

Atrazine and Nutrients in Precipitation: Results from the Lake Michigan Mass Balance Study

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Atmospheric deposition of anthropogenic air pollutants contributes to degradation of water quality in the Great Lakes and other water bodies and is indicative of atmospheric pollution. In this paper, we discuss deposition of three air pollutants: atrazine; total phosphorus; and nitrogen (total Kjeldahl nitrogen and nitrate) to Lake Michigan. Throughout 18 months in 1994–1995, over 600 atmospheric samples (gas, particulate, and precipitation combined) were collected and analyzed for persistent organic pollutants and nutrients. Here the measurements and modeled deposition estimates are presented for atrazine, phosphorus, and nitrogen. Results indicate that concentrations of atrazine in precipitation have remained constant over 5 years ($0.10\text{--}0.40\ \mu\text{g L}^{-1}$), consistent with the nearly constant sales rate of the herbicide over that time period. Actual loading of atrazine to the lake was less in 1994–1995 ($1.04 \times 10^3\ \text{kg yr}^{-1}$) than in 1990–1991 ($2.6 \times 10^3\ \text{kg yr}^{-1}$). This difference in loading is due to lower overall precipitation in 1994–1995. Phosphorus concentrations in precipitation, on the other hand, have decreased from an average of $57\ \mu\text{g as P L}^{-1}$ in 1976 to an average of $6.36\ \mu\text{g as P L}^{-1}$ for 1994–1995. Nitrate deposition has decreased by a small, but not statistically significant, amount since the late 1970s.

Introduction

Atrazine is a broad-leaf herbicide applied to fields prior to plant emergence, typically during the spring months, and is the most widely used herbicide in the United States for corn and sorghum production (1–3). The Midwestern states of central Nebraska, southern Minnesota, Iowa, Illinois, Indiana, and Ohio, commonly known as the “cornbelt”, are a major source of atrazine to the Great Lakes since its use in this region is so intense (2). Overall use of atrazine has been steadily rising since 1966 (4). Atrazine’s herbicidal properties can disrupt nontarget plant and algal communities (5) and may have impact on the endocrine system in animals (6).

The presence of semivolatile organic compounds in precipitation is a function of gas transfer and particulate scavenging (7–14). The exact mechanism (gas transfer or particulate scavenging) is dependent on the physical-chemical properties of the compound and the type of precipitation (rain or snow) (15). Atrazine is soluble in water ($\log C_{\text{sat,w}} = -2.30\ \text{mol L}^{-1}$ at $20\ ^\circ\text{C}$) and is generally not detectable in the gas phase ($\log P_L^\circ = -7.86\ \text{atm}$, $\log \text{HLC} = -5.55\ \text{atm L mol}^{-1}$, at $20\ ^\circ\text{C}$). Previous estimates of atrazine loading to Lake Michigan (1) determined that 24%, or $2.79 \times 10^3\ \text{kg yr}^{-1}$, of the total loading for 1991–1994 was due to atmospheric inputs, while the other 76% was due to tributary loading. Ninety-eight percent of the atmospheric input was from precipitation ($2.6 \times 10^3\ \text{kg yr}^{-1}$), while less than 2% was from gas exchange ($0.03 \times 10^3\ \text{kg yr}^{-1}$) and particulate deposition ($0.16 \times 10^3\ \text{kg yr}^{-1}$) combined. In 1990–1991, Goolsby et al. (2) studied the temporal variability of atrazine in precipitation and estimated deposition loadings and their relationship to crop application. Atrazine was found at its highest concentration in precipitation during periods of greatest application (mid-April through June).

Overall loadings of phosphorus to the Great Lakes have been reduced through a combination of regulatory pressure to reduce point source loadings and improved agricultural practices to reduce nonpoint source loadings (16–18). The total load of phosphorus to Lake Michigan from tributary, atmospheric, and point source loadings decreased by 50% between 1970 and 1990 to nearly 2000 tons yr^{-1} (19). This overall reduction in phosphorus loading to Lake Michigan has been credited with improved water quality by reducing primary production. During the same 20-year period, turbidity and algal blooms in the lake’s water column have decreased, while clarity, light penetration, and dissolved oxygen have all increased (20). The loading of nitrogen and phosphorus from the atmosphere may play an important role in the overall loading of these nutrients to Lake Michigan. Inputs of nitrogen and phosphorus through precipitation to a nutrient limited system may cause episodic stimulation of primary productivity (21). However, this effect has not been reported in the Great Lakes, in general, or in Lake Michigan, specifically, primarily because atmospheric loading is a small fraction of the overall loading of nutrients to the lake. It is expected, however, that changes in atmospheric loading of nutrients are a reflection of overall reduction in phosphorus released to the environment and changes in industrial and agricultural practices.

The goal of the research described here was (a) to assess the quality of the field data, (b) to assess any spatial and temporal variability, and (c) to estimate precipitation loadings to Lake Michigan to be used in developing a whole-lake mass balance model. In this paper, we describe the concentrations of atrazine and the nutrient compounds measured around Lake Michigan in precipitation from April 1994 through October 1995. Concentrations are evaluated at each of eight sampling sites for atrazine and each of six sampling sites for nutrients (Figure 1). Temporal and spatial trends are investigated and compared with that previously reported. Finally, we report on the monthly atmospheric load predicted for the lake and for each of the 2318 surface area cells created for the Lake Michigan Mass Balance whole lake model. These estimates are compared to historical reports to determine long-term trends in precipitation deposition of atrazine and nutrients to Lake Michigan.

In a continuing effort to understand how chemicals behave in a large lake, the Great Lakes National Program Office (GLNPO) of the U.S. Environmental Protection Agency (U.S.

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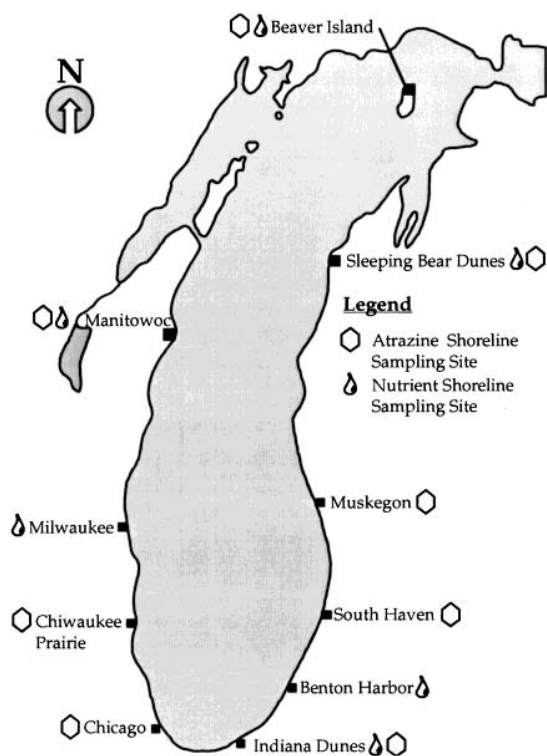


FIGURE 1. Atmospheric sampling site locations.

EPA) initiated the Lake Michigan Mass Balance (LMMB) Study. The field effort was conducted in 1994 and 1995 (22). The LMMB focuses on four potentially toxic organic compounds (polychlorinated biphenyl congeners, *trans*-nonachlor, atrazine, and mercury) as well as nutrient compounds (total phosphorus, TP; total kjeldahl nitrogen, TKN; and nitrate, NO_3^-). Phosphorus, TP, includes all forms of phosphorus in precipitation, and TKN is a measure of organic nitrogen and ammonia, while nitrate is a measure of inorganic oxidized nitrogen. Although any mass balance model includes many inputs and outputs for a large lake (23, 24), it has been shown that atmospheric sources of PCBs, for example, into the Great Lakes can be quite important (25–28). Atmospheric sources of atrazine and nutrients have also been shown to play a major role in overall loading of these compounds to Lake Michigan (1, 2, 29). For this reason, a significant effort was put into the collection and analysis of atmospheric samples to ensure a firm understanding of atmospheric loadings. Results discussed here focus on precipitation deposition estimates of atrazine and nutrients to Lake Michigan.

Methods Used During the LMMB

Field Sampling. Atmospheric sampling strategies for the LMMB are outlined in the Lake Michigan Mass Balance Methods Compendium (30, 31) but will be briefly described here. Field sampling began in April 1994 and continued through the end of October 1995.

Precipitation samples, to be analyzed for atrazine, as well as PCBs and *trans*-nonachlor were collected at eight sites located on the shore of Lake Michigan (Figure 1). A modified MIC-B (Meteorological Instruments of Canada) was used to collect precipitation. This collector consists of a stainless steel catch basin (0.2 m², fitted with a heating coil to melt any frozen precipitation) and a glass column filled with XAD-2 resin directly below it to absorb atrazine in the collected precipitation. The collector was fitted with a retractable cover and a precipitation sensor. The catch basin remained covered

when there was no precipitation (to avoid evaporation) and was uncovered when precipitation was sensed (to collect a sample). There was no fractionation between dissolved and particle-bound atrazine in the precipitation samples. Each MIC-B was in operation throughout the year to collect all the precipitation that fell. Samples were collected every 4 weeks resulting in 13 samples per year at each site. These samples were later analyzed for atrazine and used to represent a monthly averaged concentration at each of the eight shoreline sites (144 samples, total).

Precipitation samples, to be analyzed for nitrogen and phosphorus, were collected at six sites located on the shore of Lake Michigan (Figure 1). A MIC-B sampler, similar to that used to collect atrazine samples, was used for nitrogen and phosphorus sample collection. However, precipitation was collected in 250 mL high-density polyethylene containers and retrieved every 7 days from each site for analysis (approximately 380 samples, total). Samples were preserved in the field with the addition of 1 mL of concentrated H_2SO_4 per liter of sample (31).

Sample Analysis. Samples collected at the Sleeping Bear Dunes site between August 1994 and October 1995 were analyzed for atrazine at Indiana University. Samples collected at the other seven shoreline sites were analyzed for atrazine at the Illinois State Water Survey. Samples collected at the other six shoreline sites were analyzed for total phosphorus, total Kjeldahl nitrogen, and nitrate at the Grace Analytical Laboratory.

Three PCB surrogates (3,5-dichlorobiphenyl, IUPAC no. 14; 2,3,5,6-tetrachlorobiphenyl, IUPAC no. 65; and 2,3,4,4',5,6-hexachlorobiphenyl, IUPAC no. 166) were added prior to sample extraction. Each sample was extracted (using a Soxhlet extractor), the extract volume was reduced, and the reduced volume was fractionated into three parts on a silica liquid/solid column using hexane, 40% methylene chloride in hexane, and methanol as the eluting solvents. Atrazine was eluted in the methanol fraction. Prior to volume reduction, a back extraction step was included to remove water from the precipitation samples. The methanol fraction was analyzed for atrazine by gas chromatography with ion trap mass spectrometry (GC/ion trap MS). An internal standard solution containing *d*₁₀-anthracene, triphenylmethane, *d*₁₂-benzo[*a*]anthracene, and *d*₁₂-perylene was added prior to GC analysis for quantification.

An aliquot of each precipitation event-based sample collected at the six shoreline sites was transported to the Grace Analytical Laboratory for analysis. Nitrate (NO_3^-) was analyzed by automated flow injection method, while total phosphorus (TP) and total Kjeldahl nitrogen (TKN) were analyzed by semiautomated flow injection method as detailed in the Lake Michigan Mass Balance Method Compendium (31).

Quality Control. The quality of a data set is assessed through measures of accuracy, precision, representativeness, completeness, and comparability with other data sets. These quality assurance measures were an integral part of the LMMB, the results of which are summarized through the discussion of five quantitative measures: method detection limits, surrogate recoveries, field and laboratory matrix blanks, matrix spike recoveries, and replicate sampling.

Method detection limits were determined for each of the target compounds and are summarized in Table 1. Any samples below these limits were excluded from subsequent analysis. Recovery of PCB congener IUPAC no. 65 was used to measure the accuracy of atrazine measurement ($91.0\% \pm 16.5\%$, $n = 144$). To assess the accuracy with which the instrument measures nutrient concentrations, duplicate analysis of high and low concentration performance standards were evaluated with each sample set for each nutrient group. For each analyte, there was a high degree of

TABLE 1. Method Detection Limits (MDLs) for Atrazine (Atr) and the Nutrient Compounds^a

compd	method detection limit	
Atr	22.1 ng (1.77 ng L ⁻¹)	
TP	1.0 µg as P L ⁻¹	
TKN	0.1 mg as N L ⁻¹	
NO ₃ ⁻	0.03 mg as N L ⁻¹	
	relative % difference	N pairs
Replicate Analyses of a Standard at High Concentration (Standard Concentration)		
TP (15.00 µg as P L ⁻¹)	3.3 ± 4.7	77
TKN (1.15 mg as N L ⁻¹)	5.5 ± 4.9	86
NO ₃ ⁻ (0.60 mg as N L ⁻¹)	4.1 ± 3.8	86
Replicate Analyses of a Standard at Low Concentration (Standard Concentration)		
TP (3.00 µg as P L ⁻¹)	14.9 ± 19.1	77
TKN (0.45 mg as N L ⁻¹)	28.9 ± 34.8	86
NO ₃ ⁻ (0.20 mg as N L ⁻¹)	26.1 ± 39.2	86
Field Replicates		
Atr	68.4 ± 54.7	14
TP	17.8 ± 29.0	5
TKN	12.2 ± 5.6	5
NO ₃ ⁻	7.1 ± 3.2	5

^a The MDL concentration for atrazine was determined by dividing the MDL mass by the average sample precipitation volume (12.5 L). Summary of performance standards to evaluate the measurement accuracy of total phosphorus (TP), total Kjeldahl nitrogen (TKN), and nitrate (NO₃⁻). Field replicates for atrazine, total phosphorus, total Kjeldahl nitrogen, and nitrate in precipitation.

reproducibility as demonstrated by the low relative percent difference (RPD) (Table 1).

A matrix blank was used to determine background concentrations of the target analyte on sampling media after it had been cleaned. A portion of XAD-2 was set aside, stored, then extracted, and analyzed with the field samples. Mass of atrazine measured on the 38 matrix blanks analyzed was below the method detection limit and reported as zero. Since measurements of the nutrient compounds were made directly, there were no matrix blanks associated with the nutrient methods. A matrix spike recovery was used to evaluate the overall quality of the analytical procedure. Additional portions of pre-cleaned XAD-2 were set aside, stored, and then injected with a known amount of atrazine. A matrix spike was extracted and analyzed with a batch of field samples. Recovery of atrazine was 92.6% ± 27.0% (*n* = 38). There were no matrix spikes for the nutrient compounds. A field blank was used to evaluate the conditions near the sampling site and possible contamination during transport from the laboratory to the sampling site. XAD-2 was pre-cleaned, packed, transported, and exposed to the sampling site environment; however, precipitation was not sampled through the media. Mass of atrazine measured on the six field blanks collected during the sampling season was below the method detection limit. There were no field blanks for the nutrient compounds.

Field replicates were used to evaluate sampler reproducibility and natural sampling variability. At select sampling sites, two sample collectors were operated side-by-side. The agreement between samplers was determined by the RPD and summarized in Table 1. The RPD is due to real variability in the matrix between two samples: the random error in the collection method and the random error in sample treatment and analysis.

Results

Concentration Variations in Space and Time. Atrazine concentrations in precipitation have a very well defined

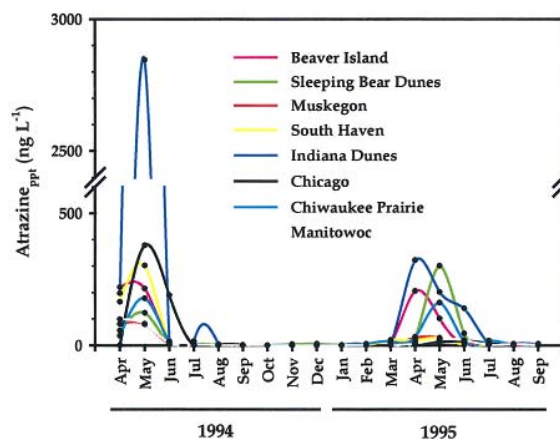


FIGURE 2. Concentration of atrazine in monthly precipitation samples collected between April 1994 and September 1995.

TABLE 2. Monthly, Lake-Wide Volume Weighted Mean (VWM) Concentrations for Atrazine in Precipitation and Lake-Wide Average Precipitation Rates for Lake Michigan

year	month	VWM (ng L ⁻¹)	<i>r</i> _{ppt} (m mo ⁻¹)
1994	April	123.9	no data
	May	160.4	no data
	June	21.2	no data
	July	3.15	0.104
	August	0.915	0.104
	September	0.360	0.081
	October	0.0867	0.047
	November	0.153	0.088
	December	0.365	0.022
1995	January	0.136	0.062
	February	0.672	0.023
	March	6.70	0.048
	April	44.3	0.094
	May	72.5	0.074
	June	114.2	0.039
	July	24.4	0.072
	August	4.12	0.107
	September	2.18	0.051

temporal variation (Figure 2). The temporal variation corresponds with the application of atrazine during the spring months. However, there is no statistically significant spatial variation. The higher concentration observed at Indiana Dunes in May 1994 is a suspected outlier. This data point is approximately six times that of the others for May 1994. It is possible that during the collection of this particular sample, a relatively small precipitation event (low volume) coincided with emissions from nearby fields (high mass) producing a high concentration. The volume of precipitation collected for that sample was 3.7 L compared to a mean volume for the whole data set of 12.5 ± 8.7 L. Monthly volume weighted mean (VWM) concentrations of atrazine are shown in Table 2.

The concentrations of TP, TKN, and NO₃⁻ in each regular precipitation sample exhibit no apparent seasonal or spatial variability. This is best illustrated in Figure 3 for TKN. Similar plots of TP and NO₃⁻ demonstrate the same lack of seasonal and temporal variability. Although there are variations in concentrations from month to month, this variation is not predictable and has not been interpreted as a seasonal trend. This lack of predictable variation is evident in NO₃⁻ data collected by the National Atmospheric Deposition Program (NADP) for sites around Lake Michigan (32).

There is limited spatial variability in nutrient precipitation concentrations that can be explained, in general, by the relationship between concentrations and precipitation vol-

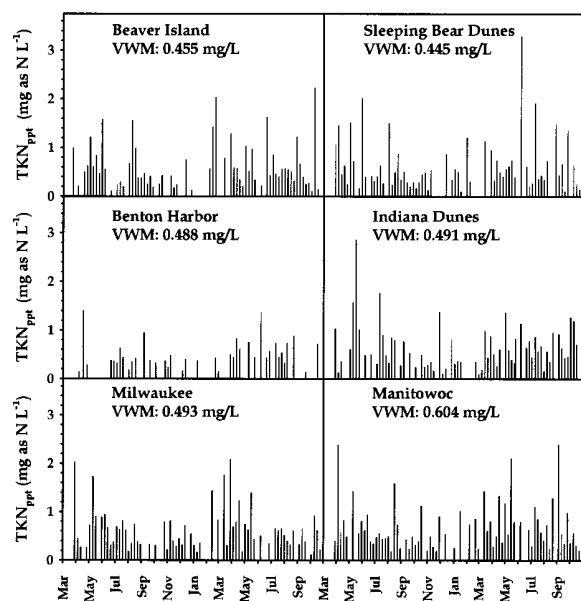


FIGURE 3. Concentration of total Kjeldahl nitrogen (TKN) in precipitation samples collected between April 1994 and October 1995.

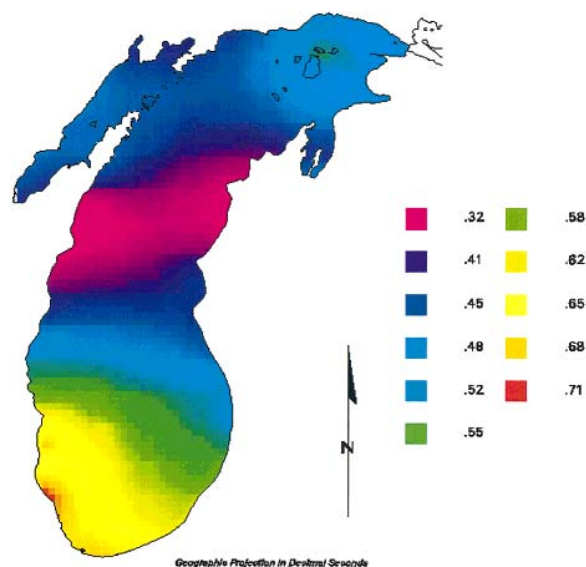


FIGURE 4. Annual deposition of atrazine in precipitation to Lake Michigan. The higher load to the southern portion of the lake is primarily a result of variation in precipitation amount. The legend units are $\text{kg cell}^{-1} \text{yr}^{-1}$.

ume collected. For example, concentrations of TP at Beaver Island exhibited spikes of high concentration during two different sampling events. However, precipitation volumes collected during these events were small (0.63 L and 0.05 L) compared to other sampling events ($1.18 \pm 1.18 \text{ L}$) with lower concentrations. Samples resulting from short duration precipitation events with smaller sample volumes tended to have higher concentrations. This may be a result of particulate scavenging at the beginning of a precipitation event. Concentrations tended to be diluted for those samples resulting from long duration precipitation events with larger sample volumes. Hence, VWM concentrations are used to describe concentrations of the nutrients at each site (Table 3).

There is a lack of a north-south variation in VWM nutrient concentrations. It will be discussed later that although there

is no spatial variation in concentration, there is a variation in loading due to spatial variation in precipitation amount.

Deposition Variations in Space and Time. Precipitation deposition of atrazine and each of the nutrients was calculated as the VWM concentration of the compound measured in precipitation multiplied by the amount or rate at which precipitation falls for each of the 2318 cells in the hydrodynamic grid

$$\text{load}_{\text{ppt},i,m} = \nu_{\text{ppt},i,m} \text{VWM}_m \text{SA} \quad (1)$$

where ν_{ppt} is the precipitation deposition rate (m mo^{-1}), VWM is the concentration of the target compound in precipitation (ng L^{-1} , $\mu\text{g L}^{-1}$, or mg L^{-1}) for grid cell i in month m , and SA is the grid cell surface area (25 km^2). Because of the lack of spatial variability in atrazine concentration, a whole-lake monthly VWM concentration was used to estimate monthly atrazine loads. Similarly, because of the lack of spatial and temporal variability in nutrient concentration, a whole-lake annual VWM concentration was used to estimate monthly nutrient loads.

Landis (33) estimated monthly precipitation rates from July 1994 through September 1995 for each of the 2318 cells of the National Oceanic and Atmospheric Administration/ Great Lakes Environmental Research Laboratory (NOAA/ GLERL) over-water Lake Michigan 5 km regular grid (34) by the krigging method of spatial interpolation. Data from approximately 700 National Weather Stations in Illinois, Michigan, and Wisconsin were used for confirmation. An example of the lake-wide precipitation deposition rates determined by this method is shown in Table 2 as the monthly average of the 2318 grid cells. Monthly lake-wide precipitation deposition loads of atrazine and nutrients were calculated by taking the sum of the load for each of the 2318 grid cells and are summarized in Table 4. Loads were calculated only for the months with modeled precipitation rates (July 1994 through September 1995). The spatial variation in the annual load of atrazine is illustrated in Figure 4. This plot illustrates higher deposition in the southern portion of the lake. These higher loads are the result of higher predicted precipitation in this region, not higher concentrations of atrazine. Although not shown here, plots of TP, TKN, and NO_3^- are similar because of the same precipitation effect.

Discussion

Atrazine Deposition. Precipitation deposition of atrazine to Lake Michigan reported here is about 2.5 times less than that reported by Schottler and Eisenreich (1). For 1990–1994, Schottler and Eisenreich estimated annual precipitation deposition of $2.6 \times 10^3 \text{ kg yr}^{-1}$ based on loading rate estimates determined by Goolsby et al. (2). For this study, deposition of atrazine for 1994–1995 was estimated to be $1.04 \times 10^3 \text{ kg yr}^{-1}$. This difference in loading estimates is mainly due to the difference in annual precipitation deposition and not a difference in concentration. For 1990–1991, Goolsby et al. (2) observed VWM concentrations of atrazine in precipitation around Lake Michigan in the range of $0.11\text{--}0.40 \mu\text{g L}^{-1}$. Similarly, for 1994–1995, concentrations ranged from 0.10 to $0.38 \mu\text{g L}^{-1}$. However, precipitation for July 1990 through June 1991 was reported as 1.2 m compared to 0.78 m for July 1994 through June 1995. Approximately 1.5 times more precipitation fell in 1990–1991 than in 1994–1995. The concentration of atrazine observed in precipitation is related to the amount of it used in agricultural production. Annual use of atrazine in agricultural production has remained constant since 1987 (3). It has been estimated that 71–76 million pounds of atrazine was used in agricultural production in 1987, compared to 70–75 million pounds in 1993 and 68–73 million pounds in 1995.

TABLE 3. Volume Weighted Mean (VWM) Concentrations of Total Phosphorus (TP), total Kjeldahl Nitrogen (TKN), and Nitrate (NO₃⁻) in Lake Michigan Precipitation

site	n	TP $\mu\text{g as P L}^{-1}$		TKN mg as N L ⁻¹		NO ₃ ⁻ mg as N L ⁻¹ (mg as NO ₃ ⁻ L ⁻¹)	
		VWM	range	VWM	range	VWM	range
Beaver Island	67	4.30	0.10–99.2	0.455	0.02–2.23	0.388 (1.72)	0.08–1.88 (0.35–8.33)
Sleeping Bear Dunes	71	4.64	0.10–48.0	0.445	0.02–3.29	0.378 (1.67)	0.08–3.27 (0.35–14.5)
Benton Harbor	40	9.04	0.30–64.2	0.488	0.01–1.40	0.461 (2.04)	0.11–1.37 (0.49–6.07)
Indiana Dunes	72	11.20	0.20–84.8	0.491	0.07–2.86	0.437 (1.94)	0.09–2.34 (0.40–10.4)
Milwaukee	64	4.07	0.80–41.2	0.493	0.12–2.09	0.457 (2.02)	0.11–2.13 (0.49–9.44)
Manitowoc	69	5.33	0.90–143.0	0.604	0.05–2.40	0.489 (2.17)	0.09–3.31 (0.40–14.7)
overall	383	6.36		0.497		0.435 (1.93)	

TABLE 4. Monthly Whole-Lake Precipitation Loads of Atrazine (Atr), Total Phosphorus (TP), Total Kjeldahl Nitrogen (TKN), and Nitrate (NO₃⁻) to Lake Michigan

year	month	Atr kg	TP $\times 10^4$ kg as P	TKN $\times 10^6$ kg as N	NO ₃ ⁻ $\times 10^6$ kg as N (kg as NO ₃ ⁻)
1994	July	14.9	3.82	2.98	2.61 (11.6)
	August	7.10	3.83	2.99	2.62 (11.6)
	September	1.16	2.99	2.34	2.04 (9.05)
	October	0.403	1.73	1.35	1.18 (5.24)
	November	0.545	3.24	2.53	2.21 (9.81)
	December	0.409	0.794	0.620	0.542 (2.40)
1995	January	0.636	2.27	1.78	1.55 (6.88)
	February	0.121	0.843	0.659	0.576 (2.55)
	March	23.2	1.76	1.37	1.20 (5.31)
	April	460	3.47	2.71	2.37 (10.5)
	May	425	2.75	2.15	1.88 (8.31)
	June	107	1.44	1.13	0.985 (4.36)
	July	29.1	2.65	2.07	1.81 (8.00)
	August	11.8	3.95	3.08	2.69 (11.9)
	September	3.95	1.89	1.48	1.29 (5.71)
annual (Jul 94– Jun 95)		1.04×10^3	2.89×10^5	2.26×10^7	1.98×10^7 (8.75×10^7)

It is important to note that there is a potential for particulate deposition of atrazine to be as significant as precipitation deposition. The overall estimated load of atrazine due to atmospheric particulates is largely due to the deposition rate chosen. In the past, a deposition rate of 0.2 cm s⁻¹ has been used for atrazine and other contaminants associated with atmospheric particulates (1, 35). Holsen and Noll (36) have suggested that pollutants associated with larger particles dominate atmospheric particulate deposition. Franz et al. (37) have estimated average summertime deposition rates for polycyclic aromatic hydrocarbons (PAHs), combustion-related pollutants that are primarily in the fine fraction, and total suspended particles (TSP) for use in calculating dry deposition to off-shore areas of Lake Michigan. These values are 0.6 for PAHs and 0.9 cm s⁻¹ for TSP. Since mechanical processes (farm machinery) or wind blown dust probably generate particles associated with atrazine, they are most likely to be in the larger size range (3–20 μm diameter). Since particle size fractionation was not part of the LMMB analysis, there is much uncertainty in the best choice of deposition rate to use. It is likely that larger particles deposit within a few kilometers of the shore, and applying the larger deposition rate (0.9 cm s⁻¹) to the entire lake would possibly overestimate the load. With the lack of particle-size associated concentrations, a more conservative approach is to apply the smaller deposition rate (0.2 cm s⁻¹) to the entire lake. Based on a

lake-wide average concentration of 0.2 ng m⁻³ (± 0.3 ng m⁻³, $n > \text{MDL} = 38$, MDL = 0.009 ng m⁻³) for the spring months (April through June) of 1994–1995 (38), the loading of particulate-associated atrazine may vary from 230 to 1000 kg yr⁻¹ or 18–50% of the total atmospheric deposition (see Table 1S in Supporting Information). Future efforts to determine the relative contribution of precipitation and particle deposition require over-lake measurements of atrazine in precipitation during the application and chemical analysis of size-separated particles. This has been difficult, even under the concentrated efforts of the LMMB because of the episodic nature of atrazine in precipitation, the absence of permanent buoys for collecting samples, and the very low (< detection limits) atrazine concentrations on bulk particles.

Deposition of Nutrients. Concentrations of total phosphorus for 1994–1995 reported here are approximately 10 times less than reported for Lake Michigan 20 years earlier (29). The lake-wide volume weighted mean concentration decreased from 57 $\mu\text{g as P L}^{-1}$ for 1976 to 6.36 $\mu\text{g as P L}^{-1}$ for 1994–1995. Similarly, loading estimates reported here for 1994–1995 are substantially lower than for 1976. Eisenreich et al. (29) estimated annual precipitation deposition loading to be 16.9×10^5 kg as P yr⁻¹ for 1976 compared to 2.9×10^5 kg as P yr⁻¹ for 1994–1995. Many of the same sites were sampled in 1994–1995 as were sampled in 1976, allowing a direct comparison of the VWM concentration. For example,

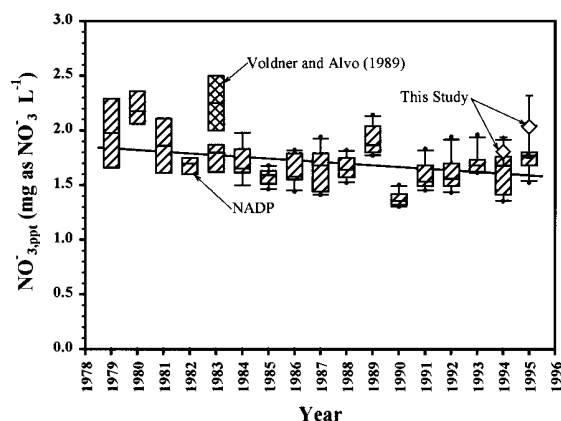


FIGURE 5. Historical comparison of NO_3^- in precipitation around Lake Michigan. Using the standard MANOVA procedure, there was not a significant linear trend component ($F(1,5) = 1.11$, $p = 0.34$) to the NADP data.

the VWM concentration of total phosphorus near Milwaukee has decreased by an order of magnitude from $31 \mu\text{g as P L}^{-1}$ in 1976 to $4.07 \mu\text{g as P L}^{-1}$ in 1994–1995.

Spring storms that cause sediment resuspension events within the lake may be more important than precipitation as an episodic source of TP to Lake Michigan. Springtime events that resuspend sediments and mix the lake from top to bottom are expected to deliver more bioavailable nitrogen and phosphorus to the lake than all other sources combined (39). Preliminary results of this episodic resuspension event support this hypothesis (40).

The VWM concentration of NO_3^- around the lake were about $1.9 \text{ mg as NO}_3^- \text{ L}^{-1}$ ($0.44 \text{ mg as N L}^{-1}$) for 1994–1995 compared to 2.0 – $2.5 \text{ mg as NO}_3^- \text{ L}^{-1}$ for 1983 (41). Deposition of nitrogen for 1983 was estimated at 9.3 to $11.6 \times 10^7 \text{ kg as NO}_3^- \text{ yr}^{-1}$ based on average precipitation of 80 cm compared to $8.9 \times 10^7 \text{ kg as NO}_3^- \text{ yr}^{-1}$ ($2.0 \times 10^7 \text{ kg as N yr}^{-1}$) and 113 cm for 1994–1995. Voldner and Alvo (41) demonstrated a general downward trend in nitrogen concentration in precipitation and loading to Lake Michigan. Clearly, there have been reductions in releases of nutrients to the atmosphere in the Lake Michigan region over the last 20 years. This is supported by over 20 years of NO_3^- data collected at NADP (32) sites around Lake Michigan that suggest decreasing, but not statistically significant ($p = 0.34$), concentrations (Figure 5). Data for NO_3^- in precipitation from this study agree with that reported by NADP.

Observed concentrations of atrazine and nutrients in precipitation appear to be declining or remaining approximately the same over time. Loading estimates appear to be following the same trend as concentration. However, loading estimates are highly dependent on precipitation rates. Since concentrations do not seem to vary with time or space in the Lake Michigan region, precipitation loading estimates will be higher during years with greater amounts of precipitation compared to those with less.

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Supporting Information Available

Table 1S (atrazine in precipitation). This material is available free of charge via the Internet at <http://pubs.acs.org>

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