Predicting Atrazine Levels in Water Utility Intake Water for MCL Compliance

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To protect human health, atrazine concentrations in finished municipal drinking water must not exceed a maximum contaminant level (MCL) of 3 μg/L, as determined by a specific monitoring regime mandated by the United States Environmental Protection Agency. Atrazine levels were monitored along tile-fed drainage ditches draining to a major drinking water source and used to predict MCL exceedance frequencies of intake and finished drinking water. Water samples were collected daily at eight monitoring sites located at the outlets of subbasins draining 298–19 341 ha (736–47 794 ac). Flow-weighted average (FWA) atrazine concentrations ranged from 0.9 to 9.8 μg/L, and were above 3 μg/L for the majority of sites, including the largest site, which represents water quality at the intake of the local municipal water treatment plant. However, a relatively low percentage of samples near the water utility intake exceeding 3 μg/L atrazine (10.4%) made this problem difficult to detect. In order to have a 95% probability of detecting any intake sample exceeding 3 μg/L atrazine in a drainage system exceeding 3 μg/L atrazine on a FWA basis, sampling frequency would need to be every 7 days or more often during the second quarter when the potentials for field atrazine losses and temporal variability of atrazine concentrations are highest.

Introduction

The St. Joseph River watershed is a largely agricultural watershed that provides the drinking water supply for the City of Fort Wayne, Indiana and its more than 200 000 residents. The herbicide atrazine [2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine] (trade names: Aatrex, Bicep II Magneum (with metolachlor), Bullet (with alachlor), Lariat (with alachlor), Dicambazine (with dicamba), Simazat (with simazine) and others) is used in the study area, where corn (*Zea mays*) and soybean (*Glycine max*) in rotation is common. Most of the corn in the region receives some level of preemergent atrazine application. Fort Wayne tap water has a history of contamination by atrazine (*1*), and requires extensive treatment in order to meet the safe drinking water maximum contaminant level (MCL) for atrazine set forth by the U.S. Environmental Protection Agency (USEPA). Since atrazine has been linked to several human health effects, including cardiovascular, kidney, and endocrine problems (*2*), the MCL for atrazine was set at 3 μg/L in 1991 and has not been changed since.

Previous studies have found atrazine to be frequently detected in surface waters in regions where it is used (*3–6*), with levels sometimes significantly higher than 3 μg/L (*7–10*). Atrazine concentrations in surface water have been observed to be a highly seasonal phenomenon (*11–13*), with greatest losses occurring during the first runoff events following application (*5, 14, 15*). However, atrazine has been shown to persist on a year round basis in river systems (*16*). According to monitoring requirements under the 1986 amendment to the Safe Drinking Water Act (SDWA) that went into effect in 1993, finished municipal drinking water must be sampled quarterly for atrazine, and MCL compliance is based upon a running annual average of these samples. If a running annual average is above MCL, a more intensive sampling requirement may be imposed and the USEPA can require that an alternate water source or additional treatment measures be employed. Municipalities such as the City of Fort Wayne often voluntarily sample intake water on a daily or weekly basis to ensure proper treatment methods are used for adequate removal of atrazine from finished drinking water, but this is not required.

In accordance with the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), atrazine and other pesticides must undergo an extensive environmental and human health safety review and reregistration process every six years. As part of one such review decision agreement, the Monsanto Company agreed to conduct surface drinking water monitoring for atrazine and acetochlor at several municipal drinking water treatment plants from 1995–2001. Based largely on biweekly sampling, intake water atrazine levels exceeded the MCL of 3 μg/L in 13.8% of samples, and atrazine levels in finished drinking water exceeded the MCL about 40% as often (or in 5.5% of samples) (*17*). This study included data from water utilities employing a variety of water treatment methods, and individual water utility atrazine removal efficiency varied greatly. These and other data, usually based upon weekly, biweekly or quarterly sampling are used by the USEPA as a basis for decision in the atrazine reregistration process. The USEPA issued a positive Interim Reregistration Eligibility Decision (IRED) for atrazine in 2003, making it possible for individual products containing atrazine to be reregistered in 2006.

The primary objectives of this study were to evaluate levels of atrazine in a set of surface drainage ditches and one natural stream contributing to a major drinking water source, and to predict whether quarterly sampling of finished drinking water can be expected to indicate one or more daily samples having atrazine concentrations >3 μg/L, where one or more are likely to exist.

Materials and Methods

Site Description. The study site was located in northeastern Indiana within the Cedar Creek sub-basin of the St. Joseph River watershed. Cedar Creek is the largest tributary of the St. Joseph River, and represents about 25% of the St. Joseph River drainage area. Predominant soils are Blount silt loams (fine, illitic, mesic, Aeric Epiaqualfs), Pewamo silty clays (fine, mixed, active, mesic Typic Argiaquolls) and Glynwood loams (fine, illitic, mesic Aquic Hapludalfs). Approximately 80% of the land area within the studied basins is agricultural, with the majority cropped to corn and soybean in annual rotation (Table 1). The area receives an average of 93 cm (36.6 in) of precipitation annually, and the average temperature is 10 °C (50 °F). Most of this land would be too wet to farm without the use of artificial drainage systems. Nearly all fields in the

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TABLE 1. Experimental Watershed Characteristics

site	area (ha)	predominant soil types	land management
XXL	19341	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam, Morley silty clay loam	58% agriculture
			17% grass/pasture 14% forest
AXL	4303	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Rensselaer loam, Sebewa sandy loam	78% agriculture
			14% grass/pasture 6% forest
ALG	1934	Blount silt loam, Pewamo silty clay, Glynwood loam, Rawson sandy loam, Morley silty clay loam	77% agriculture
			16% grass/pasture 6% forest
BLG	1417	Blount silt loam, Pewamo silty clay, Glynwood loam, Sebewa sandy loam, Rensselaer loam	83% agriculture
			12% grass/pasture 3% forest
CLG	1380	Blount silt loam, Pewamo silty clay, Glynwood loam, Morley silty clay loam	73% agriculture
			17% grass/pasture 5% forest
AME	298	Rawson sandy loam, Pewamo silty clay, Morley silty clay loam, Blount silt loam	79% agriculture
			15% grass/pasture 4% forest
BME	311	Blount silt loam, Pewamo silty clay, Glynwood loam	85% agriculture 8% grass/pasture 6% forest
CME	373	Glynwood loam, Blount silt loam, Pewamo silty clay	83% agriculture 10% grass/pasture 4% forest

study area are drained by a network of subsurface drainage tile (usually located about 1 m (3.3 ft) deep), into drainage ditches. Field drainage is then conveyed from the ditches into natural waterways.

Seven sampling locations were selected along three tile-fed ditches draining watersheds A, B, and C for daily water quality monitoring (Figure 1). These nominally represented three "replications" each of medium (ME)-sized (298−373 ha (736−921 ac)) and large (LG)-sized (1380−1934 ha (3411−4780 ac)) watersheds, and one extra-large (XL)-sized (4303 ha (10 634 ac)) watershed. Additionally, one extra-extra large (XXL)-sized (19 341 ha (47 794 ac)) watershed was monitored along the main channel of Cedar Creek, closest to the water utility intake. The XXL atrazine data was highly correlated (93%) with the atrazine data at the actual water utility intake, for the duration that both were available. However, actual water quality intake data were only available for April, May, and June.

Water Sampling and Analysis. The seven ditches were sampled daily during the 2004−2007 cropping seasons (April−November), while the XXL Cedar Creek site was sampled during the 2006 and 2007 crop growing seasons. Because corn is usually rotated annually with soybean in the study region, and corn and soybean require different weed management regimes, we use even numbers of consecutive years in order to represent the majority of fields in corn and soybean, and related weed management, equally. Each 300 mL (10.1 fl oz) daily sample represented a composite of six 50 mL (1.69 fl oz) samples taken every four hours using ISCO 6712 autosamplers (ISCO, Inc., Lincoln, NE). All samples were immediately refrigerated until processing. Hydrologic and climatologic data were collected on 10 min intervals. Discharge was monitored using ISCO 2150 area velocity flow modules (ISCO, Inc., Lincoln, NE). Sharp rises in ditch discharge during or after rainfall were recorded as runoff events.

All samples were filtered (0.45 μm) into glass vials and frozen immediately until analysis could be performed. Atrazine was preconcentrated by solid-phase microextraction according to a modified EPA method 525.2 (*18*) described by Rocha et al., 2007 (*19*), and quantified by gas chromatography with mass spectrometry (GC MS). The detection limit was determined at the signal-to-noise ratio of 3:1 as = 0.25 μg/L. Analytical uncertainty was calculated by performing a Student's *t* test using the standard deviation (σ) of seven randomly selected spike samples distributed over a four-season period. Uncertainty was calculated as the product of σ and the t-value ($\alpha = 0.05$) according to a method performance test described in EPA method 525.2 (*18*) and was found to be $\pm$0.84 μg/L.

Calculations. Seasonal flow-weighted average (FWA) concentrations were determined at each site by summing the following by cropping season: herbicide concentration of each sample (μg/L) multiplied by the discharge during the time span represented by the sample (L), and then dividing by the total seasonal discharge. For the purposes of these calculations, concentrations determined to be below detection limit were assumed to be zero. Exceedance frequencies ($P_{AC>3}$)(%) were calculated as the sum of all time intervals represented by samples having atrazine concentration >3 μg/L divided by the total time in the monitoring period. All statistical analyses were performed using SAS 9.1 (SAS Institute Inc., Cary, N.C).

Results and Discussion

Atrazine Levels. Flow-weighted average atrazine concentrations, maximum observed concentrations and $P_{AC>3}$ values are given in Table 2. The daily FWA atrazine levels ranged between sites from 0.9 to 9.8 μg/L for the four cropping seasons, and were at or above 3 μg/L at all monitoring sites except for ALG and AME.

The $P_{AC>3}$ values ranged from 5.1 to 19.4%, and averaged

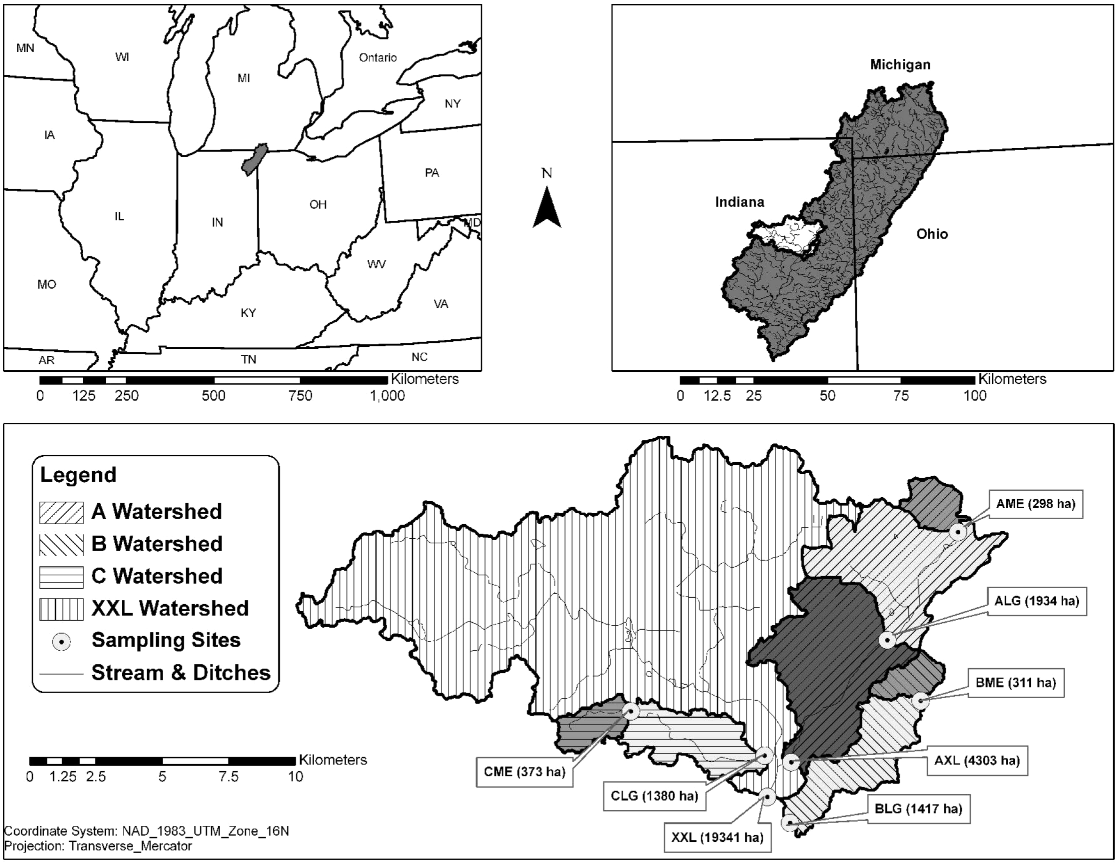

FIGURE 1. Experimental watersheds and sampling site locations.

TABLE 2. Atrazine FWA and Maximum Observed Concentrations, and Corresponding MCL Exceedance Frequencies

site	FWA concentration (μg/L)	maximum observed concentration (μg/L)	3 μg/L exceedance frequency (%)
XXL	3.5	30.5[a]	10.4
AXL	3.4	49.3[a]	12.4
ALG	2.8	59.1	11.2
BLG	7.3	79.7[a]	17.2
CLG	3.0	48.7	8.9
AME	0.9	26.7[a]	5.1
BME	9.8	85.7[a]	19.4
CME	6.3	41.0	15.5

[a] Maximum observed concentration occurred on the same day as a runoff-producing rainfall even during May or June.

TABLE 3. Atrazine 3 μg/L Exceedance Frequency ($P_{AC\,>\,3}$) by Quarter

site	atrazine 3 μg/L exceedance frequency (%) during quarter: 1	2	3	4
XXL	0	21.1	0	0
AXL	0	25.1	1.5	2.8
ALG	0	24.5	<0.1	0
BLG	0	30.7	7.9	2.7
CLG	0	15.2	5.7	0
AME	0	11.3	0.2	0
BME	0	32.2	8.9	0
CME	0	25.6	2.6	0

12.5% (Table 2). This is in agreement with the Monsanto study which found that intake water at many water utilities across the country exceeds the atrazine MCL in an average 13.8% of samples. Flow-weighted average atrazine concentrations were observed at or above 3 μg/L for watersheds exceeding 3 μg/L in relatively few samples (Table 2). Data provided by the water utility serving the City of Fort Wayne indicate a 93% agreement in daily MCL exceedance frequency at the water utility intake and at our XXL site. Atrazine losses from the upland portions of the watershed impacted intake water atrazine levels such that atrazine removal by the water utility was necessary.

Factors Potentially Affecting Observed Atrazine MCL Exceedance Frequency. *Sampling Timing.* If we break down exceedance frequency by quarter, we see that the highest exceedance frequencies occur during quarter 2 (Table 3). Atrazine levels in both intake and finished drinking water were found to be highest on average in another study of 47 water utilities across the U.S. (*13*). To determine what sampling frequency would be required to detect any one sample >3 μg/L in our largest watershed having FWA atrazine concentration >3 μg/L (XXL), we focus on the second quarter. The quarter 2 $P_{AC\,>\,3}$ value 21.1%. This value was validated by daily samples taken at the intake of the downstream water treatment plant serving the City of Fort Wayne, which were above 3 μg/L atrazine MCL 22.0% of the time during the second quarter, as determined by GC MS. If we want a 95% probability of detecting the 3 μg/L exceedance at site XXL, predictive of the 3 μg/L exceedance in water utility intake water, we use eq 1 to determine the number of samples required. By dividing the number of days in a quarter (91) by the number of samples required (*n*), we find that a sampling frequency of 7.2 (≈7) days is required.

$$n = \frac{\ln(P_0)}{\ln(P_{s<3})} = 12.64 \qquad (1)$$

Where P_0 is the accepted probability of not detecting a sample

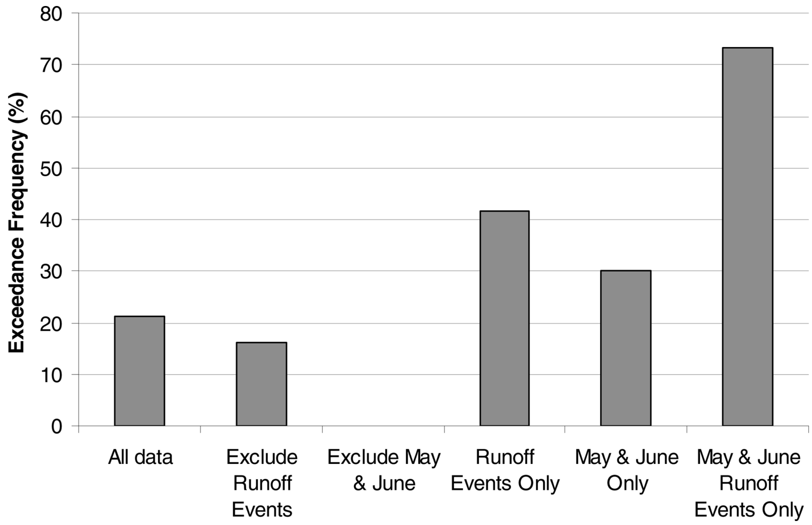

FIGURE 2. Atrazine 3 μg/L exceedance frequencies ($P_{AC > 3}$) at XXL during quarter 2 relative to the months of May and June and to runoff events.

exceeding 3 μg/L (5%) and $P_{s < 3}$ is the probability of any one sample being below 3 μg/L (78.9%).

Further, we expect that timing of sampling may impact observed $P_{AC > 3}$, especially with regard to atrazine field application and runoff events. In the study area, atrazine is typically applied to corn in May, and greatest atrazine losses typically occur during the spring precipitation and runoff events that follow. The average $P_{AC > 3}$ during May and June runoff events at site XXL was 73.4% (Figure 2). The average $P_{AC > 3}$ at XXL during the months of May and June was 30.1% (Figure 2). This was nearly 3 times greater than overall cropping season $P_{AC > 3}$ of 10.4%.

During the critical second quarter, it is possible to exclude the months of May and June by taking the required sample during April, when $P_{AC > 3}$ was zero. It is also possible to exclude sampling during a runoff event, which effectively reduced observed second quarter $P_{AC > 3}$ from 21.1 to 16.2% at our largest monitored watershed (Figure 2). Alternatively, drawing the second quarter sample during a May or June runoff event would have resulted in a $P_{AC > 3}$ of 73.4%. Assuming that finished drinking water exceeds atrazine MCL at a national average of 40% as frequently as intake water exceeds MCL (*17*), we can estimate that MCL exceedance frequency in finished drinking water during quarter 2 would be approximately 8%, but the probability of observing a single quarter two finished water sample above atrazine MCL would be close to zero if that sample was taken in April, approximately 6% if that sample was taken any day during quarter 2 when a runoff event did not occur, and approximately 29% if that sample was taken during a runoff event during May or June. Noting the occurrence of very high atrazine concentrations, especially during May and June runoff events (Table 2), and depending on a utility's specific atrazine removal efficiency, this suggests that specific conditions present at the time of the quarter 2 sampling may influence the annual average sufficiently to represent the difference between MCL compliance and noncompliance.

In a previous study by Battaglin et al. (2005) (*14*), streams in Midwestern regions where corn and soybean rotation is common were monitored for atrazine as well as other chemicals. Streams were sampled at only three times during the year, designed to correlate with herbicide applications and directly follow a runoff event: preemergence (May or June runoff event, when at least 50% of corn was planted), postemergence (June or July runoff event, when soybean emergence was close to 100%), and harvest (September, October, or November runoff event, during or after harvest). With this sampling regime, researchers found that atrazine exceeded 3 μg/L in 57% of preemergence samples and 33% of postemergence samples. Atrazine was not observed above 3 μg/L during the harvest sampling period. Clearly, timing of sampling with respect to atrazine application and with respect to runoff events is a major factor impacting observed atrazine FWA concentration and $P_{AC > 3}$ in these watersheds. We expect that these trends are related to finished drinking water trends. In the Monsanto Company report, finished drinking water from dozens of treatment plants using conventional treatment methods with or without activated carbon exceeded atrazine MCL an average of 40% as often as intake water exceeded atrazine MCL (*17*), although we expect that different filtration methods used by individual utilities will result in different MCL exceedance frequencies in finished drinking water.

TABLE 4. Atrazine Concentrations Measured at XXL on a Quarterly Basis for the 2nd Week in the Second Month of Each Quarter during 2006.

day	8th	9th	10th	11th	12th	13th	14th
month	atrazine concentration (μg/L)						
February[a]							
May	BDL[a]	BDL[a]	2.4	12.7	16.7	10.9	20.6
August	1.6	1.6	0.6	0.8	1.1	0.5	BDL[a]
November[a]	BDL[a]	BDL[a]	BDL[a]	0.6	0.5	BDL[a]	BDL[a]
Annual Average	0.4	0.4	0.8	3.5	4.6	2.9	5.2

[a] The unmeasured February and BDL (below detection limit) values are assumed to be zero.

Frequency of Sampling. Since observed atrazine concentrations depend heavily on whether that sample was taken during or directly after a runoff event, especially during the period immediately following field atrazine applications, and greater sampling frequency increases the probability of runoff event inclusion, it is expected that sampling frequency could significantly impact observed MCL exceedance frequency. Results of the quarterly sampling required for atrazine MCL compliance determination may vary greatly depending on the specific days sampled. Atrazine concentrations in daily samples obtained from XXL during each quarter of 2006 (February (assumed to be zero) May, August, and November) are given in Table 4. Results were calculated using samples obtained on the 8th through 14th day of the month. If every quarterly sample were taken on the same day of the second week of the second month in the quarter, then there are seven different possible annual average atrazine concentrations for the 2007 calendar year. Of these seven possibilities, three would result in average atrazine concentrations >3 μg/L (days 11, 12, and 14), and four would not (days 8, 9, 10, and 13). Since $P_{AC>3}$ between XXL and the local water utility intake is 93%, and a U.S. average finished drinking water has been found to exceed MCL 40% as often as intake water, our data indicate that the current MCL compliance sampling regime is heavily influenced by sampling date selection, especially during quarter 2. In order to have a 95% probability of detecting the 3 μg/L exceedance at our XXL site (and at the water utility intake), it is necessary to sample more frequently during quarter 2. One efficient way of achieving this is to sample weekly during quarter 2, and base the quarter 2 atrazine concentration value on the numeric average of weekly derived atrazine concentrations.

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