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Effect of Scale on the Behavior of Atrazine in Surface Waters

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Field runoff is an important transport mechanism by which agricultural pesticides, including atrazine, move into the hydrologic environment. Atrazine is chosen because it is widely used, is transported in runoff relatively easily, is widely observed in surface waters, and has relatively little loss in the stream network. Data on runoff of atrazine from experimental plot and field studies is combined with annual estimates of load in numerous streams and rivers, resulting in a data set with 408 observations that span 14 orders of magnitude in area. The load as a percent of use (LAPU) on an annual basis is the parameter that is compared among the studies. There is no difference in the mean or range of LAPU values for areas from the size of experimental field plots ($\geq$0.000023 ha) and small watersheds ($<$100 000 ha). The relatively invariant LAPU value observed across a large range of watershed areas implies that the characteristics of atrazine itself (application method and chemical properties) are important in determining the extent of runoff. The variable influences on the extent of runoff from individual watershed characteristics and weather events are superimposed on the relatively invariant LAPU value observed across the range of watershed areas. The results from this study establish the direct relevance for agricultural field plot studies to watershed studies across the full range of scale.

Introduction

There is a continuum in the movement of water, solids, and solutes (e.g., atrazine) from a terrestrial environment, such as an agricultural field, through a surface water system and eventually to the marine environment. The surface water system begins in the field in the form of interflow and overland flow (*1*) and concentrates to streamflow. The water moves through some combination of drainage ditches, streams, small rivers, and large integrating rivers, ultimately ending in the marine environment. This continuum can be divided into two parts—soil and stream—determined from the relative abundance of solids and water. In agricultural science, the process that connects these two parts of the continuum is termed “field runoff”.

The occurrence of soil particles and agricultural chemicals in field runoff has been a concern to the agricultural and environmental communities for decades. This is one of the predominant pathways that move agricultural chemicals from their point of use to the broader environment where unintentional adverse effects may occur. Through numerous field and laboratory studies, the important factors that govern the extent of particles and chemicals in runoff have been identified (*1−3*). For the pesticides, these factors include the attributes of the soil, weather, pesticide properties, and agricultural management practices (Table 1). It is the specific spatial and temporal combination of these factors that determines the amounts of water, soil particles, and chemicals transported in runoff.

Once a pesticide reaches a stream, a somewhat different set of governing factors becomes important in determining the extent of its transport through the surface water system to the marine environment. These factors also are summarized in Table 1. For a given pesticide, the chemical property factors are largely the same, but the attributes of the environment (aquatic and weather) that affect a chemical’s behavior and fate are quite different. Pesticides can be lost from the water column through three processes or groups of processes: sorption followed by sedimentation to the bed; volatilization to the atmosphere; and transformation through biological-, chemical-, and/or physical-induced reactions (*4*).

The attributes that control the extent of runoff from fields and loss from the stream are not only a function of the environments (terrestrial and aquatic) but also a function of scale. The soil processes that determine runoff begin at the particle scale and are aggregated to the scale of agricultural fields (*5*). Intermediate is the research plot scale at which most of the controlled runoff studies of pesticides have been conducted. Agricultural fields are aggregated to the scale of small watersheds, and the small watersheds can be aggregated up to the scale of the major regional watersheds. At each point in this continuum of scale, environmental measurements are made to determine the concentrations and loads of pesticides. In literature, the question has often been asked “Is there a relation between results of pesticides runoff studies from small field plots and the observations of pesticides in streams and rivers?” (*2*, *6−8*).

In many ways, atrazine is an excellent surrogate pesticide in terms of its behavior in the surface water system (from field to ocean). In 1996, atrazine was the most commonly used agricultural pesticide in the United States, with a total use of about 33 million kg. It is widely used on corn (84% of its total use) and sorghum (11%). It is also used, to a much lesser extent, on fallow land, millet, pasture, seed crops, sugar cane, and sweet corn ($\leq$2% each) (*9*). Generally, atrazine is applied once a year to the soil surface as a preemergent or postemergent herbicide and has a long lifetime in soil (half-life of about 6 months; *10*). Most transport of pesticides in runoff occurs during the first few rain or irrigation events after application; thus, most of the annual load in streams occurs over a relatively short time period (days to weeks; *11*, *12*). Atrazine was the most frequently detected pesticide in surface waters during the early 1990s (*13*). In the riverine system, atrazine shows minimal loss by any of the three major loss processes—volatilization, sorption followed by sedimentation, and transformation. On the basis of its physical/chemical properties and field observations, atrazine has almost no tendency to volatilize because of its low Henry’s law constant (2.48×10^{-4} Pa m^{-3} mol^{-1}). It has little tendency to sorb to aquatic particles (K_{oc}: $\sim$150 L/kg, $<$1% measured in the particulate phase in the Mississippi River; *14*) and has a relatively long aquatic lifetime because it is not prone to chemical or microbiological transformation processes (aquatic half-lives of 42 day−10 yr, median value 63 day; *12*, *15−19*).

Thus, once atrazine reaches the surface water system, it is transported to the ocean without substantial loss, except

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TABLE 1. Some Important Factors Affecting the Extent That Pesticides Runoff from Agricultural Fields and Are Transported through Surface Waters

	Runoff from agricultural fields (after Leonard, 1990)
weather factors	rainfall timing with respect to application, rainfall intensity, rainfall duration/amount, time to runoff field after inception of rainfall, water temperature
soil factors	soil texture and organic matter content, surface crusting and compaction, water content, slope, degree of aggregation and stability
pesticide property factors	sorption properties (water solubility/polarity/ionic nature), resistance to transformation in soil (via biodegradation, hydrolysis, etc.), formulation
management practice factors	erosion control practices, residue management, vegetative buffer strips, irrigation, application placement and timing
	Transport through Surface Waters
atmospheric factors	air temperature, wind speed
stream factors	
physical	depth, velocity, turbulence, suspended sediment concentration, particle-size distribution
chemical/biological	pH, dissolved organic carbon, particulate organic carbon, color/turbidity, microbial population
pesticide property factors	sorption properties (water solubility/polarity/ionic nature), resistance to transformation in water (via biodegradation, hydrolysis, etc.), volatilization properties (Henry's law constant)

when it undergoes long-term storage in large lakes, reservoirs, and alluvial aquifers. In many ways, its behavior in the surface water system can be thought of as an organic chemical analogue of the chloride ion. That is, atrazine has a geographically diffuse source readily available (at least following application) to enter surface waters where it is conservatively transported without substantial loss. The water residence times in many lakes, reservoirs, and alluvial aquifers are quite long (months to years) as compared to the residence time in most rivers (days to weeks). These longer residence times could allow for a substantial loss of atrazine, even with its long aquatic lifetime (*15*, *18*, *19*).

Concentrations of numerous current-use pesticides, including atrazine, have been measured in rivers draining watersheds across the United States in two U.S. Geological Survey programs [National Stream-Quality Accounting Network (NASQAN) and National Water-Quality Assessment (NAWQA)] over a number of years. These two programs represent a wide range of watershed areas (2700−315 620 000 ha). This paper combines the data on atrazine concentrations from these two programs with data available in the scientific literature from numerous studies on agricultural field plots and watersheds (see Supporting Information) to gain insight into the runoff process and the effect of scale on the behavior and transport of atrazine in streams. The focus of this paper is on atrazine as an example of how a relatively conservative pesticide can behave. A companion paper (*20*) extends the understanding obtained from atrazine to other pesticides that are less conservative and/or less likely to be lost from agricultural fields in runoff.

Methods

Sampling and Analysis. Samples were obtained from the largest rivers in the United States from October 1996 through September 1998 as part of the NASQAN Program. Thirteen of these watersheds from the Mississippi River Basin are included in this analysis (Table 2). The other NASQAN watersheds did not meet the predetermined minimum atrazine use criteria (1 kg/km^2), an empirical value, derived from observations from the NASQAN and NAWQA studies that was used to screen watersheds that had numerous nondetections. A more detailed description of the watersheds as well as the details of the sampling schedule and sampling techniques are described elsewhere (*21*). The pesticide concentration and discharge data are also available (*22*). In general, in these very large watersheds, water samples were collected monthly, except in the spring runoff period when they were collected biweekly.

Samples were also obtained from 43 streams and rivers from October 1992 through September 1994 as part of the NAWQA Program. Twenty-two of these watersheds meet the minimum atrazine use criteria and are included in this analysis (Table 2). The smaller watersheds generally were intensively cropped and indicative of the agriculture of the area. A more detailed description of the watersheds as well as the details of the sampling schedule and sampling techniques are described elsewhere (*23*, *24*). The pesticide concentration and discharge data are also available (*25*). In general, 4−8 samples were collected each month during critical periods of high pesticide use and runoff, and 1−2 samples were collected each month during other periods. Samples were collected more frequently for some sites where short-term fluctuations were a concern (*23*). In addition, the previously unpublished data from the NAWQA Program from October 1996 through September 1998 for the White River and Sugar Creek watersheds (Indiana) provided a direct temporal correspondence with the NASQAN program data.

The NASQAN and NAWQA programs used the same analytical procedure for the pesticides. A 1-L water sample was processed through a combusted 142-mm glass-fiber filter (nominal 0.7-μm pore openings). The filtered water was spiked with terbutylazine as a surrogate. The pesticides were isolated from the water with a 500-mg octadecyl solid-phase extraction column. After the column was dried, the pesticides were eluted with solvent. The solvent volume was reduced with a gentle stream of nitrogen. The extract then was analyzed by gas chromatography/mass spectrometry in the selected-ion monitoring mode. The method detection limit was about 1 ng/L for atrazine. Details of the analytical procedure, including quality assurance results, can be found in Zaugg et al. (*26*).

Literature Data for Atrazine in Runoff and Streams. A search of the scientific literature for studies that quantified atrazine in field runoff or streams was done on two computerized bibliographic databases—Chemical Abstracts and AGRICOLA. Only the data from papers that contained information essential to the calculation of the atrazine mass in runoff (as a percentage of the mass applied) were retained. Furthermore, only data from studies conducted in field environments and lasting more than 1 day were retained. The duration of most field studies was weeks to months. A few, with a shorter duration, employed simulated rain. Because the majority of atrazine runoff almost always occurs in the first major runoff event following application, the results of the short duration studies are similar to the results of the studies of longer duration. The a priori decision to

TABLE 2. Locations and Selected Characteristics of the Watersheds Included in the USGS NASQAN or NAWQA Programs

stream/river	location (state or basin)	watershed area (ha)	area in row crops (%)	HGA[a] (%)	HGB[a] (%)	HGC[a] (%)	HGD[a] (%)	sand[a] (%)	clay[a] (%)	log atrazine-transport-inducing water yield[b]	atrazine LAPU (%)	atrazine use (kg)[c]
Muddy Creek	VA	3 700	20.6	0.2	68.7	24.3	5.5	25.8	36.6	3.88	0.65	478
Zollner Creek	OR	3 900	46.2	2.4	24.6	14.8	58.3	18.5	24.4	4.09	2.94	259
Pete Mitchell Swamp	NC	4 400	40.3	0.7	7.5	1.2	52.4	40.2	26.8	3.99	0.33	239
East Mahantango Creek	PA	11 600	27.5	8.8	38.6	46.5	0.7	30.3	18.7	4.79	0.55	1 385
North Branch Milwaukee R.	WI	13 300	47.1	–[d]	–	–	–	–	–	4.56	0.21	1 448
Mill Creek	PA	14 100	49.3	0.1	84.2	13.5	1.2	18.7	28.8	4.13	0.28	3 866
Crab Creek Lateral	WA	14 600	55.1	1.3	66.7	9.7	22.4	28.7	8.9	3.93	0.24	354
Kessinger Ditch	IN	14 600	87.2	0.0	67.9	32.1	0.0	12.1	23.0	4.06	1.61	7 372
Lime Creek	GA	16 100	30.4	20.4	60.5	6.2	12.9	53.2	28.3	4.65	0.083	1 701
Sugar Creek	IN	24 600	75.8	0.0	25.5	43.1	0.0	25.2	24.7	4.33	0.81	11 787
Duck Creek	WI	24 700	48.9	0.8	10.7	75.3	1.3	27.8	25.6	4.07	2.70	3 566
Aycocks Creek	GA	27 300	23.9	3.1	59.9	12.3	17.8	54.6	26.4	4.72	0.030	2 779
Prairie Creek	NB	36 400	63.3	10.4	66.5	0.1	23.0	15.6	21.0	3.79	0.32	18 556
Tucsawhatchee Creek	GA	42 000	30.2	13.6	65.2	6.2	13.0	53.9	28.0	4.57	0.067	1 037
Shell Creek	NB	76 200	70.4	0.0	99.5	0.0	0.5	4.8	24.4	4.18	0.64	35 279
Maple Creek	NB	95 500	67.9	0.0	92.7	0.3	4.3	4.6	25.7	3.81	1.41	36 929
Pudding River	OR	126 100	22.4	0.6	30.9	51.2	17.4	17.6	30.2	4.69	3.12	4 070
Lonetree Creek	CO	147 300	15.0	10.3	50.2	19.6	20.0	48.9	16.8	2.81	0.13	3 949
Milwaukee R.	WI	180 400	36.6	4.1	53.0	23.4	0.8	37.3	17.2	3.94	0.50	16 389
Tar R.	NC	575 400	16.8	9.6	56.9	18.3	9.3	41.4	30.5	4.30	0.50	7 080
Shenandoah R.	VA	788 000	7.9	0.5	49.2	39.6	4.5	25.2	31.1	3.81	0.92	33 689
White R.	IN	2 929 100	44.3	0.6	31.3	48.9	3.9	21.4	24.8	3.68	1.74	864 710
Wabash R.	OH River	7 571 606	57.7	1.5	30.6	44.0	3.8	21.7	25.2	4.47	4.04	2 639 528
Tennessee R.	OH River	10 445 470	5.1	0.2	60.4	26.1	12.7	25.4	28.6	4.37	3.21	261 085
Ohio R. at Greenup Dam	OH River	16 058 000	6.4	4.0	25.0	56.0	11.8	22.1	24.5	4.11	3.53	442 726
Platte R.	MO River	22 110 830	16.5	23.6	49.4	11.0	15.6	46.6	15.7	3.33	0.87	1 762 371
Mississippi R. at Clinton, IA	MS River	22 170 400	32.3	11.5	49.5	13.1	3.8	41.6	16.7	3.20	0.50	1 480 253
Ohio R. at Cannelton Dam	OH River	25 123 000	7.8	2.6	26.1	55.3	11.4	19.8	26.9	4.30	4.24	1 479 153
Arkansas R. Terry Dam	MS River	40 996 592	17.1	6.0	48.8	22.5	22.8	29.1	26.5	3.67	1.08	1 266 802
Mississippi R. at Grafton, IL	MS River	44 366 700	31.1	6.7	51.8	14.8	5.1	30.6	22.0	3.57	1.32	7 057 136
Ohio R. near Grand Chain, IL	OH River	52 602 900	8.9	1.5	37.6	44.8	10.3	20.3	27.4	4.39	6.80	5 325 651
Missouri R. at Omaha, NB	MO River	83 605 200	5.8	4.7	41.5	20.5	31.8	28.4	26.8	3.26	0.51	1 195 544
Missouri at Hermann, MO	MO River	135 767 800	6.9	7.4	46.5	19.7	25.0	28.4	25.5	3.25	1.04	6 769 425
Mississippi R. at Thebes, IL	MS River	184 718 800	7.7	7.1	47.6	19.0	19.9	28.6	24.7	3.33	0.76	14 416 096
Mississippi + Atchafalaya R.	MS River	315 621 544	6.7	5.4	43.7	25.3	20.6	26.3	26.2	3.76	2.54	22 232 508

[a] From ref 28. [b] Units of m^3 km^{-2} 30-day^{-1}. [c] From ref 9. [d] –, missing data.

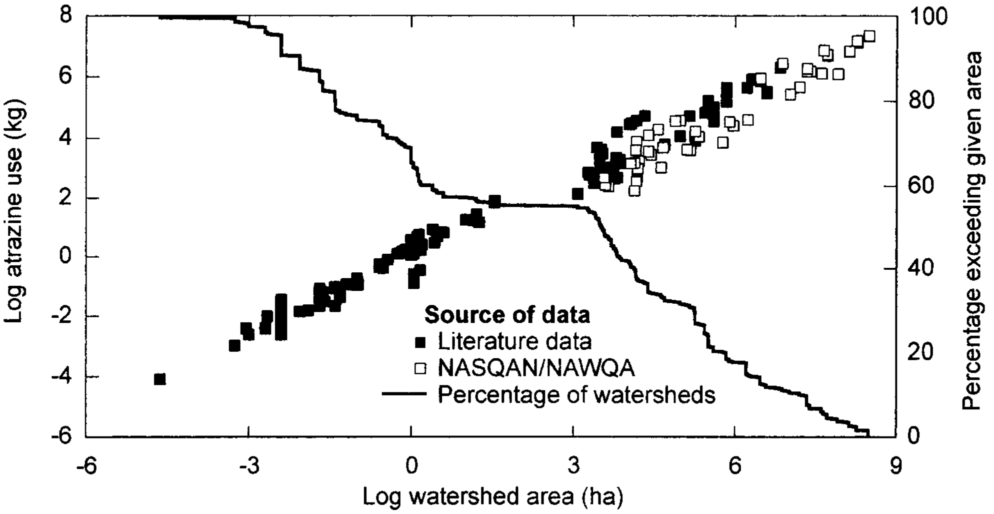

FIGURE 1. Log atrazine use and distribution of watershed areas as a function of log watershed area.

include all studies with duration greater than 1 day was made to limit any bias that would be introduced by deleting certain field studies. The areas of the controlled field studies ranged from 0.000023 to 60 ha. The areas of the watershed studies ranged from 58 to 315 620 000 ha (see Supporting Information). Throughout this paper, both of these groups will be referred to as watersheds. The distribution of watershed areas in the various studies is shown in Figure 1.

Load and Water Yield Calculations. The loads of atrazine from studies published in the literature were used as reported. The annual loads for the data from both the NASQAN and NAWQA programs were calculated as described in Larson et al. (*11*, *23*) by summing up estimated daily loads. The daily loads were calculated by multiplying the stream discharge at the time of sample collection by the daily concentration. Daily discharge values were available, but atrazine concentrations were measured less frequently. Atrazine concentrations for days that were not sampled were estimated by linear interpolation from the concentrations measured on the closest preceding and following days in which pesticides were quantified. If atrazine was not detected, a value of zero was used for the concentration.

All calculated loads of atrazine are estimates since there are never enough data available to calculate a true load. The fewest numbers of samples per year (about 15) were collected in the largest rivers (*22*); therefore, these rivers would possibly yield the largest errors in estimated loads. But because the changes in discharge and atrazine concentration are relatively slow in these large rivers, this frequency of sample collection is believed to be adequate to estimate loads with small enough errors to make them useful for the purpose of this study. As an example, two studies (*27*, *22*) collected samples from the Mississippi River near Baton Rouge, LA, and estimated loads for two overlapping years. The study by Clark et al. (*27*) collected 52 weekly samples per year, whereas the NASQAN study (*22*) collected 15 samples per year. The annual loads calculated in the two studies for 1996 and 1997 differed by only +18 and −3%, respectively.

In an attempt to quantify the parcel of water that caused the greatest amount of atrazine to runoff the fields into the stream, a parameter referred to as the "atrazine-transport-inducing water yield" was calculated. First, the 30-day period that had the maximum atrazine load for each year for each stream was identified. This was commonly in May or June but occurred at other times of the year in some streams. The summed total water discharge during this period (m^3/30-day) was calculated from the daily discharge measurements. Because "baseflow" (water from reservoirs or groundwater) would not be involved in the runoff of atrazine from fields, a summed "baseflow" (m^3/30-day), calculated by multiplying by 30 the 10th percentile of the daily discharge values for the year of interest, was subtracted from the value from the summed 30-day total water discharge value. Finally, this difference was divided by the area of the watershed to give the atrazine-transport-inducing water yield (m^3 km^{-2} 30-day^{-1}).

A total of 408 annual load values were obtained from the NASQAN, NAWQA, and the scientific literature. Twelve of these were reported as "<" and were removed from the statistical analysis described below when the data set was transformed by the base-10 logarithm. A minimum significance level ($\alpha = 0.05$) was used on all of the statistical tests.

Watershed Characteristics and Pesticide Use Estimates. The boundary of each NASQAN and NAWQA watershed area was delineated in a GIS and used to obtain spatial information on the watersheds (Table 2). Soil and topographical characteristics were obtained from the STATSGO database (*28*). The topographical characteristics included slope (unitless fraction). The soil characteristics included the soil hydrologic group, particle size classification, organic matter content, permeability, and available water capacity. STATSGO defines four hydrologic soil groups—HGA, HGB, HGC, and HGD—on the basis of water drainage. HGA includes the soils with the best drainage characteristics; HGD includes the soils with the poorest drainage characteristics. The percent of the watershed in row crop agriculture was obtained from the 1987 agricultural census (*29*).

Atrazine use was based on county-level use estimates (*9*). The estimated use of atrazine in each county in the watershed was summed to yield a total use value. For counties that only had part of their area in the watershed, the atrazine use was prorated using the ratio of row-crop in the watershed to row-crop area in the county. As a screening criteria, the total area of each watershed area was divided by the annual use estimate for atrazine; only the watersheds that had an average use ≥ 1 kg/km^2 were retained in this analysis.

The county-based atrazine use estimates (*9*) were compared to yearly state-based use estimates (*30*) to obtain an idea of the error associated with using a single-year use estimate with multiple-year riverine measurements. As an example, annual state-based use estimates for the states across the center of the Cornbelt have an average 8.3% difference (absolute value) for the years 1991−1996 for atrazine use on corn as compared with the county-based use estimate. These differences (absolute values) vary from state to state (average differences: Nebraska, 4.2%; Iowa,

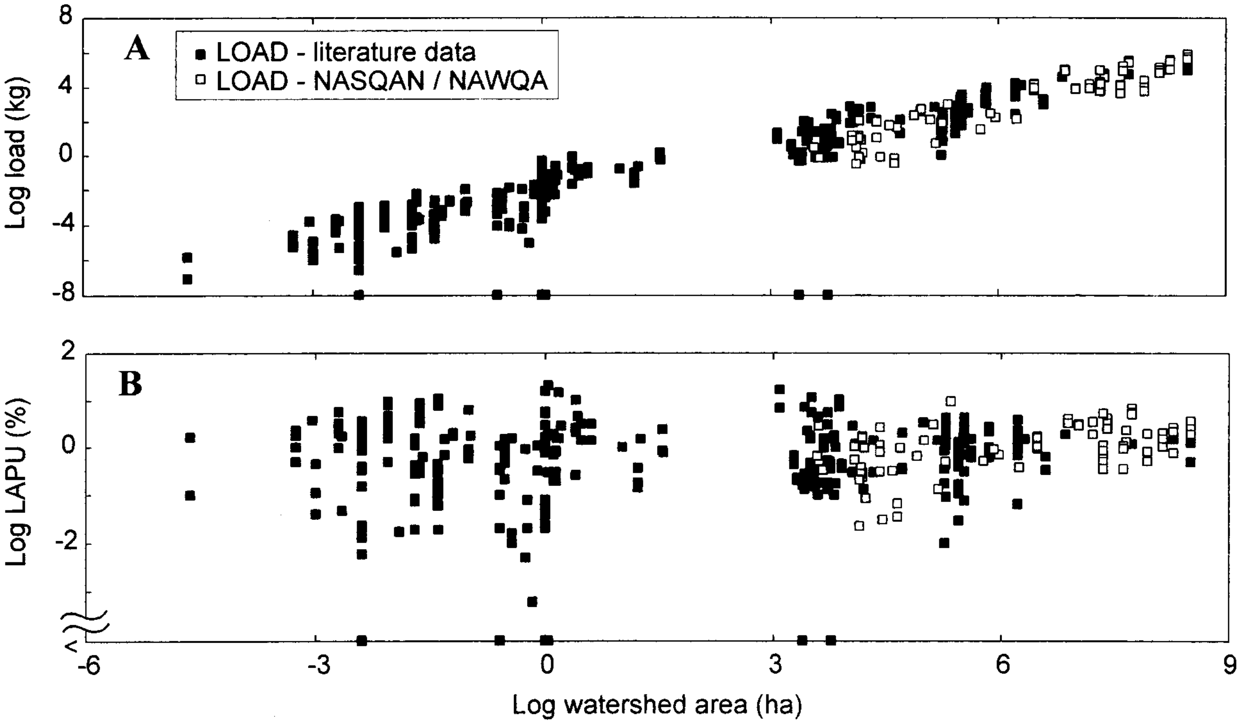

FIGURE 2. (A) Annual atrazine load and (B) load as a percentage of use (LAPU) as a function of log watershed area.

10.0%; Illinois, 10.1%; Indiana, 8.7%; and Ohio, 8.3%) and from year to year (average differences [absolute values]: 1991, 7.3%; 1992, 2.4%; 1993, 8.5%; 1994, 2.9%; 1995, 18.3%; and 1996, 9.8%). Although it would be better to use individual-year county-based (or watershed-based) atrazine use estimates, these data are not available.

Results

Atrazine Use as a Function of Watershed Size. There is a significant relation between total atrazine use and watershed area. In these 408 observations, there is a positive correlation ($r^2 = 0.98$) between log atrazine used and log watershed area (Figure 1). This relation is largely due to the fact that the application rates for atrazine used on corn and sorghum are similar throughout the country (~1–4 kg/ha; *9*) and that corn and/or sorghum are grown in most agricultural areas. To a lesser extent, the relation may be due to the choice of watersheds included in this analysis because only those watersheds that had a normalized use of ≥1 kg/km^2 of atrazine were retained; the choice of watersheds in the NAWQA program was purposely biased toward row-crop agriculture. Nineteen of the 22 smaller watersheds have >20% of their areas dedicated to row-crops (Table 2). The strong relation between atrazine use and watershed area enhances the choice of atrazine as an excellent surrogate for other pesticides because its source function is similar among all of the watersheds.

Load as a Function of Watershed Size. The log of the annual loads (kg/yr) of atrazine is also strongly correlated with the log of watershed area (Figure 2A, $r^2 = 0.938$) over the whole range of scale. This relation is partly due to the strong positive relation between atrazine use and basin size (Figure 1). If the field plots (<1 ha) and the watersheds (>1 ha) are considered independently, the correlation between annual load and area is significant but not as strong (field plots: $r^2 = 0.378$; watersheds: $r^2 = 0.882$).

The log of the annual loads (kg/yr) of atrazine is strongly correlated with log of annual atrazine use ($r^2 = 0.953$). The resultant slope is 1.04 ± 0.02, and the intercept is −2.24 ± 0.86. The slope near unity suggests that, on average, the same relative fraction of atrazine is moved from the terrestrial environment to the surface water system over the whole range of scale, as represented by different atrazine use amounts.

In many watersheds, the period of atrazine application coincides with a period of elevated flows in the surface water systems from rain. This combination produces a period of both relatively high atrazine concentration and high atrazine load in the streams. Of the 73 NASQAN and NAWQA watershed and year combinations included in this study, 47% of the maximum loads (consecutive 30-day period) occurred during June and 22% occurred during May. Only 31% had their maximum load at another time of the year. These 30-day periods of maximum loads comprised a substantial portion of the annual load in many watersheds (mean ± SD: 50 ± 19%; range: 13–90%). No relation was observed between the percentage of the annual load occurring in the 30-day period and watershed area ($r^2 = 0.13$).

Load as a Percent of Use (LAPU) as a Function of Watershed Size. The absolute loads of the atrazine coming from the various watersheds are difficult to compare because the amount of atrazine used in each watershed is different. To help overcome this confounding factor, the annual load of atrazine (kg/yr) from a watershed can be normalized to the annual amount of atrazine used (kg/yr) in that watershed. The annual load can then be expressed as a percentage of use (LAPU, load as a percentage of use). The LAPU value for atrazine is not a function of watershed area, but rather it is relatively invariant across the full range of watershed areas (Figure 2B). A linear regression between log LAPU and log watershed area yields a slope that is significantly different than, but very close to, zero (0.038 ± 0.019; slope ± 95% confidence limit) and an intercept of −0.236.

To further investigate the relation between LAPU and watershed area, the data were divided into three groups based on area: fields and study plots (<100 ha), small watersheds (101–100 000 ha), and large watersheds (>100 001 ha). These three groups had 180, 95, and 133 observations of LAPU, respectively. The cumulative frequency distribution of the LAPU values is shown in Figure 3. All three groups have the same range of LAPU values (<0.001 to 15–20%). The median

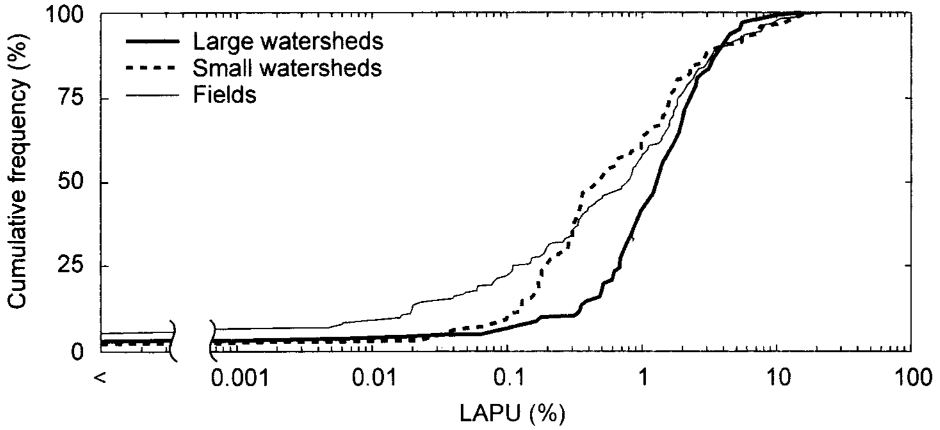

FIGURE 3. Cumulative frequency diagram of atrazine LAPUs for three groups based on watershed area: fields and study plots ($<$100 ha), small watersheds (101–100 000 ha) and large watersheds ($>$100 001 ha).

[and mean ± SD] LAPU values (in %) for the fields, small watersheds, and large watersheds are 0.78 [1.71 ± 2.98], 0.47 [1.67 ± 2.97], and 1.30 [1.82 ± 1.94], respectively. Because the data are not normally distributed, a nonparametric analysis of the LAPU as a function of watershed area was conducted using two tests. A Kruskall–Wallace test showed that while the LAPU values for the fields and small watersheds were not statistically different from each other, the values for large watersheds were different than those of the other two groups. A LOWESS analysis was also performed on the data. The LOWESS line was virtually flat for watershed areas $<$10 000 ha and then slowly curved upward for larger watersheds. Both of these tests imply that the average LAPU values are relatively invariant on the scale of fields and smaller watersheds but that the largest watersheds have higher values. The result of these statistical analyses does not make physical sense. That is, there is no way that the more atrazine will run off of a large watershed than will run off the sum of its smaller watersheds.

Therefore, a number of possible physical explanations for the observation of slightly higher LAPUs in the large watersheds were examined. One explanation is that the LAPUs are overestimated for the large watersheds. This could be a result of an underestimation of use or an overestimation of load. Previously, it was shown that about a 10% error is associated with the county-based atrazine use estimates (*9*) as compared to the yearly state-based estimates (*30*). The error associated with the load calculation is unknown, but the procedure used here probably underestimates the load for two reasons: (a) all concentrations measured as “less than” the detection limit were assumed to be zero, and (b) there is a relatively high probability of missing the day(s) with the peak concentration. Another possible explanation is the systematic underestimation of LAPU in the smaller watersheds. The smaller watersheds generally have short-term (hours to days) changes in discharge and atrazine concentrations (*11–13*, *23*); the annual load can be underestimated if a few important days are not sampled. But this does not apply to most of the controlled field studies. The LAPU values from these field studies are generally more accurate that the watershed studies because the use is known more exactly and the runoff sample collection is generally better. Since the LAPU values of the field studies agree quite well with the small and medium size watersheds, this explanation is unlikely. A third explanation is that there is a bias in the data set for the larger watersheds. All of the larger watersheds ($>$ log 6.3 ha) included in this study are in the Mississippi River Basin, and many of these are in the Ohio River Basin. Also, a disproportionately high number of observations obtained from the literature were made in Ohio (*31*). A Mann–Whitney test shows that the LAPU values from the Ohio River watersheds are significantly higher than LAPU values for the other watersheds ($p < 0.001$). If these data are removed, the LOWESS analysis results in a curve that is essentially flat throughout the entire range of basin areas. This suggests that the environmental conditions (soil type and significant rainfall in both spring and winter) in the Ohio River watershed are likely to yield more atrazine in runoff than is typical of most other environments. The field-scale studies conducted in this area are inconclusive to prove this hypothesis. Four atrazine runoff studies conducted in Ohio under natural rain conditions made 31 LAPU measurements (*32–35*). The mean LAPU value was 0.55%, but the standard deviation was 1.3% (median: 0.11; range: 0.00–5.7%). In Kentucky, one study was conducted, resulting in six reported LAPU values (*36*). The mean LAPU value was 0.55 ± 0.66% (median: 0.25; range: 0.019–1.4%). In nearby Ontario, three studies were conducted, resulting in eight reported LAPU values (*6*, *37*, *38*), and the mean LAPU value was 1.8 ± 2.0% (median: 0.98; range: 0.06–6.3%). Although there are not enough data to conclusively show excess runoff of atrazine, these studies do show that this area can produce very high LAPU values.

On the basis of the available data (Figure 2B), the median small-scale LAPU is calculated based on the extent of atrazine runoff across a variety of environmental conditions and across scale (small scale means agricultural fields and watersheds $<$100 000 ha). This value can be considered a characteristic property of atrazine and be used as a basis to compare the extent of runoff of atrazine to the extent of runoff of other pesticides (*20*). Only small watersheds were used in this calculation to minimize a negative bias in the loads of atrazine due to its in-stream loss. Although in-stream losses generally will be minimal for atrazine, the in-stream losses could be substantial for other pesticides (*20*). The median small-scale LAPU value is equal to 0.66%.

Discussion

Atrazine’s chemical properties, formulation, and application method are generally the same for all watersheds. For a given watershed, the unique combination of the natural terrestrial characteristics (soil type, slope, etc.), the agricultural practices used in the watershed (buffer strips, cultivation methods, etc.) and the weather determine the extent of runoff of atrazine (Table 1). Figure 3 illustrates the variability in atrazine runoff from different agricultural fields determined from 180 observations of LAPU from 40 studies (see Supporting Information). In reality, the influence of the terrestrial watershed characteristics cannot be separated from the influences of weather because both are necessary for runoff to occur, but conceptually they can be considered separately.

TABLE 3. Results of the Spearman's ρ Correlation between Median LAPU and Watershed Characteristics for 34 Watersheds

watershed parameter	R^a	p value
HGC[b] (%)	0.673	0.00010
sand (%)	−0.554	0.00070
HGB[b] (%)	−0.544	0.00090
permeability rate (in./h)	−0.528	0.00130
silt (%)	0.483	0.00380
organic matter (%)	0.473	0.00470
slope	−0.341	0.04810
available water capacity (in.)	0.331	0.05580
HGA[b] (%)	−0.319	0.06580
HGD[b] (%)	−0.126	0.47910
clay (%)	0.077	0.66570

[a] R = Spearman's ρ correlation coefficient. [b] HGA, HGB, HGC, HGD: hydrologic soil groups A−D. See ref *28*.

The watershed characteristics can be thought of as establishing a baseline value for the extent of runoff with the weather determining the degree of year-to-year variability around that baseline value. As a simple example, the baseline value of atrazine runoff (as quantified by the LAPU) will inherently be greater from a watershed that has clayey soils and a slope of 10° than from a watershed with sandy soils and a 1° slope given identical weather. The effect on the LAPU caused by watershed characteristics and the effect caused by weather will be examined individually. Then the effects of watershed characteristics and weather will be combined through the use of the atrazine-transport-inducing water yield parameter.

Influence of Watershed Characteristics on LAPU. The importance of various watershed characteristics (soil, topography, and land use) was independently regressed against the median LAPU values from the watersheds listed in Table 2 using the nonparametric Spearman's ρ test. Median LAPU values were used to help reduce the year-to-year variability caused by the weather. The strongest relation was found between the median LAPU values and the fraction of the watershed with soils that are categorized in the hydrologic soil group C (HGC: $R = 0.673$, $p = 0.0001$; Table 3). The percentages of HGC soils ranged from 0.0 to 75.3% of the soils for the watersheds included in this analysis. This parameter describes soils that have characteristically slow infiltration rates, commonly with a fine to moderately fine texture (*28*). Other soil parameters that had a highly significant, positive relation with median LAPU include silt and organic matter. Because the organic matter is generally higher in fine-grained soils as compared with course-grained soils, all three of the parameters with strong positive relations describe soils that generally would have relatively low infiltration and high runoff. The three soil parameters that have strong inverse relations with the median LAPU include sand, HGB, and permeability rate. All three of these parameters describe soils that generally have relatively high infiltration and lower runoff. Together these results agree well with theoretical and observed relation between soil type and extent of water runoff.

Influence of Weather on LAPU. The influence of weather, particularly the duration, intensity, and timing of rain with respect to application, on the variability of atrazine transport in runoff has been well-documented in field plot studies. This influence has been more difficult to document at the watershed scale, particularly for larger watersheds. One way of examining the influence of weather on the extent of runoff is by comparing the year-to-year variability of the LAPU. The inherent assumption is that all other factors are constant. This is completely valid for the natural watershed characteristics (soil, slope, etc.) and partially valid for agricultural management practices (amount of atrazine, tillage, buffer strips, etc.) because year-to-year changes in practices by specific farmers would influence only relatively small portions of most watersheds.

The multiple-year data sets for the LAPU in various watersheds come from the NASQAN and NAWQA programs and from the literature (*11*, *14*, *27*, *31*, *39*−*43*). The year-to-year variability in LAPU can be substantial. One example is the small, predominately agricultural watershed of Sugar Creek in north-central Indiana. The atrazine LAPU values for six years (1993−1998) were 1.3, 0.80, 0.82, 2.2, 14, and 2.3%. The LAPU of 14% was for a year when an unexpected storm occurred soon after atrazine was applied (Charles Crawford, USGS, written communication). Although this scenario is atypical, it is part of the real continuum of how the weather influences the extent of runoff. The atrazine LAPU values for the whole Mississippi River Basin were 0.49, 0.69, 1.3, 1.4, 1.6, 1.9, 2.0, 2.1, 2.3, 2.5, 2.5, and 3.6% for the 12 observations that were made in 10 years (1987, 1989, 1991−1998; there were concurrent studies by different research groups in two years.) The LAPU value in 1993, a year when much of the north-central and northwestern portions of the basin had substantial flooding, was only 2.3%. There are 21 watersheds with enough data to calculate LAPU values for 3 yr or more. The year-to-year variability in LAPU values as a function of watershed area is shown in Figure 4. There is a distinct trend in decreasing variability (as expressed by the % RSD of the multiple LAPU values) with increasing watershed area ($r^2 = 0.69$). This is due largely to the influence of weather but also incorporates changes in agricultural management practices. The decreasing variability is expected because rainstorms are frequently just local events; therefore, the variability in runoff would be greater for smaller watersheds and would decrease in the larger watersheds because of the integration of water from the various subbasins. This observation is also confirmed in the complete data set of 408 observations of LAPU (Figure 2B). The degree of variability decreased in the large watersheds as compared to the fields and small watersheds, as evidenced by the standard deviations around the mean LAPUs.

Influence of Atrazine-Transport-Inducing Water Yield on LAPU. For atrazine, weather, soil, and most agricultural management practices combine to determine the extent of runoff (Table 1). The process is driven by excess rain or irrigation (specifically the duration, intensity, and timing with respect to application) but can be strongly influenced by soil and management factors. One way to examine all of these combined factors at the critical time for each watershed is to consider the relation between the LAPU and the yield of water from the watershed during the time of greatest atrazine runoff (Figure 5). This atrazine-transport-inducing water yield (volume/area/time period) integrates all the weather and terrestrial attributes of a watershed that determine the extent of both water and atrazine in runoff for the given period of time. The atrazine-transport-inducing water yields in Figure 5 were calculated in a manner that attempts to quantify the water in the stream that actually caused the runoff of the atrazine. The critical period was determined to be the consecutive, 30-day period that had the greatest load of atrazine in the stream. For all of the watersheds in the Mississippi River Basin except the Arkansas River, the critical period occurred in May to early July. For streams in other parts of the country, the critical period occurred at other times of the year, which was determined by the local agricultural practices and rainfall characteristics of the year(s) in which the stream was sampled. Because many of the streams were sampled for more than 1 year, the median LAPU and median atrazine-transport-inducing water yields are used in Figure 5.

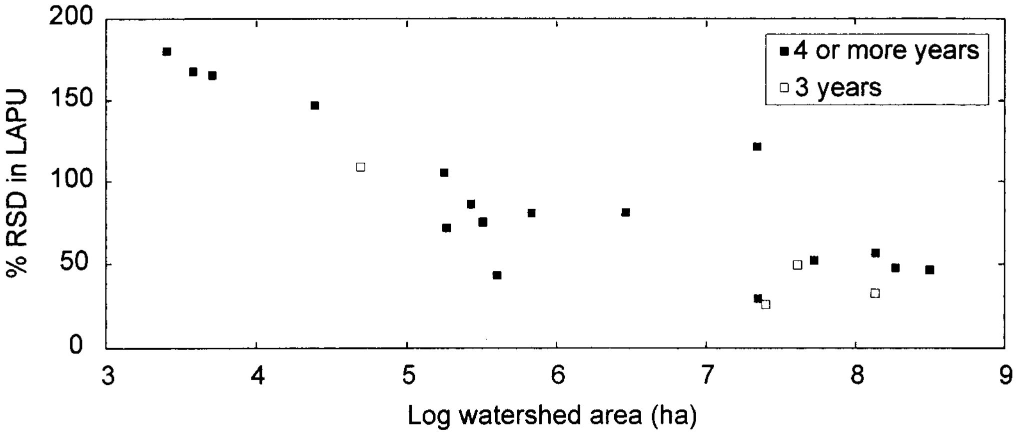

FIGURE 4. Year-to-year variability of the LAPU value in 21 watersheds, as quantified by their percent relative standard deviation (% RSD) for the period of record as a function of log watershed area. The year-to-year variability on the LAPU value is driven predominately by the year-to-year differences in rainfall. The equation of the regression line is % RSD = (−24 × log LAPU) + 232 with $r^2 = 0.69$.

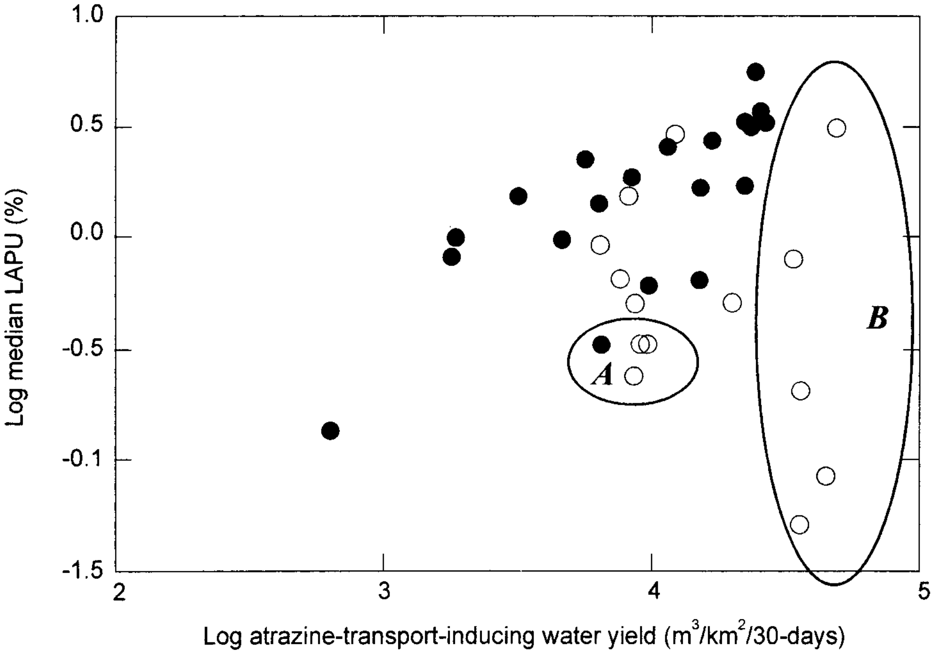

FIGURE 5. Relation between log median LAPU and log median atrazine-transport-inducing water yield for the watersheds in Table 2. The solid symbols are watersheds within the Mississippi River Basin. The two ovals group the sites (A) that have substantial irrigation and (B) that had their maximum 30-day load of atrazine in the winter (November−March).

There is a significant positive correlation between log median LAPU and log median atrazine-transport-inducing water yield for the 20 watersheds within the Mississippi River Basin ($r^2 = 0.546$; Figure 5 solid symbols). (If the data point with the lowest log median atrazine-transport-inducing water yield is deleted, the regression is still significant with a $r^2 = 0.351$.) The relation is improved by including in the regression equation the percentage of the watershed area planted in row-crops ($r^2 = 0.706$). This relation is independent of watershed area. [The residuals of the regression were not related to log watershed area ($r^2 = 0.054$, $p = 0.322$.) It should be noted that there is a significant inverse relation between the percentage of watershed area planted in row-crops and the watershed area ($r^2 = 0.712$).] These results suggest that as more water enters the surface water system after being processed in areas of atrazine use, the greater is the percentage of atrazine (higher LAPU) that is moved into the surface water system. This simple hydrologic parameter, which is based only on watershed area, percentage of watershed planted in row crops, and discharge during the period of maximum atrazine load, accounts for a substantial portion of the variability in atrazine transport in runoff from watersheds in the Mississippi River Basin that range 5 orders of magnitude in area. When all of the data for individual years are included in the regression, the strength of the relation decreases ($r^2 = 0.49$), but it is still significant.

If all of the watersheds in Table 2 are included, the relation between log LAPU and log atrazine-transport-inducing water yield is not significant because in many watersheds the runoff characteristics are very different from the normal pattern of the Mississippi River Basin (open circles in Figure 5). Usually, these watersheds had their critical period (greatest load of atrazine) occurring in months other than May, June, and July (Figure 5, oval B). Many of these watersheds are in the mid-Atlantic, southeastern, and northwestern regions of the United States where winter rains caused substantial runoff of atrazine. Others watersheds are in Wisconsin, which had snowmelt-inducing runoff, and in the more arid portions of the United States, which are heavily irrigated. The watersheds that have substantial irrigation clustered together and away from the rainfall-dominated Mississippi River Basins' regression line (Figure 5, oval A). On the basis of these results, the atrazine-transport-inducing water yield parameter may be a good first approximation of the atrazine LAPU value for watersheds, regardless of area, that exhibit spring rain-driven runoff that occurs soon after application, such as in much of the Mississippi River Basin. It is less useful when runoff is driven by other sources of water (winter rains, snowmelt, and irrigation) that occur before or long after the atrazine application.

Significance of Comparable LAPUs from Field Plots and Watersheds. The observation that there is no difference in the mean or range of LAPU values for areas from the size of experimental field plots (0.000023−100 ha) and smaller watersheds (101−100 000 ha) is quite important. It establishes the relevance of stream measurements to agricultural management by allowing the extrapolation of stream load to field runoff. The observation that the variability in the LAPU values decreases with increasing watershed area suggests that the streams will yield an integrated, area-weighted average of runoff from the agricultural fields in that watershed. Such information will be valuable to scientific and regulatory personnel trying to develop a holistic understanding of atrazine runoff. Second, it establishes the direct relevance of field plot studies to the broader hydrologic environment. It enables the extrapolation of our understanding of the processes involved in runoff from field plots to all scales, particularly through the use of process-based models such as GLEAMS and PRZM (*44*−*46*). A few studies have combined these models with GIS technology and spatial data to extrapolate the field-scale process understanding to larger areas. The runoff potentials of atrazine have been estimated for a county in Minnesota (*44*), the state of Michigan (*45*), and for the entire United States (*46*). The observation of similar LAPUs over 14 orders of magnitude suggests that there is value in these modeling efforts both to help interpret stream measurements or to predict stream loads (and concentrations) using field-scale information.

The observation of a relatively invariant LAPU value for atrazine over 14 orders of magnitude of watershed area suggests that, on average, atrazine behaves in a similar manner in very diverse agricultural environments. Even though there is this relatively invariant LAPU, the influence on the extent of runoff caused by differences in soils, weather, management practices, and other parameters can be observed in the variability of the LAPU values, both in space and in time. The LAPU was zero or very small in studies in which little or no runoff occurred because of the lack of rain. In other studies in which a “catastrophic” rain occurred (e.g., ref *2*), the LAPU value was very high. The relatively invariant LAPU values across these diverse environments implies that the characteristics of atrazine itself (application method and chemical properties) are important in determining the extent of runoff. The variable influences on the extent of runoff caused by individual watershed characteristics and weather events are superimposed on the relatively invariant LAPU value. Capel et al. (*20*) explores this hypothesis further for 38 other pesticides that were analyzed as part of the NASQAN and NAWQA programs.

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Supporting Information Available

Summary of data from the scientific literature and two USGS national programs (NASQAN and NAWQA) on atrazine in field runoff and streams; the data includes the area and location of the watershed, type of soil (fields only), type of precipitation, atrazine use, annual atrazine load, load as a percent of use (LAPU), and year of study (17 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

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