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Mass Balance Model To Quantify Atrazine Sources, Transformation Rates, and Trends in the Great Lakes

SHAWN P. SCHOTTLER† AND
STEVEN J. EISENREICH*,‡

Gray Freshwater Biological Institute, University of Minnesota, Navarre, Minnesota 55392, and Department of Environmental Sciences, Rutgers University, P.O. Box 231, New Brunswick, New Jersey 08903

A dynamic mass balance model for atrazine was constructed for the Great Lakes to estimate in situ transformation rates and the relative importance of sources. Annual atrazine inputs ranged from ~1 ton/yr in Lakes Superior to 10−25 ton/yr in Lakes Erie and Ontario. Annual inputs were <10% of lakewide atrazine inventories in all lakes except Erie. Tributaries plus connecting channel inputs account for >75% of the total load to Lakes Erie, Ontario, Huron, and Michigan. Atmospheric inputs account for 95% of the inputs to Lake Superior. Internal transformation rates are similar throughout the Great Lakes, ranging from ~0.05 to 0.13 yr^{-1}. Internal transformation and outflow produce an atrazine water column residence time of ~2 yr in Lake Erie and >5 yr in the other lakes. Approximately 5−10% of the lakewide atrazine inventory is lost annually through internal transformation.

Introduction

Atrazine has been intensively used in the Great Lakes basin for about 25 yr and has a long half-life in cold, low productivity aquatic systems such as groundwaters and oligotrophic lakes (*1*, *2*). Thus the Great Lakes having water residence times ranging from 3 to 180 yr (*3*) may act as end points in the environmental transport of atrazine, with lake wide inventories increasing since the onset of atrazine usage in the 1960s. Temporal and spatial trends of atrazine concentrations in the Great Lakes (*4*, *5*) suggest that water column atrazine transformation rates are slow, with half-lives exceeding 1 yr. An accounting of the input and elimination mechanisms is required to quantify the environmental behavior of atrazine in the Great Lakes. A dynamic mass balance model was constructed to address the questions on sources and fate of atrazine in the Great Lakes. Specifically, the model is used to estimate the *in situ* transformation rate of atrazine, to compare the relative importance of different sources, and as a predictive tool to estimate how the Great Lakes will respond to changes in atrazine use.

A simple, but robust, approach to modeling interactive and complicated systems is the use of the computer modeling shell *Stella* (*6*). *Stella* allows the user to construct a unique mass balance model with the ability to manipulate inputs and outputs on varying time scales. The overall approach, using this model, will be to manipulate independent variables such as transformation rates or atmospheric loading until model solutions for water column concentrations match measured concentrations. Water column concentration trends reported by Schottler et al. (*4*, *5*) will serve as the calibration for model output.

The strategy for using the model to decipher the fate and source of atrazine to the lakes will rely on supplying known inputs and losses and manipulating unknown parameters until model results fit measured values. An initial value is assigned to each lake for January 1991 (based on 1991 measurements), and model results are subsequently calculated through 1994. Model results are then compared to measured values over this time period. Average values and standard deviation of measured concentrations used as calibration points are shown in Table 1. Parameters such as sedimentation, air/water exchange, and dry deposition are estimated from chemical and physical properties of the herbicides, lake hydrology/climatology, and published reports. Other parameters such as tributary and precipitation loadings are entered directly from existing data or estimated from physical properties in combination with herbicide use trends and watershed hydrology. Transformation rates of herbicides in the water column are unknown and will be an independent variable for each lake. While it will be impossible to model each of the inputs precisely, careful estimation of the mass balance unknowns will produce a range of possible values for water column transformation rates and relative source loadings.

Method

A mass balance approach for the Great Lakes, using Lakes Huron, Erie, and Ontario as examples, is shown in Figure 1. A similar approach, modeling atrazine in Swiss lakes, has been used by Ulrich et al. (*2*). The concentration of atrazine in a lake (or basin) can be described by

$$\text{concentration} = \sum_{t=0}^{t} (\text{mass in} - \text{mass out})/\text{volume} \qquad (1)$$

The premise of eq 1 is incorporated into a unique dynamic mass balance model constructed on the basis of

$$\text{mass}_t = \text{mass}_{(t-\mathrm{d}t)} + (\text{inputs}_t - \text{outputs}_t)\,\mathrm{d}t \qquad (2)$$

where mass_t is the mass of herbicide in the lake at a particular time, inputs_t and outputs_t (kg/yr) are the inputs and output at any particular time, and dt is a unit interval of time change. Solutions to this general equation for a selected time period are solved iteratively using a fourth-order Runge Kutta algorithm (*6*).

Combining the premise of eq 1, into the format of eq 2, a model was constructed that continuously (dt = 0.001 yr) calculates water concentrations based on changing inputs and outputs. Figure 1 shows the general outline of inputs and outputs that was used for this model. Tributary and precipitation loadings varied monthly based on known data (*7*−*12*). In addition, tributary loading was varied annually based on trends in atrazine use. Air/water exchange and dry deposition varied monthly based on seasonal estimates of atrazine air concentration. Losses through internal transformation and sedimentation are dependent on the atrazine concentration in the lake and therefore varied as lake concentrations varied. Atrazine concentrations in Lakes Huron, Michigan, Ontario, and Superior showed no significant spatial trends (*4*, *5*) from 1991 to 1995. Therefore, these lakes were treated as one-box, well-mixed systems. Lake Erie, showing a strong west to east concentration gradient, was

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* To whom correspondence should be addressed; e-mail: eisenreich@aesop.rutgers.edu.

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TABLE 1. Measured Concentrations (ng/L) of Atrazine in the Great Lakes (*4*, *5*)[a]

year	Superior	Michigan	Huron	Erie-west	Erie-central	Erie-east	Ontario
1991	3.5 (0.5)	35 (2.0)	21 (1.4)	30 (5)	109 (3.6)	112 (5.0)	85 (3.8)
1992		37 (1.8)	23 (1.4)	68 (2)	85 (9.2)	93 (4.1)	95 (6.5)
1993	4.5 (1.0)				87 (3.1)	87 (3.1)	
1994	3.5 (0.5)	37 (2.2)	21 (1.0)	46 (8)	62 (2.5)	68 (1.5)	72 (2.4)

[a] Values in parentheses are one standard deviation about the average. Values for Lake Superior in 1991 are based on measurements made in 1990.

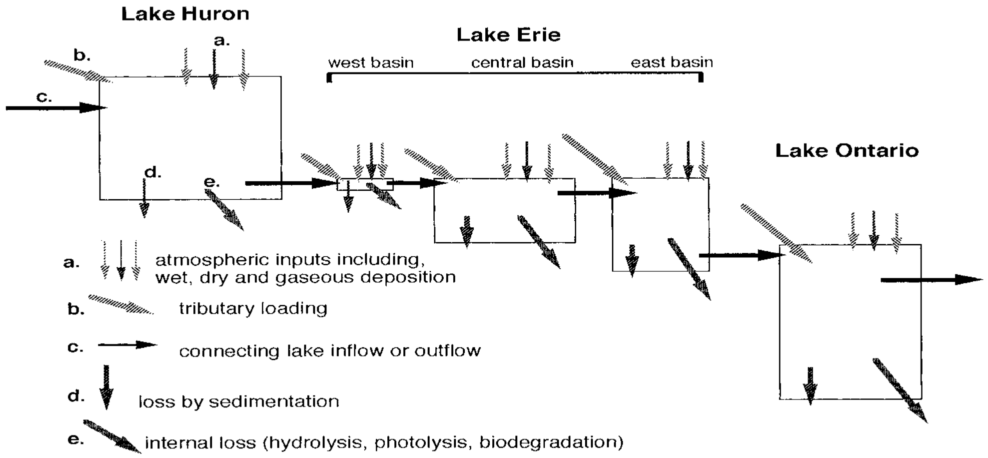

FIGURE 1. Mass balance approach for inputs and outputs to the Great Lakes using Lakes Huron, Erie, and Ontario as an example. Concentrations in Lake Erie showed large lateral variations, thus each of the major basins of Lake Erie were modeled separately. Lakes Superior, Michigan, Huron, and Ontario were modeled as one-box well-mixed systems.

divided into three basins; as defined by hydrology, morphology, and existing tanks in series models of Lake Erie (*4*).

Model Setup: Inputs and Outputs. Inputs to the lakes are

$$\text{tributary loading} = UPS_{(i)} \tag{3}$$

$$\text{precipitation loading} = WSAS_{(i)} \tag{4}$$

$$\text{connecting channel loading} = Q_{cc}C_{cc} \tag{5}$$

$$\text{air–water exchange} = v_{tot}[C_{w(i)} - C_{a(i)}(1 - f)/K_h]\mathrm{SA} \tag{6}$$

$$\text{dry deposition} = C_{a(i)}f\mathrm{SA}V_d \tag{7}$$

where U is the annual use of atrazine (kg/yr); P is the percent of use removed by runoff (%); W is the areal deposition flux (kg m^{-2} yr^{-1}; SA is the surface area of lake (m^2); Q_{cc} is the connecting channel inflow (m^3/month); $C_{a(i)}$ is the total air concentration in any month (kg/m^3); C_{cc} is the concentration of upstream lake (kg/m^3); v_{tot} is the mass transfer velocity (m/month); C_w is the mean water concentration in lake (kg/m^3); K_h is the Henry's law constant (dimensionless); V_d is the dry deposition velocity (m/month); f is the fraction of total air concentration sorbed on particles; and $S_{(i)}$ is fraction of annual load occurring during any month (yr/month$_i$).

Losses from the lake are

$$\text{outflow} = Q_oC_{w(i)} \tag{8}$$

$$\text{sedimentation} = C_{s(i)}A_{cc}\mathrm{SA}f_s \tag{9}$$

$$\text{transformation} = C_{w(i)}k_t \tag{10}$$

where Q_o is the outflow (m^3/month); $C_{w(i)}$ is the concentration in lake during any month (kg/m^3); k_t is the transformation rate (month^{-1}); $C_{s(i)}$ is the concentration on particles (kg/kg); f_s is the fraction of lake with active sedimentation; and A_{cc} is the sediment accumulation rate (kg m^{-2} month^{-1}). For eqs 3–10 the subscript symbol (i) is used to denote parameters that vary monthly.

Tributary Loading. The traditional method for calculating tributary loading would be to multiply concentration by discharge on a daily basis for each tributary entering the lake. Since the data required for this method do not exist, a less direct approach was used. Instead, tributary loading was calculated based on the amount of atrazine used in each basin and the percentage of applied atrazine that is typically removed by runoff. Tributary flux is described according to eq 3. A spring flush phenomenon of atrazine in Midwestern rivers has been well described, where 60–90% of annual riverine atrazine flux occurs in the 90 days following application (*7, 10, 12–18*). Inputs in the model are calculated on a monthly basis, and each month is given a coefficient, $S_{(i)}$, weighting its importance for tributary loading. $S_{(i)}$ is used to describe the fraction of the annual load that occurs in a particular month (yr/month$_i$) and was estimated from the studies presented in Table 2. For tributary inputs the $S_{(i)}$, coefficients were as follows: June = 0.5, May = 0.2, July = 0.15, April = 0.05, August = 0.03, and January, Febrary, March, September, October, November, and December = 0.01.

For most of the lakes, tributary loading is the most important input; therefore, good estimates of atrazine use and removal by tributaries are required. Studies on large agricultural watersheds have shown that the atrazine flux from large watersheds is ~0.25–1.5% of the amount applied annually (*14–22*). Table 2 demonstrates how consistent this percentage is from one watershed to another. Based on these studies, a value of 1% was chosen for the annual percent of application removed by tributaries.

Annual application of atrazine was estimated from two sources. Gianessi and others (*23*, *24*) and Kirschner (*25*) estimated annual atrazine use for the periods 1988–1990 and 1992–1993 (Table 3). Gianessi's estimates were for the United States only, while Kirschner's were for both the United States and Canada. Both sources estimated atrazine usage on a county or province level. Using only the counties (or portions of counties) that are part of each Great Lake watershed, the

TABLE 2. Comparison of Percentage of Annual Atrazine Application Removed by Runoff in Various Watersheds

river/watershed	annual application removed by rivers (%)	comments	ref
Mississippi (1991)	0.9	based on flux at Gulf of Mexico	17, 19
Minnesota (1990, 1991)	0.33 and 0.62	Minnesota River at Mankato, MN	18
Mississippi (1987, 1981)	0.4 and 1.7	Based on flux at Gulf of Mexico	20
S. W. Ontario (1983)	0.6−2.2	Thames, Grand, and Saugeen Rivers in S. W. Ontario, Canada	14
S. W. Ontario (1988)	0.6−1.5		
Cedar River (1985)	1.5	Cedar River at Bertram, IA	21
S. Ontario (1975−1977)	1.0	average based on 11 watersheds in southern Ontario, Canada from 1975 to 1977	15
Maumee (1991, 1992, 1993, 1994)	1.4, 0.6, 2.3, 0.4	Maumee River in western Lake Erie basin, calculated from watershed use (*7*, *23*−*25*) and annual loads (*7*)	
Sandusky 1991, 1992, 1993, 1994	0.5, 0.2, 1.3, 0.6		
Mississippi River tributaries (1991−1992)	0.84−1.9	results for White, Ohio, Platte, Illinois, and Missouri Rivers	22
Quebec (1974)	1.2−2.9	based on five tributaries of Yamaska River in Quebec Canada	16
Quebec (1975)	0.1−0.3		

TABLE 3. Estimated Atrazine Use in the United States and Canada (kg)[a] and Total Use Estimates Applied to Model Calculations[b]

(A) Estimated Atrazine Use

	United States				Canada	
	Kirschner		Gianessi		Kirschner	
	1988−1990	1992−1993	1988−1990	1992−1993	1988−1990	1992−1993
Superior	3 200	1 400	1 400	1 000	0	0
Michigan	1 297 800	89 7800	1 110 500	813 600	0	0
Huron	302 100	270 700	356500	278 200	148 900	104 900
Erie-west	997 900	733 200	748 200	612 200	297 600	170 500
Erie-central	159 100	102 700	131 100	126 700	68 900	39 800
Erie-east	14 200	8 500	13 100	12 000	101 100	59 600
Ontario	342 200	290 400	296 100	273 600	15 2500	61 500

(B) Annual Atrazine Use Estimates Used in Model (kg)

	1990	1991	1992	1993	1994
Superior	2 300	1 900	1 600	1 200	800
Michigan	1 204 000	1 088 000	972 000	856 000	740 000
Huron	503 000	462 700	422 300	382 000	341 700
Erie-west	1 086 000	995 000	904 000	813 000	722 000
Erie-central	201 000	188 300	175 700	163 000	150 300
Erie-east	107 000	101 300	95 700	90 000	84 300
Ontario	450 000	413 300	376 700	340 000	303 300

[a] Estimates of atrazine calculated from both Kirschner (*25*) and Gianessi et al. (*23*, *24*) are presented for comparison. [b] Values used in model were estimated from Section A and include use in the United States and Canada.

annual atrazine use for each Great Lake basin was calculated. In the case of Lake Erie, this breakdown was done for the east, west, and central basin watersheds. Use estimates (*23*−*25*), compared in Table 3, were averaged to produce an estimate for 1990 and 1993 atrazine use in the United States. The amount used in Canada was estimated from Kirschner (*25*) and weighted according to the percent difference between Kirschner's and Gianessi's U.S. values. The amount of atrazine used in 1990 and 1993 was linearly interpolated to determine the amounts used in 1991, 1992, and 1994. Final atrazine use estimates used in the model are shown in Table 3B.

A more detailed calculation of tributary loading can be performed for Lake Erie. Richards et al. (*7*) have calculated the annual flux of atrazine from five major tributaries to Lake Erie from 1983 to 1994. Using county use data (*23*−*25*), the amount of atrazine used in each of the five watersheds in 1990 and 1993 was calculated, and the amounts used in 1991, 1992, and 1994 were linearly interpolated. By comparing the loading from each watershed against the use in each watershed, the percent of use removed by each tributary was calculated. These calculations show that the percentage of applied atrazine removed was highest in 1993 and 1991 and lower in 1992 and 1994. Results from the two most important tributaries (Maumee and Sandusky Rivers) are shown in Table 2. Based on the results observed for these rivers, the value for percentage of atrazine removed was treated as a variable in the Lake Erie model. Values for the percent of atrazine removed by Lake Erie tributaries were as follows: 1991 = 1.0%; 1992 = 0.5%; 1993 = 2.0%; and 1994 = 0.5%.

Precipitation Loading. Atrazine loading to the lakes from precipitation was allowed to vary monthly and is described by eq 4, where W is the annual areal atrazine deposition rate (kg m^{-2} yr^{-1}); and $S_{(i)}$ is the same coefficient used in tributary loading, which describes the percentage of the annual loading that occurs in any month. Precipitation deposition of atrazine to the Great Lakes was based on areal fluxes reported by Goolsby et al. (*8*); lakewide average flux (μg m^{-2} yr^{-1}) estimates used in the model were as follows: Superior = 10; Michigan = 40; Huron = 15; Erie-west = 60; Erie-central = 40; Erie-east = 20; and Ontario = 20. In addition to these estimates, Cromwell and Thurman (*26*) measured deposition rates of atrazine to Isle Royale in Lake Superior. For the period 1992−1994, precipitation loading of atrazine ranged from 2 to 24 μg m^{-2} yr^{-1}, and averaged ~10 μg m^{-2} yr^{-1}. These values agree with Goolsby's Lake Superior estimates of <25 μg m^{-2}

TABLE 4. Estimates of Total Air Concentrations of Atrazine over the Great Lakes (ng/m^3)[a]

month	Michigan and Huron	Superior	Ontario and Erie-east	Erie-west and Erie-central
March	0.01	<0.01	0.01	0.01
April	0.20	0.03	0.05	0.5
May	0.35	0.18	0.15	0.6
June	0.07	0.01	0.05	1.0
July	0.01	<0.01	0.01	0.05
all other months	<0.01	<0.01	<0.01	<0.01

[a] Estimates were summarized from Sweet et al. (*28*)

yr^{-1}. This agreement is important since precipitation proves to be the major source of atrazine to Lake Superior.

Dry Deposition. Inputs of atrazine via atmospheric dry deposition are estimated according to eq 7. Dry deposition flux is directly proportional to the dry deposition velocity and concentration of atrazine on airborne particles. Eisenreich and Strachan (*27*) estimate a dry particle deposition velocity of 0.2 cm/s for submicrometer particles, and this is the estimate used for the model. The Illinois State Water Survey (*28*) has measured total air concentrations of atrazine near the Great Lakes and the partitioning between the gas and particulate phases. Measurement of particulate and gas phase atrazine concentrations show that over 90% ($f = 0.9$) of the total air concentration is in the particulate phase. This agrees with Eisenreich and Strachan's estimate for f of ~0.8, which was based on the vapor pressure of atrazine (*27*). Total air concentrations were measured at 12 sites around the Great Lakes from 1992 to 1994 (*28*). Samples were collected and analyzed according to the Lake Michigan Mass Balance Quality Assurance Project Plan (*29*). Eight sites were sampled around Lake Michigan representing both agricultural and non-agricultural regions. Based on these sites, monthly total atrazine air concentrations (ng/m^3) were estimated (Table 4). No sites were sampled around Lake Huron, thus Lake Michigan estimates were applied for Lake Huron. While there are certainly differences in air concentrations over Lake Michigan and Lake Huron, model results presented later show that these lakes are not highly sensitive to atmospheric inputs. Two sites were located near Lake Superior: Brule River, WI, and Eagle Harbor, MI. Average monthly concentrations for Lake Superior based on these sites are shown in Table 4. Total air concentrations for Lake Ontario and eastern Lake Erie were based on measurements made at Sturgeon Point in eastern Lake Erie (Table 4).

The western and central basins of Lake Erie are surrounded by areas of intense atrazine use. No air concentration measurements were made in this region; however, measurements were taken in Bondville, IL, Indiana Dunes, IN, and South Haven, MI. These sites are analogous to the agricultural region around western and central Lake Erie. Average monthly atrazine air concentrations at these sites were used for western and central Lake Erie (Table 4). Total air concentrations at Bondville, South Haven, and Indiana Dunes are similar to concentrations measured in other Midwestern areas of intense atrazine use (*30, 31*) and are likely representative of concentrations in the Lake Erie basin.

The air concentrations estimates used in the model have an unknown uncertainty. The potential effect of this uncertainty was tested by using a range of estimates for atmospheric inputs. These results are presented later, but in general dry deposition and air/water exchange have a small effect on atrazine concentrations in the lakes. The air concentrations in Table 4 are the best estimates available and are useful as a starting point for estimating atmospheric loading in the mass balance model.

Air/Water Exchange. Air/water exchange can be either an output or an input to the lake depending on the concentration gradient and the Henry's law constant. Using a modified two-layer model, the transfer of atrazine across the air/water interface can be expressed by eq 6. With Henry's law constant equal to 10^{-7} (dimensionless) (*32*), air/water exchange flux calculated from eq 6 shows a net transfer of atrazine from the air into the lake. Gas phase concentrations of atrazine were estimated from total air concentrations (*28*) and the fraction of the total concentration on air particles (f). The mass transfer velocity, v_{tot}, was determined according to Schwarzenbach et al. (*33*) and estimates by Muir et al. (*32*). For an average wind speed of 3 m/s and temperatures of 5−20 °C, v_{tot} was estimated to be between 10^{-3} and 10^{-4} m/month. These values of v_{tot} are small, and in conjunction with the low air concentrations, air/water exchange of atrazine is a minor process (sensitivity analysis presented later). Thus, the mass transfer coefficient was treated as constant, and the estimate of 10^{-3} m/month was used.

Outflow and Connecting Channel Inputs. Connecting channel inputs, eq 5, describe the contribution of one lake to the downstream lake. For example inputs enter Lake Huron from Lake Superior and Lake Michigan via the St. Mary River and the Straits of Mackinaw, respectively. Similarly, loss of atrazine from a lake by outflow is described by eq 8. Values for outflow, connecting channel inflows, and inter-basin flow were estimated from Quinn et al. (*3*) and Bolsenga et al (*34*).

Sedimentation. Net removal by sedimentation is described by eq 9. Concentration of atrazine on particles during any month ($C_{s(i)}$, kg/kg) is predicted from

$$C_{s(i)} = C_{w(i)}K_{oc}f_{oc} \times 10^{-3} \qquad (11)$$

where C_{wi} is the dissolved concentration of atrazine in the lake (kg/m^3) during any month, and K_{oc} (L/kg) describes the partitioning of atrazine between dissolved and particulate phase normalized to the fraction of particulate organic carbon (f_{oc}). K_{oc} measurements for atrazine range between 150 and 250 L/kg (*35, 36*); a value of 200 was used in the model. An f_{oc} of 0.25 was used based on the characteristics of suspended sediments in the Great Lakes. Sediment accumulation rates and the fraction of area with active sedimentation for each of the Great Lakes have been summarized by Strachan and Eisenreich (*37*).

Internal Loss. Internal loss is a parameter used to encompass any loss processes that occur within a lake other than sedimentation. Internal loss includes the processes of photolysis, hydrolysis, and biotransformation. Each of these processes may be treated as a pseudo-first-order loss, and the total removal from these processes is expressed by eq 10, where k_t is overall first-order loss rate of atrazine (month^{-1}) and is treated as a constant within each lake or basin. The overall loss rate, k_t, represents the sum of the loss rates from photolysis, hydrolysis, and biotransformation. The internal loss rate, k_t, is an unknown. Estimates for k_t will be entered into the model, and the model will calculate monthly concentrations of atrazine. Model results will be compared to measured values (Table 1) to determine the best estimate of k_t for each lake.

Results

Transformation Rates and Sensitivity. The first objective was to use the model as a tool to determine transformation rates of atrazine in the Great Lakes. The model was run iteratively using the best estimates of inputs and outputs described above but with changing values for *in situ* transformation rate (k_t). Model concentration trends were compared to measured concentration trends to determine the best estimate of a transformation rate. The transformation rate (k_t) was initially set at zero and increased by increments of 0.0001 month^{-1} to a maximum value of 1.0 month^{-1}. Model results were then compared to measured concentrations (and standard deviations) to determine which value of k_t generated model concentrations and trends that approximate observed

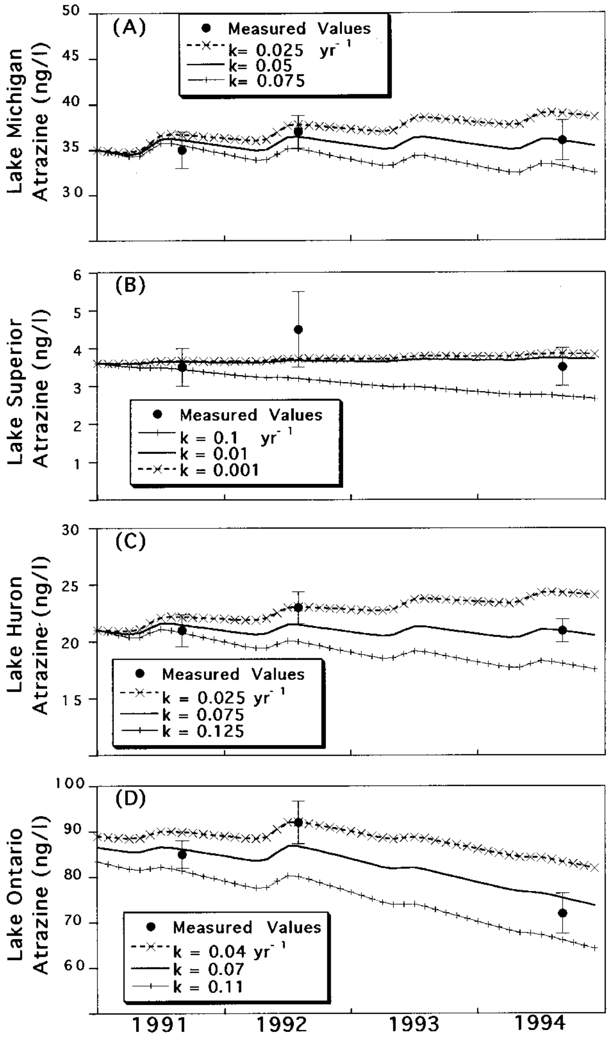

FIGURE 2. Model results compared to measured values for Lakes Michigan (A), Superior (B), Huron (C), and Ontario (D). The best match of model results to measured values (ng/L) is shown by the solid line. Model results using a range of transformation rates (yr^{-1}) are shown to demonstrate the sensitivity of the model to estimation of internal transformation.

values. The measured values, which essentially serve as calibration points, were summarized from Schottler and Eisenreich (*4*, *5*) (Table 1). Figure 2A–D shows the fit of model results as compared to measured values with different transformation rates. The solid line in Figure 2 represents the model results that most closely match measured concentration trends. Figure 2 also shows that the Great Lakes are relatively sensitive to the magnitude of the transformation rate. For example, in Lake Michigan a transformation rate constant of 0.025 yr^{-1} is clearly too low, requiring that the concentration of atrazine should have increased between 1991 and 1995. Conversely a transformation rate constant of 0.75 yr^{-1} is too large, requiring that the concentration of atrazine should have decreased between 1991 and 1995. Best estimates for internal transformation rates are summarized in Table 7.

The second objective of the model was to compare the relative importance of various sources to the lakes and the influence of these sources on the transformation rates. Table 5 shows the average annual load or loss calculated for each of the sources or outputs to Lake Michigan. Average values for annual losses were calculated using best estimates of an internal transformation rates. Table 5 also shows the relative importance of the different sources and losses. For all lakes except Superior, tributary plus connecting channel inputs are the most important source of atrazine, contributing >75% of the annual load. For the lakes with long residence times (Superior, Michigan, and Huron), internal transformation accounts for >60% of annual losses; however, only 1–10% of lakewide inventory is lost annually by *in situ* transformation (Table 6).

These results confirm that internal transformation is an important process operating in the Great Lakes. However, there is uncertainty associated with each of the inputs and outputs that creates uncertainty in the determination of transformation rate. Examining the sensitivity of the model to high and low estimates for input and outputs will define a range of possible values for transformation rates. Once transformation rates had been determined using best estimates of inputs, the model was run again using high and low estimates for each input. Using these high and low estimates, the sensitivity of atrazine concentration to a particular source was determined. In addition, transformation rates were recalculated at the high and low input estimates to determine a range of extreme values. The estimation of internal transformation rate will be discussed individually for each of the Great Lakes. Lake Michigan is discussed first and will serve as an example for the other lakes.

Lake Michigan. Figure 3 shows the sensitivity of the model for high and low estimates of inputs. Tributary inputs are the major source to the lake; consequently, the model is most sensitive to tributary estimates. A range of estimates for percent of use removed by runoff is presented in Table 2. Based on the range of values in Table 2, the model was run with the percent removed by runoff varying from 0.5% to 1.5% to test the sensitivity of the model to tributary loadings (Figure 3A). (Increasing or decreasing the percent removed by runoff to 1.5% or 0.5% is equivalent to increasing or decreasing total tributary loading estimates by ±50%.) In the case where tributary loading is increased by 50%, the transformation rate constant would have to be increased to 0.08 yr^{-1} to make model results reflect measured concentration trends. Likewise, for a 50% decrease in tributary inputs, k_t would have to decrease to 0.02 yr^{-1} to make model results match measured concentrations. While this sensitivity analysis shows that variation in tributary inputs effects the subsequent estimation of transformation rate, the total variation is within a factor of 4. An input of ~9000 kg/yr from tributaries to Lake Michigan seems large, and a ±50% variation might be expected to have a larger effect on the observed concentrations. However, total annual inputs are only 7% of the atrazine inventory accumulated in Lake Michigan (Table 6); thus in any one year the lake shows minimal response to fluctuations in tributary loadings.

Figure 3B shows Lake Michigan sensitivity to precipitation. Increasing or decreasing precipitation loading estimates by ±50% changes atrazine concentrations by less than 10% after 4 years. Thus, annual variations or errors in estimating precipitation loadings have little effect on the estimation of internal transformation rate. Dry deposition, air/water exchange and sedimentation have even less effect on estimation of the internal transformation rate. The importance of these processes was tested by examining a wide range of input/output estimates. Dry deposition, air/water exchange, and sedimentation estimates were each tested using a 50% decrease and a 5-fold increase. Even with this wide range of loading (or loss) estimates, the effect on modeled atrazine concentration or estimation of internal transformation rate is less than 1%.

An atrazine transformation half-life can be calculated from the transformation rate and the first-order rate law such that

$$t_{1/2\ \text{transformation}} = \frac{\ln 2}{k_t} \qquad (12)$$

where $t_{1/2\ \text{transformation}}$ is the pseudo-first-order atrazine transformation half-life in years. An overall atrazine loss rate is

TABLE 5. Average Annual Inputs and Losses (kg/yr) of Atrazine to the Great Lakes[a]

	Superior		Michigan		Huron		Erie -west		Erie-central		Erie-east		Ontario	
	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load	load (10^3 kg/yr)	% of total load
tributary	0.030	3	9.04	76	4.29	49	3.7–15	50–80	0.75–3.0	40–75	0.45–1.6	80 –93	1.5–3	10
precipitation	0.82	82	2.6	22	1.2	14	0.2	3	0.65	15–35	0.105	6–19	0.375	2
dry deposition	0.12	12	0.16	1	0.17	2	0.03	<1	0.15	4–8	0.005	<1	0.16	<1
air/water exchange	0.035	3	0.03	<1	0.03	<1	0.006	<1	0.25	6–14	0.001	<1	0.001	<1
c. channel					3.09	35	3.52	20–47	10–13[b]		13–20[b]		14–21	87
outflow	0.26	37	2.9	24	3.5	39	10–13	98	13–20	80	14–21	93	16–19	68
transform	0.45	63	8.89	76	5.5	61	0.2–0.8	1	3–4.8	20	1.1–1.5	7	7.8–8.5	32
sediment	0.003	<1	0.025	<1	0.015	<1	0.03	<1	0.06	<1	0.025	<1	0.026	<1

[a] Inputs are relatively constant for Lakes Superior, Michigan and Huron, thus inputs (outputs) from 1991 to 1994 were averaged. Lakes Erie and Ontario have large annual variations in inputs, thus a range of model results is presented. Transformation for the western basin of Lake Erie was calculated at $k_t = 0.05$ and 0.5 yr^{-1}. Superior inputs/outputs were calculated with internal transformation rate = 0.01 yr^{-1}. [b] Interbasin input/output dominate the source apportionment in the central and eastern basins of Lake Erie and were excluded when calculating the percentage from each source.

TABLE 6. Comparison of Atrazine Inventory in the Great Lakes to Annual Input of Atrazine Annual Loss though Internal Transformation

	inventory[a] (10^3 kg)	annual input (10^3 kg/yr)	annual input divided by inventory (%)	inventory lost annually by transformation (%)
Superior	36	1.03	3	1
Michigan	176	11.8	7	5
Huron	75	8.78	12	7
Erie[b,c]	30–60	10–25	30–40	10
Ontario[b]	125–140	16–24.5	12–18	6

[a] Inventory was calculated from average lakewide concentrations (Table 1) and volume of the lake. [b] Concentrations and loadings to Lakes Erie and Ontario vary yearly, thus a range of values is presented. [c] The three basins of Lake Erie were combined to give total annual inputs, loss by transformation, and a lakewide inventory.

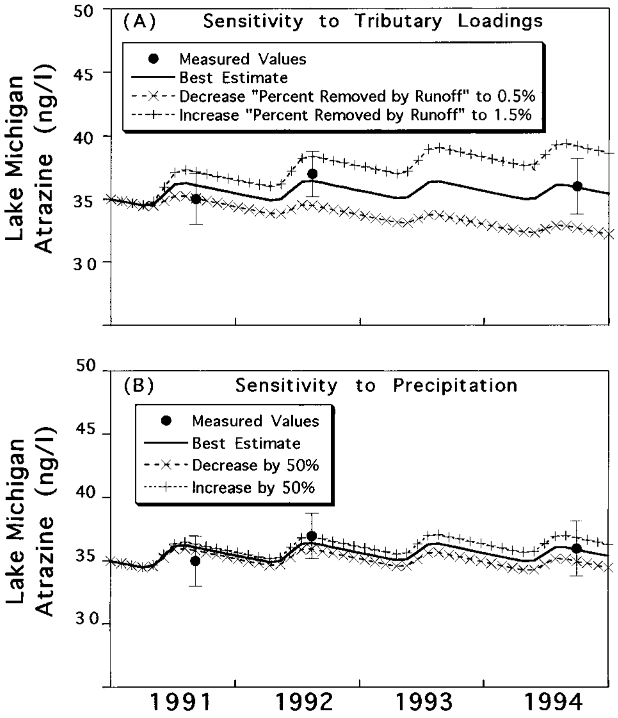

FIGURE 3. Sensitivity of Lake Michigan to estimation of tributary and precipitation loadings. In each case the internal transformation rate constant, k_t, was 0.05 yr^{-1}. Varying tributary inputs by ±50% requires k_t to range from 0.02 to 0.08 yr^{-1} in order for model results to match measured concentrations. Varying precipitation by ±50% changes model results by <5% after four years.

calculated as the sum of the individual loss rates:

$$k_{\text{total}} = k_t + k_f + k_s \tag{13}$$

where k_{total} is overall atrazine loss rate constant (yr^{-1}), k_t is the *in situ* transformation rate constant (yr^{-1}), k_f is the loss rate constant due to outflow (yr^{-1}), and k_s is the loss rate constant (yr^{-1}) from sedimentation. The loss rate constant by outflow (flushing), k_f, is simply the reciprocal of the lake residence time (Table 7). In the Great Lakes, sedimentation accounts for ≪1% of annual atrazine loss, thus k_{total} is essentially $k_t + k_f$. Finally, the overall water column residence time for atrazine is simply

$$R_{\text{atz}} = 1/(k_{\text{total}}) \tag{14}$$

where R_{atz} is the atrazine water column residence time in years.

Applying eq 12, the *in situ* atrazine transformation half-life in Lake Michigan is ~14 yr. Using 0.05 yr^{-1} k_t and 0.016 for k_f (Table 7) in eq 13, the overall atrazine pseudo-first-order loss rate for Lake Michigan is 0.066 yr^{-1}, which is equivalent to a water column residence time (eq 14) of 15 yr. Using the range of k_t determined previously from high and low estimations of inputs ($k_t = 0.02–0.08\ yr^{-1}$; $k_{\text{total}} = 0.036–0.096$), the overall water column residence time for atrazine in Lake Michigan ranges from 10 to 27 yr.

Lake Superior. The low atrazine concentrations coupled to the long residence time makes estimation of internal transformation rate in Lake Superior difficult. The 10-fold difference between $k_t = 0.01$ and $k_t = 0.001\ yr^{-1}$ in Figure 2B produces essentially no difference in model output. The insensitivity of Lake Superior to transformation rate means that k_t can only be quantified as being something <0.1 yr^{-1}. The best model results are achieved using an internal transformation rate of 0.01 yr^{-1}. The cold, oligotrophic waters of Lake Superior likely support a transformation rate much slower than Lake Michigan, thus model results using $k_t = 0.01\ yr^{-1}$ seem reasonable. The accumulated atrazine inventory of ~36 t (Table 6) in Lake Superior is also evidence of slow rate of *in situ* transformation. Atrazine has been registered for use since 1959 (*38*). Thus, assuming historical inputs were similar to current inputs of ~1 t/yr (Table 5), the internal loss rate from the lake must be slow in order for the inventory to have reached ~36 ton in approximately 35 yr.

Sensitivity to estimation of inputs was tested in the same manner as in Lake Michigan. Using the same percentage of increases or decreases in load estimates as used in Lake Michigan, atrazine concentrations were not sensitive to any of the sources. Precipitation, constituting 80% of the annual inputs would be the most likely source to effect atrazine concentration. However, precipitation contributes <1 ton per year to Lake Superior, which is less than 3% of the ~36

TABLE 7. Summary of Loss Rates and Water Column Residence Time of Atrazine in the Great Lakes

	internal transformation[a]			
lake	$t_{1/2}$ (yr)	k_t (yr^{-1})	flushing rate[b] k_f (yr^{-1})	water column residence time[c] $(k_t + k_f)^{-1}$ (yr)
Superior	>7	<0.1	0.005	>10
Michigan	13.9	0.05	0.016	10–27
Huron	9.2	0.075	0.048	6–11
Erie-west	2.3	0.3	7.7	<0.13
Erie-central	5.5	0.13	0.61	1.1–1.5
Erie-east	7.7	0.09	1.25	0.72–0.77
Ontario	9.9	0.07	0.13	4.3–5.9

[a] Internal transformation values represent the best estimate; a range of values is discussed in the text. [b] Flushing rates are the reciprocal of lake residence times estimated from Quinn et al. (*3*). [c] Range for atrazine water column residence time was based on the range of k_t values determined at high and low estimates of inputs discussed in text.

ton of atrazine inventory accumulated in the Lake (Table 6). Thus, a ±50% change in the estimation of precipitation loading has little effect on the atrazine concentration over a 4-yr period.

Lake Huron. Using best estimates of inputs and outputs, an *in situ* transformation rate of 0.075 yr^{-1} is predicted for Lake Huron (Figure 2C). Sensitivity of Lake Huron to estimation of inputs was tested in a fashion similar to that done for Lake Michigan. High and low estimates (decrease of 50%, increases of 5×) of dry deposition, air/water exchange, and sedimentation had no effect on model concentration output. A ±50% increase or decrease in total precipitation loading resulted in a model concentration change of <10% over 4-yr. Estimation of tributary inputs had the greatest effect on model results. When tributary inputs were increased by 50%, k_t had to be increased to 0.11 yr^{-1} for model concentration trends to match measured concentration trends. Similarly, when tributary estimates were decreased by 50%, k_t had to be decreased to 0.047 yr^{-1}.

Incorporating $k_t = 0.075\ yr^{-1}$ into eq 12, the *in situ* atrazine transformation half-life in Lake Huron is ~9 yr. Combining the range of k_t determined at high and low estimations of inputs ($k_t = 0.047-0.11\ yr^{-1}$) with the flushing rate (Table 7) into eq 14, the water column residence time for atrazine in Lake Huron ranges from 6 to 11 yr (Table 7).

Lake Erie. Because the water residence in each of the Lake Erie basins is <2 yr (*3*), and annual inputs are large, model results were optimized for each of the basins simultaneously. Figure 4 shows model results for the central and eastern basins of Lake Erie, using several combinations of internal transformation rates. Model concentration trends most closely matched measured concentrations when internal transformation was slightly faster in the central basin (k_t = 0.13 yr^{-1}) than in the eastern basin (k_t = 0.09 yr^{-1}). The western basin of Lake Erie is poorly mixed with respect to tributary loadings and inputs from the St. Clair River (*34*). Therefore, it is difficult to match model results with the limited western basin concentration measurements. However, due to the high tributary loadings that enter the western basin, output from the western basin is an important factor in modeling the rest of Lake Erie. Fortunately, output from the western basin is not particularly sensitive to transformation rate. Water residence of the western basin is only ~1.5 months, thus using a range of k_t for the western basin of 0.05–0.5 yr^{-1} changes output from the western basin by <10%. The best model results for the central and eastern basins were achieved using a k_t = 0.3 yr^{-1} for the western basin.

Tributaries are the major source of atrazine to Lake Erie, supplying 60–90% of the total annual input (Table 5). As a result, model output is most sensitive to estimates of tributary loading. High and low estimates for other model parameters affect model output by ≪1%. When tributary inputs are increased by 50%, k_t would have to increase to 0.3 and 0.15 yr^{-1} for the central and eastern basins, respectively, in order for model results to match measured concentrations. Likewise if tributary inputs are decreased by 50%, k_t would have to decrease to <0.05 yr^{-1} in each basin. This sensitivity test demonstrates that even though estimation of tributary loading is an important factor in determining Lake Erie concentrations, the dependence is not so large that estimation of internal transformation becomes impossible.

Applying eq 12, the atrazine transformation half-life in central and eastern basins is 5 and 7.7 yr, respectively. Using the best estimates for internal transformation rate and flushing rates in eqs 13 and 14, the combined atrazine residence time for Lake Erie is ~2 yr (Table 7). Using the ranges of k_t determined previously for the central and eastern basin at high and low estimates of tributary inputs, the water column residence time of atrazine in Lake Erie ranges from 1.8 to 2.2 yr.

Lake Ontario. Figure 2D shows model results for Lake Ontario using a range of transformation rates. Model results best approximate measured concentrations when k_t = 0.07 yr^{-1}, which is equal to a transformation half-life of ~10 yr (Table 7). However, predicted concentrations show large deviations from measured values using best estimates of inputs and k_t. The lack of fit between model results and measured values is probably a result of the spatial variability in Lake Ontario concentrations. Lake Ontario atrazine concentrations show a spatial variation of 5–10 ng/L throughout the lake in any particular year (*4*). Thus, differences between measured values and model results is partially due to the estimation of the lakewide average.

The spatial variation in concentration is in part due to heterogeneous mixing with inputs from Lake Erie. Depending on mixing patterns and rates, annual inputs from Lake Erie will be more evident in some portions of Lake Ontario and diluted in others. This mixing effect complicates the determination of a lakewide average and contributes to the disparity between model results and measured concentrations. Tributaries (excluding the Niagara River/Lake Erie) are the second most important source to Lake Ontario, contributing about 20% of the total annual load. Estimates of tributary inputs were varied by ±50% to examine the effect on model results. At high and low estimates of tributary inputs, k_t only needed to vary between 0.08 and 0.045 yr^{-1} for model results to approximate measured concentration trends. Thus, even though model results do not entirely match measured values, it is possible to constrain the range of k_t as 0.04–0.08 yr^{-1}. Using this range of internal transformation rates and the flushing rate for Lake Ontario in eqs 13 and 14, the water column residence time for atrazine in Lake Ontario ranges from ~4 to 6 yr (Table 7).

Future Concentrations. Using the best estimates of atrazine loadings and transformation rate, the model was used to examine how the lakes would respond to future changes in the use of atrazine. Figure 5A–C shows the response of the Great Lakes for three scenarios of future atrazine use:

(1) Atrazine use remains constant (Figure 5A). The model was run until 2010, with atrazine use remaining constant starting in 1994. During the period 1994–2010, all inputs were held at 1994 estimates.

(2) Atrazine use decreases by 5% annually (Figure 5B).

(3) Zero atrazine use 1995–2010. Figure 5C models the hypothetical scenario if the use of atrazine were banned in 1995. In this scenario, atrazine loading is decreased by 95% in 1995, allowing for small residual loadings. From 1996–2010, the model is run with annual atrazine inputs as zero. The year 1995 was chosen as the cutoff year because model parameters are only estimated to 1994, and this scenario is

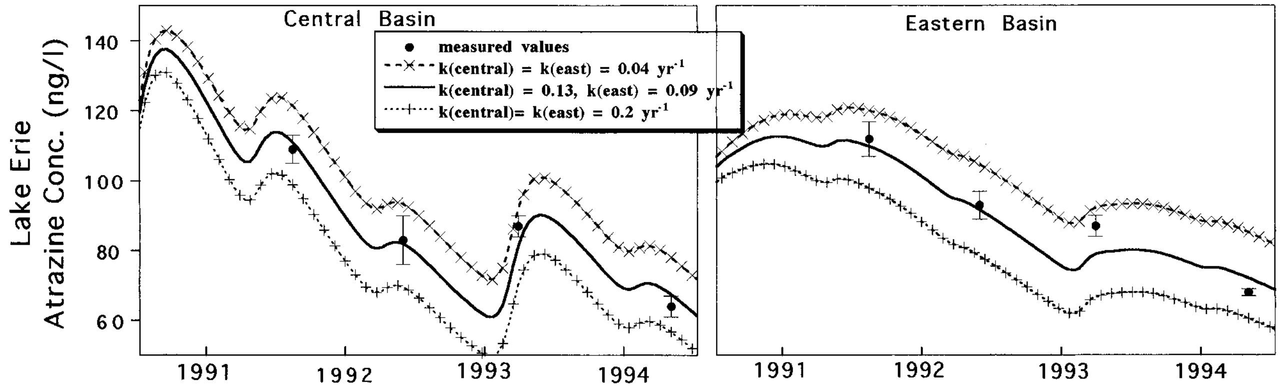

FIGURE 4. Model results compared to measured values (ng/L) for the central and eastern basins of Lake Erie. Model results that best match measured concentrations are shown by the solid line. The over- or underprediction of concentrations using a range of internal transformation rates demonstrates the sensitivity of Lake Erie to estimation of k_t.

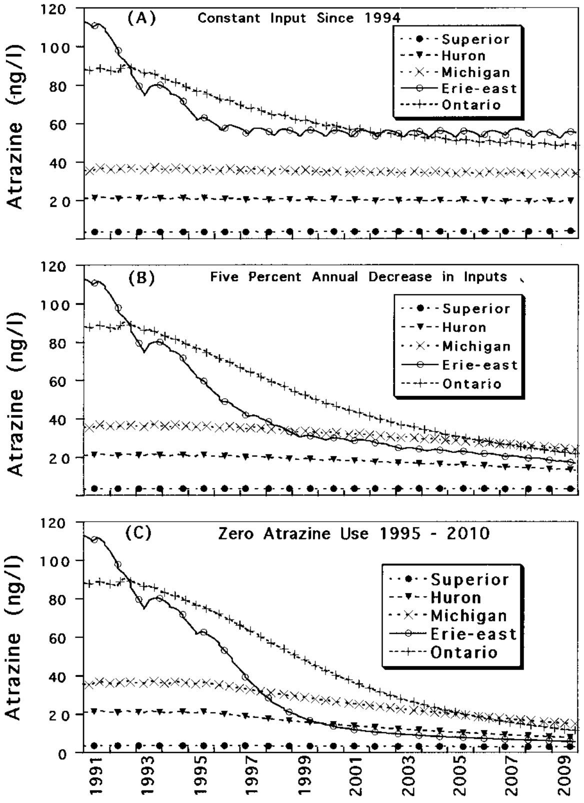

FIGURE 5. Great Lakes response to changes in atrazine use.

simply an exercise to examine lake response if inputs are reduced to zero at sometime in the future.

Figure 5A shows that if future atrazine use remains constant at 1994 levels, the atrazine concentrations in Lakes Michigan, Huron, and Superior will also remain relatively constant, changing by less than 2% over the next 15 yr. Atrazine use and concentrations in Lakes Erie and Ontario already exhibited decreases from 1991 to 1994. Thus, by keeping inputs constant at 1994 estimates, concentrations in Lakes Erie and Ontario continued to decrease for a period before reaching a nearly steady-state concentration of ~55 ng/L.

If inputs decrease by 5% annually, concentrations in the lakes will decrease according to the water residence time of the lake (Figure 5B). Lakes Erie and Ontario have the shortest residence time and thus show the largest and most rapid change in concentrations. Lakes Michigan, Huron, and Superior with their long residence times show overall decreases of <15% by 2010. If atrazine inputs are reduced to zero by 1996, concentrations still only decline by 30–40% in Lakes Michigan and Huron by 2010 (Figure 5C). With inputs reduced to zero, concentration in Lakes Erie and Ontario respond quickly, decreasing by >80% from 1994 to 2010. Continuing inputs from Lake Huron to Lake Erie, and likewise from Lake Erie to Lake Ontario, prevent the concentrations in Erie and Ontario from decreasing faster.

Model Validation. Atrazine has been registered for use in the United States since 1959 (*38*). A crude validation of the model can be accomplished by running the model since the inception of atrazine use and determining if model results predict current concentrations. Lake Michigan is the simplest for performing this validation since there are no connecting lake inflows and concentrations currently appear near steady state. Validation of the Lake Michigan model was examined by running the model from 1960 to 1995 using (1) historic inputs of atrazine estimated by normalizing current inputs against the production curve for atrazine; (2) historic annual loss from Lake Michigan calculated using the best estimate for k_{total} (k_f = 0.016, k_t = 0.05, $k_s \ll k_t$) from Table 7. Concentrations predicted by the model after 35 yr of atrazine input were compared against observed values to determine the validity of k_{total} ($k_t + k_f$).

Figure 6A shows the estimated total use of atrazine in the United States from 1960 to 1994 (1960–1976 (*39–41*); 1984–1994 (*38*)). Assuming that loading to Lake Michigan is proportional to the national use of atrazine, inputs to Lake Michigan over the last 35 yr can be estimated by normalizing current inputs against the historic use curve of atrazine (Figure 6B). Annual loss from Lake Michigan for any year is the mass accumulated in the lake multiplied by the overall first-order loss rate, k_{total}.

Figure 6C shows predicted atrazine concentrations in Lake Michigan from 1960 to 1995 using the above modeling assumptions. This scenario predicts an atrazine concentration of ~34 ng/L by 1994, which is not different from the observed concentration of ~36 ng/L. In addition, the predicted concentrations are relatively constant since the late 1980s, which is also consistent with observed trends. The similarity between predicted and observed concentrations in Figure 6C supports the validity of the value estimated for k_{total} (and hence k_t) in the mass balance model. While the results in Figure 6C are based on an approximation of historical loading, it is the only validation exercise possible with the available data. In any case, Figure 6C shows that for an input function proportional to the historic use curve and the current load of 12 t/yr (Figure 6B), the value of 0.066 yr^{-1} estimated for k_{total} (k_t = 0.05, k_f = 0.16) is appropriate.

Discussion

Internal transformation rate constants of atrazine are similar throughout the Great Lakes and ranged from 0.05 to 0.075 yr^{-1} for Lakes Michigan, Huron, and Ontario. The warmer more eutrophic waters of Lake Erie have rates within about

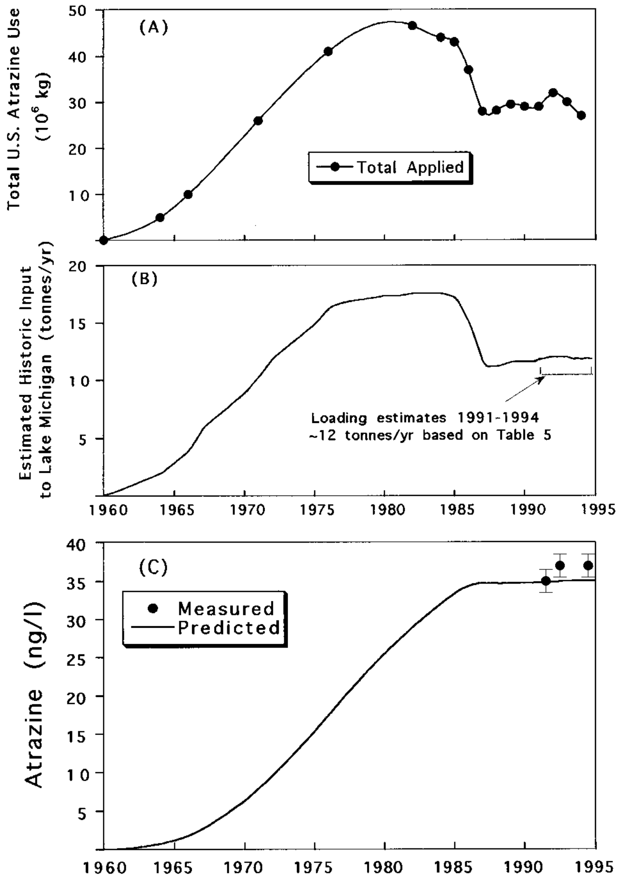

FIGURE 6. Model validation. A model scenario, based on estimated historic inputs to Lake Michigan (A and B), was constructed to validate the appropriateness of the estimated overall first-order loss rate ($k_t + k_f = 0.066$ yr^{-1}). (A) Estimated historical annual use of atrazine. (B) Input function of atrazine to Lake Michigan based on the historic use of atrazine and current annual loading. (C) Predicted concentration since 1960 using panel B and $k_{total} = 0.066$ yr^{-1}. Concentrations for 1991−1994 are within 10% of observed concentrations.

a factor of 2 higher (Table 7). Combining internal transformation rates with the flushing rate (eqs 13 and 14), the water column half-life for atrazine exceeds 5 yr in all Lakes except Erie. Because of its short residence time, the atrazine water column half-life in Lake Erie is only ~2 yr. The long water column half-lives determined from modeling results support the empirical evidence presented by Schottler et al (*4*), in which a lack of temporal or spatial variation in atrazine concentration was used to suggest a long half-life.

The long water column half-life also supports the premise of the Great Lakes as integrators in the environmental processing of atrazine. This is demonstrated by the ratio of annual inputs to inventory in the lakes. Annual inputs of atrazine to each of the Great Lakes (except Superior) are ~10−25 t/yr, constituting only 3−18% of the inventory in each lake (Table 6). This demonstrates that atrazine's long water column half-life has allowed it to accumulate in the Great Lakes over the last few decades. Model results until the year 2010 suggest that concentrations in Lakes Michigan, Huron, and Superior are now near steady state and that if use remains at current amounts, the atrazine inventory will show little change in the future (Figure 5). Lakes Erie and Ontario with shorter water column half-lives respond more quickly to changes in use, and lakewide inventories may drop if current use trends continue.

The results from this mass balance model confirm that atrazine undergoes *in situ* transformation within the Great Lakes. If internal loss is ignored or reduced to very small values, model results cannot be matched to measured concentrations. In the model, internal transformation is defined as any internal loss process other than sedimentation and encompasses photolysis, hydrolysis, and biotransformation. These processes would include the conversion of atrazine to desethylatrazine (DEA). Based on ratios of DEA to atrazine, Schottler et al. (*4*) estimated that 1.5, 0.9, 4.0, and 5.0% of total atrazine inventory is converted to DEA annually in Lakes Michigan, Ontario, Erie, and Huron, respectively. Dividing these percentages by the total percentage of inventory lost annually via *in situ* transformation in each lake (Table 6) suggests that about 15−40% of internal loss is by transformation to DEA in Lakes Michigan, Ontario, and Erie. For Lake Huron, conversion to DEA would account for 70% of total annual internal transformation. Conversion of atrazine to DEA is considered a biologically mediated process (*42*−*46*). Given the amount of atrazine that is estimated to be lost through just this one biotransformation pathway (atrazine to DEA) suggests that biotransformation may be the dominant internal loss process in the Great Lakes.

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