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Atrazine fate and transport in the Des Plaines Wetlands

H.H. Alvord, R.H. Kadlec *

Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136, USA

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Abstract

Atrazine fate and transport in three constructed pond and island wetlands in north east Illinois, USA, were studied in the field (1991) and modeled. The wetlands received pumped inflow from the Des Plaines River. The nominal residence time was about eight days for two, but was longer for the third.

The river atrazine chemograph had two peaks that rose quickly after heavy spring rains and then subsided slowly. Maximum concentrations exceeded the United States federal drinking water standard (3 μg/l). The wetlands delayed, reduced, and spread out the peaks, removing 26 to 64% of their inflows depending on residence time.

Flow and mixing models idealized the wetlands as single flow reactors or as networks of them. Atrazine reactions on biofilms with mass transfer rate limitation and when sorbed to sediments and litter were postulated.

Simulation results were consistent with almost all atrazine reactions on biofilms. Mass transfer coefficients were 10–15 m/year with the wetland bottom taken as the biofilm area. The corresponding wetland half-lives were about 10 days. Best calibration resulted when most of the reaction took place near the pumping inlet.

Model coefficients were similar to values for BOD and nutrients in other surface flow wetlands or to those derived from tracer data. The results suggest that observed removal rates of many pollutants in wetlands may reflect similar underlying mass transfer rate limitations.

Keywords: Flow networks; Pesticides; Residence time; Wetland ecosystems

1. Introduction

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, a triazine herbicide) annual use in the United States is about 35 million kg (Gianessi and Puffer, 1990). It is not highly persistent in the environment but due to continued use trace levels are often found in surface waters. A few per cent of applications in the Cedar River basin in Iowa reached river water (Squillace and Thurman, 1992). Chemographs of streams in Quebec, Canada, had peaks after spring rains (Muir et al., 1978). Its Safe Drinking Water Act (USEPA) maximum contaminant level (MCL) is 3 μg/l (Sittig, 1994).

Atrazine water concentrations in dosed natural and laboratory wetlands are known to decrease with time (Brockway et al., 1984; Huckins et al., 1986; Isensee, 1987). Water solutions however are stable at wetland pH values and temperatures (Widmer et al., 1993). The site and mechanism of atrazine reaction(s) in wetlands is not certain. Typical wetland models of flow, mixing, and reaction assume plug flow.

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* Corresponding author. Fax: (+1-313) 763-0459; e-mail: rhkad@engin.umich.edu

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This study investigated the effectiveness of wetlands for atrazine removal from river water. Models, including some describing non-ideal flow and mixing, were constructed and field calibrated. The possibility of laboratory parameter estimation was evaluated.

2. Materials and methods

2.1. Wetlands

Experimental wetlands EW3, EW4, and EW5 were constructed in 1986–87 at the Des Plaines Wetland Demonstration Project in Wadsworth, Illinois. Their areas and depth profiles were similar (Table 1). The schemes of Cowardin et al. (1979) and Shaw and Fredine (1956) classified them as Palustrine System and type 4 inland deep marshes respectively.

Wetland inflow was from pumping from the Des Plaines River, usually for 3 to 5 h on weekdays. Loading rates for EW3 and EW5 were similar but for EW4 it was much lower. More pumping was done early in the season when river levels were high than during dry weather later on. Weirs controlled outflows. Average rates declined as the season progressed. Outflow from EW4 stopped completely for some time.

The wetlands were non-linear accumulators with water volumes and outflows going up and down in response to pumping. Maximum deviations from average volumes were less than 10%.

Hourly data for pumping, precipitation, and evapotranspiration were available. Hydrologic models provided weir outflows and wetland water volumes that agreed with measurements reasonably well (Hey et al., 1994). Infiltration to ground water, as inferred from water budgets, was insignificant.

Tracer studies in June 1991 allowed estimation of dispersion numbers (Kadlec, 1994), residence time distributions, and flow and mixing model parameters.

By 1991 EW3 and EW5 had about 30% of their areas in dense vegetation; EW4 had 60%. Cattail (*Typha latifolia*), common pond weed (*Polygonum amphibium*), and white water lily (*Nymphaea tuberosa*) were abundant.

Atrazine, cyanazine, alachlor, and metachlor were commonly used pesticides in the Des Plaines River watershed (Schaefer, 1987).

2.2. Field studies

In 1991 more than 600 timed samples were collected manually or with ISCO™ automatic devices. River and wetland outflows were sampled on pumping days from late April into September. From May 26 to June 8 outflow sampling was at 4-h intervals. Samples were stored in amber glass bottles at 5°C until analyzed.

Continuous chemographs were approximated by connecting available data points. Atrazine flow rates were products of data or hydrologic model water flows with data concentrations, interpolated if necessary.

Wetland atrazine conversion (X), for 55 days from May 28, was,

$$\frac{\Sigma Q_{\mathrm{p}} C_{\mathrm{r}} \Delta t - \Sigma Q_{\mathrm{ow}} C_{\mathrm{ow}} \Delta t + I_{\mathrm{i}} - I_{\mathrm{f}}}{\Sigma Q_{\mathrm{p}} C_{\mathrm{r}} \Delta t} = X \qquad (1)$$

Table 1
Des Plaines experimental wetlands, 1991

Wetland	Area (ha)	Depth [a] (m)	Loading [b] (m^3/day)	NDT [c] (days)	% P [d]	% E [e]
EW3	2.22	0.50	1560	6.8	4	7
EW4	2.33	0.59	250	51.2	17	30
EW5	1.86	0.57	1220	8.4	4	6

[a] Averaged over wetland area and for simulation season.
[b] Averaged for simulation season.
[c] Nominal detention time: average volume/average flow rate.
[d] Precipitation as % of total season inflow (precipitation and pumping).
[e] Evapotranspiration as % of total season outflow (evapotranspiration and weir outflow).

where Q_p and Q_{ow} were pumping and (over the) weir flow rates (m^3/h), C_r and C_{ow} river and outflow concentrations (g/m^3 or $\mu g/l$), and Δt the time interval between flow and concentration measurements (h). Initial and final inventory (I_i and I_f, mg/m^3) calculations assumed outflows and represented entire wetlands. Atrazine in precipitation, evapotranspiration, and sediment convection were neglected.

2.3. Atrazine analysis

Water samples were subject to solid phase extraction, eluted with methanol, and analyzed by gas chromatography with thermionic detection. The analysis protocols are described in detail elsewhere (Alvord, 1995).

2.4. Modeling

Wetlands were idealized as having constant areas with uniform depths with respect to position but not necessarily to time.

Atrazine reactions on biofilms with mass transfer rate limitation or while sorbed to sediments and litter were postulated.

Biofilm reaction was described by a first-order rate law based on active area per unit of water volume V_w (dm^3 or l),

$$-r_f = k_a(S_a/V_w)C_w \tag{2}$$

where r_f was the reaction rate ($\mu g\ l^{-1}\ day^{-1}$), k_a a mass transfer coefficient (dm/day), S_a the active area (dm^2), and C_w the water phase atrazine concentration ($\mu g/dm^3$ or $\mu g/l$). No a priori estimates for k_a and S_a were available. However, Eq. 2 could be written as

$$-r_f = k_w C_w \tag{3}$$

where the water-based coefficient k_w (day^{-1}),

$$k_w = k_a(S_a/V_w) \tag{4}$$

assumed constant system water volume V_w. For well-mixed water parcels traversing the wetland with reaction described by Eq. 3, the final concentration, C_f, was,

$$C_f = C_i \exp(-k_w t) \tag{5}$$

in terms of initial concentration C_i and transit time t (days). This equation allowed calculation of water-based atrazine half-lives.

Sorbed phase reaction was presumed to occur on specified densities (dry kg/m^2) of sediments and litter. They were modeled as always being in reversible (dynamic) equilibrium with water.

Equilibrium sorption was described by the Freundlich isotherm,

$$C_s = KC_w^n \tag{6}$$

with C_s (μg (dry kg)$^{-1}$) the sorbent atrazine concentration. It related the sorbed and water phase concentration changes:

$$\frac{dC_s}{dt} = KnC_w^{n-1}\left\{\frac{dC_w}{dt}\right\} \tag{7}$$

Sorbed reaction was described by first-order kinetics,

$$-r = k_d C_s \tag{8}$$

where r was the reaction rate (μg (dry kg)$^{-1}$ day^{-1}) and k_d the sorbed reaction or disappearance rate constant (day^{-1}). An equation analogous to Eq. 5,

Table 2
EW3 materials

Material	Density	Freundlich isotherm (Eq. 6)		Sorbed reaction (Eq. 8)	
		K [a]	n	k_d (1/days)	$t_{1/2}$ (days)
Sediments (dry)	$0.4\ g/cm^3$ [b]	64.3	0.93	0.021	33
Litter (dry)	$1.0\ kg/m^2$ [c]	363	0.84	0.1	7

[a] $[K]$ [μg/(kg dry sorbent)][μg/(l water)]$^{-n}$.

[b] In situ density (coring).

[c] Vegetated area inventory.

with k_d replacing k_w, gave sorbed atrazine concentrations in terms of initial ones and elapsed time.

Isotherm parameters (K, n) and sorbed-phase reaction rate constants (k_d) were independently available (Table 2) from previous laboratory studies (Alvord, 1995).

2.5. Model I

Water flows and volumes were steady state. Pumped inflow and weir outflow were the same at a season-averaged value. Precipitation and evapotranspiration were ignored. The time step was one day.

Water mixing was described by residence time distributions (RTD). These functions define how long various "elements" of incoming water remain in flow systems. Wetlands with no, perfect, and tracer-defined mixing were examined.

The no mixing or plug flow wetland (PFR) had RTD,

$$\delta(t-\tau)=\mathrm{RTD} \tag{9}$$

where δ is the Dirac delta functional and τ the nominal residence time. All elements remain in PFR-modeled wetlands exactly one residence time.

The perfect mixing or continuously stirred tank reactor wetland (CSTR) had RTD,

$$(1/\tau)\exp(-t/\tau)=\mathrm{RTD} \tag{10}$$

with instantaneous concentrations the same everywhere and equal to outflow values. Water entering CSTRs has a continuous distribution of residence times with some appearing in the outflows immediately and some remaining inside much longer than the nominal residence time.

Tracer-defined wetlands were intermediate between PFRs and CSTRs: some, but not complete, mixing occurred.

Continuous RTDs were truncated and discretized into 20 one-day impulse functions with heights F_i (dimensionless, summing to 1) corresponding to flow fractions. They defined water elements with separate identities, not mixed with others, while in the wetlands. Outflows from elements from the previous 20 days were completely mixed.

Model I reaction was on biofilms only with mass transfer rate limitation (Eq. 3). Water in wetlands at the beginning of a simulation had no atrazine content.

PFR-defined wetland outflow concentrations were from Eq. 5, with C_i the river atrazine concentration when pumped in and the transit time t equal to one residence time. CSTR and tracer-defined values on day j ($C_{\mathrm{out},j}$) came from summing the products of water element final concentrations and flow fractions:

$$C_{\mathrm{out},j}=\sum_{i=1}^{k-1} F_i C_{\mathrm{r},j-i}\exp(-k_w\tau_i)$$
$$k=\min(21,j) \tag{11}$$

Starting concentrations $C_{\mathrm{r},j-i}$ were those of the river when elements entered the wetland.

Excel™ spreadsheets implemented simulations running for 55 days from May 28. Values for k_w (Eq. 4) were varied to give results with the best

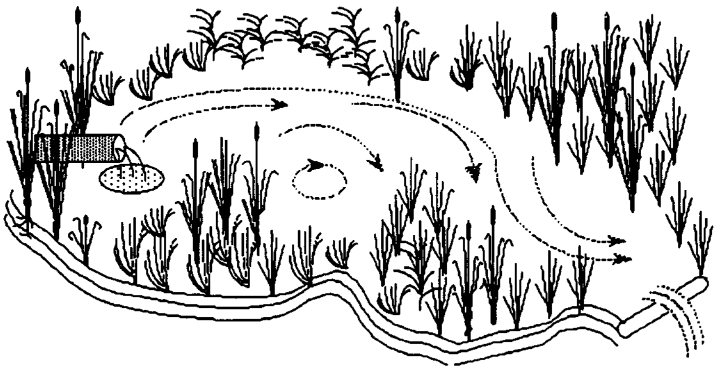

Fig. 1. Wetland idealization as a main channel with flow and vegetated, stagnant dead zones.

visual fit to data. Mass transfer coefficients k_a were calculated in units of meters per year (m/year) to allow comparison with literature values. The active area S_a was assumed to be the wetland bottom.

2.6. Model II

Water flows, including precipitation and evapotranspiration, and wetland volumes were dynamic and cyclical, based on hourly data and hydrologic models.

Water mixing was described by conceptualizing wetlands as central open water channels, with vegetated dead zones to the sides (Fig. 1). These regions were modeled by networks of flow reactors (Fig. 2). Levenspiel (1972) developed this method for non-ideal mixing in flow reactors.

A PFR and three CSTRs (of equal size) in series modeled the channel. Three other CSTRs (also of equal size) modeled the dead zone. The complete flow and mixing model has been described in detail elsewhere (Kadlec and Bastiaens, 1992). Four parameters were from tracer tests. Network flow rates, including those needed to model diffusion and to keep water levels the same everywhere, were from appropriate water balances.

PFR water from individual pumping hours were separate batch systems until pushed out. Each had its own residence time varying from hours to many days and initial (river) and final concentration (Eq. 5). Outflow, normally from several pumping hours, was perfectly mixed.

In a CSTR with water volume V_w, atrazine could be in both the water and sorbed phases with total mass, M_t,

$$M_t = C_w V_w + W_s C_s + W_l C_l \tag{12}$$

where W was the mass of a sorbent (kg) in dynamic equilibrium with the water (equilibrated density times CSTR area) and subscript s and l meant sediments and litter. Product rule differentiation (variable water volume, constant weights), gave the accumulation rate,

$$\frac{dM_t}{dt} = C_w \frac{dV_w}{dt} + V_w \frac{dC_w}{dt} + W_s \frac{dC_s}{dt} + W_l \frac{dC_l}{dt} \tag{13}$$

which could also be written in terms of flows (Q_{in}, Q_{out}), concentrations (C_{in}, C_{out}), and reaction rates:

$$\frac{dM_t}{dt} = \Sigma Q_{in} C_{in} - \Sigma Q_{out} C_{out} - (r_f + r_s + r_l) V_w \tag{14}$$

where r_s and r_l were sorbed reaction rates (Eq. 8). Combining Eqs. 13 and 14 eliminated the M_t derivative. Sorbed concentration derivatives in terms of water ones were given by Eq. 7. The water volume and its derivative were available, in terms of overall water depth h and height of the water surface over the weir, h_{ow}, (dm) from hydrologic models. Substitutions and rearrangement gave an equation (for

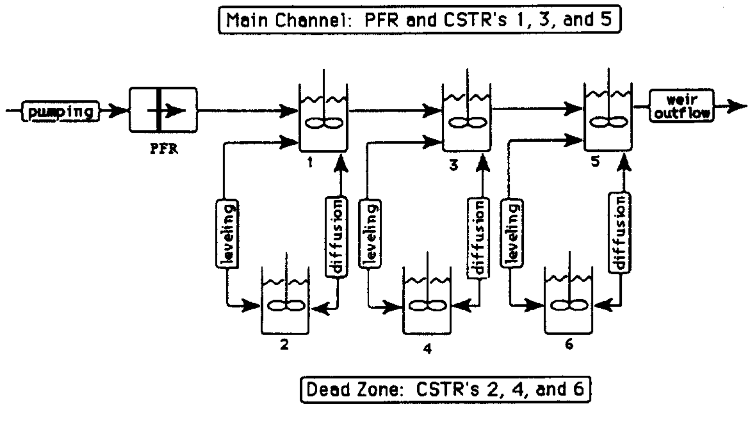

Fig. 2. Wetland flow and mixing model consisting of a plug flow reactor and six continuously stirred tank reactors.

$h_{ow} > 0$) in these variables, the water phase atrazine concentrations C_w, and their derivatives only:

$$\frac{dC_w}{dt} = \Big\{\Sigma Q_{in}C_{in} - \Sigma Q_{out}C_{out} - k_a S_a C_w - W_s k_{ds} K_s C_w^{n_s} - W_l k_{dl} K_l C_w^{n_l} - A C_w \frac{dh_{ow}}{dt}\Big\}\big\{Ah + W_s K_s n_s C_w^{n_s-1} + W_l K_l n_l C_w^{n_l-1}\big\}^{-1} \quad (15)$$

The specific equation for the second main channel CSTR with biofilm and sorbed reaction on sediments only, was (for $h_{ow} > 0$, and leveling flow Q_l going from main channel CSTR 3 to dead zone CSTR 4),

$$\frac{dC_3}{dt} = \Big\{C_1 Q_{13} + C_4 Q_{int} - C_3\Big(Q_{35} + Q_{int} + Q_l + A_3 \frac{dh_{ow}}{dt}\Big) - k_a S_a C_3 - W_s k_{ds} K_s C_s^{n_s}\Big\} \times \big\{A_3 h + W_s K_s n_s C_3^{n_s-1}\big\}^{-1} \quad (16)$$

where number subscripts refer to CSTRs and Q_{int} is the diffusion flow (Fig. 2).

Model II had 16 adjustable reaction rate parameters. Biofilm reactions in the network reactors gave seven. Mass transfer coefficients k_a and k_w values (Eq. 4) were related using season-averaged water volumes and wetland bottom area. Sorbed-phase reaction in the main channel (sediments) and dead zone (sediments and litter) CSTRs gave nine equilibrated densities.

The six coupled non-linear differential equations from the CSTR atrazine balances were integrated by a fourth-order Runge–Kutta–Gill method with 2-h time steps. Simulations ran for 49 days from May 28. Inventory and conversion calculations included water and sorbed atrazine.

Model II generated a weighted squared deviations sum (WSDS) of simulation results (interpolated) from data. The outflow peaks, with high data densities, and the tail, with a lower one, had the same total weight. First peak points (33, 0–185 h) had weights of 0.952; second peak points (25, 185–430 h) 1.33; and tail points (11, 430–1045 h) 3.03. A simulation missing all data points by 1 μg/l would have a WSDS value of 33.

There were two QuickBasic™ compiled applications that implemented Model II. One sought optimum values for subsets of adjustable parameters (without allowing atrazine generation or equilibrated litter densities exceeding inventory estimates) but kept no information from individual simulations. Another produced one simulation from a set parameter list and printed flow rates, concentrations, and inventories for all the reactors as functions of time.

Optimization was by steepest descent along a vector of partial derivatives of WSDS values with respect to parameters. Forward differences approximated derivatives with immediate updating of changes giving lower sums. Searches along the vector found three bracketing points and then isolated the minimum by golden section searches (Sprott, 1991). Simulations ran until two significant figures for parameters and three for the WSDS value did not change.

3. Results

3.1. Field studies

Over 200 water samples taken in 1991 were analyzed for atrazine, including all those from the Des Plaines River and EW3 outflow.

The river chemograph had two peaks after a 50 mm late May rain. No peaks followed the next significant rainfall, in mid June. River concentrations exceeded the MCL on two pumping days. They returned to background levels in about 30 days.

EW3 (Fig. 3) and EW5 (Fig. 4) delayed, reduced, and spread out the river peaks. Outflow concentra-

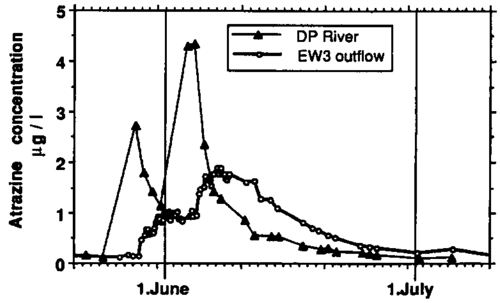

Fig. 3. Des Plaines River and EW3 outflow 1991 chemographs of atrazine.

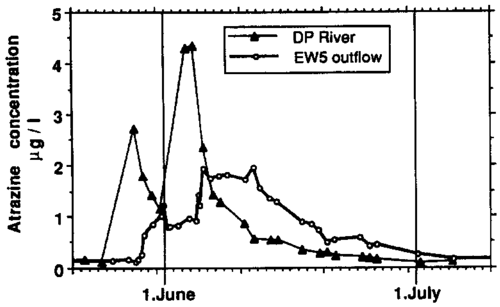

Fig. 4. Des Plaines River and EW5 outflow 1991 chemographs of atrazine.

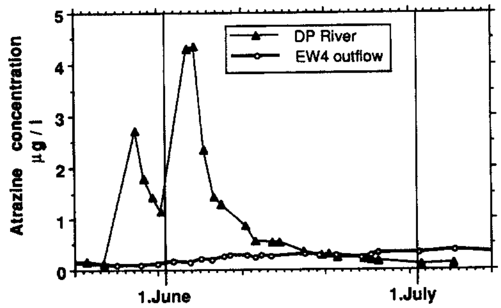

Fig. 5. Des Plaines River and EW4 outflow 1991 chemographs (high concentration) of atrazine.

tions exceeded river values for about 30 days before returning to background levels. EW4 concentrations were much lower (Fig. 5). The first river peak was barely discernible (Fig. 6). Atrazine conversions were similar in EW3 and EW5 but higher in EW4 (Table 3).

3.2. Modeling

Model I EW3 simulations gave best results with k_a of 12.6 m/year, with S_a the bottom area, corre-

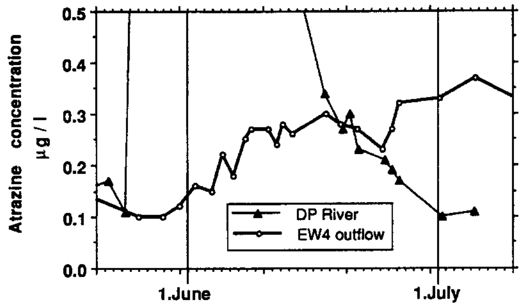

Fig. 6. Des Plaines River and EW4 outflow 1991 chemographs (low concentration) of atrazine.

Table 3

Atrazine mass balances, during 55 days from 28 May 1991

Wetland	Flows (g)		Inventories (g)		X (Eq. 1)
	in	out	initial	final	
EW3	70.3	47.8	1.6	1.1	0.33
EW4	12.1	1.5	2.1	5.0	0.64
EW5	53.5	40.1	1.6	1.1	0.26

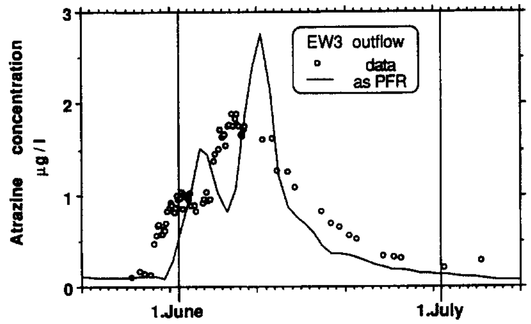

Fig. 7. Model I outflow chemograph of atrazine of EW3 as PFR and data.

Table 4

Model I-optimized parameter values and results for EW3 1991 simulations

Flow reactor	k_a [a] (m/year)	Flow (g)		Inventory (g)		X (Eq. 1)
		in	out	initial	final	
PFR	12.6	62.8	40.3	1.6	0.4	0.38
CSTR	12.6	62.8	47.3	1.6	0.4	0.27
tracer defined	12.6	62.8	41.5	1.6	0.4	0.36

[a] (Eq. 4) with S_a the wetland bottom area.

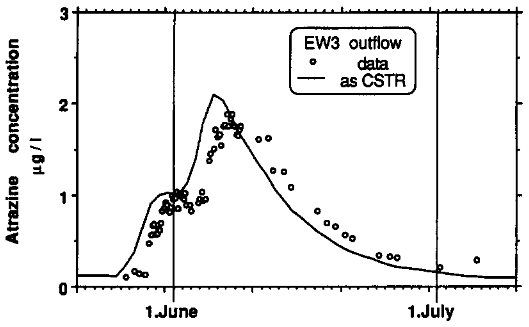

Fig. 8. Model I outflow chemograph of atrazine of EW3 as CSTR and data.

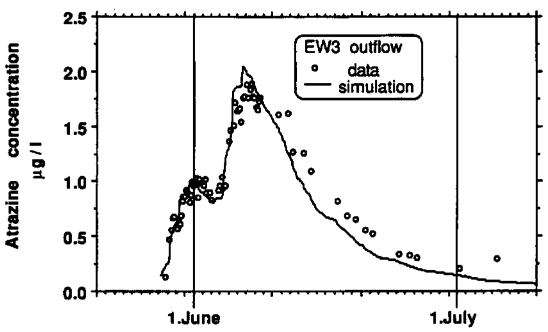

Fig. 10. Model II-optimized EW3 simulation with biofilm reaction only with the same mass transfer coefficients in all reactors and data.

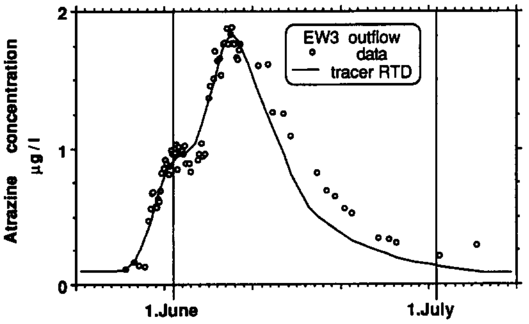

Fig. 9. Model I outflow chemograph of atrazine of EW3 as tracer-defined flow reactor and data.

sponding to a 10-day wetland half-life. Results underestimated atrazine inflows, but conversions were not far from data values (Table 4). The PFR outflow chemograph differed from data in peak size, timing, and shape (Fig. 7). The CSTR matched the data shape but without initial delay (Fig. 8). The tracer-defined reactor gave reasonable fit to the main peaks (Fig. 9). EW5 results were similar to those for EW3.

Model II-optimized EW3 simulations with sorbed-phase reaction only did not match data well but those with mass transfer-limited biofilm reaction only did. With the same coefficient in all reactors, the optimized chemograph had some main peak overshoot and tail undershoot (Fig. 10). Coefficients were similar to Model I values (Table 5). With variable coefficients all the reactions shifted to the PFR where the atrazine half-life was only about one day. The resulting improvement in the WSDS value was small.

Optimized simulations with both reactions had better fits in the tail. Only a few per cent of reaction was sorbed phase; none was on equilibrated litter.

Table 5
Model II-optimized parameter values for EW3 1991 simulations

Run [a]	k_a [b] (m/year)							Equilibrated sediments [c] (cm)					
	PFR	CSTR MC 1	CSTR MC 3	CSTR MC 5	CSTR DZ 2	CSTR DZ 4	CSTR DZ 6	CSTR MC 1	CSTR MC 3	CSTR MC 5	CSTR DZ 2	CSTR DZ 4	CSTR DZ 6
1	14.4	14.4	14.4	14.4	14.4	14.4	14.4	–	–	–	–	–	–
2	10.0	10.0	10.0	10.0	10.0	10.0	10.0	0.85	0.85	0.85	0.85	0.85	0.85
3	135	–	–	–	–	–	–	–	–	–	–	–	–
4	121	–	–	–	–	–	–	0.25	0.25	0.25	0.25	0.25	0.25
5	108	–	–	–	–	–	13.7	0.18	0.022	0.55	1.4	0.29	0.023

[a] 1: Biofilm reaction only, the same mass transfer coefficient in all reactors; 2: both reactions, the same coefficients and densities in all appropriate reactors; 3: biofilm reaction only, variable coefficients; 4: both reactions, variable coefficients but the same densities; 5: both reactions, variable coefficients and densities.

[b] (Eq. 4) with S_a the wetland bottom area and V_w the season-averaged depth.

[c] Simulation-equilibrated density (dry kg/m^2)/in situ density (Table 2).

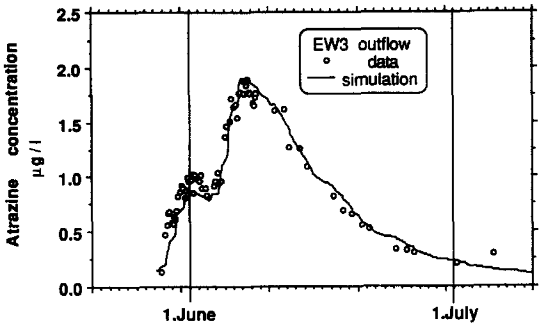

Fig. 11. Model II-optimized EW3 chemograph with biofilm and sorbed reactions with the same coefficients and densities in appropriate reactors and data.

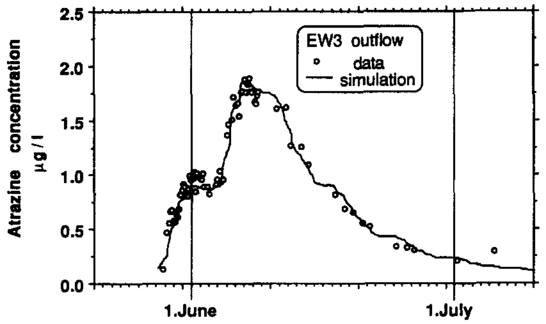

Fig. 12. Model II-optimized EW3 chemograph with biofilm and sorbed reaction with all parameters variable and data.

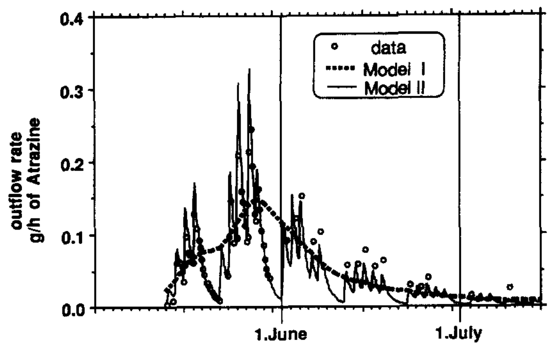

Fig. 13. EW3 atrazine mass outflows from Model I (tracer-defined flow reactor, biofilm reaction) and Model II (biofilm reaction only, the same mass transfer coefficients in all reactors) and data (data outflow concentrations times hydrologic model weir outflows).

With the same coefficients and densities there were 0.75 cm of equilibrated sediments (Fig. 11). With variable coefficients but the same densities, the biofilm reaction all moved to the PFR and sediment density decreased. With all parameters free, most of the biofilm reaction was in the PFR but some also occurred in one CSTR. Equilibrated sediments were concentrated in a few other CSTRs. The results followed data closely almost everywhere (Fig. 12).

The optimizing application searched only for the lowest WSDS value but conversions tended to approach the data as it decreased (Table 6).

The Model II atrazine flow rate fit the available data fairly well (Fig. 13). Model I by comparison eliminated its spikiness, underestimating it early in the chemograph, and overestimating it later.

4. Discussion and conclusions

4.1. *Field studies*

The 1991 Des Plaines River chemograph peaks were at high water flow periods. Most of the yearly

Table 6
Model II-optimized results for EW3 1991 simulations

Run [a]	Atrazine				X (Eq. 1)	% of X in/on		WSDS
	Σ flow (g)		inventory (g)			biofilms	sediments	
	in	out	initial	final				
1	68.9	43.0	1.38	0.40	0.390	100	–	2.85
2	68.9	46.2	2.30	0.90	0.350	93	7	1.03
3	68.9	46.2	1.38	0.55	0.342	100	–	0.850
4	68.9	47.3	1.59	0.62	0.327	96	4	0.765
5	68.9	46.9	1.70	0.80	0.333	96	4	0.749

[a] 1: Biofilm reaction only, the same mass transfer coefficient in all reactors; 2: both reactions, the same coefficients and densities in all appropriate reactors; 3: biofilm reaction only, variable coefficients; 4: both reactions, variable coefficients but the same densities; 5: both reactions, variable coefficients and densities.

atrazine flow seems to occur in a few weeks. Wetlands offer a passive method for attenuating these transient runoff peaks. They provide reaction in addition to mixing and dilution. Conversion obviously depended on residence time but three points were not enough to define functionality. It is probably well behaved since EW3 and EW5 conversions with comparable residence times were similar.

Before peak arrival, river and wetland outflows had the same low concentrations, indicating little if any wetland function. Possible explanations include inert analytical interferences or changes in wetland processes after the rains.

Deposition of atrazine by rain (Nations and Hallberg, 1992) can be significant. Concentrations are highly variable, depending on regional usage, time, and location. One $\mu g/l$ is not unusual. During the study three small rains (5 mm or less) and one larger one (17 mm) occurred without corresponding surges in chemographs.

Pesticide volatilization from water is generally insignificant if the Henry's Law constant is less than 1 Pa m^3/mol (Mackay and Leinonen, 1975; Glotfelty et al., 1988). The atrazine value is estimated (solid vapor pressure divided by solubility) as 0.0003.

Wetland in and out flows typically contained 0.10 and 0.0035 g/l of dry suspended solids. If equilibrated with water containing 1 $\mu g/l$ of atrazine (sediments, Table 2), they would have 0.64 and 0.02% of the river load.

Neglecting atrazine flows from evapotranspiration and sediment convection appears reasonable for this study. The data does not indicate major interferences from atrazine in rain water but its determination in future work would be worthwhile.

4.2. Modeling

Results from both models are consistent with atrazine reaction mainly on biofilms, as is the disappearance of BOD and nutrients in some other wetlands (Kadlec and Knight, 1995) where coefficients were 12–35 m/year. The similarity of these numbers to model results of this study (with reaction everywhere) suggest that the reaction or disappearance of many species in wetlands may be limited by mass transfer.

Mass transfer coefficient correlations for free surface water bodies like EW3 have been suggested, for example by Agunwamba et al. (1992). Unfortunately they are derived from few cases and estimates are very dependent on values for Manning's friction coefficient.

For EW3 tracer dispersion constants of 8.40 $m^2/year$ were obtained for the plug flow with dispersion model. Division by an average depth gives a mass transfer coefficient of 16.8 m/year, close to best calibrated model values. Tracer tests may provide estimates of wetland pollutant abatement performance but only after they are built.

The interpretation of Model II-optimized results needs caution. Parameters were many and changes in WSDS values small. However, in the most general cases many parameters were eliminated and the results have reasonable interpretations. High PFR mass transfer coefficients could be due to pumping induced turbulence near the inlet, indicating that reaction occurs mostly in a small part of the wetland with the rest "wasted".

Biofilm and sorbed-phase reactions in different Model II reactors are plausible. Mass transfer limitation implies zero atrazine concentration at the water–solid interface, while sorption equilibrium requires equal bulk water and interface concentrations. The biofilm may be inactive in some places, allowing atrazine to diffuse into sorbents, establish equilibrium, and react while sorbed.

All EW3 simulations undershot the first outflow peak when wetland atrazine was from the first high concentration pumping days. A few river sample analyses with expected (low) errors could cause such results. Later their effects should cancel.

The investigated models are useful for pond type wetlands with a single known inflow function, water surface areas that do not change greatly with basin water volume, and no exchanges with groundwater. Good data from an impulse tracer test are necessary. Model I needs an inflow function that can at least be approximated by a steady flow. It also requires that precipitation and evapotranspiration be small terms in the wetland water budget; hence it was not suitable for EW4 in 1991. Model II can accommodate transient inflows, precipitation, evapotranspiration, and weir controlled outflows if sufficiently detailed data are available. With 1500 lines of code, it gave some, but not a great deal, more information than Model I did with a few pages of spreadsheet.

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