



## RELATIONS BETWEEN PESTICIDE USE AND RIVERINE FLUX IN THE MISSISSIPPI RIVER BASIN

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(Received in USA 30 March 1995; accepted 6 July 1995)

### ABSTRACT

In an intensive subcontinental study of pesticides in surface waters of the United States, concentrations of 26 high-use pesticides were measured at nine sites in the Mississippi River basin from May 1991 through March 1992. Calculated total fluxes were combined with agricultural-use data to estimate the percentage of applied pesticide reaching the mouths of the Mississippi River and six major tributaries. For most pesticides, the riverine flux was less than 2% of the mass applied agriculturally. The fluxes were only marginally related to runoff-potential ratings based solely on the pesticides' chemical and environmental properties. The insecticide diazinon was detected frequently in rivers draining the three basins with the highest population densities, apparently as a result of urban use.

### INTRODUCTION

Agricultural pesticide residues in surface waters have been a concern since the 1940s [1-3]. Before 1970, attention was primarily focused on contamination by organochlorine insecticides, such as DDT, dieldrin, and heptachlor. Since that time, new agricultural practices and less persistent pesticides have been developed, in part to reduce the potential for pesticide contamination of surface waters. Agricultural use of these new pesticides, particularly herbicides, has increased dramatically since the 1960s [4-6]. Many of these pesticides are more water soluble than the organochlorines used previously, increasing the likelihood of transport to surface waters.

Pesticides are primarily moved from agricultural fields to surface waters in surface runoff [3]. The amount lost from fields and transported to surface waters depends on several factors, including soil characteristics, topography, weather, agricultural management practices, and the chemical and environmental properties of individual pesticides [7]. The combined effect of these factors on the temporal and spatial magnitude of pesticide concentrations and fluxes (mass per unit time at a specific location) in large integrating river systems is largely unknown. Mathematical models developed to simulate the behavior of pesticides applied to agricultural fields have been used mainly to predict losses of pesticides from individual fields and small watersheds [7]. At this scale, a number of the important variables (such as soil type, rainfall, and agricultural-management practices) can be controlled or measured. It is not known whether predictions from models applied at this small scale can be extrapolated to account for pesticide transport and fate on a regional scale, or if chemical and environmental properties of pesticides alone can account for the flux of pesticides to major rivers.

Pesticide properties most directly affecting runoff of pesticides include the dissipation rate in soil, water solubility, and the extent of sorption to soil particles [7,8]. Values of these three properties for the pesticides included in this study are shown in Table 1. The interaction of these three properties, and their influence on the amount of specific pesticides transported in runoff water, is complex, and no single property can be used to predict even the relative amounts of various pesticides lost from fields in runoff. Computer simulations using the GLEAMS model [9] have been used to develop relative runoff-potential ratings for most pesticides with past or present agricultural use [8]. These ratings were derived by using combinations of a number of different soils and pesticides as inputs to the GLEAMS model, and examining the predicted runoff losses of pesticides. Based on the results from these simulations, pesticides were assigned a runoff-potential rating of small, medium, or large. The runoff-potential ratings derived for the pesticides included in this study are shown in Table 1. These ratings provide a convenient way to compare the fluxes of the pesticides included in this study, and to investigate the relation between pesticide properties and runoff losses.

In this paper, pesticide fluxes in the Mississippi River basin from May, 1991 to April, 1992 are presented, and the influence of chemical and environmental properties on the movement of pesticides from fields to large rivers is examined. The choice of which pesticides to include in this study was based on two criteria. First, the pesticides had to be amenable to isolation from water by solid-phase extraction (SPE) and analysis by gas chromatography/mass spectrometry (GC/MS). Second, they had to be important high-use agricultural pesticides both within the Mississippi River basin and throughout the United States. Table 1 shows that the herbicides and insecticides targeted in this study include many of the highest-use agricultural pesticides in the United States. The 12 herbicides and 14 insecticides included in this study accounted for approximately 67% and 62% of the total United States agricultural use of herbicides and insecticides, respectively, as of 1989-90. Agricultural use of herbicides and insecticides in the Mississippi River basin accounted for approximately 70% and 30%, respectively, of the total agricultural use in the United States [5,6].

## MATERIALS AND METHODS

### Sampling

Concentrations of the targeted pesticides (Table 1) were monitored at three sites on the Mississippi River (Clinton, Iowa; Thebes, Illinois; and Baton Rouge, Louisiana) and at six sites near the mouths of major tributaries (Figure 1) from May 1, 1991 to March 31, 1992. The 1991 spring application period for most of the pesticides included in this study was encompassed by this sampling period. The sampling schedule was based on fixed time intervals, rather than the timing of individual runoff events. Because the drainage basins studied are large, the sampling points served to integrate the effects of all of the individual runoff-inducing rain events occurring within each basin. Samples were collected every 2 to 3 days during the high flow period (May through June) and once per week thereafter, except at the Ohio River site, where samples were collected weekly throughout the summer. Samples were collected by equal-discharge-increment or equal-width-increment procedures [10] at all sites, except for the Minnesota River near Mankato, MN, where previous data have shown that a single depth-intergrated sampling yields a water sample that is representative of the entire cross-sectional area of the river. Water samples were collected in 3-L Teflon<sup>1</sup> bottles. Samples obtained at each vertical sampling point in the river were composited and split with a Teflon cone splitter into cleaned bottles for various chemical analyses [11]. The

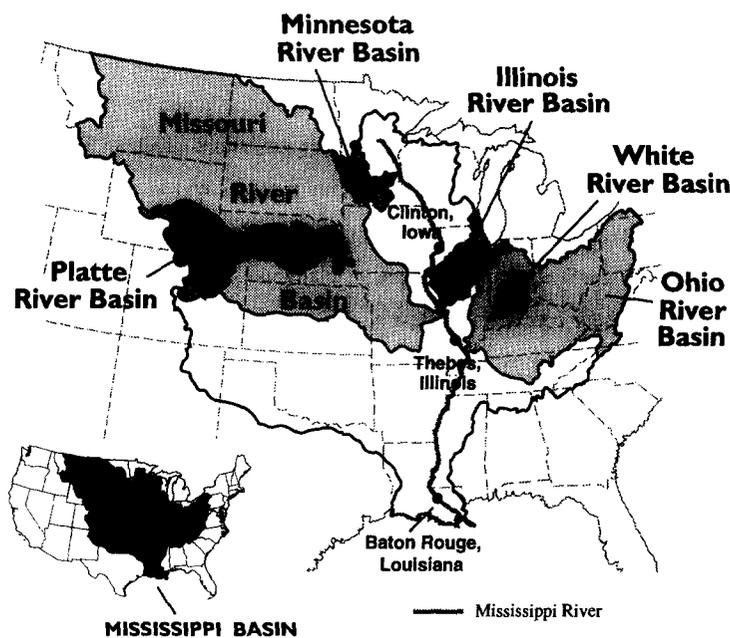


Figure 1. Map of study area. Sampling sites were near the mouths of the six tributaries, and at the three locations shown on the mississippi river.

aliquot for pesticide analysis was split directly into a clean 1-L amber glass bottle. The sample was then filtered through a glass-fiber filter (Whatman GF/F, in a stainless steel holder) into another clean 1-L amber glass bottle. The filter was discarded and the bottle was sealed and shipped overnight to the laboratory for analysis.

#### *Analytical methods*

Samples were spiked with surrogate analytes ( $D_6$ - $\gamma$ -HCH, terbutylazine, and  $D_{10}$ -diazinon) to monitor the accuracy and precision of the analytical procedure. Pesticides were isolated by solid-phase extraction (SPE). The 1-L sample was passed through a 100-mg octadecyl-SPE cartridge (Varian Associates) at a flow rate of about 20 mL/min. Water was removed from the SPE cartridge by centrifugation followed by passing dry nitrogen through the cartridge. Pesticides were eluted from the SPE cartridge with 7 mL of 5 percent isopropanol in hexane (volume:volume). The eluate was passed through a column of anhydrous sodium sulfate to remove any residual water, and was then reduced in volume to about 200  $\mu$ L under a gentle stream of nitrogen. The final extract was transferred to a glass insert in an auto-sampler vial, to which internal standard compounds (perdeutero-acenaphthalene, perdeutero-phenanthrene, and perdeutero-chrysene) were added.

All samples were analyzed on a 30-m gas chromatographic capillary column (Hewlett-Packard (HP) Ultra II, 0.3- $\mu$ m film thickness) with mass selective detection in the selective-ion monitoring mode (HP 5890 gas chromatograph equipped with an HP 5971A mass selective detector and an HP 7673 autosampler). Two microliters of the sample extract were injected into a split/splitless injection port. The column temperature was held at 100 °C for 5 min, then increased at a rate of 6 °C/min to 300 °C, and held at 300 °C for 5 min. The injector temperature was 250 °C.

Method detection limits (MDLs) for the pesticides targeted in this study are shown in Table 1. As part of the development of the analytical method, precision and accuracy were evaluated by analyzing river water spiked with the target analytes at low ( $\sim$ 0.1  $\mu$ g/L) and high ( $\sim$ 1.0  $\mu$ g/L) concentrations [12,13]. For all of the analytes included in this study, the relative standard deviation of seven replicate analyses was less than 12% at both concentration levels. For the pesticides most frequently detected in this study -- alachlor, atrazine, carbofuran, cyanazine, diazinon, EPTC, metolachlor, metribuzin, and simazine -- relative standard deviations of the seven replicate analyses were less than 6% at both concentration levels. The mean recoveries for the seven replicate analyses were between 60 and 110 percent for most analytes. Mean recoveries (both concentration levels) were lower for azinphos methyl (33%), propargite (57%), metribuzin (50%), and linuron (50%). In addition, recoveries for carbaryl and disulfoton varied widely between the low and high concentration solutions, with results biased high at the low concentration. Recoveries of the surrogate compounds (spiked at  $\sim$ 0.8  $\mu$ g/L) ranged from 74 to 85% in 14 replicate analyses, with a relative standard deviation of 3 to 7%. Pesticide concentrations in the water samples were not corrected for recovery. A complete description of the laboratory quality-assurance procedures used during the analysis of the samples from this study is included in reference [12].

#### *Flux calculations*

The flux of a pesticide is the mass transported in the river past the sampling point during a specified time period. The daily flux of each pesticide at each sampling point was calculated as the product of pesticide

**Table 1. Target analytes, method detection limits (MDLs), selected chemical and environmental properties, and runoff-potential ratings developed from simulations using the GLEAMS model (see text).**

	National use rank <sup>a</sup>	MDL (ug/L) <sup>b</sup>	Water solubility (mg/L) <sup>c</sup>	Soil half-life (days) <sup>c</sup>	Soil sorption coefficient (K <sub>oc</sub> ) <sup>c,d</sup>	Runoff-potential <sup>e</sup>	
						Solution phase	Sorbed phase
<b><u>Insecticides</u></b>							
azinphos methyl	17	0.005	29	10	1000	M	M
carbaryl	3	0.010	120	10	300	M	S
carbofuran	5	0.010	351	50	22	L	M
chlorpyrifos	1	0.004	0.4	30	6070	S	M
diazinon	21	0.002	60	40	1000	L <sup>f</sup>	L <sup>f</sup>
disulfoton	11	0.017	25	30 <sup>f</sup>	600 <sup>f</sup>	L <sup>f</sup>	S <sup>f</sup>
ethoprop	22	0.003	750	25	70	M	S
fonofos	7	0.003	17	40	870	L	S
malathion	10	0.005	130	1	1800	S	S
methyl parathion	2	0.008	60	5	5100 <sup>f</sup>	M <sup>f</sup>	M <sup>f</sup>
parathion	16	0.005	24	14	5000 <sup>f</sup>	M <sup>f</sup>	M <sup>f</sup>
phorate	6	0.003	22	60 <sup>f</sup>	1000 <sup>f</sup>	L <sup>f</sup>	L <sup>f</sup>
propargite	8	0.007	0.5	56	4000 <sup>f</sup>	M <sup>f</sup>	L <sup>f</sup>
terbufos	4	0.013	2.3	30	5000	M	M
<b><u>Herbicides</u></b>							
alachlor	2	0.002	240	15	170	M	S
atrazine	1	0.005	33	60	100	L	M
butylate	8	0.002	44	13	400	L	S
cyanazine	7	0.008	170	14	190	M	S
EPTC	4	0.002	344	6	200	M	S
linuron	29	0.010	75	60	400	L	M
metolachlor	3	0.002	530	90	200	L	M
metribuzin	13	0.005	1220	40	60 <sup>f</sup>	L <sup>f</sup>	S <sup>f</sup>
pendimethalin	9	0.005	0.3	90	5000	M	L
propachlor	20	0.007	613	6.3	80	M	S
simazine	21	0.005	6.2	60	130	L	M
trifluralin	6	0.005	0.3	60	8000	M	L

<sup>a</sup> Insecticides - national agricultural-use rank among all insecticides [6]. Herbicides - national agricultural-use rank among all herbicides [5].

<sup>b</sup> MDL - Method detection limit, in µg/L.

<sup>c</sup> Physical property data and runoff-potentials from Goss [8].

<sup>d</sup> K<sub>oc</sub> - Sorption coefficient normalized to organic carbon content.

<sup>e</sup> Runoff-potentials: L - large, M - medium, S - small [8].

<sup>f</sup> Values for physical properties are estimates, as are the runoff-potentials derived for these compounds [8].

Table 2. Agricultural use, and riverine flux as a percentage of use, for 26 pesticides in the Mississippi River basin, May, 1991 through March, 1992.

Pesticide	Rivers Sampled							
	MINNESOTA		WHITE		ILLINOIS		PLATTE	
	Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**
<b>PESTICIDES WITH LARGE RUNOFF POTENTIAL</b>								
Atrazine (H)	290	.62	710	.95	2000	1.9	1600	.84
Butylate (H)	160	no det.	270	.01	750	.02	560	<.01
Carbofuran (I)	11	no det.	42	.05	95	.38	190	.09
Diazinon (I)	0	--	.08	20.0	2.4	4.0	39	.02
Disulfoton (I)	.39	no det.	0	no det.	.24	no det.	39	no det.
Fonofos (I)	31	.45	20	.04	120	.09	100	.03
Linuron (H)	.54	no det.	44	.01	86	no det.	3.7	no det.
Metolachlor (H)	510	.65	430	.48	1800	.93	440	.74
Metribuzin (H)	32	.23	54	.21	140	.23	38	.33
Pendimethalin (H)	160	<.01	41	no det.	290	<.01	92	<.01
Phorate (I)	0	no det.	.52	no det.	.67	no det.	47	no det.
Propanil (I)	47	<.01	11	.06	73	no det.	66	no det.
Simazine (H)	.96	5.2	9.5	5.0	67	.97	4.6	2.4
Trifluralin (H)	510	<.01	79	<.01	630	.01	240	.01
<b>PESTICIDES WITH MEDIUM RUNOFF POTENTIAL</b>								
Alachlor (H)	1400	.20	850	.15	2000	.46	1000	.31
Azinphos methyl (I)	.06	no det.	.72	no det.	1.2	no det.	.18	no det.
Carbaryl (I)	8.6	nd	3.2	<.01	30	.01	140	<.01
Chlorpyrifos (I)	53	.15	60	no det.	280	.07	300	.01
Cyanazine (H)	450	1.3	210	.76	750	3.1	460	2.6
EPTC (H)	1500	<.01	42	.02	650	.05	460	<.01
Ethoprop (I)	.99	.08	0	no det.	.01	no det.	37	no det.
Methyl parathion (I)	8.5	.10	.08	no det.	9.4	no det.	140	no det.
Parathion (I)	3.3	no det.	0	no det.	0	no det.	110	no det.
Propachlor (H)	22	2.0	0	--	35	.09	70	.20
Terbufos (I)	56	.05	42	no det.	150	<.01	260	no det.
<b>PESTICIDES WITH SMALL RUNOFF POTENTIAL</b>								
Malathion (I)	0	--	.98	.12	.90	no det.	9.4	no det.

\* Total reported agricultural use in the basin, in metric tonnes (1000 kg) [5,6].

\*\* Flux calculated by substituting zero for concentrations below the detection limit (see text).

-- No agricultural use reported in basin; nd - no data.

no det. - no samples with concentrations above the detection limit; (H) - herbicide, (I) - insecticide.

concentration and river discharge (flow) for each day. Daily mean discharge values were available for all sampling points for the entire eleven month period. Concentrations of pesticides on non-sampling days were estimated by linear interpolation between the concentrations measured on the adjacent sampling days. The daily fluxes were then summed to give the total flux over the eleven-month period. The total flux of each pesticide at each sampling site was compared with data on agricultural use of that pesticide in the drainage basin (see below), and is expressed as a percentage of the amount applied in each basin in Table 2.

Table 2. (continued)

Rivers Sampled									
MISSOURI		OHIO		MISSISSIPPI					
Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**	at Clinton, IA		at Thebes, IL		at Baton Rouge, LA	
				Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**	Use in basin*	Flux as % of use**
<b>PESTICIDES WITH LARGE RUNOFF POTENTIAL</b>									
6300	1.2	4800	1.2	1500	.96	13000	1.5	21000	1.3
1900	<.01	1900	.03	470	no det.	4200	<.01	6700	nd
650	.09	370	.08	53	.28	930	.14	1800	nd
84	.07	6.6	1.10	18	no det.	110	.13	150	nd
200	no det.	3.3	no det.	11	no det.	220	no det.	470	nd
270	.02	160	.01	65	.11	660	.02	940	nd
55	no det.	270	no det.	15	no det.	240	no det.	630	nd
3500	.68	3400	.45	1700	.53	11000	.80	16000	.62
210	.41	400	.09	72	.10	610	.36	1300	.43
810	.01	480	<.01	330	<.01	2100	<.01	3700	nd
100	no det.	6.6	no det.	.32	no det.	120	no det.	190	nd
300	.05	130	no det.	64	.08	490	no det.	800	nd
52	1.4	220	3.9	3.9	10.5	170	1.6	460	2.2
2400	.01	750	<.01	810	no det.	5400	<.01	8500	nd
<b>PESTICIDES WITH MEDIUM RUNOFF POTENTIAL</b>									
4700	.16	4700	.12	2100	.30	12000	.27	19000	.17
1.5	no det.	14	no det.	4.3	no det.	11	no det.	150	nd
810	<.01	200	.08	36	no det.	920	.01	1500	nd
1100	no det.	490	<.01	250	.02	2300	<.01	3400	nd
2000	2.0	1400	.82	1600	.57	6200	1.6	8300	1.5
4200	<.01	810	.02	3900	.01	12000	.01	13000	nd
85	no det.	3.9	no det.	1.4	no det.	98	no det.	120	nd
120	no det.	19	no det.	15	no det.	150	no det.	1600	nd
360	no det.	.08	no det.	4.3	no det.	580	no det.	650	nd
1100	.01	19	no det.	66	.05	1400	<.01	1800	nd
640	no det.	280	no det.	130	no det.	1300	no det.	2000	nd
<b>PESTICIDES WITH SMALL RUNOFF POTENTIAL</b>									
85	<0.01	45	no det.	.23	no det.	100	no det.	460	nd

For most of the targeted pesticides, concentrations were below the method detection limit in some samples. All concentrations below the detection limit were assigned a value of zero for the flux calculation. Thus, the percentages reported in Table 2 may be conservative estimates for some compounds, since the actual concentrations of pesticides reported as less than the detection limit may have ranged up to the detection limit without being observed. For most of the detected compounds, however, substitution of either zero or the detection limit for "less-than" values had little effect on the reported percentages, relative to the differences in the

percentages observed for different pesticides. When both the detection frequency and the agricultural use of a specific pesticide were low, there is considerable uncertainty in the calculated percentage. For low-use pesticides, relatively small fluxes produced by concentrations below the detection limit could represent a significant percentage of the amount applied in the basin. In these cases, the percentages reported in Table 2 may be low estimates.

Several factors contribute uncertainty to the total flux estimates shown in Table 2. The error associated with the discharge measurements is approximately  $\pm 10\%$  [13]. The errors associated with the analytical method, discussed earlier, imply that concentrations of most of the analytes are underestimated. Errors in the concentrations estimated for non-sampling days are as likely to be positive as negative, and may largely cancel out. In addition, samples were collected more frequently during the spring and early summer, when pesticide concentrations were generally highest and most variable. This also helps to minimize errors due to interpolation. Thus, the actual riverine fluxes were probably greater than the flux estimates shown in Table 2, perhaps by as much as a factor of two for some compounds. Despite this uncertainty, valid comparisons can still be made between the fluxes of the pesticides in this study, since the fluxes for the different pesticides range over several orders of magnitude when expressed as a percentage of the amount of the pesticide applied in each drainage basin.

#### *Agricultural-use data*

Estimates of pesticide use in each river basin were obtained from databases compiled by Resources for the Future, Inc., in which herbicide and insecticide use on agricultural crops is tabulated, by county, for the 48 conterminous states [5,6]. The herbicide use estimates are primarily based on a 1989/90 survey of U.S. Department of Agriculture Extension Service weed scientists, and surveys published in the late 1980's by State and Federal agencies, academic institutions, and commodity organizations. Appropriate revisions were made so that, in general, the estimates of herbicide use reflect 1989 and 1990 use amounts. Insecticide use estimates are based on surveys by State and Federal agencies and reflect use in the 1989 to 1991 crop years. Amounts of each pesticide used in counties included in each basin were extracted from the databases and summed. Amounts from counties partially in a basin were multiplied by the appropriate fraction. Amounts from counties whose drainage enters the river downstream from the sampling point were excluded or assigned to the appropriate basin. In compiling the pesticide-use databases, pesticide use totals for each county were obtained by using estimates for the percentage of each crop treated with a particular pesticide and the average application rate on that crop. For both herbicides and insecticides, crop acreage in each county was estimated from the 1987 Census of Agriculture. Any changes in crop acreage, pesticides used on particular crops, or in application rates between the time the use data was collected and the time of pesticide application in 1991 will affect the accuracy of the use totals used in this study. Because of the regional nature of this study, however, it is unlikely that this uncertainty significantly affected the results and conclusions presented.

## RESULTS AND DISCUSSION

### Temporal patterns

Concentrations of nearly all of the detected pesticides followed a temporal pattern consistent with earlier studies on mid-continental rivers [3, 14-16]. This pattern is shown in Figure 2 for atrazine in the White, Ohio, and Mississippi Rivers. For atrazine and most other detected pesticides, concentrations were highest during May and June, immediately after pesticide application, when water discharge is high due to spring rains. During August and September, when most pesticide applications have ceased and river discharge is lower, concentrations dropped to near or below detection limits. Concentrations remained near or below detection limits through the winter, even though discharge increased during this period in several of the rivers.

In general, maximum pesticide concentrations were higher in the smaller rivers. In the White River, for example, which has the smallest drainage basin of the rivers studied, the maximum water concentrations of

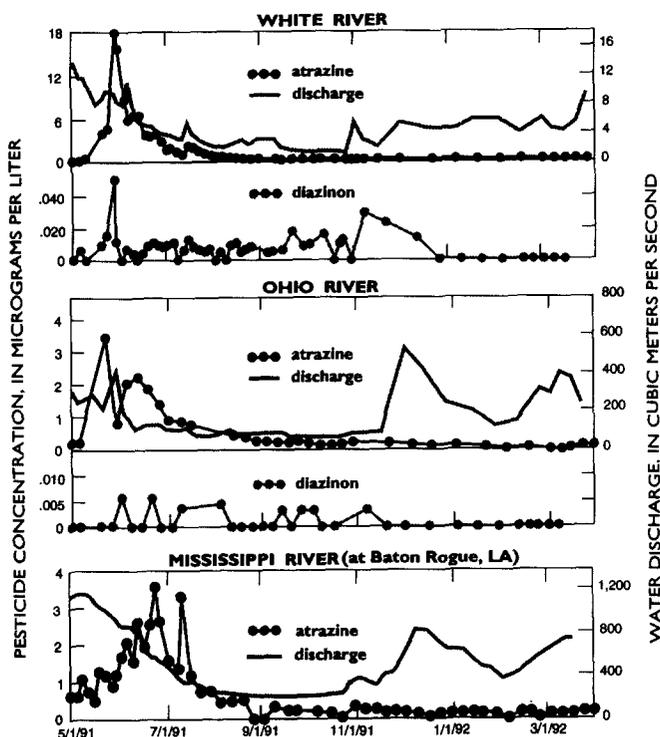


Figure 2. Plots showing relations between pesticide concentration, river discharge, and time for atrazine and diazinon in three river basins. Diazinon concentrations were not measured at Baton Rouge.

atrazine and alachlor were 18 and 5.3  $\mu\text{g/L}$ , respectively. Maximum concentrations of atrazine and alachlor were 3.3 and 0.35  $\mu\text{g/L}$  in the larger Ohio River, and 3.6 and 0.86  $\mu\text{g/L}$  in the Mississippi River at Baton Rouge. (As a comparison, the U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) for concentrations of atrazine and alachlor in drinking water are 3 and 2  $\mu\text{g/L}$ , respectively. The MCL refers to the annual mean concentration in finished drinking water [17]. Annual mean concentrations of the pesticides in this study were all less than established MCLs.) There were also differences in the shapes of the concentration-versus-time profiles between the smaller and larger rivers (Figure 2). In the rivers with smaller drainage basins (Illinois, Minnesota, Platte, and White), pesticide concentrations increased abruptly and the period of elevated concentrations was relatively short, as pesticides were transported in runoff from local spring rains in the relatively "small" area. In the larger rivers (Ohio, Missouri, and Mississippi), elevated pesticide concentrations were more spread out over the summer months, due to the integrating effects of the many tributaries in these larger drainage basins. Maximum concentrations of most pesticides also occur later in the year in the larger rivers (Figure 2). For nearly all detected pesticides, however, more than 90% of the total flux had occurred by mid-July in all of the rivers studied.

Concentrations of the insecticide diazinon were an exception to this pattern in the White, Illinois, and Ohio Rivers (Figure 2). In these rivers, diazinon concentrations remained constant or increased in late summer, probably due to non-agricultural use. The USEPA estimates that non-agricultural use accounts for as much as two-thirds of the total use of diazinon in the United States, occurring primarily in urban areas (R. Torla, USEPA, personal communication). Urban applications of this chemical are more variable and occur over a longer time period than agricultural applications. The anomalously high values for flux of diazinon as a percentage of agricultural use in these three basins (Table 2) also imply that non-agricultural use is significant. These three basins have the highest population densities of the basins studied [18], and agricultural-use data undoubtedly underestimate total diazinon use. Non-agricultural use must also be considered as a possible source of variability in the percentages calculated for simazine. The USEPA estimates that non-agricultural use of simazine accounted for 30 to 40% of total use during this period [5].

#### *Pesticide flux in relation to use*

The total flux of herbicides was much greater than the total flux of insecticides at each sampling point (Table 3). The combined fluxes at the Baton Rouge, Louisiana site show that approximately 550,000 kg of the herbicides measured in this study were discharged to the Gulf of Mexico during the study period. Insecticide concentrations were not measured at the Baton Rouge site, but a approximately 2,500 kg were discharged from the combined Ohio, Missouri, and upper Mississippi River basins during the study period, compared to 520,000 kg of herbicides. Thus, the flux of herbicides was approximately 200 times greater than the flux of insecticides. The much greater flux of herbicides was not simply due to higher agricultural use, since herbicide use in the Mississippi River basin was approximately 35 times greater than insecticide use. Alachlor, atrazine, cyanazine, and metolachlor accounted for more than 90% of the total herbicide flux at all sites. Carbofuran, diazinon, carbaryl, fonofos, and chlorpyrifos accounted for more than 80% of the total flux of insecticides at all sites.

Table 3. Total herbicide and insecticide fluxes in the Mississippi River and major tributaries, May, 1991 through March, 1992.

	Herbicide flux (kg)	Insecticide flux (kg)	Total pesticide flux (kg)	Percent of total pesticide flux *
Minnesota River	15,000	300	15,300	3
Illinois River	90,000	800	91,800	17
White River	12,000	100	12,100	2
Platte River	32,000	300	32,300	6
Ohio River	100,000	600	101,000	18
Missouri River	150,000	1,000	151,000	27
Mississippi River at Clinton, Iowa	39,000	300	39,300	7
Upper Mississippi River**	270,000	1,000	271,000	49
Mississippi River at Thebes, Illinois (includes Missouri R.)	420,000	1,900	422,000	76
Mississippi River downstream of Ohio and Missouri Rivers***	520,000	2,500	523,000	95
Mississippi River at Baton Rouge, Louisiana	550,000	nd	~553,000	--

\* Percent of the estimated total flux (herbicides plus insecticides) in the Mississippi River at Baton Rouge, Louisiana.

\*\* Fluxes in Mississippi River upstream of Missouri River confluence (flux at Thebes minus the flux from the Missouri River).

\*\*\* Calculated as the flux at Thebes plus the flux from the Ohio River.

nd - No data (insecticide concentrations not measured at Baton Rouge).

The fluxes of the different pesticides can not be compared without accounting for differences in the amounts used in each basin. In Table 2, the flux of each pesticide is expressed as a percentage of the amount applied agriculturally in each basin. A number of the targeted pesticides were seldom or never detected, and the percentage of agricultural use represented by riverine flux could not be calculated in some basins. These compounds include the insecticides azinphos methyl, disulfoton, ethoprop, malathion, methyl parathion, parathion, phorate, propargite, and terbufos, and the herbicide linuron. Fluxes of the insecticides carbaryl, and chlorpyrifos, and the herbicides butylate, EPTC, pendimethalin, and trifluralin were below 0.1% of the amount applied in the basins at most sampling sites. Fluxes of the insecticides carbofuran and fonofos ranged from less than 0.1% in some basins to nearly 0.5% in others. Propachlor flux in the Minnesota River was 2% of the amount applied in the basin, but 0.2% or less in all other rivers. Fluxes of the herbicides alachlor and metribuzin were between 0.1 and 0.5% of the amount applied in all basins. The herbicides atrazine, cyanazine, and metolachlor had

consistently higher fluxes, ranging from 0.4 to 2% of the amount applied in most basins, and up to 3.1% for cyanazine in the Illinois River. The percentages for diazinon and simazine were quite variable, and anomalously high in some basins. This is probably due to non-agricultural use of these compounds, which is not accounted for in the use totals shown in Table 2, as discussed earlier.

For most of the pesticides, the flux for the 11-month period ranged from 0 to 2% of the amount applied in each basin. This range of values for flux in these large river basins is in general agreement with earlier studies of these pesticides in runoff water from the edges of agricultural fields, and in surface waters draining small agricultural watersheds [7,19]. In addition, for pesticides with measurable fluxes in all basins (alachlor, atrazine, cyanazine, metolachlor, metribuzin, and simazine), the percent reaching the rivers was relatively constant as basin size increased (Figure 3). If losses of these pesticides from the rivers were significant, lower percentages would be expected in the larger basins, due to the longer average travel time in the water from the source of the pesticide to the sampling point. An important implication of this study is that, at least for these six pesticides, once they are removed from agricultural fields in runoff water, they are transported with relatively little loss into large, integrating river systems and eventually into the ocean.

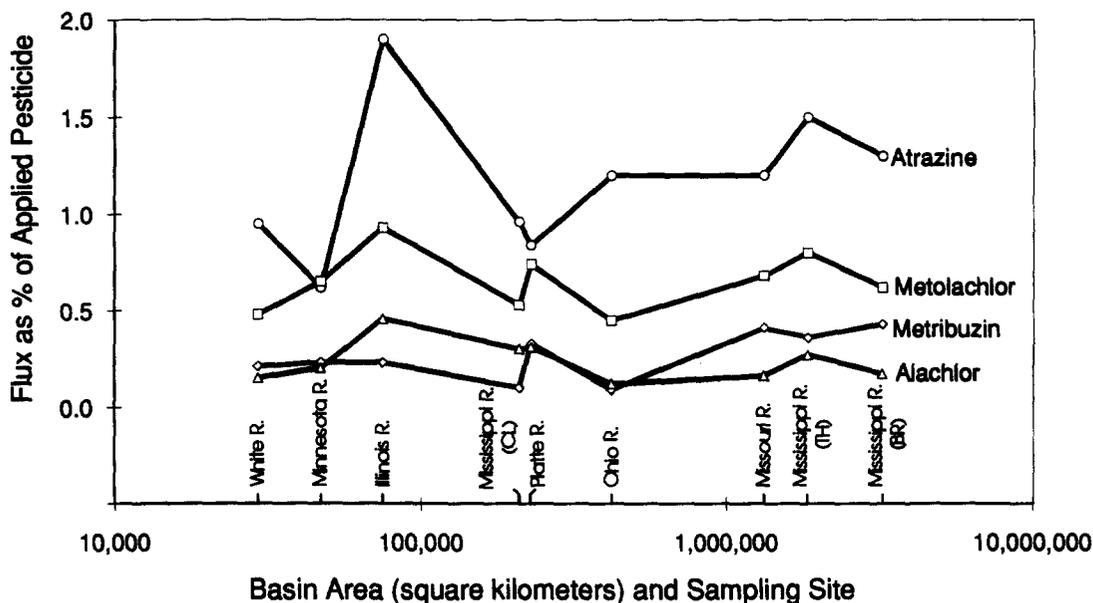


Figure 3. Riverine flux, as a percentage of the amount applied in each drainage basin, for atrazine, metolachlor, metribuzin, and alachlor. Sampling sites are arranged in order of increasing basin area. Mississippi River sites: CL - Clinton, Iowa; TH - Thebes, Illinois; BR - Baton Rouge, Louisiana.

### *Factors affecting pesticide flux*

The runoff-potential ratings discussed earlier (Table 1) can be used to examine the relation between the amounts of specific pesticides reaching these large rivers and the chemical and environmental properties of the pesticides. The runoff potentials were developed as a "first tier" evaluation tool, however, and several limitations should be noted [8]. The GLEAMS simulations used one set of meteorological conditions, and assumed that pesticides were applied to bare, fallow soil. One value for half-life in soil was used for each pesticide, ignoring the effects of temperature and soil moisture. The runoff potentials, then, reflect the influence of the chemical and environmental properties of the pesticides under a specific set of environmental conditions and application techniques. In addition, to determine the actual runoff potential for a particular pesticide/soil combination, the pesticide runoff potential must be combined with runoff potentials derived for specific soil types [8]. Although accounting for different soil types in these large river basins is beyond the scope of this study, the effects of variation in soil types can be reduced by comparing concentrations and fluxes for the different pesticides within each basin. Within a basin, it must be assumed that the pesticides are used on the same assortment of soil types. This is more likely in the smaller basins studied (Minnesota, Platte, Illinois, and White) than in the larger basins, in which there are areas with distinctly different soil types and crops.

In Table 2, the targeted pesticides are grouped by runoff potential for comparison of the observed fluxes. All but four of these pesticides have a higher potential for runoff in the dissolved phase than in the sorbed phase, and are grouped according to their dissolved-phase runoff potentials. Chlorpyrifos, pendimethalin, propargite, and trifluralin have higher potentials for runoff in the sorbed-phase, and they are grouped according to their sorbed-phase runoff potentials in Table 2. The only pesticide in the small runoff-potential group -- malathion -- was detected in only two of the rivers, and fluxes were low. Most of the pesticides for which the riverine flux represented more than 0.2% of the amount applied in the basin were in the large runoff-potential group (atrazine, carbofuran, diazinon, fonofos, metolachlor, metribuzin, and simazine), although some were in the medium potential group (alachlor, cyanazine, methyl parathion, and propachlor). In contrast, seven pesticides in the large runoff-potential group (butylate, disulfoton, linuron, pendimethalin, phorate, propargite, and trifluralin) and four in the medium potential group (EPTC, ethoprop, parathion, and chlorpyrifos) were either not detected or had very low percentages of applied pesticide detected in the rivers.

A distinct difference in the percentage reaching the rivers was evident between herbicides of different chemical classes. As a group, the triazines (atrazine, cyanazine, metribuzin, and simazine) and acetanilides (alachlor, metolachlor, and propachlor) had higher percentages reaching the rivers than the other targeted herbicides (butylate, EPTC, linuron, pendimethalin, and trifluralin) (Figure 4). Percentages for the triazines and acetanilides were nearly all in the 0.1 to 5% range in all basins, while percentages for the other herbicides were all below 0.1%, with many below 0.01%, despite the fact that they have medium to large runoff potentials. The observed difference between these two groups of herbicides may be primarily due to differences in how they are applied. The triazines and acetanilides are normally applied as pre-emergent sprays to the soil surface. Butylate, EPTC, pendimethalin, and trifluralin, on the other hand, are normally incorporated into the soil when applied [20,21]. Incorporation of pesticides decreases the amount available for runoff, but was not considered in the

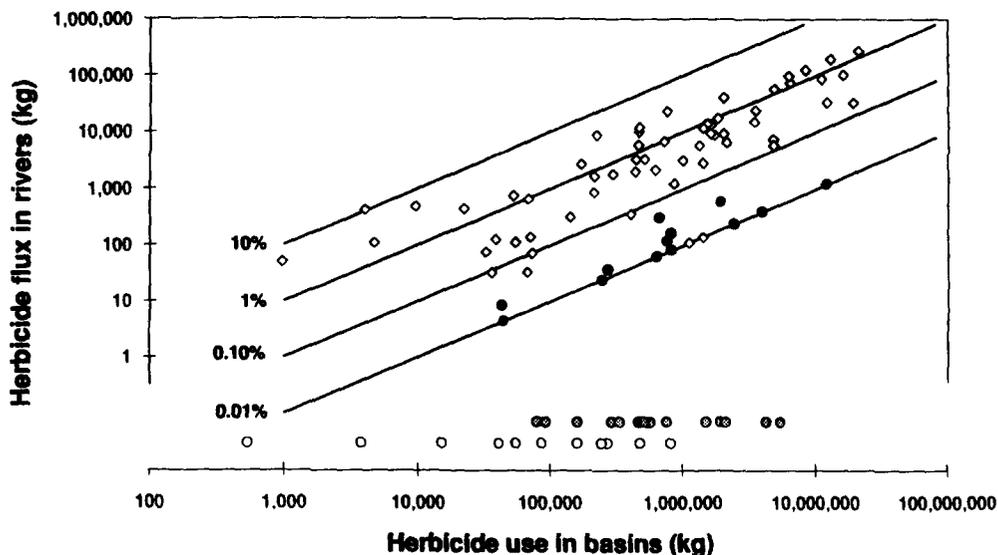


Figure 4. Riverine flux of herbicides versus the amount applied agriculturally in the river basins, for three sites on the Mississippi River and sites on six tributaries in 1991. Lines represent fluxes corresponding to 0.01%, 0.1%, 1%, and 10% of the amount applied in the basin.  $\diamond$  - Triazine and acetanilide herbicides;  $\bullet$  - Other herbicides, with flux of 0.01% or greater;  $\circ$  - Other herbicides, with flux less than 0.01%;  $\circ$  - Other herbicides, with no detections in any samples.

derivation of the runoff potentials. Linuron is not normally incorporated when applied, but use of linuron was low in all basins, and it was rarely detected in the rivers.

The percentages were relatively consistent in all basins for atrazine, metolachlor, metribuzin, and alachlor (Table 2), all of which are normally applied as pre-emergent sprays to the soil surface. This suggests that runoff of these chemicals is strongly influenced by their chemical and environmental properties and/or the application practices used -- factors which were essentially constant in all of the basins studied. Soil characteristics, topography, and weather -- factors which varied considerably among the basins -- appear to have had less influence. Percentages for cyanazine, a triazine herbicide, varied among the different basins, possibly due to its application as a post-emergent or follow-up treatment in some areas [15]. For carbofuran, fonofos, and propachlor, the percentages reaching rivers also varied among the different basins. This implies that other factors can override the influence of chemical and environmental properties in determining runoff losses of these pesticides. Diazinon and simazine percentages were also variable, probably due to lack of accurate use-data for these compounds, as mentioned earlier.

Thus, agreement between the runoff potentials and the relative amounts of various pesticides observed in these rivers is marginal. The ratings should be regarded as "potentials", however, and a number of factors, such as soil type, topography, weather, and agricultural management practices, combined with pesticide properties, determine the actual amount lost in runoff. As mentioned earlier, agricultural management practices, such as soil incorporation, can outweigh the influence of the physical and environmental properties of some pesticides. Similarly, variations in rainfall from year to year have a large effect on the magnitude of pesticide loss from agricultural fields and the resulting flux in rivers [15,19]. Rainfall in 1991 was above average in much of the Mississippi River basin [22], and fluxes of some of these pesticides may be lower in years with lower rainfall. Higher rainfall, or more frequent rainfall, is likely to influence the flux of pesticides with short soil half-lives more than the flux of those with longer soil half-lives, as runoff losses are more likely to occur before losses from other processes. This may explain the relatively high percentages of cyanazine and propachlor in some basins; these herbicides have a medium runoff potential, and soil half-lives of one to two weeks. It is possible that in a longer term study (several years), the fluxes of these two pesticides would be lower, and may be better predicted by runoff-potential ratings based on their chemical and environmental properties.

The regulatory process for pesticide registration and for determination of use restrictions is currently moving toward increased use of mathematical modeling [23]. The results of this study indicate that models must take into account the effects of weather, soil type, topography, and agricultural management practices. Reliance on chemical and environmental properties alone is not adequate to predict the actual or relative amounts of specific pesticides moving from fields to rivers. Limitations in accounting for these variables on a regional scale, and lack of sufficient data on non-agricultural use of pesticides, make extrapolation of model results from the field scale to the regional scale tenuous.

## SUMMARY

For most of the 26 pesticides included in this study, less than 2% of the amount applied agriculturally was observed in large integrating rivers. This is in agreement with many edge-of-field runoff studies, and the order of magnitude is in the range of model predictions for runoff losses. However, when the fluxes were examined in the context of pesticide-runoff potentials based on chemical and environmental properties of the pesticides, the agreement was marginal. The relative percentages of particular pesticides reaching major rivers often were not reflective of their runoff potentials. For a number of the pesticides studied, the percentages detected in the rivers were much lower than for other pesticides with similar runoff potentials. These results imply that for many of these pesticides, factors such as soil characteristics, weather, and perhaps most important, agricultural management practices, are more influential than chemical properties in the movement of pesticides from fields to rivers. Better agreement between observed and predicted runoff losses would be expected when models are applied to small watersheds, where most of these variables can be measured or controlled.

### Acknowledgements

This study was jointly sponsored and conducted by the U.S. Geological Survey's National Water Quality Assessment Program (NAWQA), Toxic Substances Hydrology Program, and National Research Program. The authors thank Naomi Nakagaki (USGS) for providing Geographic Information System (GIS) support. Thanks also to Shawn Schottler (Gray Freshwater Biological Institute, University of Minnesota) for providing herbicide data for the Minnesota River.

<sup>1</sup>Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

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