one sample. For the Pere Marquette and Kalamazoo Rivers, only three samples (one in each flow panel) were composited (Hall *et al.*, 1998). A total of 405 samples (including quality control samples) were collected.

River discharge was measured either by stage and discharge techniques for the Manistique, Pere Marquette, and Kalamazoo Rivers in Michigan or acoustic velocity meters for the Muskegon, Grand, and St. Joseph Rivers in Michigan; Grand Calumet River in Indiana; and Milwaukee, Sheboygan, Fox, and Menominee Rivers in Wisconsin (Hall *et al.* 1998).

2.2.4.2 Atrazine Load Estimation for Monitored Rivers Using the Stratified Beale Ratio Estimator (SBRE) Method

Concentration data are usually limited due to cost constraints; however, flow data are usually readily available at short-time intervals. Sampling for the LMMBP was focused on high-flow, high-concentration events. However, if the mean concentration from these limited samples were multiplied by the total annual discharge, the load estimate would be biased high. The reason it would be high is that the mean concentration observed would be disproportionately distorted by the number of high-flow, high-concentration samples.

The SBRE method is nearly bias-free when the data are sufficient to give acceptable precision to the load estimate. The SBRE method used by the USGS for the LMMBP can be found in Richards (1994). Another factor in the selection of the SBRE is that the method is robust over a range of data distributions. The method has been the method preferred by the International Joint Commission (IJC) for a number of years. The SBRE was used for the period April 4, 1995 through October 30, 1995 when atrazine was sampled.

For the unmonitored period, January 1, 1994 through April 3, 1995 and October 31, 1995 through December 31, 1995, a combination of Beale-derived daily loads and regression loads from the monitored period were used to adjust regression-produced daily loads from the unmonitored period (Hall, 2004). The Beale method does not provide an algorithm to

extend the loadings derived from the monitored period to an unmonitored period. An adjustment coefficient was computed by dividing the sum of Beale-model daily loads from the monitored period by the sum of the Estimator Regression Model loads for the same period. The adjustment coefficient was then multiplied by each daily load produced by the selected regression model for each of the two unmonitored periods to produce "corrected" daily loads. For example, if the Beale model was producing a sum of daily loads greater than the sum of the regression model daily loads for the monitored period, the adjustment coefficient would be greater than one and the adjustment multiplication would linearly increase each regression-daily load in each of the two unmonitored periods.

The 1995 USGS SBRE tributary loadings are depicted in Figure 2.2.5. Median river flows and median atrazine concentrations are also shown. The rivers are ordered based on the highest load on the left to the lowest load on the right. Note that although the Grand Calumet had the lowest atrazine load, it did have the fourth highest median atrazine concentration.

2.2.4.3 Atrazine Load Estimation for Unmonitored Watersheds

Hall (2004) presents material on the method used to estimate daily loading from watersheds in the Lake Michigan basin where no samples were taken for the analytes of interest. Loading estimates derived from the 11 monitored tributaries were used to predict loadings from the additional 25 unmonitored tributaries larger than 325 km^2. Unit area yields from the monitored basin were calculated as follows:

$$Unit\ Area\ Yield = I_i / A \qquad (2.2.4)$$

where

I_i = load estimate for any given day
A = area of the watershed for a monitored tributary

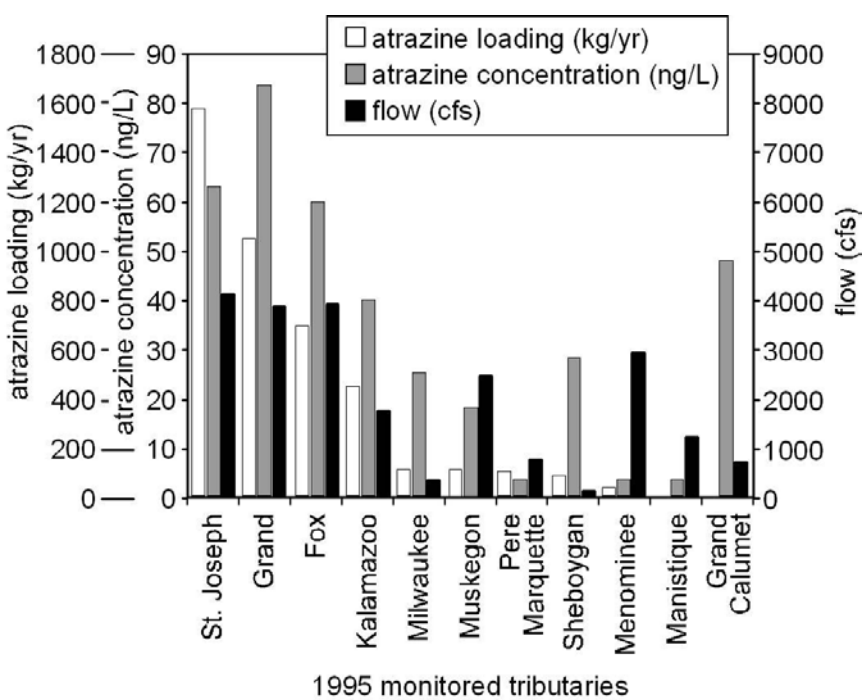

Figure 2.2.5. 1995 USGS SBRE atrazine loadings and median concentrations relative to median flow in Lake Michigan tributaries.

The USGS used Unit Area Yields from monitored watersheds that best matched unmonitored watersheds in terms of land use and nature of surficial land deposits. A GIS was used to help in the watershed classification. Once this classification was done, the areas of the 25 unmonitored watersheds were expanded to encompass smaller adjacent basins that were poorly defined in terms of land use, discharge location, and other properties. The sum of all monitored and unmonitored watershed loads were designed to represent the total loading to Lake Michigan from the entire Lake Michigan watershed.

2.2.5 Comments on Atrazine Tributary Loading Estimates

Estimates of atrazine tributary loadings to Lake Michigan for years 1994 and 1995 were made independent of the USGS estimates. These independent estimates were based on actual application of atrazine to the basin and using a literature-derived WEP of 0.6%. The following are the results:

1994 USGS:	1163 kg
1995 USGS:	1426 kg
1994 WEP-Based:	5263 kg
1995 WEP-Based:	4916 kg

The ratio of WEP-based to USGS load for 1994 is 4.5, and the ratio for 1995 is 3.4.

For a discussion on possible reasons for the discrepancy between the two load estimation techniques, see Section 5.3.3.3.1 in this report.

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PART 2

LAKE MICHIGAN MASS BALANCE PROJECT ATRAZINE LOADINGS TO LAKE MICHIGAN

Chapter 3. Estimation of Atrazine Loads in Wet Deposition (Precipitation)

2.3.1 Atmospheric Components Considered in Modeling Atrazine in Lake Michigan

Both the MICHTOX and LM2-Atrazine models utilize annualized wet deposition loadings for long-term simulations. However, LM3-Atrazine wet deposition loadings were calculated on a daily basis to capture seasonal loading variations. LM3-Atrazine was used to make predictions in lake segments on short-time scales in a fine-grid framework as a function of seasonally varying loads – both wet deposition and tributary.

Particulate deposition was not considered in the MICHTOX, LM2-Atrazine, and LM3-Atrazine models because studies have shown that atrazine deposition associated with atmospheric particulates represents a minor fraction of the total deposition of atrazine (Nations and Hallberg 1992; Siebers *et al*. 1994). In the Lake Michigan Mass Balance Project (LMMBP) (Section 1.3.2.2.2), the detection limit for atrazine associated with atmospheric particulates was relatively high. As a consequence, there was a low number of detects at land-based collection sites positioned around the lake. Attempts to measure atrazine-associated particulates over-the-lake yielded only two detects, and both of them were in the southernmost part of the lake near major atrazine sources. To make an estimate of atrazine deposition fluxes associated with particulates, one needs both reliable measurements of atrazine concentration on the particles and an estimate of the deposition rate of the particles. To calculate a rate of deposition, particle sizes are needed. Particle size fractionation was not part of the LMMBP analysis.

Some researchers have attempted to make estimates of atmospheric, particulate-associated atrazine fluxes to Lake Michigan using some assumptions about the particle sizes. Miller *et al.* (2000) roughly estimated that the load from particles for the high-loading spring months (April through June, 1994-1995), could range from 230 to 1000 kg/yr. Schottler and Eisenreich (1997) estimated that the atrazine-associated particulate load to the lake for the period 1991 to 1994 was approximately 160 kg/yr. Sweet and Harlin (1998) estimated that the 1994-1995 atrazine-associated particulate load to the lake using data from April through July to be about 220 kg/yr. Using these estimates, as well as wet deposition and tributary loadings for 1994, the relative contribution of dry particulate deposition to the total load of atrazine to the lake (wet+dry+tributary) is 2.8% to 11.4% (Miller *et al.*, 2000), 2.0% (Schottler and Eisenreich, 1997), and 2.7% for Sweet and Harlin (1998). Note that these estimates were based on particulates collected at land-based stations around the lake. However, other than the two atrazine-associated particulate detects in the southernmost part of the lake, we have no evidence that these loadings are occurring over-the-lake.

Vapor phase concentrations of atrazine were used in the models as a boundary condition; please see

Parts 4 (LM2-Atrazine) or 5 (LM3-Atrazine) for details.

2.3.2 Atrazine Wet Deposition Load Estimates Based on Measured Fluxes in the Basin

Over-the-lake wet deposition of atrazine for 1991 (Figure 2.3.1) was based on data collected from shore-based samples (Goolsby *et al.* 1993). Goolsby's study area included Midwestern and Northeastern states in a geographic rectangle defined by the states North Dakota, Kansas, Virginia, and Maine. It is interesting to note that the total amount of wet-deposited atrazine in this region is calculated to be 0.6% of the amount applied in the region. This is the same percentage used to estimate the atrazine tributary load export from the Lake Michigan watershed. Higher fluxes of atrazine to Lake Michigan are noted in the southern part of the lake compared to the northern part. This gradient is the result of higher use of the chemical in the states south and west of the lake and wind patterns.

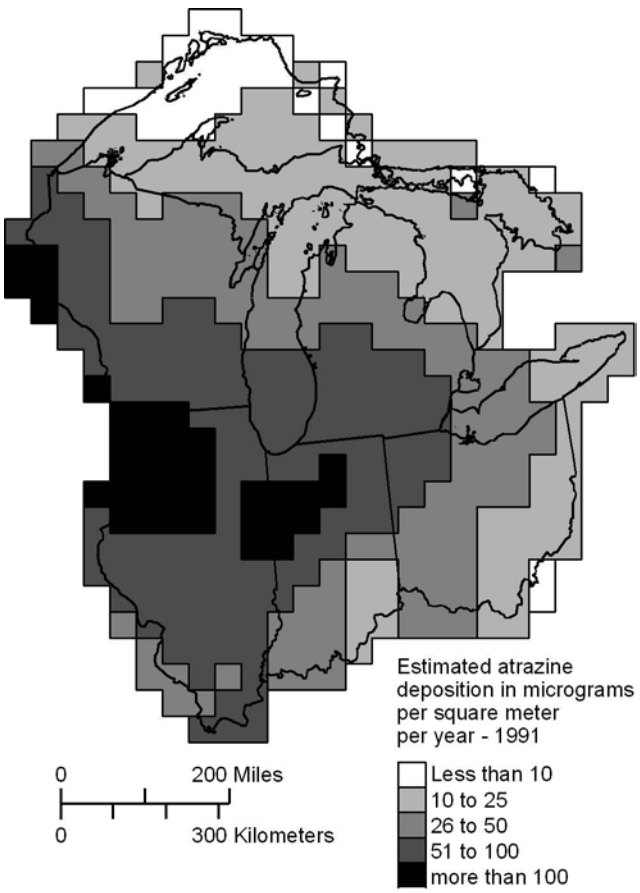

Figure 2.3.1. Wet deposition (rain and snow) of atrazine for 1991 for Midwestern United States (Figure by W.A. Battaglin, U.S. Geological Survey, 1997).

Wet deposition data for 1994 and 1995 associated with the LMMBP were received from Hornbuckle (University of Iowa, personal communication, 1999). These over-the-lake wet deposition estimates were used in all three models. Figure 2.3.2 depicts wet deposition for the month of May 1994, and again the southern region depicts higher atrazine fluxes. There is a strong seasonal trend of wet deposition loadings to the lake (Figure 2.3.3) – high loadings in the spring and early summer and very little loading during the rest of the year. Translating Hornbuckle's loadings into wet deposition fluxes over Lake Michigan and Green Bay yielded a value of 30.8 $\mu g/m^2/yr$ for 1994 and 1995. A similar calculation of flux for 1991 (Figure 2.3.1) yielded a value of 45 $\mu g/m^2/yr$.

Wet deposition to the lake other than 1991, 1994, and 1995 was estimated from total annual usage estimates in a similar manner as described for historical tributary loadings. However, instead of a "Tributary Load Ratio," a "Precipitation Load Ratio" was defined. Precipitation ratios were calculated as an average for years 1991, 1994, and 1995 as follows:

$$\textit{Precipitation Load Ratio} = (\textit{Precipitation Load to a Model Segment})/(\textit{Total Annual USA Atrazine Usage}) \quad (2.3.1)$$

For any year (y), where only total annual United States usage is known, a segment load was calculated utilizing the precipitation ratio:

$$\textit{Precipitation Load} = (\textit{Precipitation Load Ratio}) \times (\textit{Total Annual USA Usage Year } (y)) \quad (2.3.2)$$

Along with total annual usage estimates, annual atrazine wet deposition and tributary loadings for Lake Michigan and Green Bay are depicted in Figure

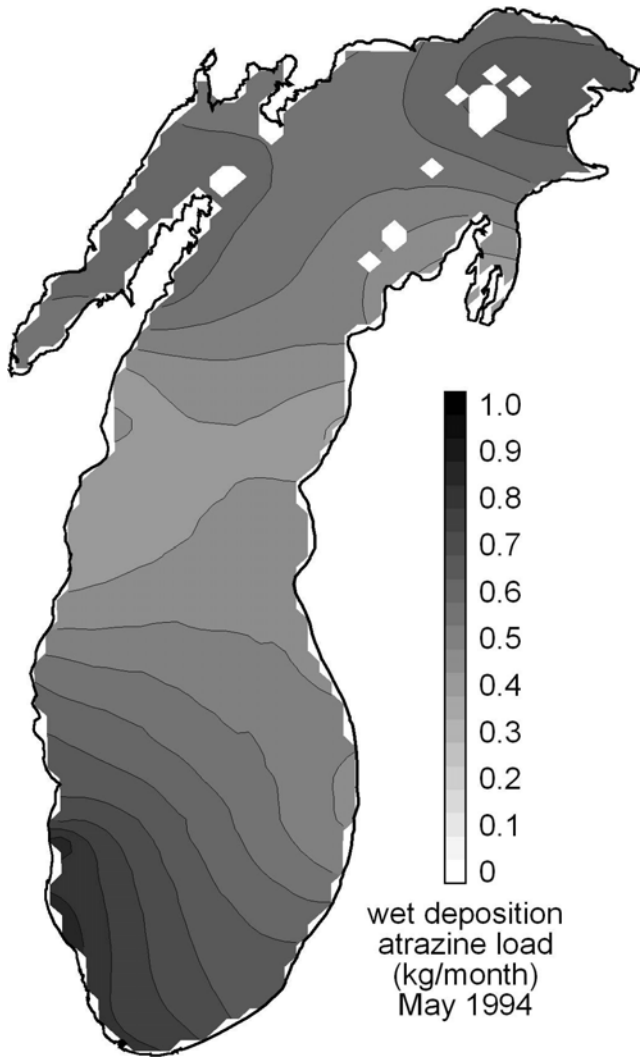

Figure 2.3.2. Gradients of atrazine in wet deposition loadings over Lake Michigan for May 1994.

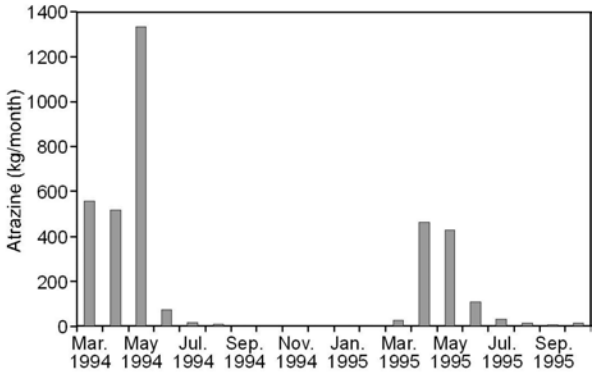

Figure 2.3.3. Seasonality of atrazine wet deposition loadings to Lake Michigan for 1994-1995.

2.3.4. The wet deposition load calculated for 1995 was very low compared to 1994 (Figures 2.3.3 and 2.3.4). It is believed that a cold and wet spring in the major corn-growing regions of the United States may explain this low estimate (see Section 1.3.2.2.3).

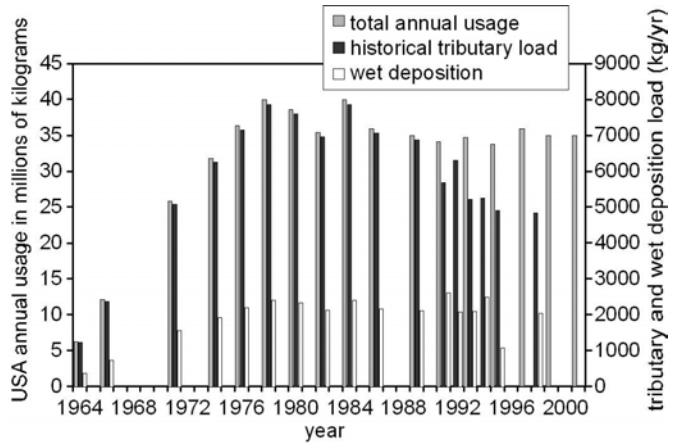

Figure 2.3.4. Total atrazine tributary loading and wet deposition loading estimates to Lake Michigan.

2.3.3 Atrazine Wet Deposition and Tributary Loads for MICHTOX and LM2-Atrazine

Both tributary and precipitation loadings for the MICHTOX and LM2-Atrazine models' surface water segments are shown in Figures 2.3.5 and 2.3.6, respectively. In MICHTOX, the southern third of the lake is identified as segment 1, the central lake region is segment 2, and the northernmost part of the lake is segment 3 (see Part 3, Figure 3.1). Note that total loadings are greater in the southern region of the lake compared to the northern region. In LM2-Atrazine, the southern third of the lake is represented by segments 1 and 2; central lake, 3 and 4; and the northern lake, 5 and 6. Segments 2, 4, and 6 are located on the eastern side of the lake. The rest of the segments are located in Green Bay. See Figure 4.1 in Part 4 for a graphic identifying segments for LM2-Atrazine. The highest load to LM2-Atrazine is in segment 2. Both MICHTOX and LM2-Atrazine perform a linear interpolation to estimate missing loads between dates that have known loads. For the whole lake, the total annual load estimates were the

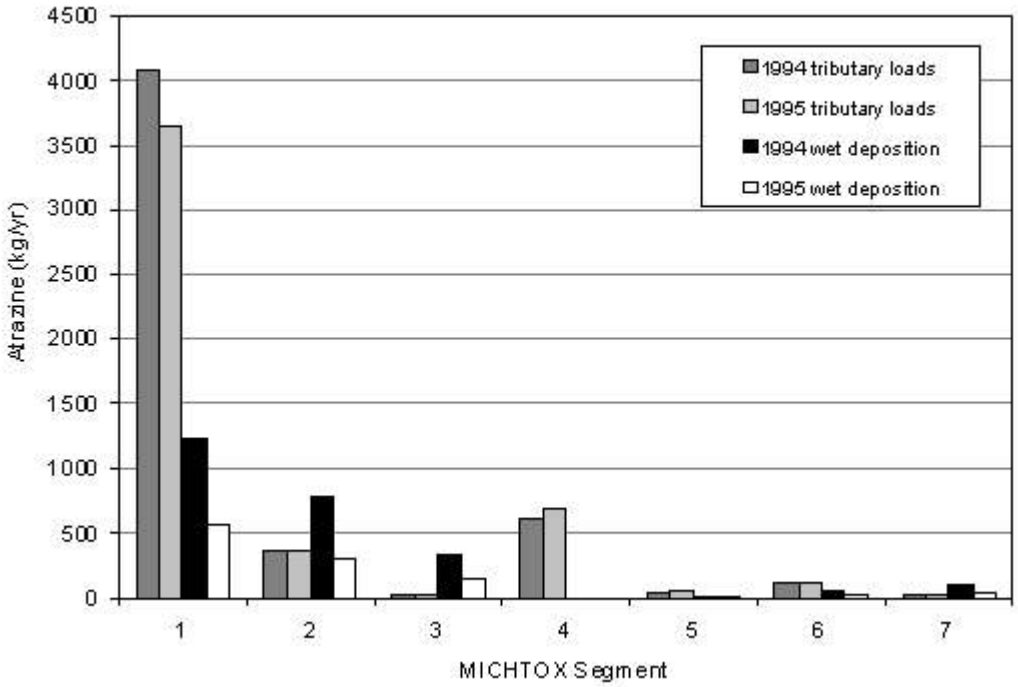

Figure 2.3.5. Tributary and wet deposition loadings to MICHTOX model segments for 1994 and 1995.

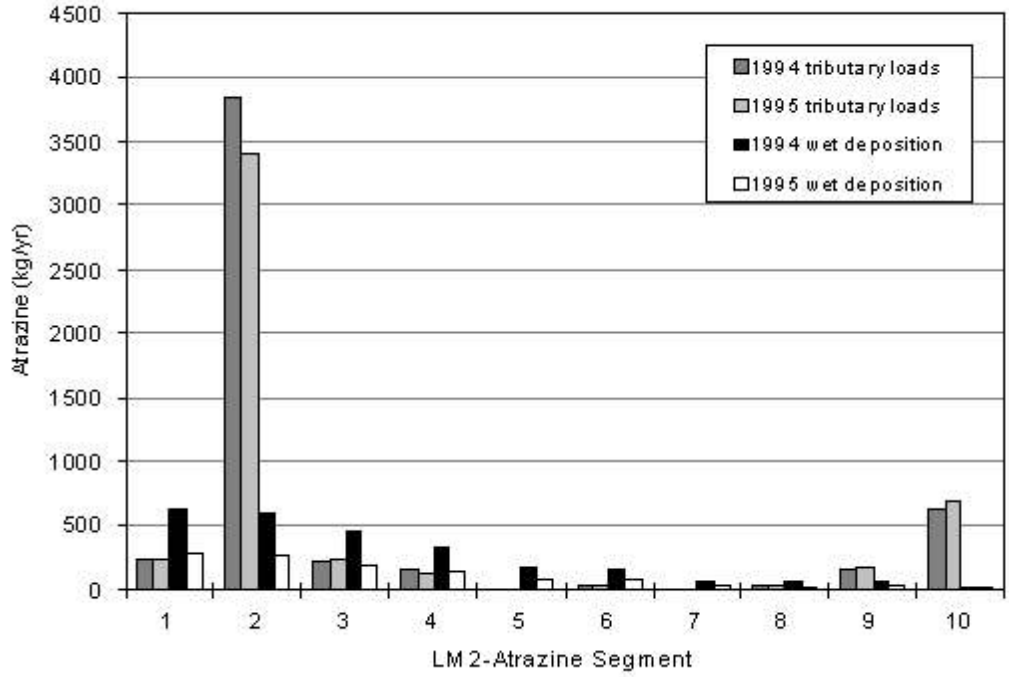

Figure 2.3.6. Tributary and wet deposition loadings to LM2-Atrazine model segments for 1994 and 1995.

same for MICHTOX and LM2-Atrazine; however, MICHTOX had seven receiving surface water segments and LM2-Atrazine had 10. See Part 5 for information on tributary loads and wet deposition estimates used in LM3-Atrazine.

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PART 3

LAKE MICHIGAN MASS BALANCE PROJECT LEVEL 1 MODEL: MICHTOX-ATRAZINE

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3.1 MICHTOX-Atrazine Executive Summary

Our coarse-segmented model, MICHTOX, was run in a hindcast and forecast mode under various load modification scenarios. A calibration run based on average boundary conditions using historical loadings of atrazine to Lake Michigan suggests that approximately 1% of the atrazine in the lake decays each year. In the forecasts of alternate futures, eliminating all loadings to the lake resulted in the largest decline in model predictions. A total loading reduction of approximately 37%, if implemented on January 1, 2005, would have been needed in order to prevent atrazine concentrations from increasing further than above those that were observed in the lake on January 1, 2005.

3.2 MICHTOX-Atrazine Recommendations

For long-term forecasts, future modeling efforts should utilize LM2-Atrazine as a model because it is more highly resolved and has advective and dispersive components that were derived from a hydrodynamic model (see Part 4). The hydrodynamic model components can be considered to best represent “average” lake conditions because the various hydrodynamic forcing functions were considered to be average (see Part 1, Chapter 4).

3.3 Model Description

3.3.1 Model Overview

For calibration purposes, the MICHTOX mass balance model (Endicott *et al.*, 2005) was used in a hindcast mode to simulate atrazine concentrations in Lake Michigan and Green Bay in response to mass loadings to these systems from the time of introduction in the early 1960s to 1995. The calibrated model was then used in a forecast mode to predict lake-wide concentrations in Lake Michigan as a function of various loading scenarios.

MICHTOX was adapted from the general water quality model WASP4 (Ambrose *et al.*, 1988). The model solves mass balance equations based on a finite volume spatial discretization (Thomann and

Mueller, 1987) and Euler time integration. The MICHTOX model framework is capable of incorporating a full range of transport and fate processes such as advection, dispersion, particle settling, sediment resuspension, sediment burial, transport in sediment pore water, partitioning to particles, chemical reaction, volatilization, and absorption.

3.3.2 MICHTOX Model Segmentation and Circulation

The segmentation schematic for Lake Michigan and Green Bay is depicted in Figure 3.1. Lake Michigan and Green Bay have nine water segments. Surface segments 1 (southern lake), 2 (central lake), and 3 (northern lake) cover the entire main lake. Segments 5 (southern bay), 6 (central bay), and 7 (northern bay) cover Green Bay. Hypolimnetic water segments in the main lake are numbered 8 (southern lake), 9 (central lake), and 10 (northern lake). Segment 4 is a very small segment located in the lower Fox River. During a period of approximately 100 days in the summer, flow and exchange across the Straits of Mackinac occurs in two discrete layers between the surface water (segment 3) and Lake Huron and between the deep hypolimnetic water (segment 10) and water that primarily originates from Lake Superior (Quinn, 1977) mixed with water from Lake Huron. During this period of stratification, surface layer flow (segment 3) is from Lake Michigan to Lake Huron, and a deeper return flow to Lake Michigan is observed. It has been observed that Lake Superior water discharging from the St. Marys River travels in a persistent westerly direction during stratification and constitutes a significant component of the return flow to Lake Michigan (Ayers *et al.,* 1956; Schelske *et al.* 1976; Saylor, J., National Oceanographic and Atmospheric Administration, personal communication, 1998). During the unstratified period, all of the flow is from Lake Michigan to Lake Huron.

Two-layered flow has been observed at the mouth of Green Bay during thermal stratification (Martin *et al.,* 1995); however, this structured flow process was not incorporated in the MICHTOX model framework. MICHTOX incorporates the flows between Green Bay and Lake Michigan as net flows.

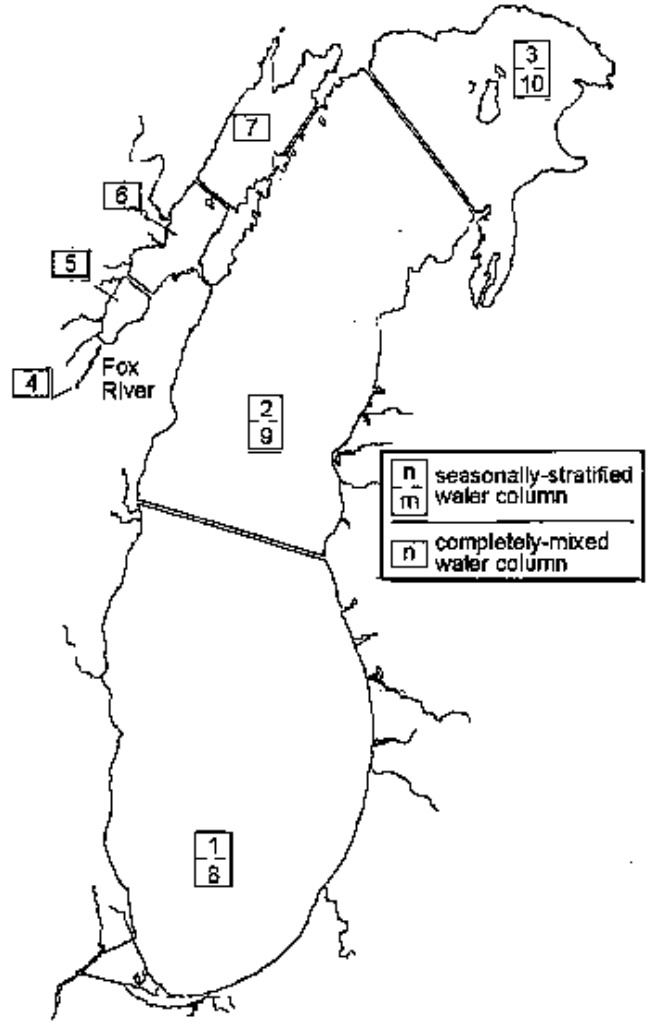

Figure 3.1. MICHTOX model segmentation.

The MICHTOX model has two water column layers for Lake Michigan to simulate the effects of summer stratification of the lake. Also, the model consists of just three horizontal compartments in the main lake. This low spatial resolution was considered adequate to address open-lake concentrations. Water column concentration profiles of atrazine at 10 stations, representing four to 10 depths per station, showed no vertical gradients during lake stratification for the years 1991 and 1992 (Schottler and Eisenreich, 1997) and 1994-1995 (Brent *et al.*, 2001). Furthermore, they reported that analysis of data from their 10 lake stations that covered a central north-south axis and an east-west axis showed no horizontal gradients in atrazine concentrations in the lake.

MICHTOX exchange coefficients were taken from the literature. Vertical exchange coefficients, which quantify the extent of mixing between epilimnetic and hypolimnetic segments in the main lake, were taken from the Lake Michigan WASP eutrophication model, MICH1 (Rodgers and Salisbury, 1981). Horizontal exchange coefficients in Green Bay were calibrated to reproduce chloride gradients. In the main lake, however, horizontal exchange coefficients were taken from work by Thomann *et al*. (1979) on Lake Ontario.

Flows in the lake were based on the whole-lake water balance by Quinn (1977), which provided monthly average changes in storage, tributary flow, outflow, diversion, precipitation, and evaporation. The hydraulic residence time (volume/outflow) for the main lake was estimated to be 62 years (Quinn, 1992).

3.4 MICHTOX Model Application to Lake Michigan

3.4.1 Screening Model Application

A screening-level model of MICHTOX was applied before Lake Michigan Mass Balance Project (LMMBP) loadings were available (Rygwelski *et al.,* 1999). This early MICHTOX application assumed that volatilization was negligible due to a very small Henry's law constant of 8.1×10^{-8} (U.S. Department of Agriculture, 2001) and that the chemical could be modeled as a conservative substance.

For this screening model, tributary loads were estimated based on atrazine applications to the basin in 1992 and 1993 using algorithms identified in Equation 2.2.1. The watershed export percentage (WEP) used was 0.6% (see Table 2.2.2). In order to predict loadings for years when application data were not available, the loads estimated for 1992 and 1993 were divided by estimates of total annual United States usage of atrazine using Equation 2.2.2 (no annual United States usage estimate was available for 1992, so an estimate for that year was calculated as a mean of United States usage reported for 1991 and 1993). A mean of these two ratios was assumed to be constant over the entire historical record of atrazine usage in the basin. For years where only total annual usage was available, an estimate of loadings could be determined by multiplying the mean load ratio by total annual usage.

Loadings of wet deposition to the lake were obtained for 1991 (Goolsby *et al.*, 1993). These wet deposition loads were based on actual measurements of atrazine in rain and snow. In a similar manner as was calculated for tributary loads, the load from Goolsby was divided by a mean of the total annual United States usage of atrazine for the years 1992 and 1993. Usage in the United States between 1989 through 1995 was relatively constant so errors in substituting a mean of 1992 and 1993 usage for 1991 were believed to be small. In a manner similar to the mean Tributary Load Ratio, a mean atmospheric load ratio was used to estimate historical wet deposition to the lake. See Figure 3.2 for both tributary and precipitation atrazine loads.

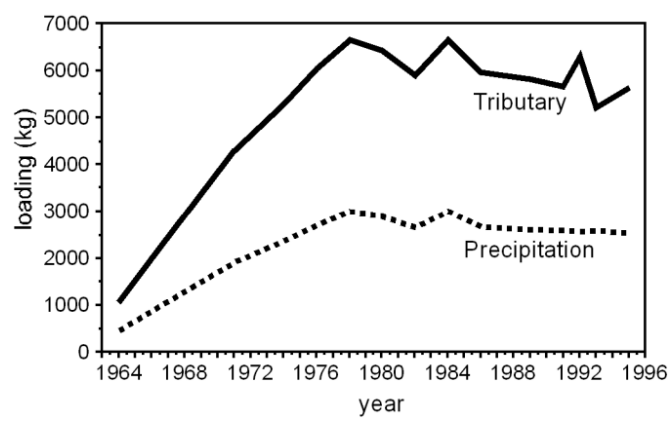

Figure 3.2. Total annual estimated tributary and precipitation loadings of atrazine to Lake Michigan.

Using the load history and assuming that atrazine decay is zero with negligible volatilization, a model hindcast run starting in 1964 yielded a good fit with lake data (see Figure 3.3). The results shown in the figure are from the main lake only and does not include Green Bay. The initial conditions in the lake model were set to an atrazine concentration of zero. No calibration of the model was needed. Also depicted are the effects of using the upper and lower 95% confidence intervals on the 0.6% WEP reported in the literature for moderate textured soils (see Part 2, Chapter 2). As a sensitivity test, a hypothetical 0.05 per year overall decay constant was incorporated into the model. The model is very

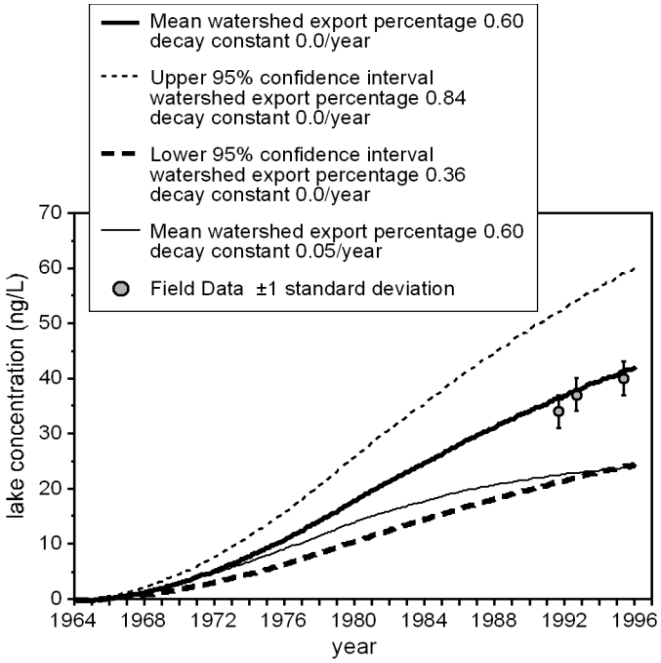

Figure 3.3. A comparison of MICHTOX – Predicted atrazine concentrations in Lake Michigan to averaged Lake Michigan data for the years 1991, 1992, and 1995 are depicted. Field data for 1991 and 1992 were obtained from the literature (Schottler and Eisenreich, 1997) and data for 1995 are LMMBP data.

sensitive to this decay as shown in Figure 3.3. "Decay" as used in this paper is internal decay likely due to the combined effects of abiotic and biotic transformation of atrazine to degradation products. Considering that the model required no calibration and relied mostly on data from the literature, it performed remarkably well.

3.4.2 Enhanced Screening Model Application

As additional county-level atrazine application data in the basin and total United States usage estimates became available, MICHTOX modeling in Lake Michigan continued to develop. In the earlier screening model application, only two years of county-level atrazine application data were available. For the enhanced screening-level model, seven years of application data were available and used. Also, due to label changes that lowered application amounts and established planting setbacks from water bodies in 1990 and 1992, a decision was made to use two Tributary Load Ratios in order to address atrazine application practices for pre- and post-label changes. New data from the LMMBP also became available to modelers. With these additional data, loading ratios for both the tributaries and wet deposition were updated (see Part 2, Chapters 2 and 3). The model was calibrated by determining a total decay that would yield a best fit of the model to observations in the lake. Also, several forecasting scenarios were run with the model. The efforts of this additional modeling are described in the following sections of this part.

3.4.2.1 Field Data

See Part 1, Chapter 3 for atrazine data obtained from lake, tributaries, and atmospheric components samples.

3.4.2.2 Model Assumptions and Calibration Procedures

Due to atrazine's physical and chemical properties (Part 1, Chapters 1 and 3), processes modeled included only advection, dispersion, and reaction (decay).

Model processes involving sediments and particulates in the water column were not included in the MICHTOX model runs because atrazine is primarily in the dissolved state in surface waters; therefore, any processes that involve sediment or suspended particle interactions are of minor significance (Section 1.2.2).

A literature review of atrazine degradation processes in surface freshwater presented in Part 1, Chapter 2 suggests that degradation is hindered in freshwater such as in Lake Michigan where the water is cold, has low solids concentrations with low dissolved organic carbon, has a high pH, and has low concentrations of nitrate ions. Degradation of atrazine is known to occur through either biotic or abiotic processes in some environmental compartments. Given the lack of any Lake Michigan-specific kinetic information on any of these processes, the approach taken in MICHTOX was to estimate the loading history of atrazine to the lake and find an overall first-order loss rate constant to fit the model to observations of atrazine in the lake

water. Loadings were not part of the calibration procedure. Considerable effort was expended to ensure that loadings were fairly represented in the model (Part 2, Chapters 2 and 3).

Due to a very small Henry's law constant, volatilization and absorption were not simulated.

3.4.2.3 Tributary Loadings

It was assumed that a WEP of 0.6% derived from the literature for fine/moderate textured soils adequately described the overall WEP of the Lake Michigan watershed. This WEP, along with historical annual atrazine usage in the United States was used to calculate atrazine loadings from the tributaries to the lake. For a complete discussion on the WEP method used to estimate MICHTOX loadings, please see Part 2, Chapter 2.

Utilizing flow and concentration data, the Stratified Beale Ratio Estimator (SBRE) method was used to estimate tributary loads in the 11 monitored tributaries during the LMMBP. Also, estimates of loads from the unmonitored watersheds were made. However, loads were apparently missed and therefore MICHTOX tributary loads were only based on WEP, county-level application data, and total United States annual usage records. See Section 5.3.3.3.1 for a discussion of this topic.

3.4.2.4 Atmospheric Loadings

Loading estimates of wet deposition to Lake Michigan and Green Bay were made for each of the top surface water segments. These loadings were estimated for MICHTOX per discussion in Part 2, Chapter 3.

3.4.2.5 Model Confirmation

In 2005, atrazine water samples were collected in Lake Michigan for the purpose of confirming the model predictions. However, as of this printing, these analyses were not available.

3.4.2.6 Model Application (Scenarios)

The calibration of the model was undertaken using three scenarios (1, 2, and 3) that included lower boundary conditions, upper boundary conditions, and a most likely or average boundary condition scenario, respectively. All of these model runs started on January 1, 1963. The model was calibrated by finding an appropriate internal decay until the model output best matched the observed atrazine concentration in the lake for samples taken in 1991, 1992, 1994, and 1995.

The scenarios 4 through 7 are referred to as load reduction scenarios. These are not necessarily management scenarios but can give managers insight as to which loads are important in the model and environment for the purpose of predicting concentrations of atrazine in the lake. It is believed that they bound the entire range of potential loads and provide some specific load scenarios within the range. Scenario 3 was used to simulate conditions from January 1, 1996 through December 31, 2004 for scenarios 4 through 7 described below. When December 31, 2004 is reached, each of the load reduction scenarios 4 through 7 began on January 1, 2005 and were run for a period of 50 years.

The Lake Superior boundary condition was assumed linear during the period modeled (0 ng/L at the beginning of year 1963 and 3.5 ng/L at 1994) and likewise for the Lake Huron boundary condition (0 ng/L at the beginning of year 1963 and 23 ng/L at 1992). The boundary conditions were assumed to be zero in 1963 because this was the year when the herbicide was first introduced to the basin. Lake Superior and Lake Huron atrazine concentrations for the years 1993 and 1992, respectively, were based on measurements of atrazine in these lakes (Schottler and Eisenreich, 1994). While the Lake Superior flow component of the return flow to Lake Michigan is primarily characteristic of concentrations of atrazine in Lake Superior, the actual concentration is probably somewhere between Lake Superior and Lake Michigan due to some mixing (see section 3.3.2).

1. **Calibration Based on Upper Estimate of Boundary Conditions** – The summer inflow concentration at the Straits of Mackinac was assumed to be 100% Lake Huron water. Lake Huron water started at 0 ng/L and was assumed to linearly rise to 23 ng/L as observed in 1995 (Station 54) and then held constant at that level for the remainder of the simulation. Tributary loading projections were set equal to an

averageof loadings for 1995 and 1998, but prior to that time, the historical loading estimates were used. Wet deposition projections were set equal to an average of loads for 1978 through 1998. Wet deposition loadings before that were based on historical load estimates. The model was calibrated by adjusting the overall internal decay to best match whole-lake volume-weighted average concentration.

2. **Calibration Based on Lower Estimate of Boundary Conditions** – The summer inflow concentration at the Straits of Mackinac was assumed to be 100% Lake Superior water. Lake Superior was assumed to begin with an atrazine concentration of 0 ng/L, was then assumed to linearly rise to 3.5 ng/L as observed in 1994 (Schottler and Eisenreich, 1997), and was then held constant at that level for the remainder of the simulation. Tributary loading projections were set equal to an average of loadings for 1995 and 1998, but prior to that time, the loading history estimates were used. Wet deposition projections were set equal to an average of loads for 1978 through 1998. Wet deposition loadings before that time were based on historical load estimates. The model was calibrated by adjusting the overall internal decay to best match whole-lake volume-weighted average concentration.

3. **Calibration Based on "Average" Boundary Conditions** – The inflow concentration at the Straits of Mackinac was assumed to be 50% Lake Superior and 50% Lake Huron water. This mix of water was assumed to begin with an atrazine concentration of 0 ng/L, was assumed to linearly rise to 13.25 or [(3.5+23)/2] ng/L in 1995, and was then held constant at that level for the remainder of the simulation. Tributary loading projections were set equal to an average of loadings for 1995 and 1998, but prior to that time, loading history estimates were used. Wet deposition projections were set equal to an average of loads for 1978 through 1998. Wet deposition loadings before that were based on historical load estimates. The model was calibrated by adjusting the overall internal decay to best match whole-lake volume-weighted average atrazine concentration.

4. **Virtual Elimination (Lower Bound on Model Prediction)** – This scenario simulated a 100% reduction of tributary and atmospheric loads. For the projections, the Lake Huron/Superior boundary conditions were set equal to zero. This scenario was run using scenario 3 for predictions leading up to the date when the virtual elimination scenario was to take place.

5. **No Tributary Loads** – This scenario simulated a 100% reduction of tributary loadings. Wet deposition loads were set equal to an average of loads for 1978 through 1998. This scenario was run using scenario 3 for predictions leading up to the date when the 100% tributary load reduction scenario began.

6. **No Wet Atmospheric Deposition Loadings** – Tributary loads were set equal to an average of loadings for 1995 and 1998. Atmospheric wet deposition loadings were decreased by 100%. This scenario was run using scenario 3 for predictions leading up to the date when the 100% atmospheric load reduction scenario began.

7. **No Further Degradation of Lake Water Quality** – A total load (tributary and wet deposition) was determined such that no further increase in lake-wide volume-weighted concentration was observed starting in January 1, 2005. Up through December 31, 2004, scenario 3 was used.

3.4.2.7 Discussion of Results

Total internal degradation of atrazine in the water (k_d) determined by model calibration was low in all scenarios where evaluated (see Figures 3.4 and 3.5). These rates of decay for scenarios 1, 2, and 3 were 0.0125/yr, 0.008/yr, and 0.01/yr, respectively. For the calibration based on average boundary conditions, MICHTOX predicts that approximately 1% of the atrazine in the lake decays each year due to some combination of abiotic and biotic decay in the lake.

Decay can be related to the half-life of the chemical in the lake by the following:

$$Half-Life = t_{1/2} = (\ln 2)/k_d \qquad (3.1)$$

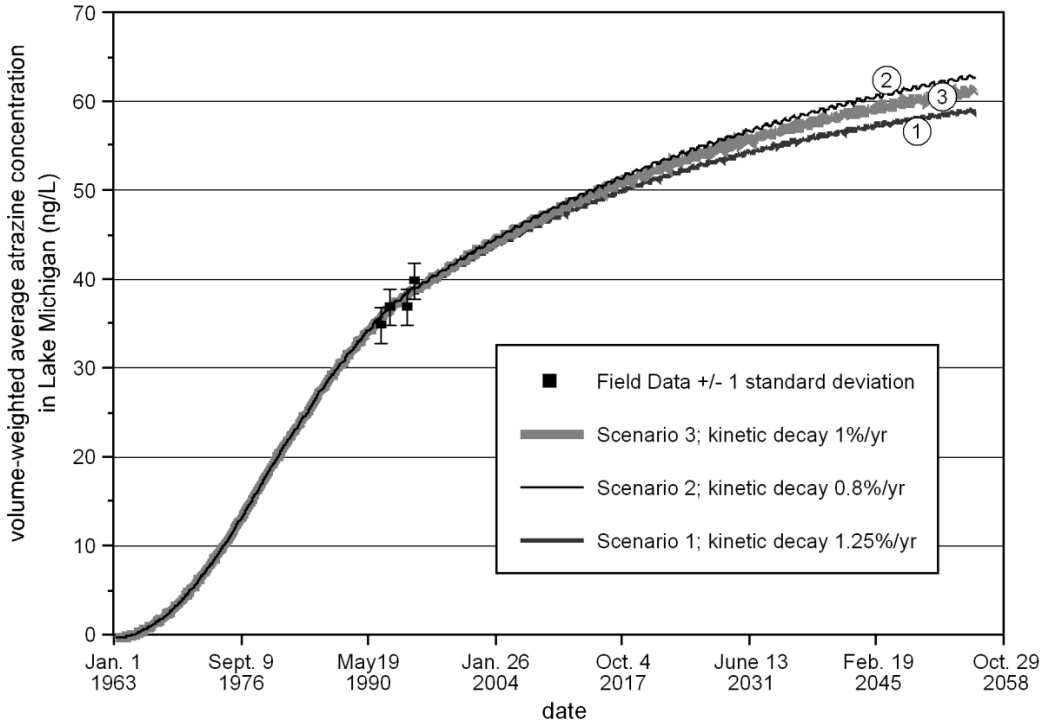

Figure 3.4. Lake Michigan (open-lake) forecast scenarios: 1 – upper estimate of boundary condition, 2 – lower estimate of boundary condition, and 3 – estimate of average boundary condition.

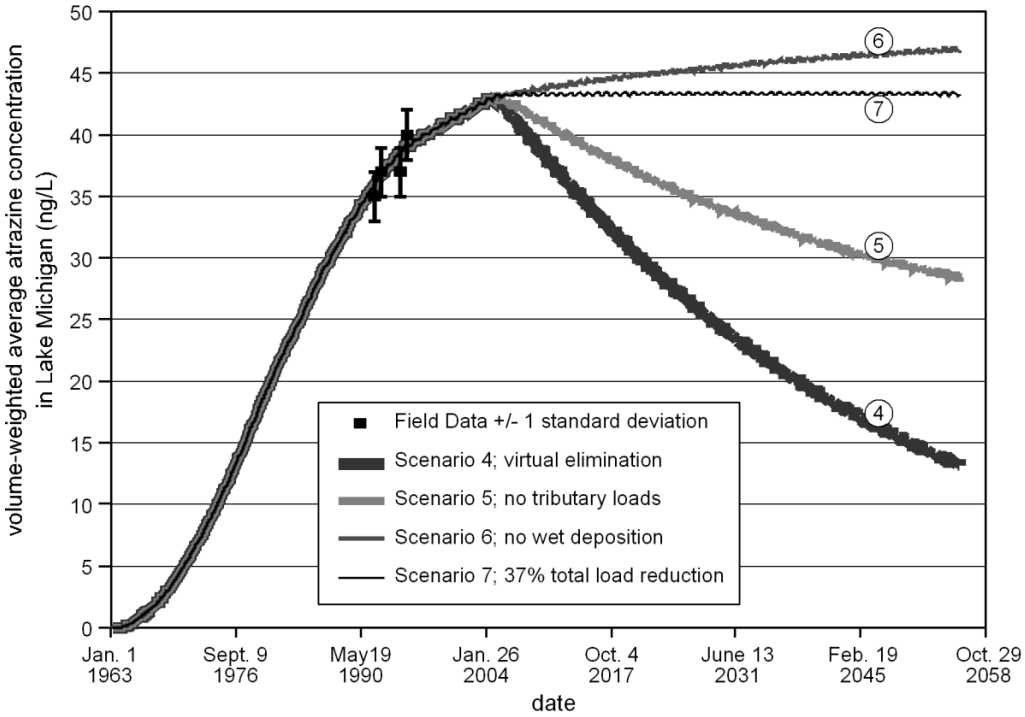

Figure 3.5. Lake Michigan (open-lake) hindcast and scenario forecasts: 4 – virtual elimination of all loadings and 0.0 ng/L atrazine at the Straits of Mackinac boundary, 5 – no tributary loads, 6 – no wet deposition, 7 – no further degradation of lake water quality.

Assuming that scenario 3 captures typical conditions, then the 1% internal decay associated with this scenario represents a half-life of the chemical in the lake of 69.3 years. In scenario 3, the water at the Straits of Mackinac was assumed to be half Lake Superior water and half Lake Huron water and is believed to be a fair assessment of the conditions during summer stratification. It is intuitive that the decay rate associated with scenario 1 that has the highest boundary condition concentrations of atrazine (assumed to be all Lake Huron water) is the one with the highest decay rate because higher boundary concentrations will mean that more atrazine is transported into the lake at the Straits of Mackinac. This higher loading will result in a higher decay needed in the modeling calibration exercise in order for model output to match observations. The opposite argument is true for the scenario where the boundary condition at the Straits of Mackinac is based solely on the lower concentrations of atrazine from Lake Superior.

In the forecasts of alternate futures (Figure 3.5), eliminating all loadings to the lake resulted in the largest atrazine decline in model predictions. A total loading reduction of approximately 37%, if implemented on January 1, 2005, would be needed in order to prevent atrazine concentrations from increasing higher than what was estimated in the lake on January 1, 2005. If only the atmospheric loadings ceased (scenario 6), concentrations would continue to increase. However, if only the tributary loadings ceased (scenario 5), concentrations in the lake would decline relative to scenario 3 predictions.

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PART 4

LAKE MICHIGAN MASS BALANCE PROJECT LEVEL 2 MODEL: LM2-ATRAZINE

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4.1 LM2-Atrazine Executive Summary

LM-2 Atrazine was run in a hindcast and forecast mode under various load and modified boundary condition scenarios. A calibration run, based on average boundary conditions using historical loadings of atrazine to Lake Michigan, suggests that only 0.9% of the atrazine in the lake decays each year. Net volatilization of atrazine is negligible. Tributaries, transporting the atrazine run-off load from farm fields, contribute most of the atrazine load to Lake Michigan. In the forecasts of alternate futures, eliminating all loadings to the lake resulted in the largest decline in model predictions. A total load reduction of approximately 35%, if implemented on January 1, 2005, would have been needed in order to prevent atrazine concentrations from increasing above those that were estimated in the lake on January 1, 2005.

4.2 LM2-Atrazine Recommendations

Due to its fast run-time speed, LM2-Atrazine can be used to perform long-term model forecasts of lake concentrations. As additional loading data become available, the updated loading history can easily be added to existing model input files. For additional model confirmation purposes, it is recommended that the model predictions be compared to data from lake samples that were collected in 2005 when these data become available.

4.3 Model Description

4.3.1 Model Overview

As one of the models in the Lake Michigan Mass Balance Project (LMMBP), LM2-Toxic was specifically developed to simulate the transport and fate of hydrophobic toxic chemicals, such as polychlorinated biphenyl (PCB) congeners, in both

the water and sediment of Lake Michigan (Zhang, 2006). LM2-Toxic is a descendant of the WASP4 water quality modeling framework (Ambrose *et al*., 1988). The model solves mass balance equations based on a finite volume spatial discretization (Thomann and Mueller, 1987) and Euler time integration. Compared to WASP4, LM2-Toxic has an updated air-water exchange formulation that includes a Henry's law temperature-corrected coefficient as described by Bamford *et al*. (1999); water phase mass transfer coefficient per Wanninkhoff *et al*. (1991); and the air phase mass transfer coefficient by Schwarzenbach *et al*. (1993). The LM2-Toxic model is capable of incorporating a full range of transport and fate processes such as advection, dispersion, particle settling, sediment resuspension, sediment burial, transport in sediment pore water, partitioning to particles in the water column and sediment, reaction, volatilization, and gas absorption.

The LM2-Atrazine model is identical to LM2-Toxic except for differences in the volatilization algorithms. In LM2-Atrazine, the algorithm for calculating the temperature-dependent Henry's law coefficient follows that of Scholtz *et al*. (1999) and Miller (1999). The dimensionless value for the Henry's law constant was set to 8.1×10^{-8} (U.S. Department of Agriculture, 2001). The water and air phase mass transfer coefficients were that of the O'Connor "long form" and O'Connor, respectively (O'Connor, 1983). The volatilization algorithm differences between LM2-Toxic and LM2-Atrazine would not be expected to have a significant impact on atrazine model predictions because of the low value of the Henry's law constant for atrazine. As a non-hydrophobic chemical, atrazine was not associated with particulates in LM2-Atrazine. Therefore, processes such as resuspension, settling, burial in sediment, transport in sediment pore water, and partitioning to solids in the water column and sediment were not operative. Processes such as advection, dispersion, reaction, volatilization, and gas absorption were active. For information on the physical and chemical properties of atrazine, see Part 1, Chapter 2.

In a manner similar to MICHTOX (see Part 3), LM2-Atrazine was used in a hindcast mode to simulate atrazine concentrations in Lake Michigan and Green Bay in response to mass loadings to those systems from the time of introduction in 1964 up to 1995. The calibrated model was then used in a forecast mode to predict lake-wide atrazine concentrations in Lake Michigan as a function of various loading scenarios.

4.3.2 LM2-Atrazine Model Segmentation and Circulation

Compared to MICHTOX (Level 1 contaminant transport and fate model developed for Lake Michigan) segmentation (Figure 1.5.1), the LM2-Atrazine model has a finer resolution (Figure 4.1). Most water column segments in the LM2-Atrazine model segmentation schematic share the same or portions of the segment boundaries used in the MICHTOX atrazine model. The spatial segmentation for the LM2-Atrazine model was developed from digitized bathymetric (5 km x 5 km grid) and shoreline data for Lake Michigan provided by Dr. David Schwab, National Oceanic and Atmospheric Administration (NOAA) (Schwab and Beletsky, 1998). The lake, including Green Bay, was divided into 10 horizontal columns, five water column layers, and one surficial sediment layer. A detailed spatial and cross sectional display of the water segments for LM2-Atrazine is illustrated in Figure 4.1. There are 41 segments in total. Segments 1-10 are surface water segments with an interface with the atmosphere. The rest of the segments lie below these surface segments.

Water balance is one of the major components in a traditional water quality modeling framework. Water movement directly controls the transport of solids and chemicals in dissolved and particulate phases in a water system. In terms of LM2-Atrazine model inputs, the data in the transport fields such as advective flows and dispersive exchanges, or mixing, were used to describe the water balance in the model. The components and their sources used in LM2-Atrazine model transport fields are listed below:

1. Bi-direction horizontal advective flows (provided by David Schwab, NOAA; originally based on Schwab and Beletsky (1998).

2. Net vertical advective flows (provided by David Schwab, NOAA; originally based on Schwab and Beletsky (1998).

3. Tributary flows and bi-directional flows across the Straits of Mackinac (Endicott *et al.*, 2005; Quinn, 1977).

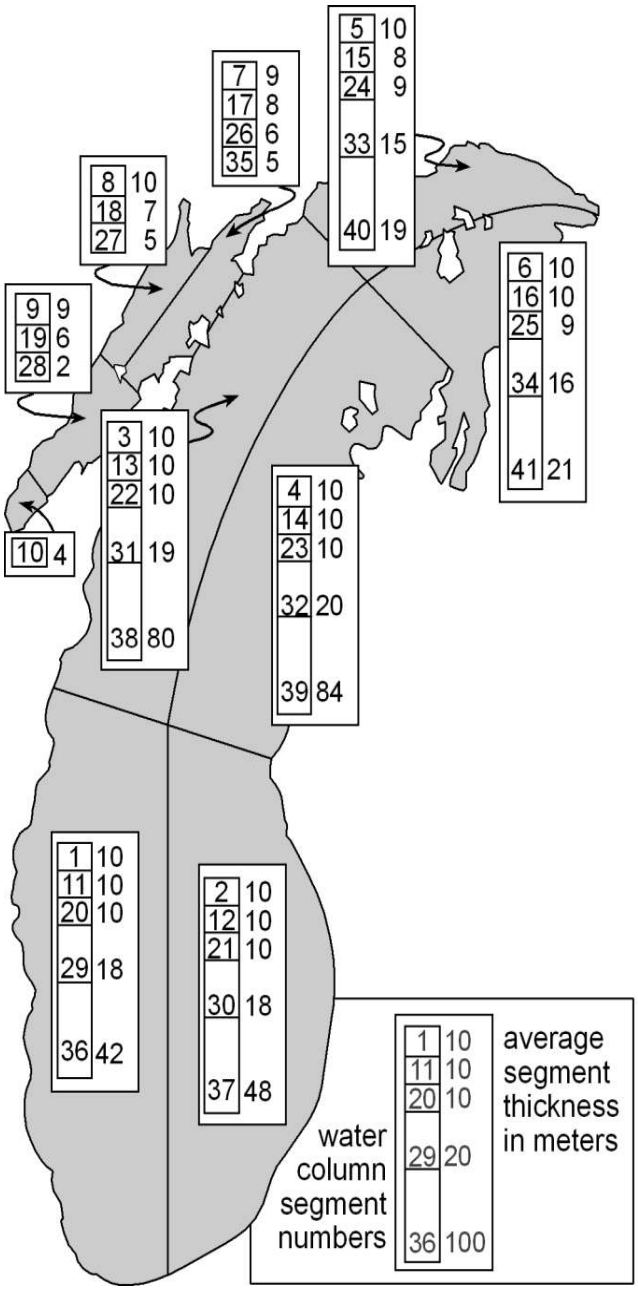

Figure 4.1. Water column segmentation for LM2-Atrazine.

4. Water balancing flows.

5. Vertical dispersion coefficients.

Components such as precipitation, evaporation, and groundwater infiltration were not considered in the water transport fields used in the LM2-Atrazine model.

Correct water circulation is essential for the accuracy of outputs from the LM2-Atrazine model. The Princeton Ocean Model (POM) has been demonstrated to accurately simulate water movement for a given large water body (Schwab and Beletsky, 1997; Blumberg and Mellor, 1987). Using an extensively tested version of POM for the Great Lakes (POMGL), transport fields were generated for Lake Michigan at different spatial and temporal resolutions for use in a series of mass balance models adapted for LMMBP (Schwab and Beletsky, 1998). The hydrodynamic model for Lake Michigan had 20 vertical layers and a uniform horizontal grid size of 5 km x 5 km (Schwab and Beletsky, 1998). Because the LM2-Atrazine model segmentation was constructed based on the 5 x 5 km^2 grid used in the POMGL for Lake Michigan, the hydrodynamic model results were relatively easily aggregated to the resolution used in LM2-Atrazine (Schwab and Beletsky, 1998). The aggregated horizontal bi-direction flows at each interface provided a good approximation of horizontal advective and dispersive transport components at the interface. The advantage of using bi-directional flows at an interface was that it bypassed the tedious and necessary horizontal dispersion coefficient calibration procedure required when only net flow is available at the interface.

The vertical transport field was calculated in the form of net vertical flow [provided by David Schwab, NOAA and originally based on Schwab and Beletsky (1998)]. Therefore, vertical exchange coefficients were calculated and calibrated to define the vertical mixing process between vertically adjacent segments. A summer period of strong stratification and a non-stratified period of intense vertical mixing are important limnological features of the Great Lakes (Chapra and Reckhow, 1983; Thomann and Mueller, 1987). Therefore, determining the dynamics of vertical mixing was considered an important model development task for the LMMBP.

A thermal balance model was constructed to calibrate the vertical exchange coefficients at the interfaces (Zhang *et al*., 1998, 2000). The coefficients were calibrated using 250 observed vertical temperature profiles collected at 40 stations in Lake Michigan during the 1994-1995 LMMBP period (Zhang, 2006).

Water balancing flow was another advective component added into the water transport field for LM2-Atrazine. The aggregated advective flows provided by NOAA were not balanced in individual segments over the two-year LMMBP period. However, the total water mass was perfectly balanced on a whole - lake basis. Over the two-year LMMBP period, some segments lost or gained a certain amount of water. This problem could be very significant for long-term simulations for the LM2-Atrazine model because the model simulation stops once the volume of a segment reaches zero. To counter the amount lost or gained in each segment, a water balancing flow was introduced to keep the volume of water unchanged in each segment at any time during the simulation. The balancing flows were generated based on the aggregated advective flows [provided by David Schwab, NOAA, and originally based on Schwab and Beletsky (1998)], original volume of each segment, and the general water circulation patterns during the LMMBP period.

Tributary flows and flows through the Straits of Mackinac were based on MICHTOX model inputs (Endicott *et al*., 2005), the literature (Quinn, 1977), and water circulation patterns during the LMMBP period [provided by David Schwab, NOAA, and originally based on Schwab and Beletsky (1998)]. During a period of approximately 100 days in the summer, flow and exchange across the Straits of Mackinac occurs in two discrete layers formed by the surface water and deep, cold, hypolimnetic water. During this period of stratification, surface layer flow is from Lake Michigan to Lake Huron, and a deeper return flow to Lake Michigan is observed. It has been observed that Lake Superior water discharging from the St. Marys River travels in a persistent westerly direction during stratification and constitutes a significant component of the return flow to Lake Michigan (Ayers *et al.,* 1956; Schelske *et al.*, 1976; J. Saylor, NOAA, personal communication, 1998). The remainder of this return flow to Lake Michigan is Lake Huron water.

Hydraulic residence times (volume/outflow) for the main lake has been estimated to be 62 years (Quinn, 1992).

After vertical exchange coefficients were calibrated, a conservative constituent, chloride, was simulated using the LM2 model configuration to verify that the water transport components described above were a good representation of the overall water transport field for atrazine. The chloride model was run just once without adjusting any parameters or coefficients. The model results agreed very well with the observations during the LMMBP period (Zhang, 2006).

Water column concentration profiles of atrazine at 10 open-lake stations representing four to 10 depths per station showed no vertical gradients during lake stratification for the years 1991-1992 (Schottler and Eisenreich, 1997) and 1994-1995 (Brent *et al.*, 2001). Furthermore, Schottler and Eisenreich reported that analysis of data from their 10 lake stations that covered a central north-south axis and an east-west axis showed no horizontal gradients of atrazine concentrations in the lake.

4.4 LM2-Atrazine Model Application to Lake Michigan

4.4.1 Enhanced Screening Model Application

For the LM2-Atrazine model runs, seven years of atrazine application data were available and used. Also, due to label changes that lowered application amounts and established planting setbacks from water bodies in 1990 and 1992, a decision was made to use two tributary load ratios in order to address atrazine application practices for pre- and post-label changes. New data from the LMMBP also became available to modelers. With these additional data, loading ratios for both the tributaries and wet deposition were updated (see Part 2, Chapters 2 and 3). The model was calibrated by determining a total decay that would yield a best fit of the model to observations in the lake. Also, several forecasting scenarios were run with the model. The efforts of this additional modeling are described in the following sections of this part.

4.4.2 Field Data

See Part 1, Chapter 3 for atrazine field data from the lake, tributaries, and atmospheric components.

4.4.3 Tributary Loadings

It was assumed that a Watershed Export Percentage (WEP) of 0.6% derived from the literature for fine/moderate textured soils adequately described the overall WEP of the Lake Michigan watershed. This WEP, along with historical annual atrazine usage in the United States, was used to calculate atrazine loadings from the tributaries to the lake. For a complete discussion on the WEP method used to estimate LM2-Atrazine loadings, please see Part 2, Chapter 2.

The Stratified Beale Ratio Estimator (SBRE) method was used to estimate tributary loads in the 11 monitored tributaries during the LMMBP utilizing tributary flow and concentration data. Also, estimates of loads from the unmonitored watersheds were made. However, loads were apparently missed, and therefore, LM2-Atrazine tributary loads were based only on WEP, county-level application data and total United States annual usage records. See Section 5.3.3.3.1 for a discussion of this topic.

4.4.4 Atmospheric Loadings

Loading estimates of wet deposition to Lake Michigan and Green Bay were made for each of the top surface water segments. These loadings were estimated for LM2-Atrazine per the discussion in Part 2, Chapter 3.

4.4.5 Model Assumptions

Model processes involving sediments and particulates in the water column were not included in the LM2-Atrazine model runs because atrazine is primarily in the dissolved state in surface waters; therefore, any processes that involve sediment or suspended particle interactions were concluded to be of minor significance (Section 1.2.2).

A literature review of atrazine degradation processes in surface freshwater presented in Part 1, Chapter 2 suggests that degradation is hindered in freshwaters such as in Lake Michigan where the water is cold, has low solids concentrations, low dissolved organic carbon, a high pH, and low concentration of nitrate ions. Degradation of atrazine is known to occur through either biotic or abiotic processes in some environmental compartments. Given the lack of any Lake Michigan-specific kinetic information on any of these processes, the approach taken in LM2-Atrazine was to estimate the loading history of atrazine to the lake and then find an overall first-order loss rate constant to fit the model to observations of atrazine in the lake water.

Therefore, due to atrazine's physical and chemical properties (Part 1, Chapters 2 and 3), processes modeled included only advection, dispersion, volatilization, absorption, and reaction (atrazine decay).

4.4.6 Model Calibration and Application (Scenarios)

The calibration of the model was undertaken using three scenarios (1, 2, and 3) that included lower boundary condition, upper boundary condition, and a most likely or average boundary condition scenario, respectively. All of these model runs started on January 1, 1963 with a zero load. The model was calibrated by finding an appropriate internal decay until the model output best matched the observed atrazine concentration in the lake for samples taken in 1991, 1992, 1994, and 1995.

The scenarios 4 through 8 are referred to as load reduction scenarios. These are not necessarily management scenarios, but they can give managers insight as to which loads are important in the model and environment for the purpose of predicting concentrations of atrazine in the lake. It is believed that they provide bounds on the entire range of potential loads. Scenario 3 was used to simulate conditions from January 1, 1996 through December 31, 2004. Then on January 1, 2005, the load reduction scenarios 4 through 8 began and ran for a period of 50 years.

Scenario 1 – Calibration Based on an Upper Estimate of Boundary Conditions: In this scenario, the initial vapor phase concentration was 0 ng/m^3 and increased linearly until December 31, 1977. Starting on January 1, 1978, the vapor phase concentration was held constant at the atrazine detection limit of 0.00926 ng/m^3 (Miller, 1999) throughout the remainder of the simulation period. The summer inflow concentration at the Straits of Mackinac was assumed to be 100% Lake Huron water. Lake Huron water was initially set at 0 ng/L

and was assumed to rise linearly to 23 ng/L observed in 1995 (Station 54), and then remained constant for the remainder of the simulation. Tributary loading projections were set equal to an average of loadings for 1995 and 1998, but prior to that time, the historical loading estimates were used. Wet deposition loads beyond 1998 were set equal to an average of loads 1978 through 1998. Wet deposition loadings before that were based on historical load estimates. Volatilization, absorption, and other processes were active in the model. An internal decay was then selected for the model run that yielded a best fit to whole-lake volume-weighted average concentrations.

Scenario 2 – Calibration Based on a Lower Estimate of Boundary Conditions: In this scenario, the vapor phase concentration was initially set at 0 ng/m^3 and remained at that concentration for the entire simulation period. The summer inflow concentration at the Straits of Mackinac was assumed to be 100% Lake Superior water. Lake Superior water was initially set at 0 ng/L, and was assumed to rise linearly to 3.5 ng/L observed in 1994, and then held constant at that level for the remainder of the simulation. Tributary loading projections were set equal to an average of loadings for 1995 and 1998, but prior to that time, the historical loading estimates were used. Wet deposition projections beyond 1998 were set equal to an average of loads for 1978 through 1998. Wet deposition loadings before that were based on historical load estimates. Volatilization, absorption, and other processes were active in the model. An internal decay was then selected for the model run that yielded a best fit to whole-lake volume-weighted average concentrations.

Scenario 3 – Calibration Based on "Average" Boundary Conditions: In this scenario, the vapor phase concentration was initially set at 0 ng/m^3 and then increased linearly up to 0.00463 ng/m^3 (one-half detection limit) until December 31, 1977. Starting on January 1, 1978, this vapor phase concentration was held constant at 0.00463 ng/m^3 throughout the remainder of the simulation period. The inflow concentration at the Straits of Mackinac was assumed to be 50% Lake Superior and 50% Lake Huron water. This mix of water started out at 0 ng/L and was assumed to linearly rise to 13.25 ng/L or (½ x (3.5+23)) ng/L as observed in 1995 in Lake Superior and Lake Huron, respectively, and then held constant at that level for the remainder of the simulation. Tributary loading projections were set equal to an average of loadings for 1995 and 1998, but prior to that time the variable loading estimates were used. Wet deposition projections beyond 1998 were set equal to an average of loads for 1978 through 1998. Wet deposition loading before that were based on historical load estimates. Volatilization, absorption, and other processes were active in the model. An internal decay was then selected for the model run that yielded a best fit to whole-lake volume-weighted average concentrations.

Scenario 4 – Virtual Elimination (Lower Bound on Model Predictions): In this scenario, tributary and atmospheric loads were reduced by 100%. For the projections, vapor phase concentrations and the Lake Huron/Superior boundary conditions were set to zero. All modeling processes were active. This scenario was run using scenario 3 for predictions leading up to the date when the virtual elimination scenario began (January 1, 2005).

Scenario 5 – No Tributary Loads: In this scenario, the tributary loadings were reduced by 100%. Wet deposition loads were set equal to an average of loads for 1978 through 1998. This scenario was run using scenario 3 for predictions leading up to the date when the 100% tributary load reduction scenario was began (January 1, 2005). All other modeling processes were active.

Scenario 6 – No Wet Atmospheric Deposition Loadings: Tributary loads were set equal to an average of loadings for 1995 and 1998. Atmospheric wet deposition loadings were decreased by 100%. This scenario was run using scenario 3 for predictions leading up to the date when the 100% atmospheric load reduction scenario began (January 1, 2005). All other modeling processes were active.

Scenario 7 – Zero Vapor Phase Concentration: Tributary loads were set equal to an average of loadings for 1995 and 1998. Wet deposition loads were set equal to an average of loads for 1978 through 1998. Vapor phase concentration were set equal to zero. This scenario was run using scenario 3 for predictions leading up to the date when the zero vapor phase concentration scenario began

(January 1, 2005). All other modeling processes were active.

Scenario 8 – No Further Degradation: A total load (tributary and wet deposition) was determined using the model such that no further increase in lake-wide volume-weighted concentration would be observed after January 1, 2005. Up through December 31, 2004, scenario 3 was used.

4.4.7 Model Confirmation

In 2005, atrazine water samples were collected in Lake Michigan for the purposes of confirming the model predictions. However, as of this printing, these analyses were not available.

4.4.8 Discussion of Results

In terms of mass flow rates, LM2-Atrazine results from scenario 3 are depicted in Figure 4.2 for 1994. As shown, the highest load to the lake is from the tributaries followed by the load from the atmosphere in the form of wet deposition. The greatest loss of atrazine from the system is *via* export through the Straits of Mackinac. Loss due to internal decay is the second highest loss mechanism in the lake. Volatilization and gas absorption are minor processes in terms of mass flow gain and loss.

Total internal degradation of atrazine in the water (k_d) determined by model calibration was low in all scenarios evaluated. These rates of decay for scenarios 1, 2, and 3 were 0.012/yr, 0.004/yr, and 0.009/yr, respectively. For the calibration based on average boundary conditions (scenario 3), LM2-Atrazine predicts that approximately 0.9% of the atrazine in the lake decays each year due to some combination of abiotic and biotic decay in the lake. Decay can be related to the half-life of the chemical in the lake by the following:

$$\text{Half-Life} = t_{1/2} = (\ln 2)/k_d \qquad (4.1)$$

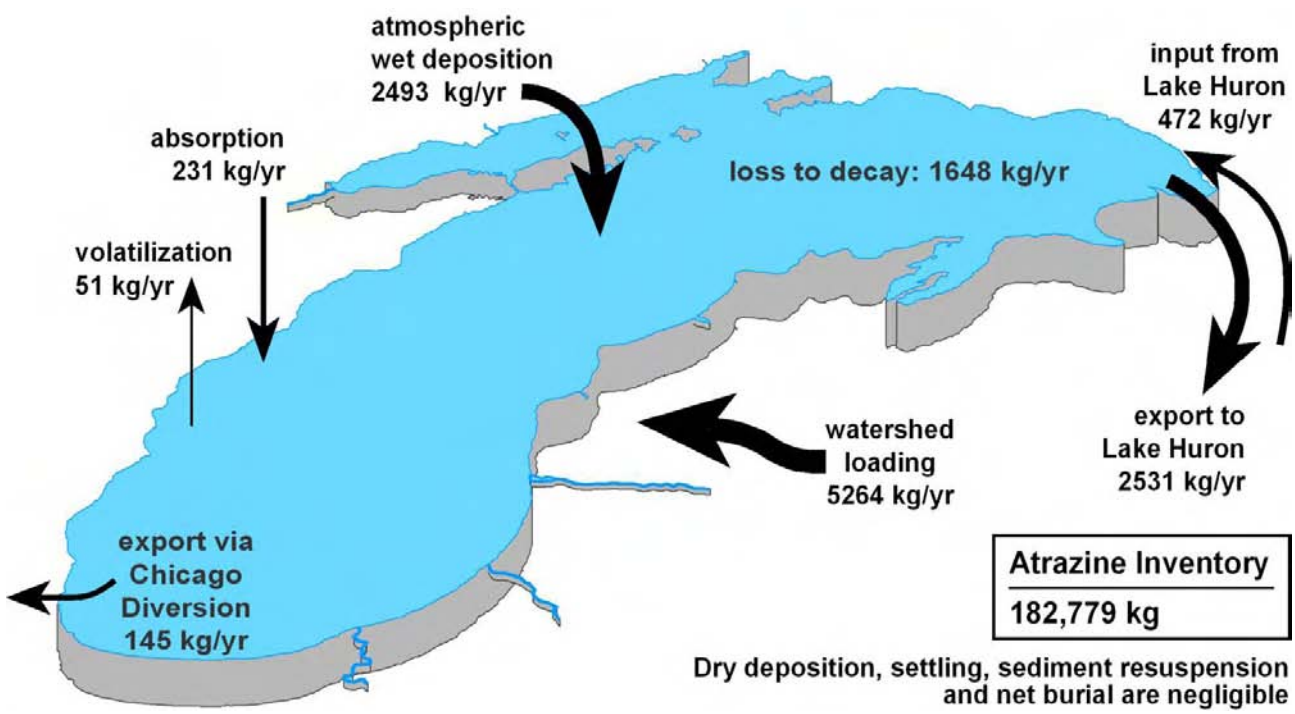

Figure 4.2. LM2-Atrazine model results for Lake Michigan and Green Bay for the year 1994.

Assuming that scenario 3 captures typical conditions, then the 0.9% internal decay associated with this scenario represents a half-life of the chemical in the lake of 77 years. In scenario 3, the water at the Straits of Mackinac is assumed to be half Lake Superior water and half Lake Huron water. It is intuitive that the decay rate associated with scenario 1 that has the highest boundary concentrations of atrazine (assumed to be all Lake Huron water) is the one with the highest decay rate because higher boundary concentrations will mean that more atrazine is transported into the lake at the Straits of Mackinac. Furthermore, the increased vapor phase concentration in scenario 1 will also contribute slightly more to gas absorption than the other scenarios. This cumulative higher mass flow will result in a higher decay needed in the modeling calibration exercise in order for model output to match lake concentration observations. The opposite argument is true for scenario 2 where the boundary condition at the Straits of Mackinac is based solely on the lower concentrations of atrazine from Lake Superior, and the vapor phase concentration of atrazine is assumed to be equal to zero throughout the entire simulation.

In the forecasts of alternate futures (Figure 4.3), constant conditions scenario 3 results in lake concentrations increasing until a value of approximately 66 ng/L is attained. Scenario 3 is based on average boundary conditions, and the forecasts using this scenario are based on constant loadings that were observed in the mid to late 1990's. Eliminating all loadings to the lake (scenario 4) resulted in the largest decline in model predictions. A total loading reduction of approximately 35% (scenario 8), if implemented on January 1, 2005, would be needed in order to prevent atrazine concentrations from increasing further than what was estimated in the lake on January 1, 2005. If only the atmospheric loadings ceased (scenario 6), then concentrations in the lake would not be expected to change much after January 1, 2005, and the model-predicted concentrations in the lake would be expected to be only slightly higher than that predicted by scenario 8. However, if only the tributary loadings ceased (scenario 5), then atrazine concentrations in the lake would decline relative to scenario 3 predictions. Maintaining the vapor phase concentration at 0 ng/l (scenario 7) has very little effect compared to the constant condition scenario 3. This is intuitive because scenario 3 vapor phase concentrations are set to one-half the detection limit of atrazine in the vapor phase.

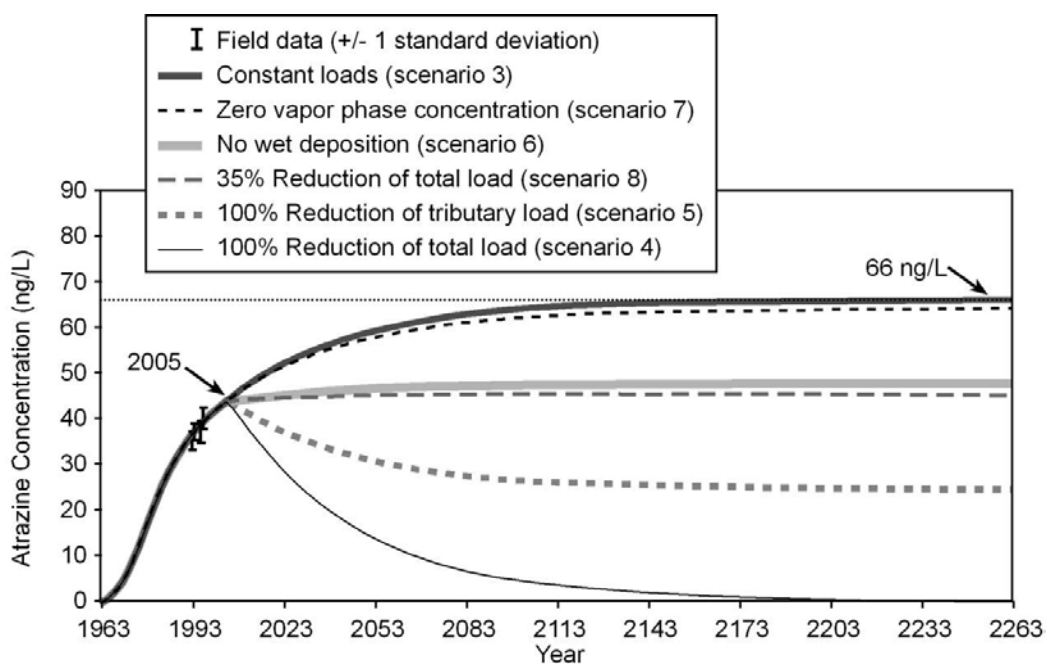

Figure 4.3. LM2-Atrazine model runs of scenarios.

Related to the production of ethanol for motor vehicles in this country, the demand for corn increased the United States corn acreage planted in 2007 to 93.6 million acres, exceeding the acreage planted in 2006 by 19.5 % (U.S. Department of Agriculture, 2007). This also represents an increase of 24.5% of the average acreage planted during the project period, 1994-1995 (see Figure 4.4 for corn acreage in the United States from 1986 to 2007). This was the largest amount of corn planted in the United States since 1944 when farmers planted 95.5 million acres. It can be assumed that this increase in corn acreage has resulted in an increase in the use of atrazine in the Lake Michigan watershed. To estimate the potential impact on this increased usage of atrazine in the Lake Michigan basin, both atmospheric and tributary loadings were increased by 15% and 30% starting in 2007 in scenario 3 (see Figure 4.5). For these increases, the lake reaches steady-state at approximately 75.2 ng/L and 84.2 ng/L, respectively. At the time of this printing, data on the actual usage amounts of atrazine applied to the Lake Michigan basin were not available. Thus the range of percent increases for the basin is probably the best current estimate of the potential impact of increased loadings to the lake.

In conclusion, the net volatilization of atrazine is negligible in Lake Michigan. Furthermore, model calibration over a hindcast suggests that very little of the atrazine inventory in the lake decays each year. The chemical almost behaves as a conservative substance in the cold, deep waters of Lake Michigan. If loadings stay that same or increase over what was observed in the 1990s, then the lake concentration of atrazine is expected to increase.

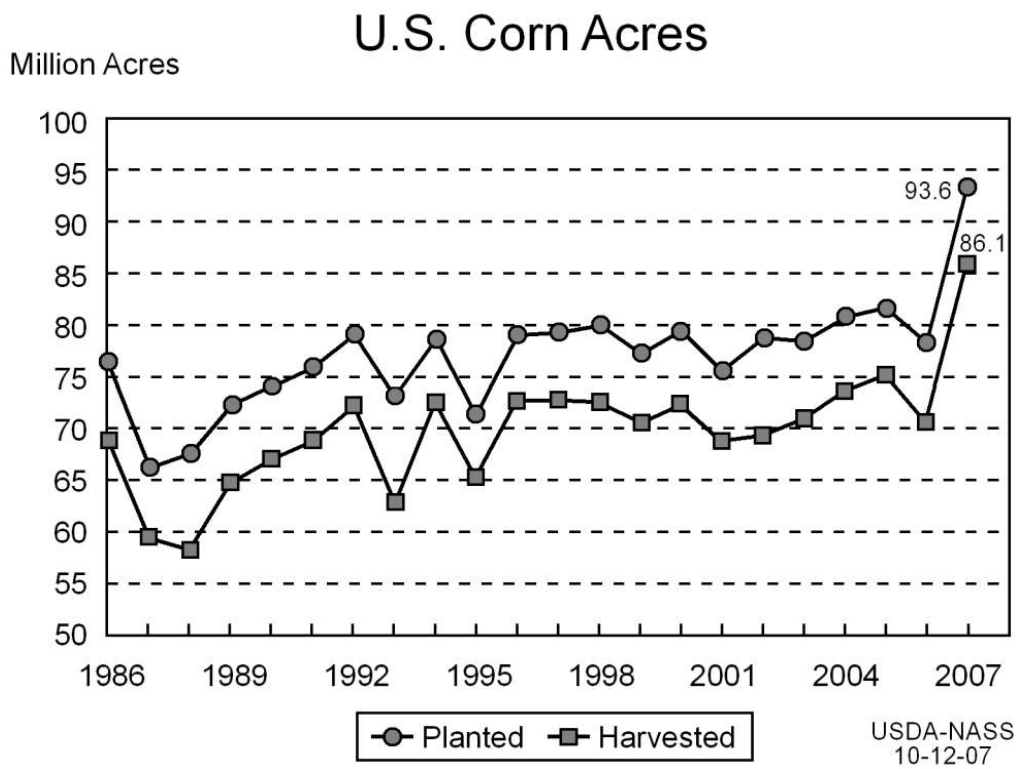

Figure 4.4. Historical trends of United States corn acreage planted and harvested from 1986 to 2007 (U.S. Department of Agriculture, 2007).

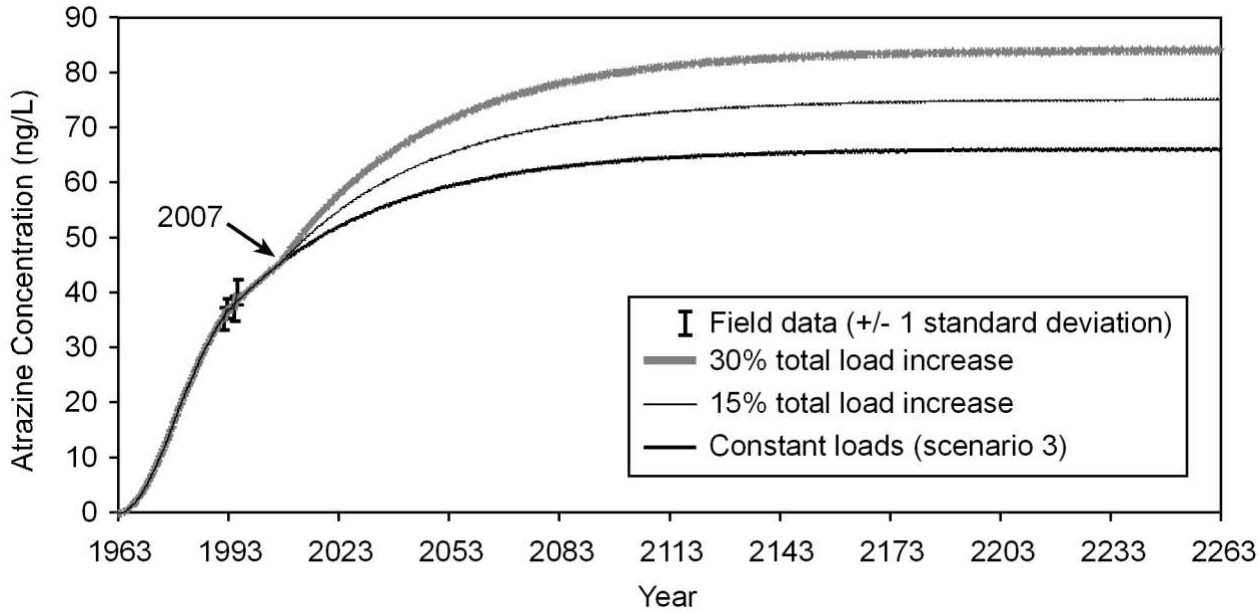

Figure 4.5. Model-predicted lake-wide averaged atrazine concentrations in water related to increases in atrazine loadings resulting from corn crop acreage increases are depicted. The actual Lake Michigan response is believed to be bracketed by the 15% to 30% total atrazine load increase to the lake related to the corn-to-ethanol biofuels program.

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PART 5

LAKE MICHIGAN MASS BALANCE PROJECT
LEVEL 3 MODEL: LM3-ATRAZINE

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5.1 LM3-Atrazine Executive Summary

Most previous Great Lakes water quality models were developed using large spatial scales. These models were capable of predictions on a lake-wide or regional scale but were not suitable for evaluating differences on smaller spatial scales, such as between off-shore and near-shore concentrations. The LM3-Atrazine model is a high-resolution model that is suitable for evaluating fine-scale spatial and temporal changes in water quality.

The LM3-Atrazine model was based upon the same framework as the United States Environmental Protection Agency's (USEPA) other LM3 models. The hydrodynamic transport was provided by the National Oceanic and Atmospheric Administration's (NOAA) Great Lakes Princeton Ocean Model (POM). The water quality framework was the same as used by the LM3 chloride and eutrophication models. Water quality components for the atrazine model were developed at the USEPA Large Lakes Research Station (LLRS) and included a small first-order decay rate and volatilization. The model spatial resolution consisted of a 5 km x 5 km horizontal grid with 19 vertical layers, for a total of 44,042 model cells. The model was run using a time step of three hours.

Tributary loads, atmospheric loads, and boundary conditions for the model were estimated as part of the Lake Michigan Mass Balance Project (LMMBP). Model simulations were conducted using tributary loads for the 1994-1995 LMMBP period estimated by

the United States Geological Survey (USGS) and alternative loads with a spring seasonal adjustment based upon long-term historical loading trends.

The LM3-Atrazine model could not be fully calibrated because only one year of in-lake data and one year of tributary loading data were collected during the LMMBP. However, confidence in model results was provided by the favorable comparison of model results to available data without adjustment of kinetic parameters, by successful calibration of the hydrodynamic model, by successful calibration of the high-resolution model transport (in the form of a chloride model), and by the long-term hindcast calibrations of coarser segmented atrazine models using the same water quality kinetics.

The high-resolution model was useful in demonstrating the effects of tributary loadings on near-shore water quality. Predicted mid-lake atrazine concentrations varied annually less than 5 ng/L during the two-year simulations. In comparison, the model segment receiving loads from the largest tributary, the St. Joseph River, ranged from winter concentrations of 37 ng/L to spring peaks of 100-350 ng/L depending upon whether 1994-1995 or long-term tributary loads were used in the simulation.

The USEPA collected atrazine samples from Lake Michigan during the 2005 field season; however, the results were not available at the time the atrazine modeling was conducted. To estimate potential expected concentrations, the LM3-Atrazine model was run for the period 1994-2005. Loads were estimated by repeating the 1994-1995 loading time-series over the 12-year period. The model was run using both the USGS-estimated loads from 1994-1995 and loads based upon long-term trends. Mid-lake concentrations were predicted to increase from the 1994 concentration of 37 ng/L to between 38 ng/L and 46 ng/L in 2005.

Inflows and outflows of atrazine from the Lake Michigan system were tracked during the 1994-1995 model simulations. Outflow through the Straits of Mackinac and decay losses were approximately equal and were the largest loss terms. Tributary inputs and atmospheric wet deposition were the largest sources of atrazine. Atmospheric exchange was minimal.

Model results and measured data were compared to toxicological endpoints to examine possible ecological effects of atrazine concentrations in Lake Michigan. Most model forecast and data concentrations were below the toxicological endpoints of concern at the spatial scales used in these modeling analyses.

5.2 LM3-Atrazine Recommendations

Because of its high-resolution (5 km x 5 km model cells), LM3-Atrazine is useful to determine seasonal effects of loadings to various cells. Of particular interest may be the effects of high run-off in the spring after application to cells at the mouths of major tributaries. Within these cells, dramatic changes in atrazine concentrations may be noted over relatively short periods of time. Some of the highest concentrations in the lake would most likely be found at these sites. The lower-resolution models, MICHTOX and LM2-Toxic, have coarse segmentation and would not respond like the high-resolution model to these spring/early summer high loading events. In the coarse segmented model, the load is instantaneously dispersed uniformly into the much larger model segment volume receiving the river load. Hence, a concentration spike would be low compared to a high-resolution segment receiving the equivalent load.

5.3 LM3-Atrazine Transport and Fate Modeling

5.3.1 Purpose of High-Resolution Model

Historically, water quality models for the Great Lakes have been developed using large spatial scales. The first eutrophication model for Lake Ontario (Thomann and Di Toro, 1975; Thomann *et al.*, 1979) was configured with only two vertical segments (epilimnion and hypolimnion). Similar scale models were also developed for Lake Erie (Di Toro and Connolly, 1980), Lake Huron (Di Toro and Matystik, 1980), and Lake Michigan (Rodgers and Salisbury, 1981). Even a more recent model of Green Bay was developed on a relatively coarse-grid scale (DePinto *et al.*, 1993). These models were capable of adequately simulating average water quality over large spatial segments and projecting future concentrations. However, they were not capable of

simulating spatial concentration gradients very well, if at all. Also, there have been questions on whether limnological processes could adequately be represented on such a large spatial scale, particularly sediment transport. During the design phase of the LMMBP, modelers were determined to construct a higher-resolution model to overcome these deficiencies.

The LM3 level models include linked high-resolution hydrodynamic and water quality components. The hydrodynamic component of the models was developed by modelers at the NOAA's Great Lakes Environmental Research Laboratory (GLERL). The transport framework was based on the U.S. Army Corps of Engineers' CE-QUAL-ICM model (Cerco and Cole, 1994). The water quality components were developed at the USEPA's LLRS. Completed water quality components included a eutrophication model (Pauer *et al.,* 2006), the atrazine model described below, and, subsequent to the LMMBP, an ecosystem model (Miller *et al.*, 2007).

Although the LM3 level models have many scientific and technological advantages, there are major challenges. First, the LM3 models required a much greater degree of computer resources to develop and operate. Second, they required more computer programming support to develop completely new programs. Third, because there are over 40,000 water segments for which concentrations are being simulated, there is much more computer output to manage and evaluate. This has presented disk storage issues and has required additional effort to develop computer programs to analyze and display model output.

The following sections describe the LM3-Atrazine model, the assumptions used in developing the model, the loading data and lake concentrations used for model confirmation, and the results of model simulations for the 1994-1995 LMMBP period and for forecasts.

5.3.2 Model Description and Framework

LM3-Atrazine, as with most mass balance models, incorporates segment geometry, advective and dispersive transport, boundary concentrations for state variables, point and diffuse source loads, kinetic parameters, constants and time functions, and initial conditions. These input data, together with the general mass balance equations and the specific chemical kinetics equations, uniquely define a special set of water quality equations. These equations are numerically integrated as the simulation proceeds in time. At user-specified print intervals, values of selected state variables are saved for subsequent evaluation in visualization and statistical post-processor programs.

In the Great Lakes environment, atrazine has the chemical properties of a mostly conservative substance. The important functions of the LM3-Atrazine model consist of hydrodynamic transport, external loads, atmospheric exchange, and a small first-order decay rate.

This section contains a description of the hydrodynamic model, the kinetic processes of the atrazine model, and the spatial and temporal configuration of the atrazine model.

5.3.2.1 POM Hydrodynamic Model

The basis of the LM3 water quality model is water movement and material transport. Hydrodynamic simulations were conducted by Schwab and Beletsky (1998) who applied the POM. Portions of the following section are excerpted from their report. Subsequent to the preparation of the report, Schwab included annual average tributary flows and average Straits of Mackinac outflow in the final submission of model results to USEPA for use in mass balance models. In addition, computational modifications were made that eliminated a minor problem with water balance [for a technical discussion of the details, see Appendix A in Melendez *et al.* (2008)]. The primary goal was to provide three-dimensional fields of currents, temperature, and wind-wave characteristics for the study period (1994-1995) for direct input to the LM3 water quality model. The model was applied to Lake Michigan using a 5 km x 5 km grid (Figure 5.1). The output of POM simulations was provided to the water quality modeling team at the USEPA/LLRS for further translation for the water quality models.

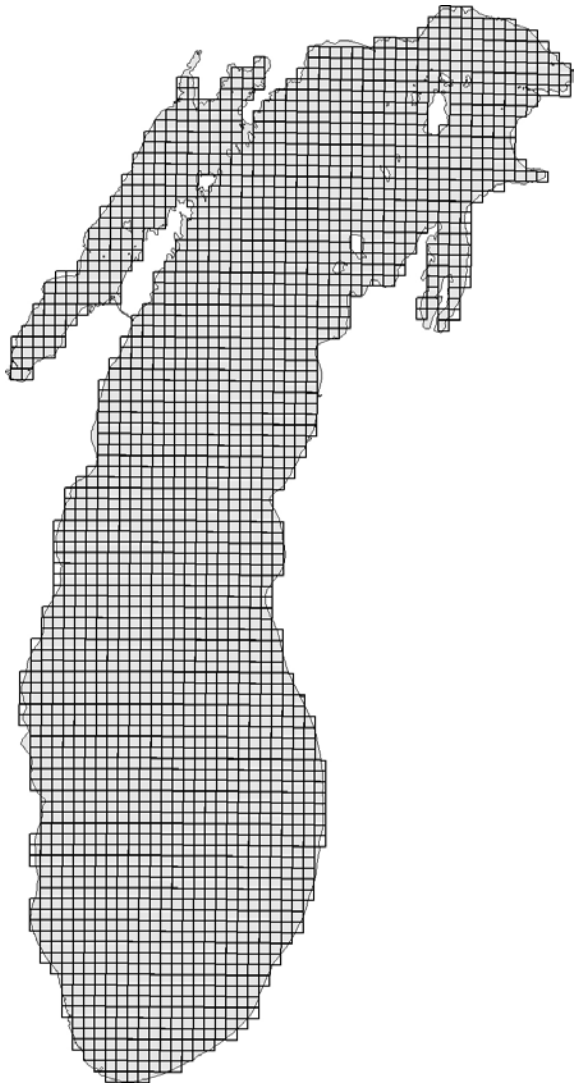

Figure 5.1. Lake Michigan hydrodynamic model 5 km x 5 km computational grid.

During the development of the POM for Lake Michigan, the model was applied for two periods: 1982-1983 and 1994-1995. The first period was chosen for model calibration because of an extensive set of observational data including surface temperature observations at two National Data Buoy Center (NDBC) weather buoys and current and temperature observations during June 1982-July 1983 at several depths from 15 subsurface moorings.

Results were output to files containing values for each of the 5 km x 5 km cells at specified time intervals. To compare model simulations with data, model results were averaged over various time periods depending on the data period. For example, the simulated temperature time-series for the 1982-1983 period are shown in Figure 5.2 and for the 1994-1995 period in Figures 5.3a and 5.3b. Statistics of temperature field validation are presented in Table 5.1 for 1982-1983 and Table 5.2 for 1994-1995. RMSD is the root mean square difference (error) between observed and computed temperatures. Maximum Error is the maximum temperature difference. Average is the arithmetic mean. The correlation coefficient provides a statistical indication of the strength of the linear relationship between computed and observed variables.

The model was able to reproduce all of the basic features of the thermal structure of Lake Michigan during the 600 day period of study: spring thermal bar, full stratification, deepening of the thermocline during the fall cooling, and the overturn in the late fall (Figure 5.4).

Another model validation was made by comparing observed temperature profiles acquired during the seven Great Lakes National Program Office (GLNPO) water quality surveys during 1994-1995 to simulated temperature profiles at 20 locations. Figure 5.5 depicts one of these locations, Station 18M. In addition, the USGS conducted several near-shore transect surveys and compared simulated and observed temperatures.

Schwab and Beletsky (1998) provided additional information on model development and validation. The basic conclusion was that, overall, the models simulated the large scale thermal structure, circulation, and waves quite realistically on the 5 km x 5 km grid. There were some qualifications, however. First, lack of an ice model will be a serious problem if the model is applied during a year with normal or severe ice conditions. It will cause both significant violations of the lake's heat balance and errors in calculating transfer of momentum from air-to-water because of the difference in surface roughness of ice and water and momentum absorption by the ice. The 1994-1995 POM simulation assumed a constant uniform water temperature of 2°C for the period January 1 to March 31, 1994. Because no hydrodynamic data

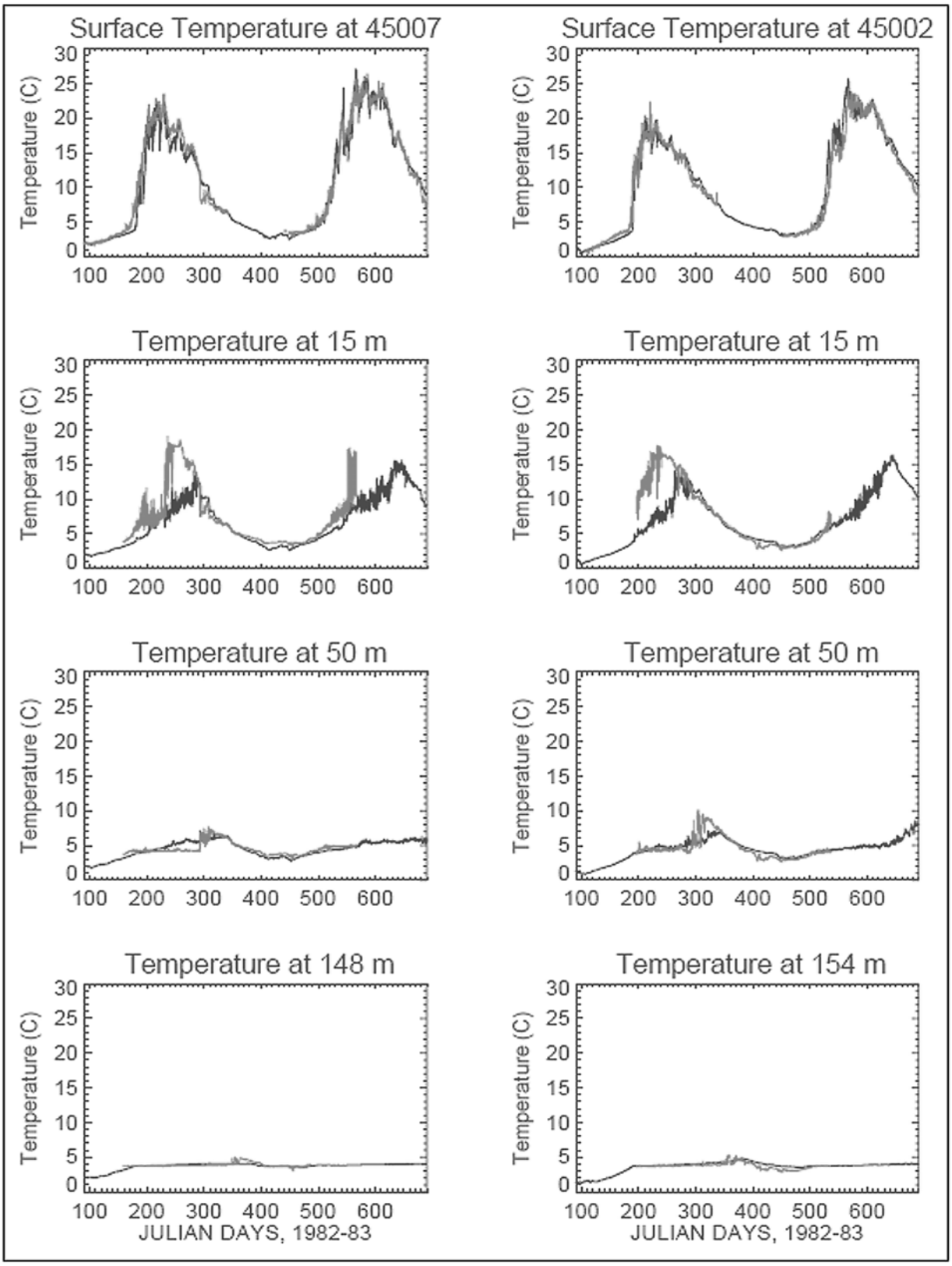

Figure 5.2. Simulated temperature (black) compared to measured temperature (gray) at two buoys in Lake Michigan for 1982-1983 (Schwab and Beletsky, 1998).

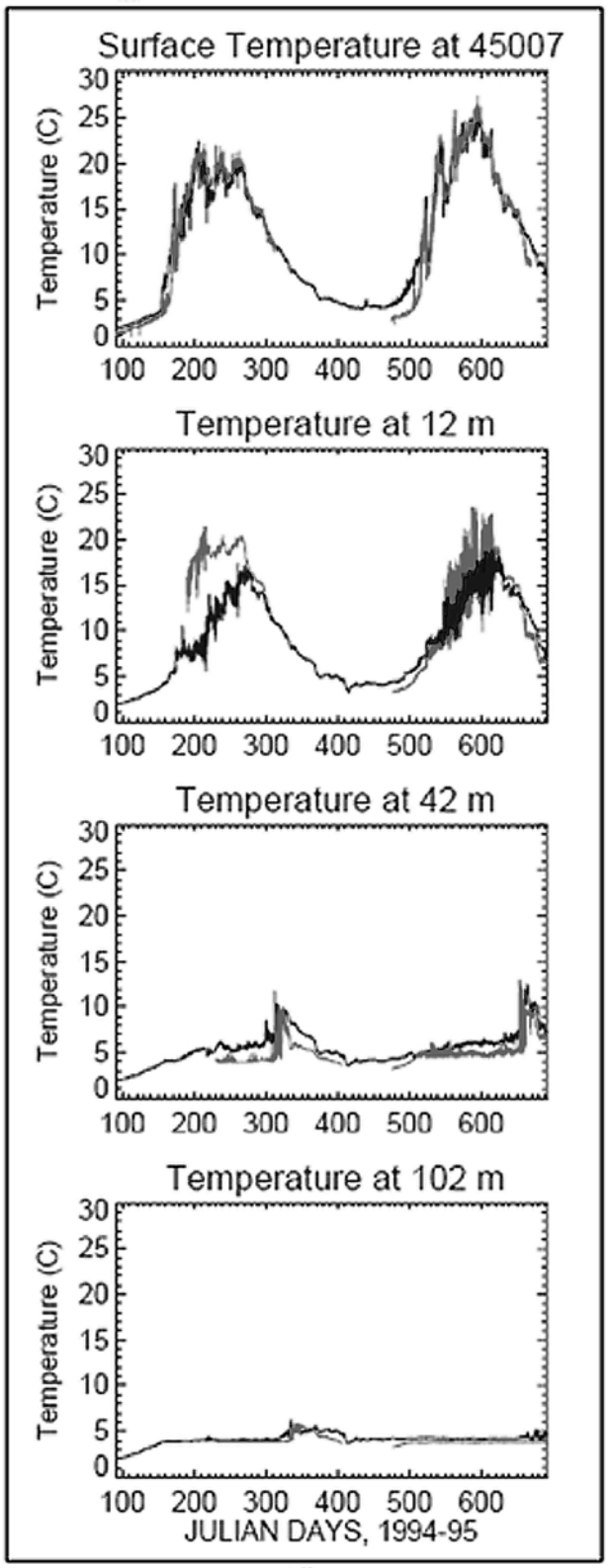

Figure 5.3a. Time-series of simulated water temperature versus observed at 45007 for 1994-1995. Gray line is observation; black line is model simulation (Schwab and Beletsky, 1998).

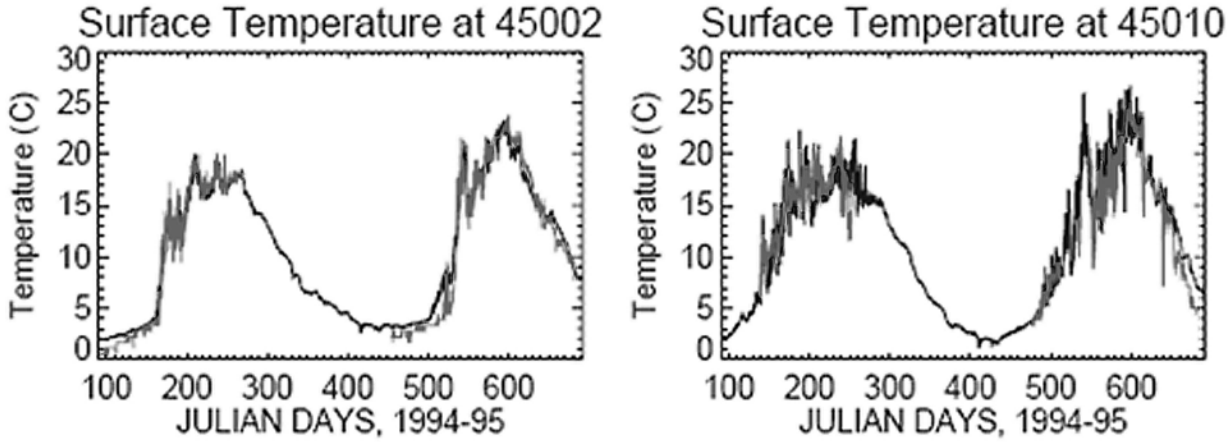

Figure 5.3b. Time-series of simulated surface water temperature versus observed at 45002 and 45010 for 1994-1995. Gray line is observation; black is model simulation (Schwab and Beletsky, 1998).

Table 5.1. 1982-1983 Hydrodynamic Model Evaluations for Surface Temperature at NDBC Buoys (45002 and 45007) and Subsurface Temperature at GLERL Current Meter Moorings (28 Instruments) (Schwab and Beletsky, 1998)

	RMSD	Maximum Error	Average Observed	Average Computed	Correlation Coefficient
Surface	1.2	6.6	12.1	12.1	0.99
Subsurface					
Epilimnion	2.5	10.6	7.1	6.4	0.87
Hypolimnion	0.7	3.3	4.2	4.3	0.78

Table 5.2. 1994-1995 Hydrodynamic Model Evaluations for Surface Temperature at NDBC Buoys (45002, 45007, and 45010) and Subsurface Temperature at GLERL Current Meter Moorings (10 Instruments) (Schwab and Beletsky, 1998)

	RMSD	Maximum Error	Average Observed	Average Computed	Correlation Coefficient
Surface	1.5	6.1	13.1	13.3	0.96
Subsurface					
Epilimnion	2.4	9.2	7.3	7.7	0.93
Hypolimnion	1.3	5.2	4.5	5.3	0.87

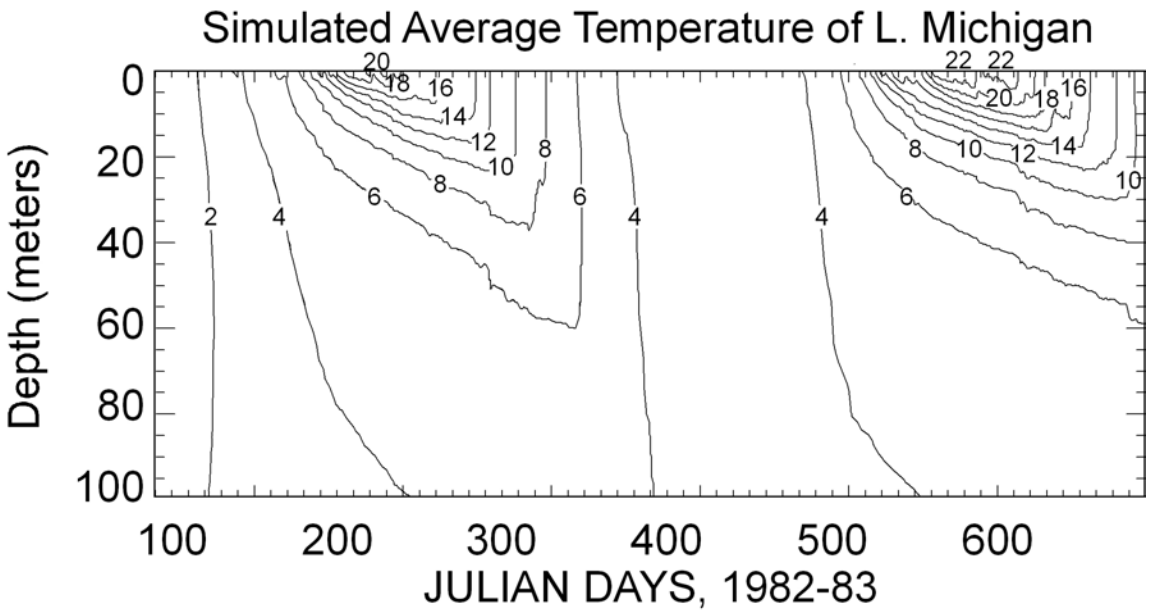

Figure 5.4. Simulated mean temperature (°C) profile for 1982-1983 (Schwab and Beletsky, 1998).

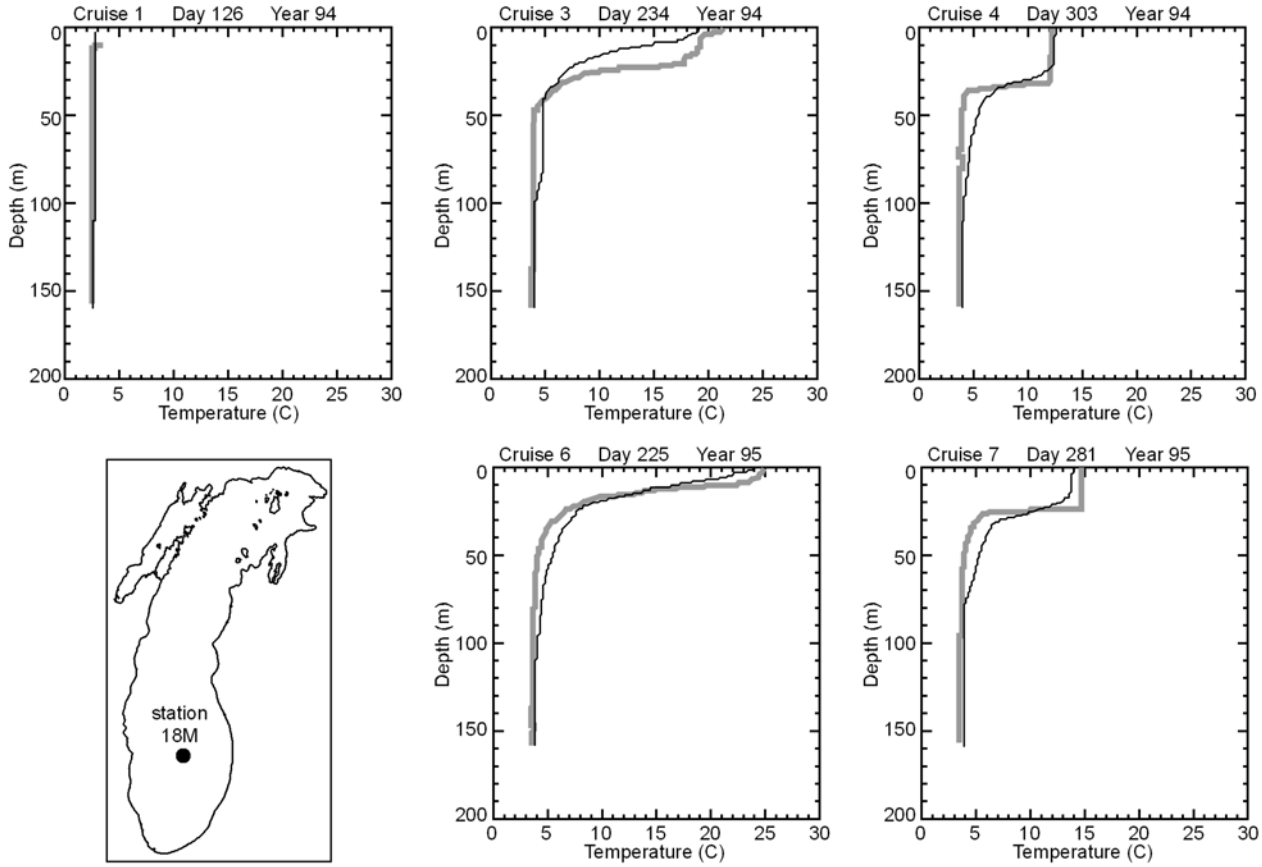

Figure 5.5. Temporal evolution of simulated versus observed temperature profiles, Station 18M (Schwab and Beletsky, 1998). Black line is model simulation; gray line is observation.

were available after December 21, 1995, the LM3-Atrazine model used the corresponding 1994 data for the last 10 days in 1995.

Second, the model did not perform as well in the thermocline area as it did near the surface. The simulated thermocline was too diffuse. Although this problem might be overcome by development of a higher-resolution model, this problem is probably not significant for the mass balance study in comparison to other uncertainties with data and chemical and biological processes.

Lastly, while the MICHTOX and LM2-Atrazine models have bidirectional flow through the Straits of Mackinac, the present configuration of LM3-Atrazine only uses a net, annual average outflow. In reality, there is a return flow to Lake Michigan at the Straits during stratification for a period of approximately 100 days in the summer. However, to include this process within POM would have required significant additional resources including the running of a simultaneous Lake Huron hydrodynamic model. The absence of bi-directional flow at the Straits was not expected to have a significant impact on circulation predictions in the main portion of the lake.

5.3.2.2 Model Framework

The LM3-Atrazine model uses the same computer code and spatial resolution as other LM3 models (LM3-Eutro and LM3-Eco). Detailed documentation of the LM3 models has been provided by Melendez *et al.* (2008). The documentation provides a history of the models' development and a complete description of the model framework, equations, and use. Documentation of the LM3-Eutro application is included in Pauer *et al.* (2006). Version 3.2.15 of the LM3 model code was used for the LM3-Atrazine model analyses.

The transport model incorporated within the LM3 framework was based on the ULTIMATE QUICKEST transport scheme, originally developed by Leonard (1991) and subsequently augmented for use with variable grid sizes by Chapman *et al*. (1997). The transport algorithm was coded in Fortran and previously applied to the Chesapeake Bay model (CE-QUAL-ICM) (Cerco and Cole, 1994, 1995). The transport model calculation performed numerical integration of spatially varying concentrations using quadratic interpolations of the concentration to infer its value at flow faces and analytic integration over space- and time-variables to account for changes in the concentration at the cell wall during the course of the time step. Further details of the dimensional derivation of the ULTIMATE QUICKEST transport method can be found in Melendez *et al*. (2008).

Because atrazine is relatively stable in Lake Michigan, only a subset of the model's kinetic processes were used: hydrodynamic transport, atmospheric exchange, and degradation. These processes, and the spatial and temporal resolution used in the simulations, are described below.

5.3.2.2.1 Water Quality Processes

The LM3 models are mass balance models based on the principle of conservation of mass. They use the same finite segment modeling approach used in the USEPA-supported WASP4 and the CE-QUAL-ICM modeling framework. The models describe where and how a mass of constituent is transported and transformed. The mass of a chemical or solid in each water segment is controlled by water movement between adjacent segments, solids and chemical dynamics within the system, internal and external loads, and boundary concentrations.

For LM3-Atrazine, external loads, hydrodynamic outflow, and chemical transformation are the most significant processes affecting atrazine concentrations in Lake Michigan. Atmospheric exchange (volatilization and absorption at the water/air interface) was also included in the model kinetic process, although the mass involved is considerably smaller than that involved with outflow or chemical transformation. Atrazine does not partition onto solids. Thus the settling and sediment interaction portions of the LM3 water quality model were not utilized.

Mass balance equations representing the above processes were used in the model to compute the change of mass of atrazine in each segment at a certain time. A general time-dependent finite differential equation in a given segment can be written to describe the change of mass for a state-variable at a certain time. The change in mass of atrazine in the LM3-Atrazine model for a given water column segment is described as:

$$V_j \frac{dC_j}{dt} = \sum_i^n Q_{ij} C_{ij} + \sum_i^n R_{ij}(C_i - C_j) + W_j + S_{aw,j} + S_{k,j} \quad (5.3.1)$$

where

V_j = volume of segment j (L^3)

C_j = concentration of water quality constituent in segment j (M/L^3)

C_i = concentration of water quality constituent in segment I (M/L^3)

C_{ij} = concentration of water quality constituent at the interface between segment I and j (M/L^3)

Q_{ij} = net flow across the interface between segment I and j (defined as positive when entering segment j and negative when leaving segment j) (L^3/T)

n = number of adjacent segments

R_{ij} = ($E_{ij}A_{ij}/\Delta X_{ij}$), bulk dispersion/diffusion coefficient (L^3/T)

E_{ij} = mixing (dispersion/diffusion) coefficient (L^2/T)

A_{ij} = interfacial area between segment I and j (L^2)

ΔX_{ij} = characteristic mixing length between segments I and j (L)

W_j = external loading rate of segment j (M/T)

$S_{aw,j}$ = mass change rate due to air-water exchange process between segment j and air directly above segment j (M/T)

$S_{k,j}$ = mass change rate due to sum of kinetic transformation processes within segment j (M/T), positive is source, negative is sink

Note: L = length; M = mass; T = time.

The mass change due to kinetic transformation processes, $S_{k,j}$, is represented in the atrazine model by a single first-order decay rate. The decay coefficient was determined during the long-term hindcast simulations using the MICHTOX and LM2-Atrazine models (Parts 3 and 4 of this report) and was set at 0.009 $year^{-1}$ (2.854×10^{-10} s^{-1}).

Gas exchange (volatilization and absorption) of atrazine between the lake and the atmosphere is a potential source or loss of atrazine to Lake Michigan. Computing the atrazine mass transfer across the water-air interface was necessary to satisfy the overall atrazine inventory and mass budget in the Lake Michigan system for the LMMBP period. The mass change rate term ($S_{aw,j}$) for atrazine due to air-water exchange processes was calculated in Equation 5.3.2 as a product of the overall net mass exchange flux and surface area of the water segment j.

$$S_{aw,j} = \left(C_{dw,j} - \frac{C_{a,j}}{H'}\right) * k_{ol} * A_j \quad (5.3.2)$$

where

k_{ol} = the overall mass exchange rate coefficient (L/T)

$C_{dw,j}$ = dissolved atrazine concentration in water (M/L^3)

$C_{a,j}$ = atmospheric atrazine concentration over segment j (M/L^3)

H' = temperature-dependent Henry's law constant (dimensionless)

A_j = surface area of the water segment j (L^2)

The overall mass exchange rate coefficient (k_{ol}) was calculated using the Whitman two-film theory formulation (Whitman, 1923) given as:

$$k_{ol} = \frac{1}{\frac{1}{k_l} + \frac{1}{k_g * H'}} \quad (5.3.3)$$

where

k_l = the liquid film mass transfer rate coefficient (L/T)

k_g = the gas film mass transfer rate coefficient (L/T)

The parameters H', k_l and k_g were calculated at every time step for each LM3 segment. The Wanninkhoff (1992) formulation for water mass transfer resistance and the Schwarzenbach (Schwarzenbach *et al*., 1993) formulation for gas mass transfer resistance were used for modeling the air-water exchange of atrazine in Lake Michigan. The Wanninkhoff equation for k_l, with correction for atrazine molecular diffusivity in reference to carbon dioxide (CO_2) molecular diffusivity across the air-water interface, is given as:

$$k_l = 0.45 * \left(\frac{D_w}{D_{l_CO_2}} \right)^{\frac{1}{2}} * u_{10}^{1.64} \qquad (5.3.4)$$

where

D_w = chemical molecular diffusivity in water (L^2/T)

D_{l_CO2} = CO_2 molecular diffusivity in water (L^2/T)

u_{10} = wind velocity measured at 10 m above water surface (L/T)

The Schwarzenbach formulation for k_g with correction of atrazine molecular diffusivity in reference to water vapor molecular diffusivity across the air-water interface is given as:

$$k_g = (0.2 * u_{10} + 0.3) * \left(\frac{D_\alpha}{D_{g_H_2O}} \right)^{0.67} \qquad (5.3.5)$$

where

D_α = chemical molecular diffusivity in air (L^2/T)

D_{g_H2O} = water vapor molecular diffusivity in gas phase (L^2/T)

The atrazine model calculated a temperature-corrected dimensionless Henry's law coefficient using equations derived from Scholtz *et al.* (1999) and Miller (1999).

$$\log H' = \log\left(H_{Tref}\right) - \Delta H_H \frac{\left(1/T - 1/T_{ref}\right)}{\left(2.303R\right)} \qquad (5.3.6)$$

where

H' = temperature-dependent Henry's law constant (dimensionless)

H_{Tref} = Henry's law constant at the reference temperature

ΔH_H = the enthalpy of phase change (kJ/mol)

R = the ideal gas constant, 8.315 x 10^{-3} kJ/(mol)(°K)

T = interfacial temperature (°K)

T_{ref} = reference temperature of 298.16 K (25° C)

The value for the dimensionless Henry's law constant at 25°C was set to 8.1 x 10^{-8} (U.S. Department of Agriculture, 2001). The enthalpy of phase change was set to 50 kJ/mol (Scholtz *et al.*, 1999; Miller, 1999).

5.3.2.2.2 Spatial Resolution

Developing the high-resolution grid for the LM3 models required compromises between different spatial configurations and the difficulties in translating the 5 km x 5 km grid hydrodynamic output. The best approach was to develop the fine-grid model at the same 5 km scale as the POM (Figure 5.1). The high-resolution LM3 grid consisted of 2,318 horizontal segments with 19 vertical "sigma" layers, resulting in a total of 44,042 water column cells.

A linkage between POM and the LM3 model was developed by Chapman *et al.* (1997). The linkage mapped POM cell numbers with ULTIMATE QUICKEST flow face numbers and the relationship between horizontal and vertical components. LM3-Atrazine inputs included POM output for water temperature, horizontal and vertical dispersion, and horizontal and vertical currents for each segment in the water column.

5.3.2.2.3 Temporal Resolution

The LM3-Atrazine model simulated the period from January 1, 1994 through December 31, 1995 for the LMMBP study period. To forecast the possible range of atrazine concentrations expected in Lake Michigan during the 2005 sampling surveys, the model was also run for the 12-year period January 1, 1994-December 31, 2005.

The LM3-Atrazine model was run using a variable time step based upon model stability. Over the course of the 1994-1995 simulation, the average value of the time step was approximately three hours. Output from the POM hydrodynamic model was averaged over three-hour intervals for input to the LM3-Atrazine model. LM3-Atrazine model results were output at a daily interval for two-year model runs. Atrazine almost behaves as a conservative constituent in Lake Michigan (has an extremely slow chemical transformation), and daily behavior provided sufficient resolution for interpretation of simulation results. Results from some of the 12-year forecast model runs were output at a six-day frequency to maintain reasonable output file sizes for long-term output animations.

5.3.2.2.4 Model Assumptions

The conceptualization of processes in the LM3-Atrazine model was based upon literature review (Part 1, Chapter 2) and previous LLRS atrazine modeling efforts (Part 3 and Part 4). Atrazine essentially behaves as a conservative substance in Lake Michigan. Previous LLRS modeling demonstrated that external loading and outflow from the Straits of Mackinac were the most important processes effecting atrazine concentrations in the lake (Part 3; Part 4; Rygwelski *et al.*, 1999). Although it occurs slowly, degradation of the chemical is also an important process because of the slow rate of export. Exchange between the water surface and atmosphere was modeled, although it only had a small effect on lake concentrations.

Atmospheric loads were assumed to be primarily through wet deposition. Dry deposition was not found to be significant based upon LMMBP sampling reports (Brent *et al.,* 2001; Miller, 1999). Sections 1.3.2.2.2 and 1.3.2.2.3 of this report summarize the atmospheric deposition sampling. Later papers have suggested that dry deposition may be significant (Miller *et al.*, 2000) but only provided a range of possible loads and no spatial or temporal resolution consistent with the LM3 models. The range of possible dry deposition loads was taken into consideration when estimating loads for long-term forecasts.

Atrazine is primarily found in the dissolved state in Lake Michigan, and sediment interactions with atrazine are minor (Part 1, Chapter 2; Rygwelski *et al*., 1999). Sediment processes were assumed to be negligible and were not included in the LM3-Atrazine model kinetics.

5.3.3 Description of Data Used

The data used for the LM3-Atrazine modeling was collected during the 1994-1995 LMMBP studies. The data were reviewed in Brent *et al.* (2001) and summarized in Part 1, Chapter 3 and Part 2 of this report.

5.3.3.1 Field Data

Model simulation results were compared to data collected during the LMMBP field surveys. Lake water samples were collected for atrazine analysis during six cruises from April 1994 through April 1995. Data from mid-lake stations were selected for comparison purposes because these stations were sampled during most cruises. While data were also collected from near-shore stations, these stations were not routinely sampled.

5.3.3.2 Initial and Boundary Conditions

The Lake Michigan atrazine model initial concentrations were estimated based upon the LMMBP field survey data. A uniform concentration of 37 ng/L was set for all main lake and northern Green Bay model cell initial concentrations based upon the average concentrations measured during the spring 1994 sampling cruise. Southern Green Bay cells nearest to the Fox River were assigned an initial concentration of 50 ng/L based upon the limited Green Bay sampling from the fall 1994 and spring 1995 cruises.

While the MICHTOX and LM2-Atrazine models have bidirectional flow through the Straits of Mackinac, the

present configuration of LM3-Atrazine only uses a net outflow. For this assumed configuration, Lake Huron boundary conditions are not necessary because there is no flow to Lake Michigan at the Straits of Mackinac.

Atmospheric atrazine vapor samples were collected from March 1994 through October 1995. Atmospheric sampling did not detect vapor phase atrazine concentrations in 86% of the samples (Brent *et al.,* 2001). For modeling purposes, the atmospheric concentration for all locations and times was set to a single value equal to one-half the average method detection limit (MDL) of the samples, 4.63 pg/m^3 (Miller 1999).

5.3.3.3 Loadings

5.3.3.3.1 Tributary

Watershed atrazine loadings to Lake Michigan were estimated by Hall and Robertson (1998). Loads were calculated for 11 tributaries that were sampled as part of the LMMBP field program and for 18 unmonitored watersheds (Figure 5.6). For the monitored tributaries, event and base flow samples were collected from April 1995 through October 1995. The Stratified Beale Ratio Estimator (SBRE) was used to calculate loads for 1995 with these sample data and the USGS flow data. Because tributary samples were not collected in 1994, loads for 1994 were estimated using USGS regression methods and the 1995 data (Hall and Robertson, 1998). Loads for the unmonitored watersheds were estimated using load to watershed area ratios from monitored watersheds with similar soils and land uses. Part 2, Chapter 2 discusses the tributary loads in more depth.

The USGS estimated loads for 1994-1995 were substantially smaller than what would have been expected based upon long-term loading patterns. Rygwelski *et al*. (1999) reviewed previous studies and found that, for soils similar to those in the corn-producing watersheds of Lake Michigan, 0.6% of the atrazine applied to the watershed reached Lake Michigan. This amount is also referred to as the Watershed Export Percentage (WEP). Rygwelski *et al*. (1999) also conducted long-term hindcast atrazine modeling that confirmed the appropriateness of the 0.6% WEP (see Parts 3 and 4). The 1994-1995

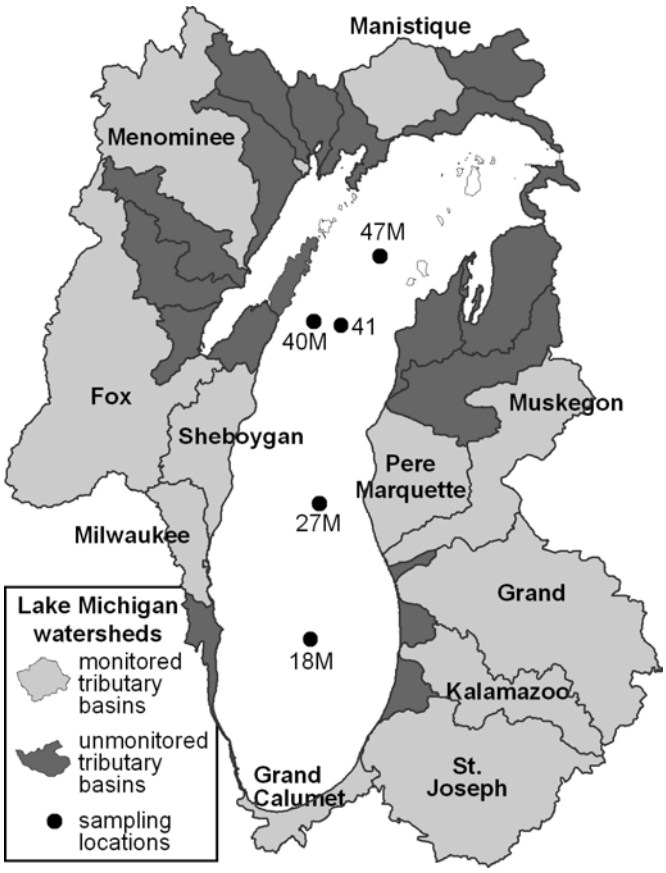

Figure 5.6. Watershed and mid-lake sampling stations for the LMMBP study.

USGS estimated tributary loads were only 30% of the load estimated using the long-term WEP and 1994-1995 atrazine application data for the Lake Michigan watershed. Using the USGS-estimated loads for 1995, a WEP of 0.12% was calculated. Using this WEP derived from the USGS load and no atrazine decay in a MICHTOX hindcast, the model-predicted less than one-half of the measured concentration in the lake as observed in the mid-1990s.

The 1994-1995 loads may have been substantially lower because of a number of possible factors: loads were lower than normal due to the WEP possibly decreasing over time because of improved agricultural management practices, significant peaks in tributary loads may have been missed because the weekly storm event sampling was discontinued too early, or atmospheric dry deposition may be higher than expected. It is known that dry years can depress atrazine watershed loadings. However,

precipitation to the lake was near long-term averages (see Sections 1.3.2.2.3, 1.4.5.1, 1.4.5.2, and 2.2.1.2 for information on rainfall and impact on WEPs). Other potential meteorological forcing functions were also near average conditions during 1994-1995 (see Part 1, Chapter 4). Therefore, weather conditions are an unlikely cause of the low USGS export estimates.

The USGS loadings were based on an average of 14 atrazine samples per year per tributary (range: seven to 20). When compared to other similar atrazine load estimation studies (Schottler *et al.*, 1994; Richards *et al*., 1996; Capel and Larson, 2001) this represents a very low number of samples collected and thus could have contributed to underestimation of loads. A study by Leu *et al.* (2004) found that a single run-off event that occurred on day 23 after application of atrazine exported 70% of the total cumulative load measured during a one- to 67-day period after application. On a fine-loamy field in Ohio, a rainstorm occurred just two days after atrazine application to a no-till field. That rain event accounted for only 3% of the yearly rainfall and 6% of the yearly run-off; yet it produced 78% of the yearly atrazine loss (Shipitalo and Owens, 2003). The Shipitalo and Owens' study also concluded that the timing of rainfall and run-off relative to atrazine application can have a much greater effect on yearly losses than agronomic management practices (till versus no-till). So, a lack of adequate sampling during an event shortly after atrazine application could cause significant underestimation of the total annual loading from a watershed. Also, Schottler *et al.* (1994) and Williams *et al.* (1995) have noted that the spring atrazine concentration often peaks in streams just before the maximum flows are achieved. One possible theory suggests that a fraction of atrazine on the soil immediately following application is readily available for transport by run-off during a precipitation event. However, later in the season, the peak concentration may actually lag the peak flow suggesting that export from the fields is associated with water that has infiltrated the soil and carried *via* shallow saturated zones or surface drainage tile networks to receiving tributaries. High frequency sampling just before, during, and after a flow event are important in order to fully capture atrazine loading events.

To evaluate the possible range of loads occurring in the Lake Michigan system, additional model runs were conducted with annual loads set equal to those expected based upon the long-term WEP of 0.6%. The USGS loads were adjusted by multiplying loads from each tributary during a 90-day period from April 15 to July 13 by a factor that resulted in the loads for that tributary being equal to the expected WEP-based load. Only the spring period was multiplied since this is the period when the majority of atrazine loads enter the lake and this is the period when tributary and atmospheric loads have the largest uncertainty. Load multiplication factors were calculated as the multiplier for the specified time period loads that set the total 1994 and 1995 USGS-calculated loads for each tributary equal to the combined WEP loads for both years for that tributary. Computer code in the LM3-Atrazine model conducted the multiplication during the model simulation by reading inputs for the scaling time periods for each year and the multiplication factors for each tributary. WEP-based loads and USGS-estimated loads are listed in Section 2.2.5. Figure 5.7 displays the USGS and WEP-based loading time-series for the three largest tributary loadings of atrazine to Lake Michigan.

A loading series for the 12-year model runs was developed by repeating the loads for the 1994-1995 period six times, using USGS-calculated or WEP-adjusted loads as appropriate. The LM3-Atrazine model did this automatically by looping over the two-year loading input deck and applying the load multiplier factors as needed.

In Figures 5.7-5.10 and for the remainder of this part, the "long-term WEP loads" in the legends refer to USGS loads that were adjusted as described in the preceding paragraphs and "USGS estimated loads" refer to the loads as received from the USGS.

5.3.3.3.2 Atmospheric

Atmospheric deposition samples were collected from March 1994 through October 1995. Wet deposition was the dominant atmospheric source of atrazine to Lake Michigan. The monthly average 1994 and 1995 wet deposition loading time-series data were provided by Hornbuckle (University of Iowa, personal communication, 2002; Miller *et al.,* 2000). Dry deposition was not included in the atmospheric loads.

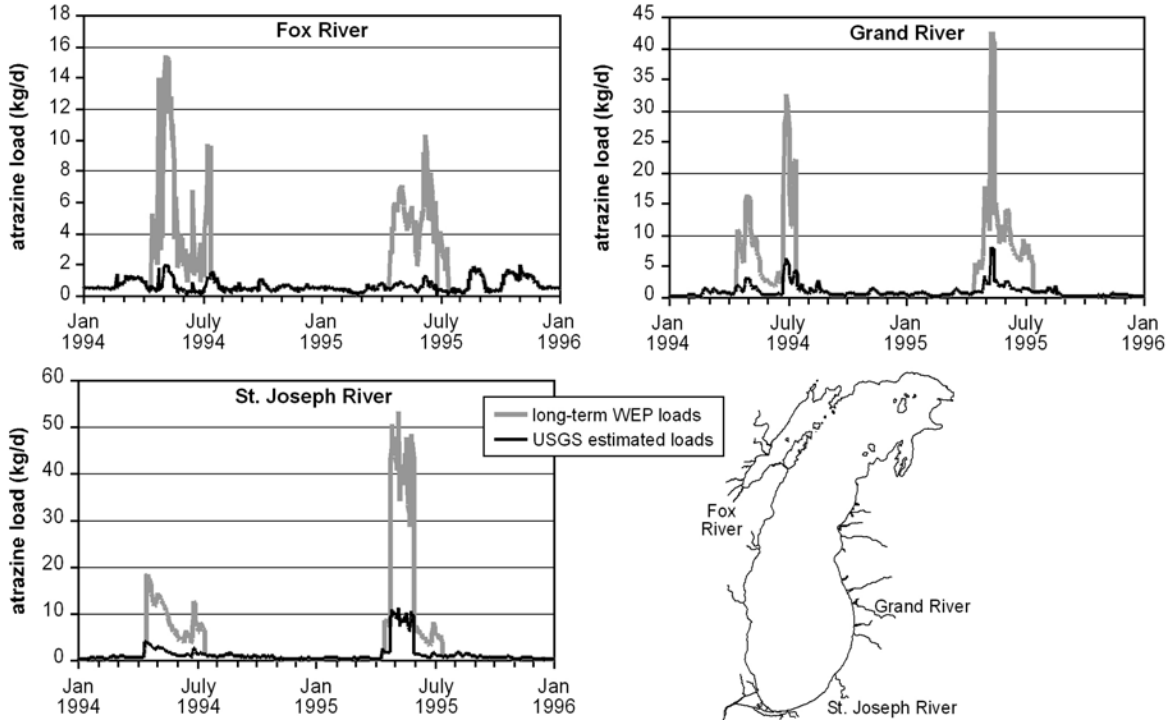

Figure 5.7. Atrazine loads for Lake Michigan tributaries, 1994-1995.

Estimates from the LMMBP study found it to be small (208 kg/year) (Miller, 1999). However, later estimates placed the range of dry deposition loads from 230-1000 kg/year (Miller *et al.*, 2000). For additional discussion on atrazine in the particulate fraction, see Part 1, Chapter 3.

5.3.4 Description of Model Simulations and Results

Model simulations were conducted for different load scenarios and time periods. Simulations were conducted with tributary loads based upon the 1994-1995 USGS estimates and with loads based upon the long-term WEP loads. Atmospheric loads were kept constant for all model runs. Time periods modeled included the two-year period of the LMMBP (1994-1995) and the 12-year period from 1994 to 2005.

For the 1994-1995 simulation using USGS tributary loads, mid-lake model results generally matched field data (Figure 5.8). Mid-lake model predictions varied little over the course of a year. The 1994-1995 simulation using the long-term WEP loads (Figure 5.8) was run to represent long-term trends of loadings. These higher loads resulted in greater seasonal increases in mid-lake concentrations compared to the USGS-estimated loads, but annual variation was still relatively small.

The high-resolution LM3 model was especially useful in demonstrating near-shore impacts resulting from various watershed loads. Higher concentrations were predicted in the areas near the mouths of major tributaries during the spring and early summer period when loadings were highest (Figure 5.9). The high-resolution model was also useful for demonstrating the impact of different loading scenarios on small spatial areas. Model results from the 5 km x 5 km model segments directly off the mouths of the major tributaries showed the largest variations of atrazine in the lake (Figure 5.10). Predicted concentrations directly off the mouth of the St. Joseph River ranged as high as 102 ng/L using the USGS-estimated loads and as high as 350 ng/L using the long-term WEP-based loads model runs.

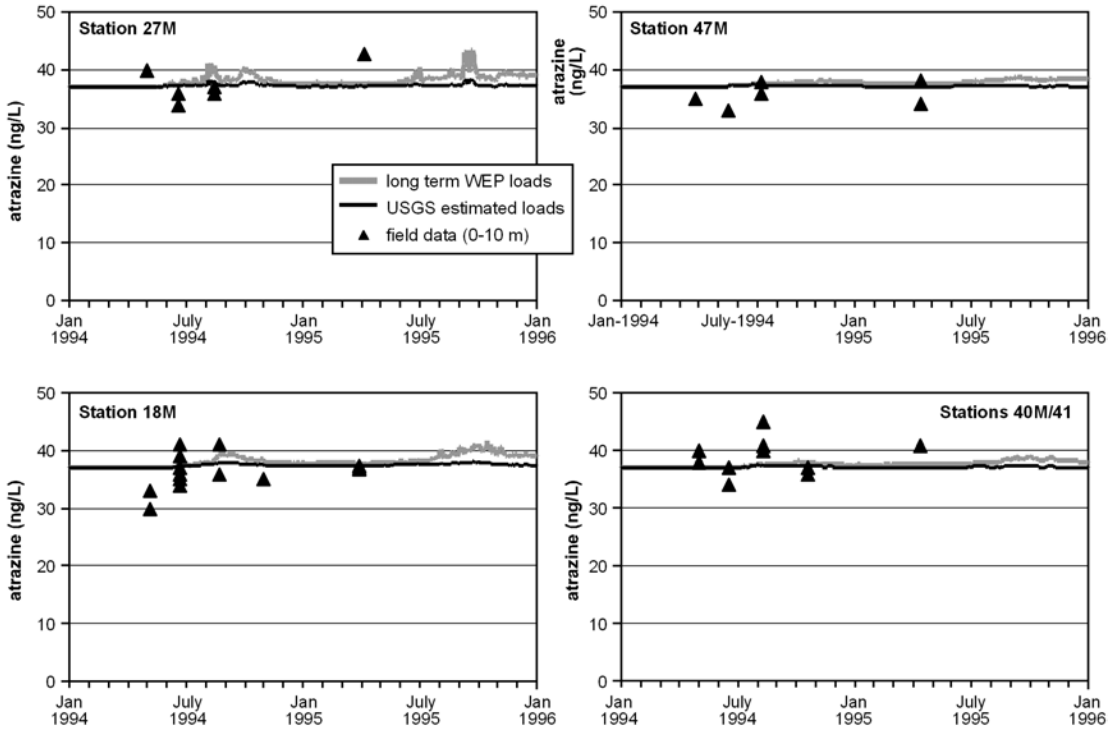

Figure 5.8. Comparison of field data to predicted mid-lake surface concentrations for the 1994-1995 model simulation and two loading conditions. Station locations are shown in Figure 5.6.

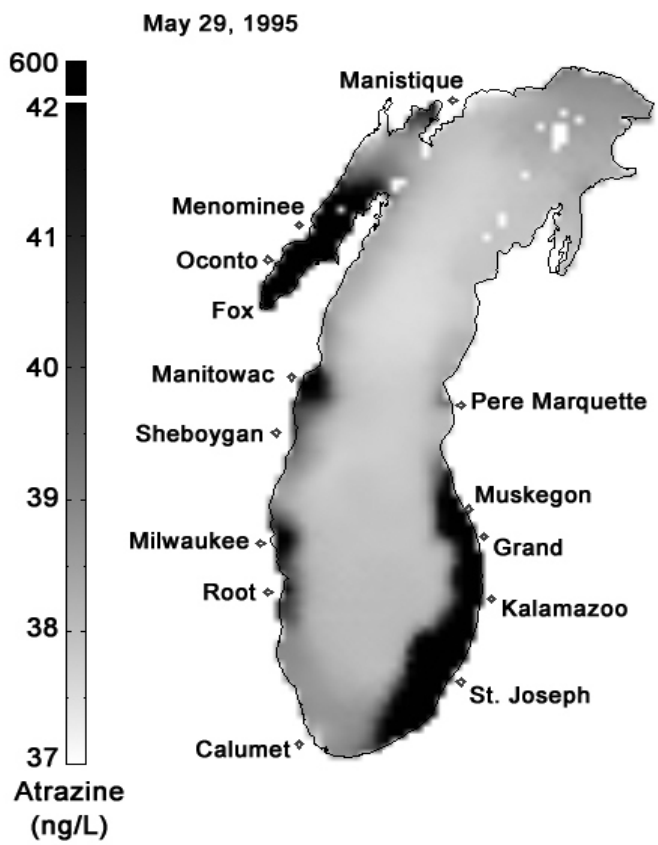

Figure 5.9. Model simulation results of surface concentrations for May 29, 1995 using long-term WEP-based loads. Selected tributary input locations are labeled.

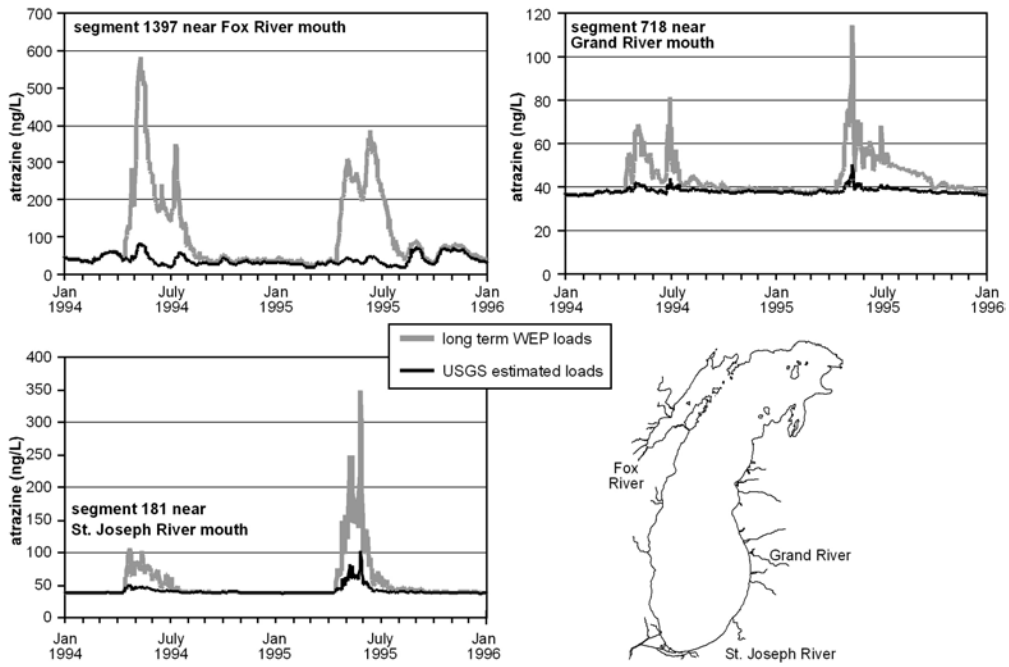

Figure 5.10. Comparison of near-shore surface cell model results for the 1994-1995 model simulation and two loading conditions.

While the model is useful for demonstrating near-shore impacts, it does not simulate concentrations in a river plume entering the lake or in the tributary itself. During model simulations, at each time step, any tributary load is immediately mixed throughout the 5 km by 5 km model cell near the tributary mouth, and thus predicted near-shore concentrations are a function of the size of the model cells and not representative of concentrations in river plumes in the lake. Furthermore, the LM3-Atrazine model was not designed to make predictions of atrazine concentrations in any of the tributaries.

The model results reasonably fit the available data, and no adjustments were made to the initial model kinetic parameters. A better model fit to data probably could have been obtained by using different initial concentrations in different regions of the main lake rather than a uniform, lake-wide initial concentration. However, since the January 1994 initial concentrations were estimated from spring 1994 data, it was believed that the sampling data were not sufficient to justify that change.

A longer-term data set would be required to fully calibrate the LM3-Atrazine model. However, confidence in model predictions was provided in two ways. First, atrazine in Lake Michigan acts as a mostly conservative chemical, and the model was previously calibrated to the conservative chemical chloride in Lake Michigan (Richardson *et al.*, 2001). Thus there is confidence that the transport of substances, one of the primary loss processes of atrazine, was being correctly simulated. The high-resolution transport is the primary difference between LM3-Atrazine and the MICHTOX and LM2-Atrazine models. Second, an acceptable simulation of atrazine concentrations was obtained using model parameters derived from literature and previous modeling studies, providing confidence in the kinetic formulations and kinetic parameterization of the model (Rygwelski *et al.*, 1999; Part 3; Part 4).

As part of the 2005 Lake Michigan sampling effort, the USEPA collected atrazine samples at multiple stations during multiple cruises. These data were not available at the time of this report, but, when available, they will provide a comparison of atrazine concentrations to those measured in 1994-1995 and an estimate of the change in atrazine mass in the system over that time period. To estimate potential changes in Lake Michigan atrazine concentrations during the 1994-2005 time period, additional LM3-Atrazine model simulations were conducted. Two

model runs were conducted: one with the 1994-1995 USGS-estimated loads and one with the WEP-based loads. The 12-year loading time-series for these runs was developed by repeating the appropriate 1994-1995 loading time-series and hydrodynamics six times. Assuming that atrazine usage in the watershed did not change significantly from that during 1994-1995, results from these model simulations will likely bracket the concentrations from the 2005 sampling period. Predicted mid-lake concentrations for 2005 ranged from 38 ng/L for the USGS tributary loading time-series to 46 ng/L for the WEP-based tributary loading time-series (Figure 5.11). Tributary loads were not sampled during the 2005 surveys, but by calculating the change in the in-lake atrazine inventory and comparing it to the load scenarios used for model runs, the actual magnitude of present watershed loads will be able to be estimated.

5.3.4.1 Mass Budgets

Inflows and outflows of atrazine to the Lake Michigan system were tabulated during the 1994-1995 model simulation runs (Table 5.3, Figure 5.12). For the model run using the USGS-estimated tributary loads for 1994-1995, the largest source of atrazine was wet deposition from the atmosphere. The percentage of loads from tributary sources was only slightly less. For the model run using the long-term WEP-based 1994-1995 tributary loads, tributary loads dominated and were almost three times higher than wet deposition. Absorption from the atmosphere (volatilization in) was minimal for both cases.

Losses from the Lake Michigan system were similar for both loading scenarios. The largest losses of atrazine were from decay and outflow through the Straits of Mackinac, though the mass lost through these processes is relatively small compared to the total atrazine inventory in the lake. Outflow through the Chicago Ship and Sanitary Canal was a small percentage of total mass lost, and volatilization from water to the air was negligible.

The annual net gain of atrazine to the system for the model run using the USGS-estimated loads was 380 kg/year, or 11% of the measured 1994-1995 loads to the system. For the model run using long-term WEP-based load estimates the net gain increased to 3,842 kg/year, equal to 55% of incoming sources.

5.3.4.2 Selected Model Versus Observation Statistics

The variability in the field data made any comparison with model results difficult. There was as much variation between atrazine field duplicate samples as there was seasonal variation predicted by the model. Fifty-seven field duplicate and two field triplicate samples were collected as part of the LMMBP atrazine sampling. The median absolute difference between field duplicate samples was 1.8 ng/L, with the average relative percent difference (RPD) equal to 6%. Maximum seasonal variation in model results from representative mid-lake stations was 1.5 ng/L for the model run using USGS-estimated loads and 6.6 ng/L for the model run using WEP-based loads.

There were also no significant spatial or temporal trends in the Lake Michigan data (Brent *et al.*, 2001) that would have assisted in evaluating model prediction capabilities. This may have been due to an actual lack of trends or because there was no near-shore sampling during the late spring and early summer period when the lake concentrations were predicted to be most affected by seasonal atmospheric and tributary loadings.

5.3.4.3 Comparison to Toxicological Endpoints

Model simulation and forecast results were plotted with measured data against toxicological endpoints to examine potential ecological effects of predicted atrazine concentrations in Lake Michigan (Figure 5.13). Most forecast and data concentrations were below the selected toxicological endpoints of concern at the spatial scale used in these modeling analyses.

The toxicological endpoints selected for Figure 5.13 were developed as part of a review of toxicity studies used for determining the eligibility of atrazine for reregistration as an herbicide (U.S. Environmental Protection Agency, 2003a). Endpoints for important ecological components of the Lake Michigan system included fish, zooplankton, other invertebrates, and phytoplankton. Mortality endpoints correspond to acute, or short-term, toxicity studies. Growth or population reduction endpoints correspond to chronic, or long-term, toxicity studies.

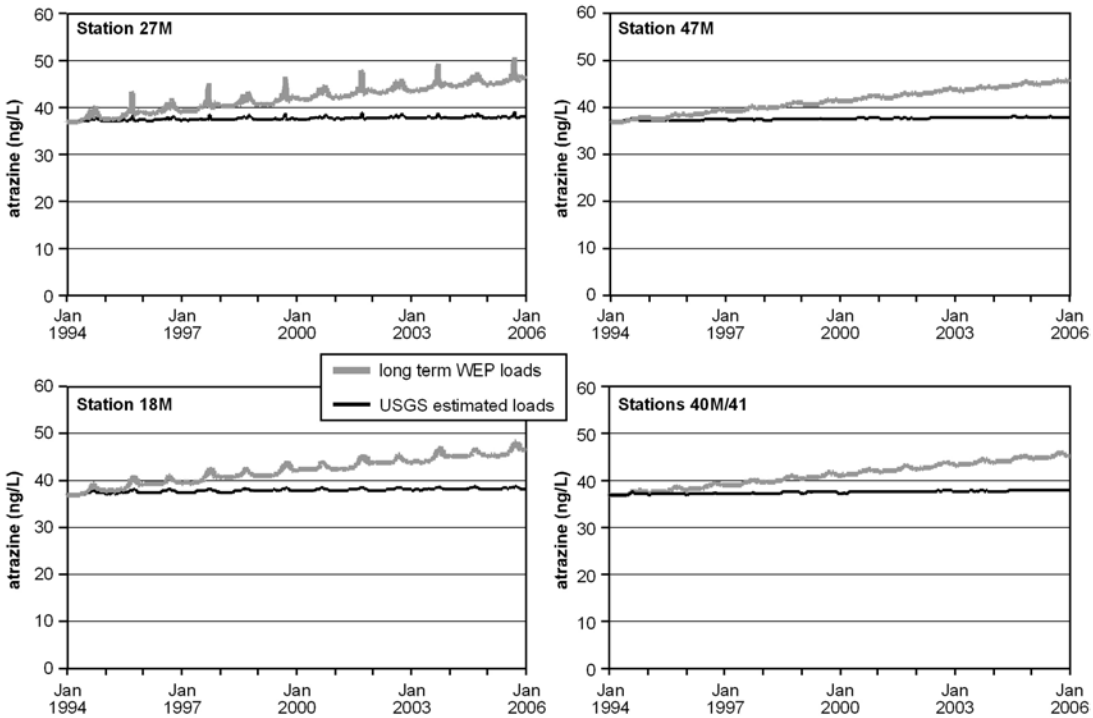

Figure 5.11. Mid-lake surface concentration model results for the 1994-2005 model simulation and two loading conditions.

Table 5.3. Mass Budget Average Annual Results for 1994-1995 Model Simulations. All are in kg/year.

	USGS Loads		Long-Term WEP-Loads	
Mass Change	380		3842	
Inflows				
Loads	3362	98%	6870	99%
Tributary	1578	(46%)	5086	(73%)
Wet Deposition	1784	(52%)	1784	(26%)
Volatilization In	58	2%	58	1%
Outflows				
Decay	1615	53%	1647	53%
Total Outflow	1412	46%	1425	46%
Chicago Outflow	110	(4%)	112	(4%)
Mackinac Outflow	1302	(43%)	1313	(43%)
Volatilization Out	13	0%	14	0%
Totals				
Net Volatilization	-45		-44	
Total In	3420		6928	
Total Out	3040		3086	
Average Mass Inventory (kg)	179,459		182,979	

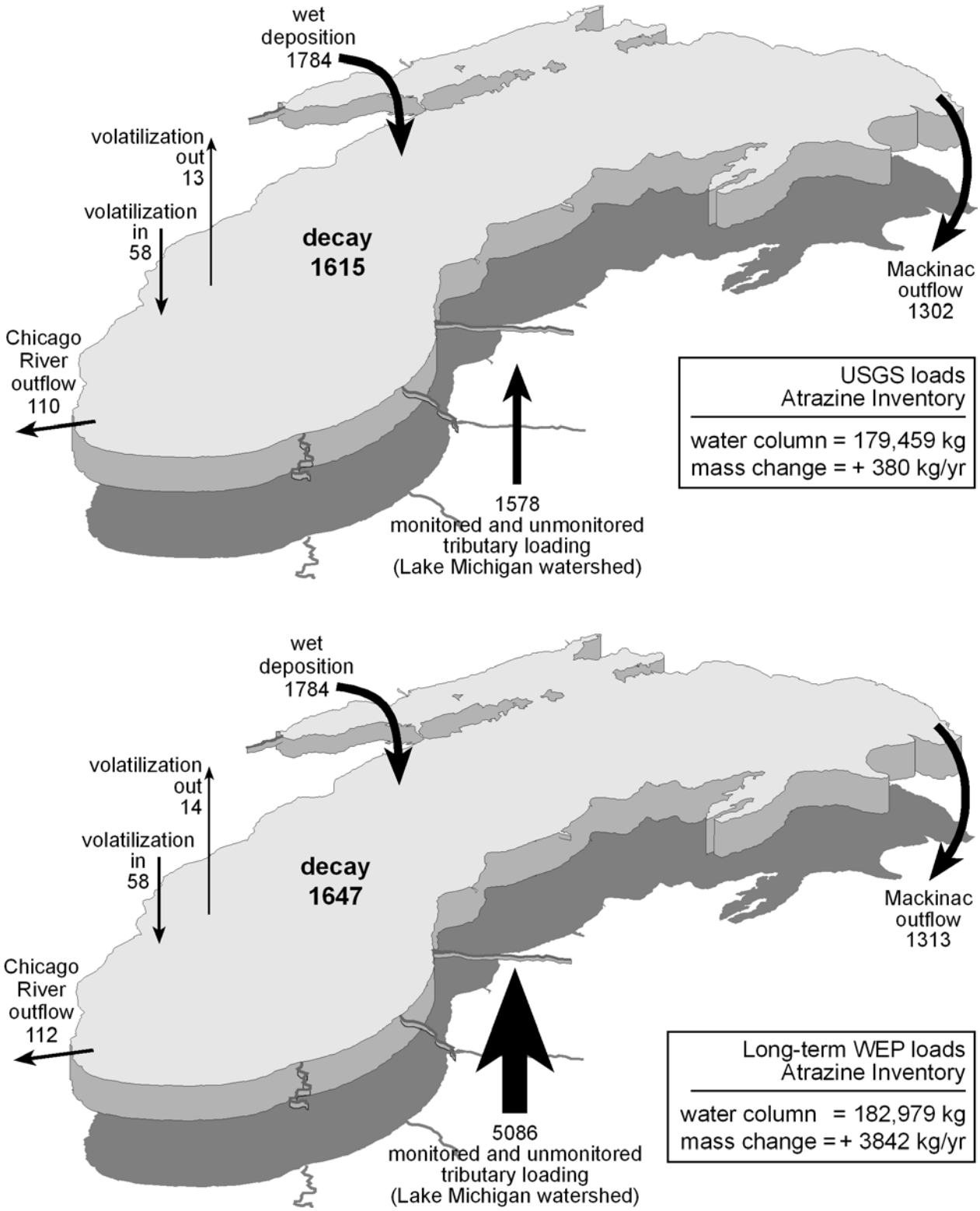

Figure 5.12. Mass budget average annual results for the 1994-1995 model simulations. All mass flow rates are in kg/yr.

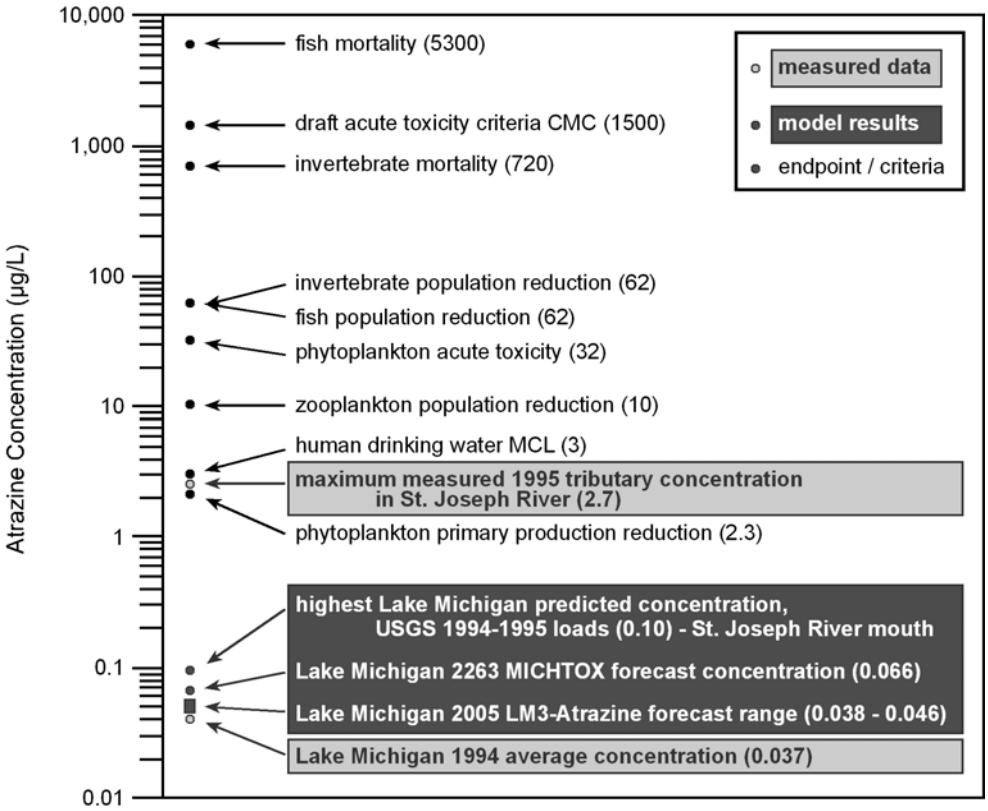

Figure 5.13. Comparison of model predictions, measured data, and selected toxicological endpoints.

Regulatory endpoints were also included in Figure 5.13. These endpoints included proposed criteria for environmental protection and established limits for human health protection. Water quality criteria for the protection of aquatic ecosystems have been proposed for atrazine (U.S. Environmental Protection Agency, 2003b) but were not finalized at the time of this report. The draft acute toxicity Criterion Maximum Concentration (CMC) was included in Figure 5.13. While a draft chronic criteria was also published, it was not included in the figure because it was not based upon a single concentration. The draft chronic criteria were based upon modeling ecological community changes in aquatic plants using both exposure concentration and duration. The human drinking water Maximum Contaminant Limit (MCL) is also included in the graph.

Measured atrazine data collected during the LMMBP were below endpoints of toxicological concern except for one tributary sample from the St. Joseph River in May 1995. This measurement, 2.7 µg/L, exceeded the endpoint of 2.3 µg/L at which reductions in primary production of phytoplankton were estimated to occur. The St. Joseph River sample was also close to the human drinking water MCL. Detailed information on determining compliance with the MCL for atrazine can be found in 40 CFR 141.24(h). The second highest measured tributary concentration, 0.55 µg/L, was a sample from the Grand River in May 1996 and was below all selected toxicological endpoints. The 1994 Lake Michigan annual average atrazine concentration of 0.037 µg/L was well below the selected toxicological endpoints.

Model forecasts were below all selected endpoints. The MICHTOX long-term steady-state forecast concentration of 0.066 µg/L was well below toxicological endpoints. The LM3-Atrazine 12-year (2005) forecast lake-wide concentration range was lower than the MICHTOX steady-state forecast concentration. The highest simulated single model cell concentration from the high-resolution LM3-Atrazine model was also below selected endpoints.

The highest simulated concentration, using the USGS loading time-series, was 0.10 µg/L near the mouth of the St. Joseph River. It must be remembered that this concentration represents an average prediction from a volume representing a 5 km by 5 km area of the lake which provides significant dilution to tributary event loads. The WEP-based loading time-series was not used in this analysis because the distribution of the long-term annual loads among seasons and short-term loading events was somewhat subjective. Thus, presenting a concentration prediction based upon this loading time-series at a single location and point in time would have a large amount of uncertainty.

5.3.5 Model Uncertainty

While the LM3-Atrazine could not be fully calibrated because of insufficient data, the basis upon which the model was developed provided confidence that model results were reasonable. The hydrodynamic model was successfully compared to two separate datasets (Schwab and Beletsky, 1998) and model transport of a conservative substance, chloride, was also calibrated (Richardson *et al*., 2001). The only additions to the chloride model for the LM3-Atrazine model were volatilization and kinetic decay terms. Volatilization was a minor effect on the fate of atrazine in the lake, and the decay term was based upon long-term hindcast calibrations with the MICHTOX and LM2-Atrazine models. Furthermore, the model provided reasonable fits to data without changing model kinetic parameters from the initial values based upon literature studies and previous atrazine model calibration studies. There may be some uncertainty about the decay term because the LM2-Atrazine model used to calibrate the term incorporated bi-directional flow at the Straits of Mackinac outflow while the LM3-Atrazine model used a net outflow from the Straits to Lake Huron. However, this would only have had a minor effect on the atrazine mass in the lake for the time periods modeled with the LM3-Atrazine model.

There was probably more uncertainty from the loading data used in the model and the field data than from the model kinetic processes. The estimated 1994-1995 tributary loads were significantly less than those expected based upon previous long-term modeling studies, and it was not known if 1995 was a year of low atrazine loading, if storm events were missed during the tributary sampling, or if there were additional significant sources of loads such as dry deposition that were not measured.

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PART 6

REVIEW OF ATRAZINE MODELS

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6.1 LMMBP Atrazine Models

6.1.1 Peer Reviews of LMMBP Atrazine Models

Two modeling science peer reviews were conducted on the Lake Michigan Mass Balance Project (LMMBP) atrazine modeling products. These reviews were conducted near the beginning and final phases of the atrazine modeling work. The first review was general in nature and was conducted on June 23-25, 1998 in Southgate, Michigan and covered all components of the LMMBP modeling effort including project design and organization; project management, including an evaluation of resources; model linkages; sediment transport; loadings; hydrodynamics; model construct; atrazine; polychlorinated biphenyls (PCBs); eutrophication; and mercury. The second review was conducted on September 27, 2000 in Romulus, Michigan and solely focused on atrazine modeling.

In the first review, panel members recommended that atrazine modeling advance to a level 2 type model (LM2-Atrazine) with more resolution than MICHTOX. Also, they recommended that management scenarios for the prediction of alternative futures include model sensitivity runs that include both zero atrazine concentrations in the vapor phase and non-zero concentrations, because measurements of the vapor phase concentrations in the basin were difficult to detect (see Part 4 for LM2-Atrazine modeling results). Reviewers encouraged the development and application of the high-resolution model, LM3-Atrazine (see Part 5 for results of LM3-Atrazine, a 5 km x 5 km gridded model). The reviewers included United States Environmental Protection Agency (USEPA), Great Lakes National Program Office (GLNPO); Dr. Paul Capel, United States Geological Survey (USGS); Dr. Miriam Diamond, University of Toronto; Dr. Kevin Farley, Manhattan College; Dr. Raymond Hoff, Environment Canada; Dr. Robert Hudson, University of Illinois - Urbana Champaign; and Dr. Barry Lesht, Argonne National Laboratory.

Review comments from the second peer review appear in Appendix 6.1 of this Part. In general, comments received on atrazine modeling for the LMMBP were very favorable. Reviewers included USEPA/GLNPO; Dr. Paul Capel, USGS; and Dr. Robert Hudson, University of Illinois.

The reviewers acknowledged that although the modified Stratified Beale Ratio Estimator (SBRE) method and the USGS ESTIMATOR used in the LMMBP are standard and reliable methods to estimate loadings, the length of the data record (one year) for the LMMBP was perhaps too short, and the number of samples taken from the tributaries to estimate loads was limited. Typically, multi-year records are used. There was follow-up discussion and evaluation of another load estimation procedure by Dr. Robert Hudson after the formal peer review comments were submitted. All of the necessary files were provided to Dr. Hudson to make loading assessments using rating curves similar to what is used in ESTIMATOR, but also to look at all the sites together rather than individually. He consulted USGS, who performed the LMMBP load estimates, before performing his analysis. The new attempt was not successful. The reviewers concluded that the load estimates made for the LMMBP using the watershed export percentage (WEP) approach were most likely the best estimates available for the project.

It was recommended that further literature research be conducted to determine what type of degradation mechanisms may be operative in Lake Michigan. This was done and the results were reported in Part 1, Chapter 2.

The reviewers concluded that there are a number of combinations of watershed export percentages (WEPs) and *in situ* decay rates that could achieve a model "fit" to the data. It is true that if the WEP were increased, the decay rate would have to increase. A concern was raised by the reviewers that these variables are somewhat unconstrained. However, the WEP was constrained by focusing only on northern freshwater drainage basins with soil texture similar to that of the Lake Michigan basin. Also, since rainfall can have an effect on measured WEPs, a balance of both wet and dry years were included in our long-term model runs. Using the mean WEP from these studies reported in the literature was the best estimate of the WEP's central tendency in the Lake Michigan basin. Indeed, one of the reviewers, Paul Capel, looked at WEPs from 408 observations across numerous types of soil textures after the peer review and calculated a mean WEP of 0.66%, which was close to our mean of 0.6% (Capel and Larsen, 2001).

Other comments included a recommendation for a follow-up atrazine sampling of Lake Michigan water to help confirm short-term model predictions. This sampling was done in 2005; however, the results were not yet available at the time of this printing. Also, the reviewers suggested that a model sensitivity analysis be conducted. Sensitivity analyses were performed using both the MICHTOX model and the LM2-Atrazine models and are reported in Parts 3 and 4 of this report.

The reviewers also were very pleased with the progress made with the LM3-Atrazine application and suggested that this high-resolution model would be very useful for making local environmental management decisions. The modelers agree with this assessment and have demonstrated local applications in the vicinity of the St. Joseph River, Fox River, Grand River, and the Kalamazoo River mouths. Some of the details of the St. Joseph application are discussed in Part 5.

6.1.2 Comparison of LMMBP Models

The LMMBP models are those discussed in this report: MICHTOX, LM2-Atrazine, and LM3-Atrazine (Part 3, 4, and 5, respectively). The differences in the model construct among these models has been discussed. Total annual atrazine loadings for all three models were the same and were based on an estimate of the 0.6% WEP. Both MICHTOX and LM2-Atrazine were calibrated using historical loading estimates and comparing model output to available lake data. Calibration consisted of selecting an appropriate *in situ* total decay so that model output matched lake data. For Scenario 3, based on average conditions and the most likely scenario, MICHTOX yielded a half-life of atrazine in the lake of 69.3 years (kinetic decay of 0.01/year). LM2-Toxic predicted a similar half-life of 77 years (kinetic decay of 0.009/year). LM3-Atrazine model used the 0.009/yr decay derived from calibration of decay in the LM2-Atrazine model.

6.2 Comparison of LMMBP Models to Other Recent Atrazine Models Applied to Lake Michigan

Within the last decade, three Lake Michigan atrazine modeling papers have been published. All three models were based on the principles of mass balance. However, the three models yielded very different estimates of *in situ* atrazine decay. Tributary loads carry the most atrazine to the lake compared to other sources. Therefore, any significant differences in the amount of atrazine delivered among the models will result in a range of internal decay estimates. There are many differences among these models, but the analysis here will specifically focus on the main reasons why these models differ.

6.2.1 Schottler and Eisenreich (1997)

Schottler and Eisenreich (1997) predicted an internal, overall, 14-year half-life for atrazine in Lake Michigan using a mass balance model called Stella. They used an atrazine WEP of 1% obtained from studies on basins outside of the Lake Michigan basin. However, their selection of WEP's did not appear to be based on soil textures that match those of the Lake Michigan basin. Also, it was not clear if the WEP they used reflected wet or dry years (or a combination of both). These considerations could have an impact on selecting a representative WEP for the Lake Michigan basin (See Part 2, Chapter 2). The watersheds were from both northern and southern regions. The higher WEP used by Schottler and Eisenreich will yield higher atrazine tributary loads to be delivered to the lake (approximately 67% more mass loading from tributaries than the LMMBP models delivered) and therefore more internal decay was required in the lake to achieve a model fit to the lake data. Their model predicted that atrazine concentrations in the lake were at a steady-state concentration of 34 ng/L in 1994, but the model predicted that the lake concentration was close to this value since the late 1980s. The LMMBP models suggest that the lake, under constant 1995 loadings into the future, will reach a steady-state concentration of 66 ng/L in the year approximately 2194.

6.2.2 Tierney et al. (1999)

Tierney *et al.* (1999) predicted that the half-life of atrazine in Lake Michigan is about two years. The authors used atrazine run-off concentration data derived from the Lake Erie basin (Richards and Baker, 1993), and from Bodo (1991), who studied watersheds in Southwestern Ontario to make estimates of atrazine loading in the Lake Michigan basin. The soils in the Lake Erie basin have much more clay (Richards and Baker, 1993) than the soils in the Lake Michigan basin and run-off (WEP) of atrazine in the Lake Erie basin would likely approach percentages over 1% (see Table 2.2.2 in Part 2 of this report). The Lake Michigan basin has moderate textured soils, and the run-off WEP would be closer to 0.6%. Using atrazine concentration data from Lake Erie tributaries with high WEPs and applying them to characterize tributaries in the Lake Michigan basin would result in more atrazine loadings to Lake Michigan than what is likely, and therefore, *in situ* decay will need to be high in their model in order for the model to match observed lake data. High decay is associated with the short half-life that they report.

Run-off loads of atrazine also is a strong function of the amount of atrazine applied to corn in the watershed. Predicted run-off concentrations in the Lake Michigan basin by Tierney *et al.* (1999) did not appear to be based on relating corn crop acreage in Lake Erie basin and Lake Michigan basin. They related flow-weighted concentrations in tributaries to % total agricultural land use and then applied them to the Lake Michigan basin. Total agricultural land use would be a poor predictor of atrazine usage/discharge if corn crop acreage per acre agricultural land varies within or between the Lake Erie and the Lake Michigan basins. The reason is that atrazine is used almost exclusively on corn crops in the Great Lakes basin. There is no indication in the paper that an analysis of corn crop acreage variation within agricultural lands was performed. To further complicate this issue, the amount of atrazine applied to corn acreage can vary from state-to-state.

Loadings in their model (both from watershed run-off and precipitation) appear to be fixed to levels observed in the early 1990's and applied for the entire historical usage period of the chemical. This would have overestimated loads from the period leading up to approximately 1978. This

overestimation of loads in those early years would require that they include a significant non-zero atrazine decay term in their mass balance.

The Tierney model predicted that Lake Michigan reached steady-state atrazine concentrations in the mid- to late-1970s with a concentration of 33 ng/L.

In contrast, Richardson and Endicott (1994) and Rygwelski *et al.* (1999) and the modeling work in this paper organized WEPs from the literature and used a WEP based on moderate textured soils typical of the Lake Michigan basin of 0.6%. Furthermore, Rygwelski *et al.* (1999) and this paper selected WEPs only from northern watersheds only and included a mix of both wet and dry years (see Part 2, Chapter 2). Also, only corn crops grown in the Lake Michigan basin were included in this analysis to determine atrazine loadings on a county-by-county basis.

The results of the three atrazine models applied to Lake Michigan are displayed in Table 6.1. A WEP of approximately 5.6% was calculated for the Tierney model, based on their estimates of loads to the lake and amount of atrazine applied to the Lake Michigan watershed. It is clear from the table, that higher WEPs are associated with shorter atrazine half-lives.

6.3 Atrazine Models Applied to Lake or Deep River Systems Outside the Lake Michigan Basin

Other atrazine models have been applied to large freshwater lakes and rivers. Consistent with the results of the LMMBP models, these models have shown that little to no atrazine decays in these lakes and that loss *via* outflow from the lakes or rivers is the primary atrazine removal mechanism.

6.3.1 Swiss Lakes

Ulrich *et al.* (1994) modeled atrazine in an eutrophic lake, Greifensee, in Switzerland. The lake has a maximum depth of 32 m with a mean of 17.8 m. They found that, except for a short time in July and August, atrazine showed a somewhat conservative behavior. Within the overall mass balance, *in situ* decay accounted for only 5% of total annual loss of atrazine from the lake. Ninety-five percent of the loss from the lake was attributed to outflow. The authors

Table 6.1 Comparison of LM2-Atrazine Model to Other Models

Model	WEP	Half-Life	Watershed Load Methods Used	Estimated Year to Reach Steady-State	Atrazine Steady-State Concentration ng/L
Rygwelski and Zhang, 2007 (Part 4 of this report)	0.6%	77 yrs.	County Application and WEP	2194	66
Schottler and Eisenreich, 1997	1.0%	14 yrs.	County Application and WEP	1994 But Approached Near Steady-State Concentration in the Late-1980s.	34
Tierney *et al.*, 1999	Not Used Directly (Approx. 5.6%)	2 yrs.	Run-off Flow and 0.23 µg/L Forested; 1.6 µg/L Agricultural (Flow-Weighted)	Mid- to Late-1970s	33

noted that decay in the epilimnion layer of 0.003 per day was needed only in July and August to get the model to fit observations. They also noted that during that time, nitrate levels in the lake increased. High nitrate concentrations and high solar energy have been associated with indirect photolytic degradation of atrazine in water (see Section 1.2.3.2 of this report). Since the lake stratified in the warm months of the year, water in the hypolimnion would be somewhat more isolated from photolytic decay than the epilimnion. During the rest of the year, atrazine was modeled without decay. Modeled processes such as volatilization and sedimentation were negligible.

Buser (1990) modeled atrazine in Lake Zurich, Switzerland. The maximum depth of the lake is 136 m with an average depth of 50 m. His results also showed atrazine to be rather stable and its removal primarily *via* outflowing waters compared to other loss processes such as sedimentation, degradation, and volatilization. This lake also stratified during the warm months of the year.

Müller *et al.* (1997) modeled atrazine in three Swiss lakes: Greifensee, Murtensee, and Sempachersee. The maximum/mean depths for the Murtensee and Sempachersee are 45.5 m / 23.3 m and 87 m / 44 m, respectively. Except for the July and August period when they used an *in situ* decay of 0.003 per day in the epilimnion, atrazine was modeled as a conservative substance. Good agreement was achieved between model output and measured concentrations of atrazine in the lakes.

6.3.2 St. Lawrence River

Over an 18 month period in 1995 and 1996, Pham *et al.* (2000) measured the inputs and outputs of loadings of atrazine to a reach of the St. Lawrence River. The atrazine load was measured in both the upper part of the river near Cornwall, Ontario, Canada and at the outflow to the estuary, near Quebec City, Quebec, Canada. Taking into account loadings from the watershed, their measurements indicated that atrazine does not degrade during the three day transit in the river. This large river has a mean discharge of approximately 12,000 m^3/s at Quebec City. At Cornwall, the depth is about 8.2 m and at Quebec City the depth is approximately 11 m.

6.4 Atrazine Models Applied to Shallow Surface Water Systems in Agricultural Areas

Atrazine degradation seems to be occurring in shallow surface water systems in agricultural areas. A hypothesis is that in these shallow systems, light energy penetrates a greater percentage of the water column than in lakes that show thermal stratification in the summer. Compared to these lakes, shallow rivers have fast mixing due to turbulence. This brings a fresh supply of atrazine close to the surface where photolysis can more easily degrade it. Rivers also generally have higher solids concentrations that could act as catalysts for hydrolysis. In deep lakes, summer stratification isolates water from photolysis in the hypolimnion and solids concentrations tend to be lower than that found in rivers. See Part 1, Chapter 2 for more discussion on this topic.

6.4.1 Saylorville Reservoir, Iowa

The Saylorville Reservoir is located on the upper Des Moines River basin in Northern Iowa near the city of Des Moines. Seventy-nine percent of the basin is cropland, mostly corn and soybeans. The reservoir is shallow, with a mean depth of only 4.3 m. Chung and Gu (2003) modeled atrazine transport and fate in 1997. During the study period, the reservoir showed very weak thermal stratification in the summer months, which allowed them to assume well-mixed conditions. The authors found a strong inverse relationship between half-life and daily hours of sunlight. This supports the notion that photolysis was probably operative as a loss mechanism. In this system, approximately 60% of the atrazine that entered the reservoir was released through discharge. Approximately 40% of atrazine in the reservoir was transformed *via* kinetic loss mechanism(s) such as photolysis, hydrolysis, etc. The half-life of atrazine in the reservoir varied from two to 58 days. Their analysis found that the half-life of atrazine did not correlate well with nitrate concentrations, suggesting that photolysis was not nitrate-mediated indirect photolysis. Rather, they indicated that direct photolysis, aided by the high concentrations of dissolved organic carbon (DOC), was probably operative.

6.4.2 Other Small Surface Water Systems

Other modeling studies in small lakes and a shallow creek in agricultural regions have shown similar, relatively short half-lives of atrazine.

Spalding *et al.* (1994) estimated the atrazine half-lives in two very small lakes in Northeastern Nebraska ranged from 124 to 193 days. Spalding suggested that hydrolysis may have been responsible for degradation of atrazine in these lakes. However, these lakes had relatively high pH's averaging 8.1 for one lake and 8.2 for the other, and some researchers have found that hydrolysis above pH 4 was difficult to achieve in the laboratory. The authors did not rule out photolytic decay. These small lakes were very turbid where average Secchi readings were less than 1 m. None of the other atrazine modeling papers reviewed suggested hydrolysis as a possible explanation of atrazine decay.

In a small creek in Iowa, Kolpin and Kalkhoff (1993) found that atrazine half-lives had a significant inverse relationship with sunlight, therefore suggesting photolysis was responsible. To rule out temperature as a confounding variable, they found that comparing atrazine half-lives to water temperature did not yield a significant correlation. The degradation in Roberts Creek was very rapid. Half-lives ranged from 168 hours (November 1990) to 35.6 hours (July 1990). The stream discharge ranged from 0.264 to 0.086 m^3/s during the sampling period, April 11, 1990 to December 2, 1990.

6.5 Conclusions

A likely reason for the discrepancies (see Table 6.1) between the three Lake Michigan atrazine modeling efforts has to do with the wide range of estimates made for tributary loadings of atrazine to the lake. Since tributary loadings are the major source of atrazine to the lake, rigorous detailed efforts need to be taken to ensure that these loads are as accurate as possible.

Atrazine decay in large surface water systems (lakes and rivers) appears to be much lower than decay found in shallow water systems. In larger systems, decay is very slow with half-lives estimated in years. In shallow, small systems with a high degree of mixing, atrazine decay can be rapid with half-lives estimated in days or even hours.

Research suggests that decay in surface water may be linked to photolysis, either direct of indirect. Modeling studies in deeper lakes suggest that this happens in the summertime when solar energy is high. Photolysis is limited in lakes that are stratified or deep rivers, because the exposure of light energy to the inventory of atrazine in these systems is limited. Systems that are well-mixed further facilitate photodegradation, because a fresh supply of atrazine is constantly being brought to the water surface where light energy would be the greatest. Atrazine in a hypolimnion layer would be less available for photolysis because it is somewhat isolated from the mixed epilimnion layer due to the thermocline.

In regards to Lake Michigan, can other degradation processes besides photodegradation explain the *in situ* decay? Per Part 1, Chapter 2, Section 1.2.3.1, biodegradation in surface waters is not likely. Hydrolysis in Lake Michigan is not likely because of the high pH of 8.4, low solids, and low DOC (see Part 1, Chapter 2, Section 1.2.3.2.1).

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PART 6

REVIEW OF ATRAZINE MODELS

Appendix 6.1 Peer Review of LMMBP Atrazine Models, September 27, 2000, Romulus, Michigan

Report of the Second Review Panel Meeting
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A.6.1.1 Overview

The second review meeting was focused solely on the work that the Lake Michigan Mass Balance Program (LMMBP) has completed on atrazine. Presentations were made on the following subjects: data quality assurance; summary statistics measurements in air, rain, tributaries, and lake water; tributary load calculations; modeling atmospheric transport and deposition; atmospheric deposition calculation results; hydrodynamic transport in the 41 segment model; hind/forecasting using MICHTOX; and, simulation results from 41-segment and high-resolution models.

The review team feels that the LMMBP has generally met its goals for modeling atrazine loading to and fate and transport within Lake Michigan. The following aspects of the work were notably strong:

A. The data management system and data quality assurance program were excellent. A great deal of work was expended to develop the platforms and communication that was needed to make such a large data set useful. This work had recently undergone an independent review.

B. The atmospheric modeling (from volatilization to deposition) is an important contribution, both to the LMMBP and to the scientific community. This is the first attempt at a regional model for a semi-volatile chemical. Although the work is still underway, the planned attempts to compare model predictions with the field measurements is commended.

C. The hydrodynamic components of the 41-segment model appear to be complete and well-calibrated, based on the results for temperature and chloride. These components of the model will be further tested when the focus shifts from atrazine, which is largely dissolved, to the particle-associated chemicals (mercury and PCBs).

D. The simulations of atrazine fate within the lake based on the MICHTOX, 41-segment, and high-resolution models agreed well with each other

and with the measured data. The fact that the measured atrazine concentrations were relatively homogeneous throughout the lake (22 to 58 µg/L) made the comparison of measured and modeled results a "relatively" straightforward, albeit necessary test of the model.

E. The use of MICHTOX (Rygwelski *et al*., 1999) to simulate the evolution of atrazine levels in the lake since atrazine use began (hindcasting) and to forecast future levels was an excellent way to tackle the issue of the rate of atrazine decay within the lake. It also plays an important role in testing the consistency of the loading and decay estimates.

F. The high-resolution modeling has significance far beyond the potential improvements in scientific understanding of atrazine fate it may bring. The model should be of great use in making local environmental management decisions. In addition, the animations produced from the daily simulations should serve as an excellent communications tool for environmental managers to reach the public with. This work should continue to be strongly encouraged.

A.6.1.2. Comments on Technical Issues

A. **Tributary Loads of Atrazine** – The LMMBP work to date indicates that about 2/3 of the atrazine load to Lake Michigan is borne by rivers. The tributary loads were estimated using various statistical approaches, such as the modified Beale method and the USGS ESTIMATOR software, to derive loads from a limited number of dissolved atrazine measurements in water from the rivers in the Lake Michigan basin. Although determining "true" loads is impossible, these estimation methods have proved reliable and are considered standard where non-point source loads need to be quantified. In this case, however, the length of the data record for each tributary (one-year) is short with a limited number of measurements in comparison to multi-year records that are typically used. Therefore, the reviewers suggest exploring other statistical approaches that can be used on the existing data set. Appendix 1 (in preparation) presents a brief description of one such approach that could be considered. [Note to readers: Appendix 1 was not completed by the review panel. However, Dr. Hudson did make some loading estimates using rating curves similar to what is used in ESTIMATOR, but looked at all of the sites together, rather than individually. He consulted USGS, who performed the LMMBP load estimates, before performing his analysis. The new attempt was not successful.]

The tributary loads were also estimated using the "watershed export percentage" (WEP) approach and the estimated annual use of atrazine in each watershed of rivers flowing into the lake. This approximate method serves as a good check on the tributary load calculations and has the benefit of allowing the tributary loads to easily be estimated each year for the hind/forecasting.

B. **Atmospheric Deposition** – The magnitude of atmospheric deposition was estimated through field measurements (for rain) and simple models (for dry deposition). It appears that inputs *via* rain are dominant. A single, typical value for the particle depositional velocity was chosen and all of the estimates based on this single value. The reviewers suggest that the model sensitivity to this approximation should be examined by choosing an appropriate range of particle depositional velocities. Large particles, coming from Chicago, have been shown to have much higher depositional velocities than the "typical" value used, although it is unknown how much atrazine is on these larger particles. [Note to readers: Only wet deposition was estimated for the Lake Michigan atrazine models, because dry deposition was negligible. See Part 1, Chapter 3 for more information.]

C. **Atrazine Decay Processes** – Atrazine was initially selected for study in the LMMBP as a model of a reactive, biodegradable compound (see Section 1.1 of Statistical Assessment of QA Data documents). A half-life of 14 years was estimated by Schottler and Eisenreich (1997) based on the assumption that atrazine should be approximately at steady-state within the lake. Rygwelski *et al*. (1999) showed that current atrazine levels within the lake could be predicted from plausible historical loading estimates

assuming no decay of atrazine within the lake. This approach leads to predictions of very large, continued increases in lake atrazine levels. Although atrazine levels are not likely to exceed current drinking water standards, this scenario is obviously of greater concern than the steady-state assumption.

Further literature review of mechanisms of atrazine decomposition is warranted to help determine which mechanisms are most likely to be significant in the lake. Given the current state of knowledge, it may be difficult to resolve this issue. However, the full range of processes – biodegradation, photochemical decomposition, and chemical hydrolysis should be considered. The possibility of more significant decay within the lake needs to be kept open.

D. **Summary** – Both the data and modeling results suggest that atrazine may not be as reactive within the lake as originally anticipated. This question is probably best resolved by continued monitoring of atrazine levels in lake water. The model results can be used to ensure that sampling locations are not unduly affected by tributary inputs. Further modeling work in this area should combine the historical approach with parameter sensitivity analyses. The results presented in the review meeting showed that the measured data can be correctly modeled by different combinations of WEP and atrazine's degradation rate in Lake Michigan. At this time, neither parameter is well-constrained. It is suggested by the panel that the LMMBP investigate the relationship between values of WEP and degradation rate that yield accurate estimates of current atrazine levels from historical loading rates. Presumably, an inverse relationship between the two will result, with an acceptable range for each.

The above discussion concerns an example of variables in the models that are constrained at this time only to a range of values, rather than a single correct value. The LMMBP might wish to consider other model variables to evaluate the model's sensitivity to the appropriate ranges of these values and to the relationships between parameters.

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