Maximum Loss of Atrazine From a Watershed Occurs During Baseline Flow

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Abstract

With the use of event responsive water samplers (hourly samples), intensive daily Samples (4/day) and continuous monitoring of flow, we calculated the event versus non-event loss of atrazine from the Glenmark Creek watershed over a single year and tested the hypothesis that maximum loss of a herbicide coincides with hydrometeorological events. During the 1997 growing season, 855 kg of atrazine was applied to cornfields with an annual loss of 1.67 kg of atrazine from the watershed to the creek. Seasonally, atrazine concentrations varied greatly and were correlated with fluctuations in precipitation ($r = 0.63$) and discharge ($r = 0.93$). Similar to many watersheds studied, pulsed losses after rain fall events were observed at Glenmark Creek linked by continuous low-level contamination similar to what was observed in the midwest and larger watersheds. Notably maximum concentrations of atrazine in Glenmark Creek occurred in the winter, not in the spring. Despite 9.7 cm of rain in June that encompassed the application period of atrazine at the Glenmark watershed, annual atrazine loss was not strongly associated with runoff events as only 26% of the annual loss of atrazine occurred during hydrometeorological events; that is, 74% of the atrazine loss from the watershed occurred during non-event or baseline conditions. Annually, 54% of the atrazine lost from the Glenmark watershed occurred during the winter and only 27.1 % in the spring. A similar pathway of loss for atrazine and dissolved nutients is suggested as event related atrazine loss from the watershed is similar to other dissolved nutrients and not particulate fractions.

Introduction

Atrazine is used to control the pre- and post-emergence of broadleaf and grass weeds in corn crops. Atrazine's occurrence in the environment reflects a balance between its predominant presence in the dissolved phase and thus mobility, hydrometeorological processes and its use pattern in tributary basins. Two seemingly opposing scenarios exist concerning seasonal fate or loss of atrazine from the watershed. Schottler and Eisenreich (1) hypothesized that the maximum lost of herbicides, such as atrazine, coincides with precipitation events that follow the spring application period - a spring flush or freshet. Thurman et al. (2) present data suggesting ground-water storage and subsequent release during base-flow conditions. Many studies on fate and transport are short term focusing in on the spring and early summer, have weekly or biweekly sampling (3), do not have event responsive sampling schemes, and often consider concentration (μg/L) not actual loss (g/day) from the watershed - a function of discharge. The goal of this study was to assess seasonal variation in atrazine loss from a watershed and to gain some insight into the transport pathways during hydrometeorlogical events and baseline flows. With the use of event responsive water samplers (hourly samples), intensive daily samples (4/day) and continuous monitoring of flow, we calculated the event versus non-event loss of atrazine from a watershed over a single year and tested the hypothesis that maximum loss of a herbicide coincides with hydrometeorological events.

Site of Research

Sodus Bay (1247 hectares) is the largest Lake Ontario embayment in the United States and is drained by six streams with Glenmark Creek accounting for ***68%*** of the annual discharge into the Bay (4). The primary land use of the Sodus Bay watershed (13,423 ha) is agriculture **(54%)** with corn (5.8%) and fruit crops dominating. Developed land represents **18%** of the land usage and the remainder is composed of wetlands, forests and open meadows (R. Williams, Wayne County Soil and Water Conservation District, NY, personal communication). Soil types in the watershed are dominated by Minoa-Phelps-Alton (51%) which is composed of very fine sand, fine sand and silt (Minoa), sand and medium texture gravely outwash (Phelps) and gravel, sand (Alton). The other major soil type in the watershed is Williamson-Elnora-Collamer (39%), made up of silt to very fine sand (Williamson), gravel free sand (Elnora) and nearly gravel free silty soils (Collamer). These soils are moderately drained with temporary high water tables in the subsoil during the spring. Drainage tiles and ditches are used in the watershed to reduce the high subsoil water tables. Between 5 May and 30 June of the study period, atrazine was applied to 772 ha of land planted in corn (application rate varied form 0.44 to 2.2 kg/ha).

Methods

Since 1990, stage height of Glenmark Creek was measured continuously using a bubbler system connected to a Campbell Scientific CR10 datalogger equipped with a Druck pressure transducer. The previously developed rating curve was confirmed using velocity (Gurley meter) and cross-sectional area measurements within the cement channel of a bridge crossing the creek (5). Hourly measurements of stream height from Glenmark Creek's permanent stream-side gauging station were converted to discharge (m^3/s) by a second order polynomial. Event loss of analyte from the watershed or event loading to the bay was calculated by adding up hourly discharge for both the rising and falling limb and multiplying them by their respective chemistries. During non-event periods, hourly discharge was summarized into a daily discharge and multiplied by that period's chemistry value. Watershed areas used in the loading calculations represent the area upstream from the monitoring station.

Daily composited (four samples, one every six hours) water samples were collected with an ISCO automatic refrigerated sampler from 1 April 1997 to 30 April 1998. An event, defined as a rise in the creek level of 2.54 cm in 30 minutes, would trigger hourly sampling collected in an American Sigma refrigerated automated sampler. Discharge and water chemistry from a network of sub-surface drain tiles from a 4.4 hectare "tiled sub-watershed" within the Glenmark watershed planted in corn and treated with atrazine (1 kg/ha) were also measured during the sampling period. Precipitation was measured at the "tiled subwatershed" with a Belfort recording rain gauge. All water samples were placed in prewashed (RBS, Pierce Inc.) rinsed polyethylene containers. Sample water for dissolved nutrient analyses was filtered immediately on collection with a 0.45-µm MCI Magma Nylon *66* membrane filters and held at 4°C until analysis.

Water samples were analyzed for atrazine, total phosphorus **(6,** Method 4500-P-F), nitrate+nitrite **(6,** Method 4500-F), total suspended solids **(6,** Method 2540-D), and volatile suspended solids **(6,** Method 2540-E). Atrazine was analyzed using an immunoassay technique (Ohmicron Rapid Assay) (2, 7, 8). By utilizing a double beam spectrophotometer and a microcell, the method detection limit was reduced to 0.020 ng/L from 0.05 ngL possible with the Ohmicrom RPA- Rapid Analyser.

The Water Chemistry Laboratory at SUNY Brockport is certified through the New

York State Department of Health's Environmental Laboratory Approval Program (ELAP - # 11439). This program includes biannual proficiency audits, annual inspections and good laboratory practices documentation of all samples, reagents and equipment. Quality control samples included laboratory and field blanks and spikes, and field duplicates. Multiple sample control charts were constructed for each parameter analyzed, except total suspended solids.

Results and Discussion

During the 1997 growing season, 855 kg of atrazine was applied to cornfields (772 ha) in the Glenmark Creek watershed (3,065 ha). Based on an annual loss of 1.67 kg of atrazine from the watershed to the creek (Table 1), the percentage annual loss (0.2%) of applied atrazine from the watershed to downstream systems was at the lower end of the range of annual losses reported from several agricultural watersheds (0.35-1.5%)(9). Loss rates during events of approximately **3%** are commonly reported during hydrometeorological events (10), although values as high as 18% of the atrazine applied to fields in late spring or early summer may be transported to surface waters (11). Pantone et al. (12) reported a loss of 15% during a heavy rainstorm within 24 hours of application. At Glenmark Creek, not only were percentage losses of atrazine low annually, but also losses of atrazine during atrazine application were low (0.03%) - a period in which 9.7 cm of rain fell. In fact, 3.8 cm of rain fell within 10 days after 80% of the planted acreage was treated. Even atrazine transport from the subsoil via the "tiled sub-watershed" was low (0.15%). Our low annual application loss ratio is probably related to one of the driest summers (10.4 cm) in years with only one precipitation event in excess of 2.54 cm that occurred in mid-September. As the time interval between application and a runoff event increases, less pesticide will be available for transport due to loss from dissipation processes, such as degradation, volatilization, sorption, and photolysis (13).

If the entire watershed acreage is considered, mass loss of atrazine (0.54 g/ha) from Glenmark Creek is comparable, but in the low range of losses reported from other watersheds planted in corn. For example, atrazine loss from Nebraskan watersheds ranged from 0.48 to 2.65 g/ha. However, if mass loss of atrazine is calculated based on atrazine loss from atrazine treated acreage only, the mass loss of atrazine (2.16 g/ha) from the Glenmark watershed is on the high end of mass losses reported from Nebraskan watersheds. Similarly, atrazine loss from the "tiled sub-watershed" entirely planted in corn within the Glenmark Creek watershed was 1.59 g/ha - a value in the middle of the range observed in Nebraska. Obviously, mass loss is a function of the percent of watershed acreage being treated with atrazine. The difference in atrazine loss within the Glenmark watershed is undoubtedly related to different application rates within the watershed and by differences in tillage practice, soil amendments, soil pH and soil organic matter among the twelve different farms growing corn (14).

With only 5.8% of the watershed planted in corn, it is not surprising that average (0.1 µg/L) and maximum (1.18 µg/L) atrazine concentrations in water draining the Glenmark Creek watershed were in the lower end of the range of those observed in other watersheds where atrazine is applied. Reported concentrations of atrazine in surface waters range from less than 1 µg/l to as much as 2,300 µg/L (10, 15). A median concentration of 3.8 µg/l for 132 samples with a maximum of 108 µg/L was noted by Thurman et al. (2) in midwestern states. In Missouri, atrazine concentrations reached 112 µg/L in Goodwater Creek; a watershed with 23% of the cropped acreage planted with corn or sorghum (16). In the Great Lakes region, Baker (17) observed concentrations of atrazine in eight Ohio and Michigan tributaries to Lake Erie to range from 0.25 to 7.67 µg/L while average concentrations in several Vermont streams were generally lower than midwestern streams ranging from 0.2 to 2.74 µg/L (8). The St. Lawrence River, which drains Lake Ontario and received runoff from Glenmark Creek, also had relatively low atrazine concentrations (10.4 and 3.4 µg/L (18) compared with midwestern watersheds.

Seasonally, atrazine concentrations varied greatly (Fig. 1) and were correlated with fluctuations in precipitation (r = 0.63) and discharge (r= 0.93). Daily composite atrazine concentrations generally increased from April and peaked in late June shortly after atrazine was applied to agricultural fields. After mid-July, very little rainfall occurred in the watershed and concentrations decreased into August and remained low until November when concentration increased through November and remained below –0.2 ug/L . Similar to many watersheds studied (see 1 for a review), pulsed losses after rain fall events were observed at Glenmark Creek linked by continuous low-level contamination similar to what was observed in the midwest (19) and larger watersheds (8). This may be a function of location of the sampling site in the watershed. Larger streams lower in the watershed exhibit more continuous low level contamination (8). Thus a sampling site at the base of the watershed, such as Glenmark Creek, would be expected to have continuous low level concentrations punctuated by pulses during hydrometeorological events.

The fact that atrazine was still being lost from the Glenmark watershed six months after application is consistent with other data. With a half-life in soils of 300 to 500 days (14), atrazine would be potentially available for transport for well over a year after application. Wu (20) estimated that 5 to 13% of the atrazine applied to fields was carried over to the next growing season. At our study in Glenmark Creek, the typical low summer flows (4) (only 5.5% of the total annual discharge during the study period) undoubtedly contributed to the low transport of atrazine during the summer (268 g, 0.01% of the total applied). Others (7, 16) have argued similarly that dry conditions during the growing season led to very low amounts of atrazine transported from the soil. During a dry summer, it follows that atrazine levels in the soils might not decrease as quickly as a wet summer and thus be available for transport either as a continuous low level transport as observed throughout the year in our study with low to moderate rainfall or as a pulse, similar to the spring flush, later in the year with a large precipitation event.

Notably maximum concentrations of atrazine in Glenmark Creek occurred in the winter not in the spring (Fig. 1). The peak concentration in winter contrasted with Schottler and Eisenreich (1) who suggested that maximum concentrations in the Great Lakes region are seasonal and focused during the April-July period. Considering the amount of atrazine lost from the watershed or loading to Sodus Bay rather than concentration, maximum loads occurred in the spring (26.9%) and winter (54.4%)(Table 1). Both the maxima in spring and winter were a function of the high atrazine concentration and of high stream discharge during the periods. A post-application peak load of atrazine attributed to late spring and early summer rainfall has been frequently observed (8, 21, 22, 23).

Fifty four percent of the atrazine lost from the Glenmark watershed occurred during the winter (Table 1). This result contrasted with Schottler and Eisenreich (1) who hypothesized that the maximum lost of herbicides, such as atrazine, coincides with precipitation events that follow the spring application period -a spring flush or freshet. The winter maxima in atrazine concentration and loading were associated with precipitation events and warm air temperature that resulted in a melt of the snow pack. Interestingly, atrazine concentrations in surface standing water (puddles) at the "tiled watershed" were high (1.3 ug/L) during April. Maxima in mass losses of atrazine other than in the spring period have been observed elsewhere and were associated with storm events (1S), snow melt (24) and substantially higher flows in the winter (25).

Thurman et al. (2) suggested that atrazine loss from ground water storage during base-flow conditions after the first flush may represent an important pathway of loss from the watershed. Despite 9.7 cm of rain in June that encompassed the application period of atrazine at the Glenmark watershed, annual atrazine loss was not strongly associated with runoff events as only 26.5% of the annual loss of atrazine occurred during hydrometeorological events; that is, 73.5% of the atrazine loss from the watershed occurred during non-event or baseline conditions (Table 2). **A** similar pathway of loss for atrazine and dissolved nutients was suggested as event related atrazine loss from the watershed was similar to other dissolved substances and dissimilar to particulate fractions. For example, the annual relative loss of particulate fractions during events were high (TP = 60.4%; **TSS** = 68.0%) while other dissolved fractions (e.g., SRP=41.1%; nitrate=27.3%) were low and similar to event losses of atrazine (Table 2). Precipitation events often scour or wash particulate fractions from the land surface, especially those in agriculture **(3).** We did analytically compare dissolved and particulate atrazine fractions and found that there was no significant difference ($P<0.05$, paired t-test) in concentration between the dissolved and particulate fractions during the spring and summer.

In summary, maximum losses of atrazine occurred during the winter months, six months after application and during baseflow conditions, not during hydrometeorological events or during the spring directly after treatment of crops. Although aspects of this conclusion have been observed elsewhere, especially in the Lake Ontario basin, the universality of this result has to be tempered by the fact that a dry summer followed the application of atrazine to the study area.

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Table 1. Annual and seasonal loss of atrazine (event plus non-event) from the Glenmark watershed, April 1997 to April 1998.

	Atrazine (kg)	Percent Loss
Spring	0.45	26.9
Summer	0.13	7.8
Autumn	0.18	10.8
Winter	0.91	54.4
Annual	1.67	–100.0

Table 2. Seasonal event losses of atrazine and selected analytes from the Glenmark Creek watershed. Values are percent loss during events for a given season. In the spring, 6.5% of the atrazine applied annually is lost during events or 93.5% of the spring loss of atrazine occurs during baseline flows. TP = Total Phosphorus, TSS = Total Suspended Solids, SRP = Soluble Reactive Phosphorus.

	Atrazine	TP	TSS	SRP	Nitrate
Spring	6.5	16.9	17.1	7.5	8.2
Summer	15.5	33.3	45.2	9.1	14.5
Autumn	2.6	34.8	48.2	11	8.7
Winter	42.7	77.3	83.8	63	38.8
Annual	26.5	60.4	68	41.1	27.3

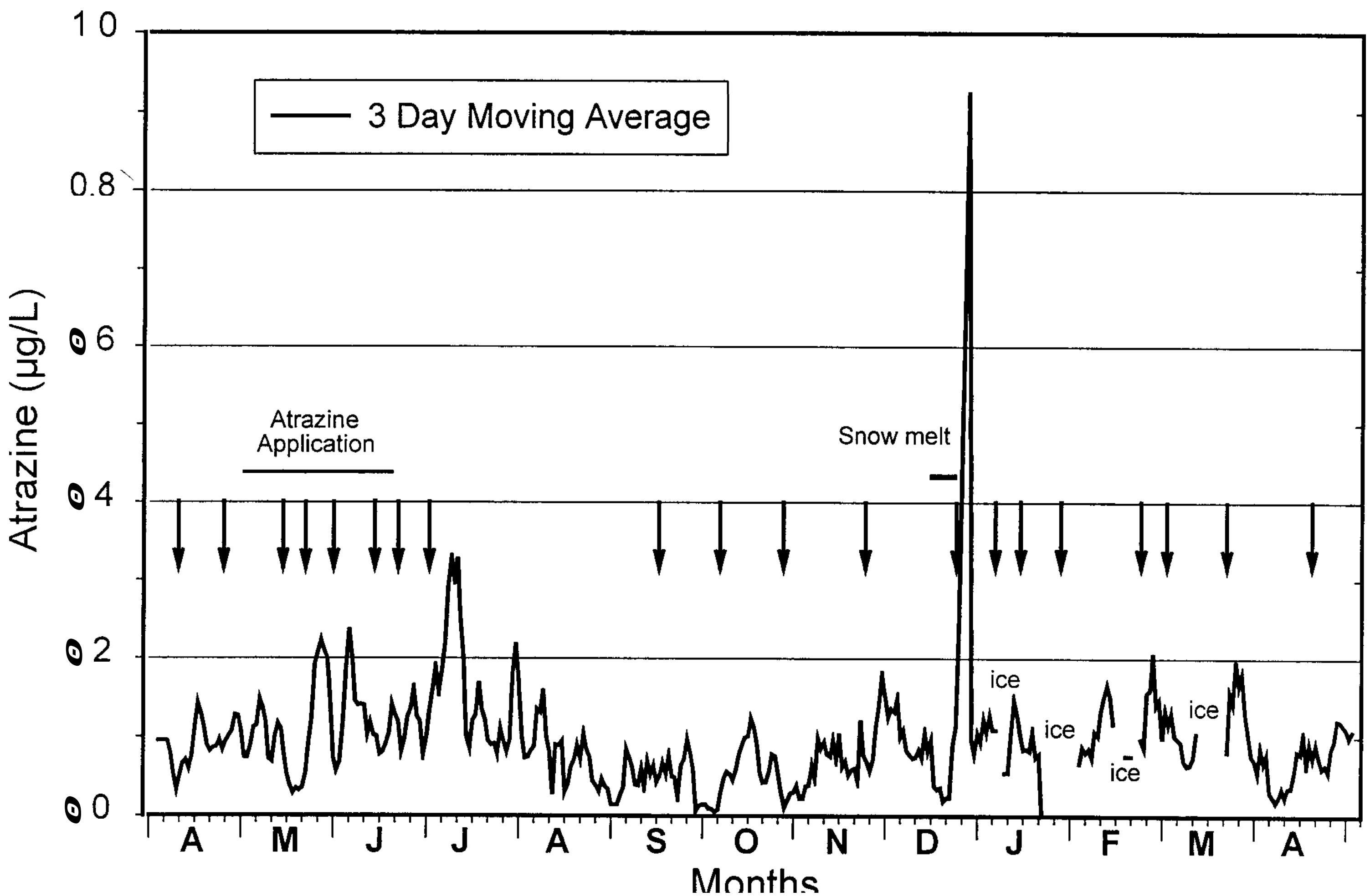

Figure 1. Seasonal atrazine concentrations in Glenmark Creek, Wayne County, New York. Values are the three day moving average. Vertical lines represent precipitation events in excess of 1.27 cm.