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2004 National Atrazine Occurrence Monitoring Program Using the Abraxis ELISA Method

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The goal of this project was to gain a better understanding of atrazine occurrence in the United States by surveying drinking water utilities' sources and finished water for atrazine on a weekly basis for seven months. Atrazine is a contaminant of interest because the United States Environmental Protection Agency (USEPA) has found short-term atrazine exposure above the drinking water maximum contaminant level (MCL) to potentially cause heart, lung, and kidney congestion, low blood pressure, muscle spasms, weight loss, and damage to the adrenal glands. Long-term exposure to atrazine concentrations above the drinking water MCL has been linked to weight loss, cardiovascular damage, retinal and muscle degeneration, and cancer. This survey effort improved upon previously conducted atrazine surveys through intensive, high frequency sampling (participating plants sampled their raw and finished water on a weekly basis for approximately seven months). Such an intensive effort allowed the authors to gain a better understanding of short-term atrazine occurrence and its variability in drinking water sources. This information can benefit the drinking water industry by facilitating (1) better atrazine occurrence management (i.e., awareness when plants may be more susceptible to atrazine), (2) more efficient atrazine control (e.g., effective treatment alternatives and more effective response to atrazine occurrence), and (3) treatment cost reduction (e.g., efficient atrazine control can result in substantial cost savings). Forty-seven drinking water treatment plants located primarily in the Midwestern United States participated in the survey and sampled their raw and finished water on a weekly basis from March through October. Samples were analyzed using the Abraxis enzyme-linked immunosorbent assay (ELISA) test kit. Confirmation samples for quality assurance/quality control (QA/QC) purposes were analyzed using solid-phase extraction (SPE) followed by gas chromatography mass spectrophotometry (GC/MS). Several important conclusions can be drawn from this study including (1) surface waters were confirmed to be more vulnerable to atrazine contamination than groundwater sources, (2) peak atrazine concentrations corresponded well to precipitation/runoff events, and (3) atrazine occurrence tended to be uniform geographically when compared by river drainage basins. In addition, this project confirmed that the Abraxis atrazine ELISA test kit tended to have a positive bias (i.e., the measured ELISA concentration was higher than the actual concentration) in most measured samples. Finished samples tended to have more of a positive bias than raw water samples. Therefore, this bias may limit the effectiveness for ELISA for regulatory monitoring. There are many other applications for ELISA, however, including frequent monitoring for early detections of atrazine concentration changes that might trigger conventional analysis by GC/MS or be used for activated carbon dosing or other treatment operating controls.

Introduction

Atrazine is the most commonly applied herbicide in the United States with an average of 51 million pounds of active ingredient applied per year (*1*). While it is mainly applied to corn crops to control many broadleaf weeds and grasses, atrazine has also been applied to other crops including soybeans, sorghum, sugarcane, macadamias, and pineapples. Generally, atrazine is applied in the midwest and south central regions of the United States for soil pre-planting or pre-emergence and to the foliage post-emergence (*2*) (Figure 1).

Atrazine, like many other herbicides, can enter the environment in a variety of ways. Once applied to the soil, atrazine may enter surface water sources by runoff, can be carried into groundwater sources by soil infiltration, or may remain in the soil through adsorptive processes (*3*). Atrazine is water soluble and relatively conservative in the environment due to little loss by volatilization, low sediment partitioning, and relatively slow rates of degradation (i.e., a half-life of months to years) (*4*).

Although the USEPA has classified atrazine as "not a likely human carcinogen" (*5*), potential reproductive and developmental health effects are a concern. The USEPA has found atrazine to potentially cause the following health effects when people are exposed to it at levels above the drinking water Maximum Contaminant Level (MCL) for relatively short periods of time: congestion of heart, lungs, and kidneys, low blood pressure, muscle spasms, weight loss, and damage to adrenal glands. Lifetime exposure to levels above the atrazine MCL may cause weight loss, cardiovascular damage, retinal and muscle degeneration, and cancer (*6*).

The current USEPA drinking water MCL for atrazine is 3 μg/L (set in 1991). However, atrazine must undergo a formal re-registration process for pesticides every six years as part of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (*7*). The goal of this program is to conduct a comprehensive review of pesticides and herbicides and to evaluate their health and environmental effects and make decisions about their future use. In 2003, the USEPA completed its Interim Re-registration Eligibility Decision (IRED) for atrazine, outlining the label changes and risk reduction steps necessary for atrazine to meet health and environmental safety standards (*8*).

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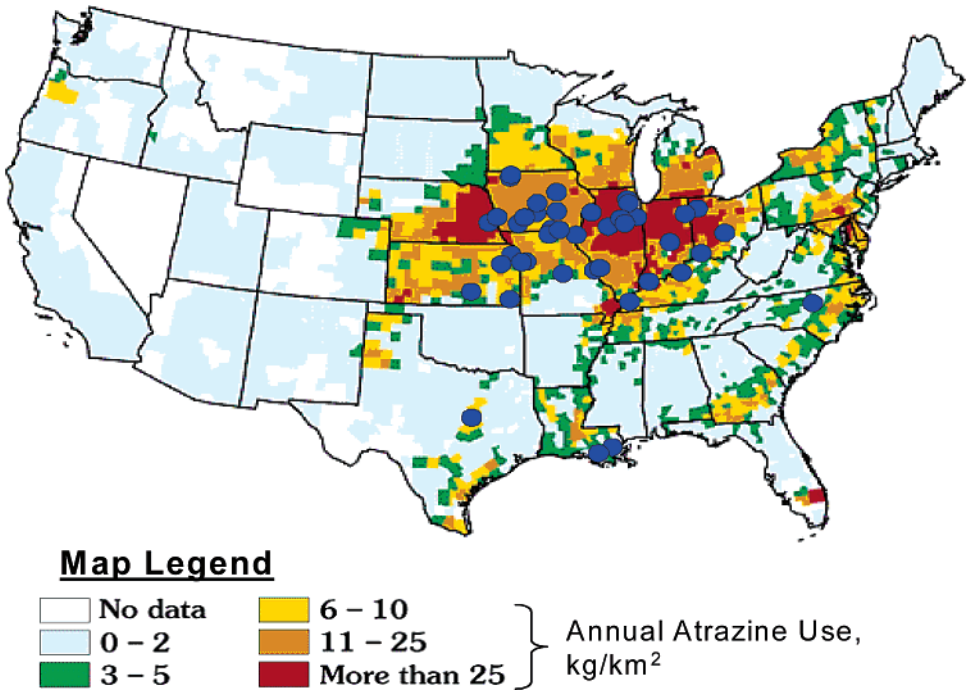

FIGURE 1. Annual atrazine use in the United States (*14*) and utilities that participated in this study.

For drinking water compliance purposes, atrazine must be monitored quarterly and compliance is based on the annual average of these quarterly samples. Minimization of health risks due to short-term exposure, however, depends on implementation of effective treatment when atrazine concentrations are at their peak. Variability in atrazine concentrations, both in source waters and throughout the growing season, is not well-characterized. Generally, frequent atrazine monitoring can be costly and time-consuming using gas chromatography/mass spectrometry (GC/MS) laboratory methods. The recent development of portable enzyme-linked immunosorbent assay methods (ELISA) for atrazine analysis has enabled drinking water utilities to begin to understand the variability of atrazine in their sources and rapidly respond to high atrazine concentration peaks with immediate application of treatment.

Atrazine occurrence has been extensively monitored in the United States. In 1990, the USEPA completed a five-year study entitled National Survey of Pesticides in Drinking Water Wells (NPS). This survey estimated that 1570 (or 1.7%) community water system wells (CWS) and 70 800 (or 0.7%) rural domestic wells nationwide contained atrazine at concentrations above the study's detection limit of 0.12 μg/L. The maximum atrazine concentrations measured in CWS and rural domestic wells were 0.92 and 7.0 μg/L, respectively.

Between 1992 and 2001, the USGS collected surface water samples at 162 sites in 49 of the nation's river basins as part of the National Water Quality Assessment Program (*9*). The goal of this USGS study was to estimate the annual frequency of pesticide detection in the United States. Of the 76 streams sampled at agricultural sites, 90% of the samples contained atrazine, 80% of the samples had atrazine concentrations exceeding 0.01 μg/L, 43% had atrazine concentrations greater than 0.1 μg/L, and no samples exceeded 1 μg/L.

As part of a pesticide registration agreement with the USEPA in 1994, the Monsanto Company agreed to complete a surface drinking water monitoring program (*10*). Sampling for atrazine and acetochlor began in 1995 and continued through December 2001. While both raw and finished water samples were collected, raw water samples were collected less frequently than finished water samples. All of the samples were collected at conventional drinking water treatment

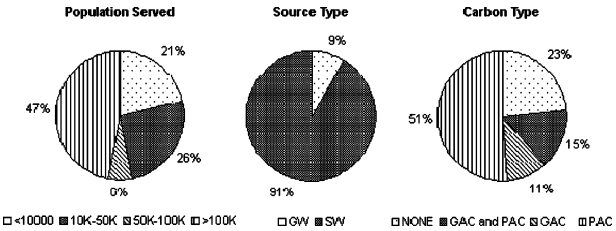

FIGURE 2. General characteristics of the participating plants.

plants, with some plants also using granulated activated carbon (GAC) or powdered activated carbon (PAC). Samples were collected biweekly from March through August each year. Additional samples were collected in November to represent autumn months and in January to represent winter months. Results from the duration of the survey showed that atrazine was detected in 90.5% of the raw water samples and 78.4% in the finished water samples. Of these samples, 13.8% of the raw water samples and 5.4% of the finished water samples exceeded the EPA atrazine MCL of 3 μg/L.

In 2003, the American Water Works Association's (AWWA) Water Industry Technical Action Fund (WITAF) sponsored an intensive year-long study to evaluate atrazine occurrence across the United States (*11*, *12*). Thirty-eight drinking water treatment plants sampled raw and finished water on a weekly basis from April 2003 through October 2003. These samples were analyzed using EPA-approved Beacon ELISA test kits. Several important conclusions resulted from this study, including the determination that the Beacon ELISA test kit was inaccurate under certain conditions due to water matrix interferences (*13*). Other observations included the following: (1) surface waters were found to be more vulnerable to atrazine contamination than groundwater sources, (2) peak atrazine occurrence corresponded well to precipitation/runoff events, and (3) atrazine occurrence was not uniform across river drainage basins. Additionally, the study demonstrated that atrazine can be effectively removed using activated carbon (either as GAC or PAC).

This project, titled the 2004 Atrazine Monitoring Program, was conducted under the joint sponsorship of the AWWA WITAF program and the American Water Works Association

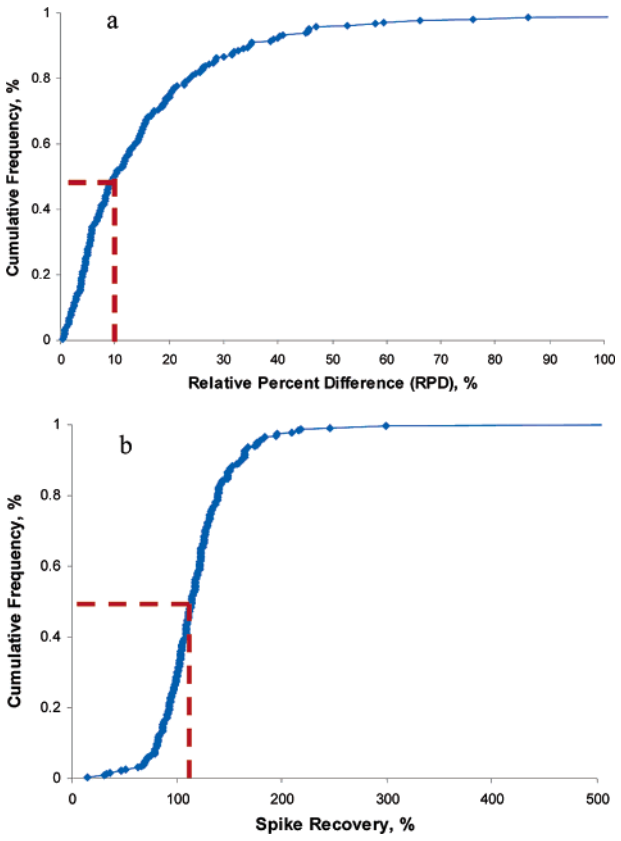

FIGURE 3. Cumulative frequency of (a) relative percent difference for duplicate samples and (b) spike recovery for spiked samples.

Research Foundation (AwwaRF). This study assessed atrazine occurrence patterns in drinking water utilities in susceptible areas of the United States. The purpose of this paper is to report the results of this national atrazine assessment program to characterize atrazine occurrence patterns using the ELISA test kit manufactured by Abraxis, which was shown to be more reliable than the Beacon kits tested in 2003.

Materials and Methods

Forty-seven drinking water plants were included in this study. Since atrazine application is highest in the midwestern and southeastern US, utilities in these regions were invited to participate. Figure 1 shows a map of the participating plants plotted against a backdrop of annual atrazine use from a previous USGS study conducted in 1998 (*14*). A broad range of drinking water treatment plants participated (i.e., in terms of population served, source type, and treatment strategies) (Figure 2).

Participating plants served from 400 to over 1 000 000 people, with 47% of the plants serving between 10 000 and 50 000 people. A majority of the plants used surface water as their primary source, and 77% employed some form of carbon in their treatment process (primarily for taste and odor control but sometimes for pesticide control).

For this study, paired weekly samples of raw and finished water were collected by the 47 participating plants from March through September 2004 and shipped to McGuire Environmental Consultants, Inc. (MEC) for analysis using the Abraxis ELISA method. Split samples for 10% of the samples were sent to the University of Missouri—Rolla (UMR) for analysis by solid-phase extraction GC/MS to provide a quality control comparison to the Abraxis ELISA method results (*15*). The GC/MS used was an Agilent 6893 with an

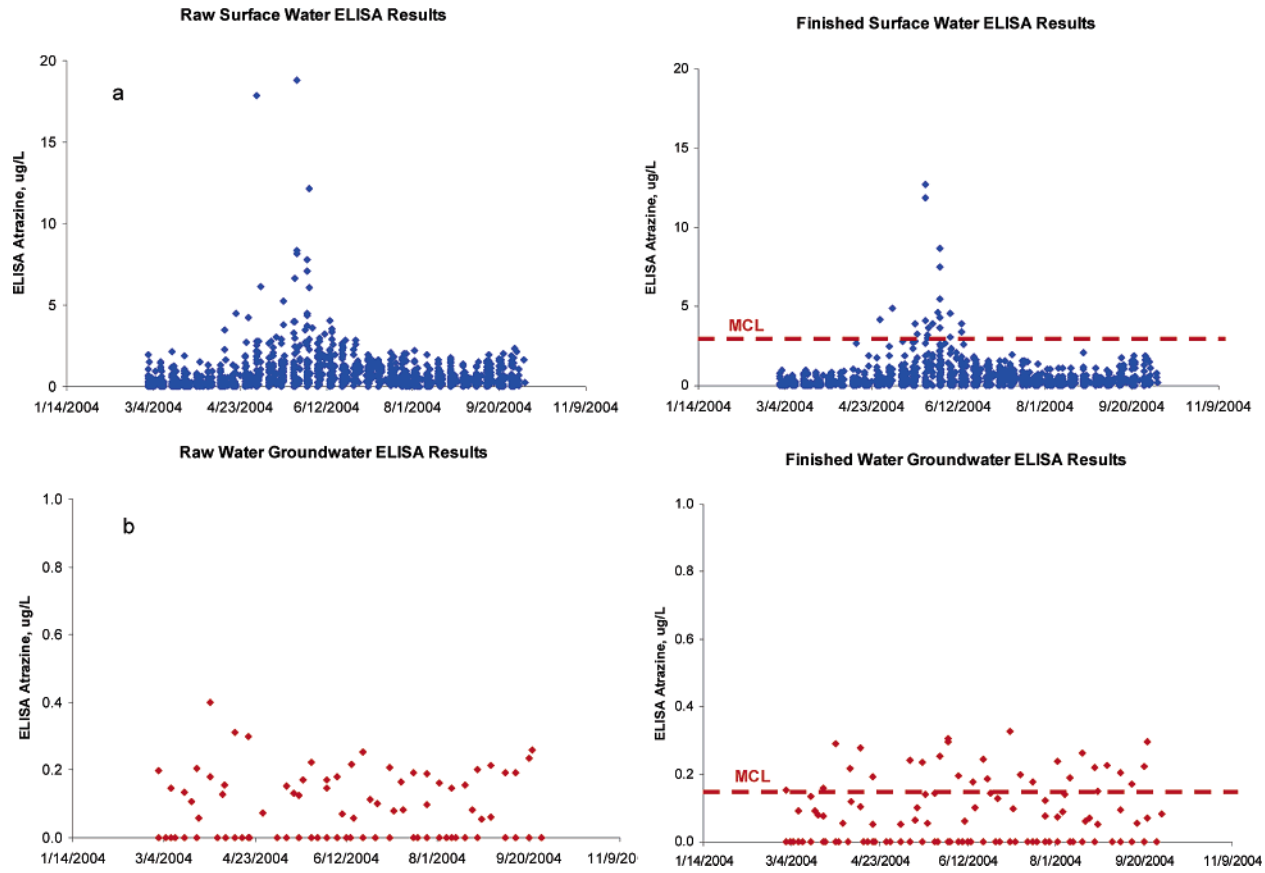

FIGURE 4. Raw and finished water atrazine in (a) surface water and (b) groundwater treatment plants.

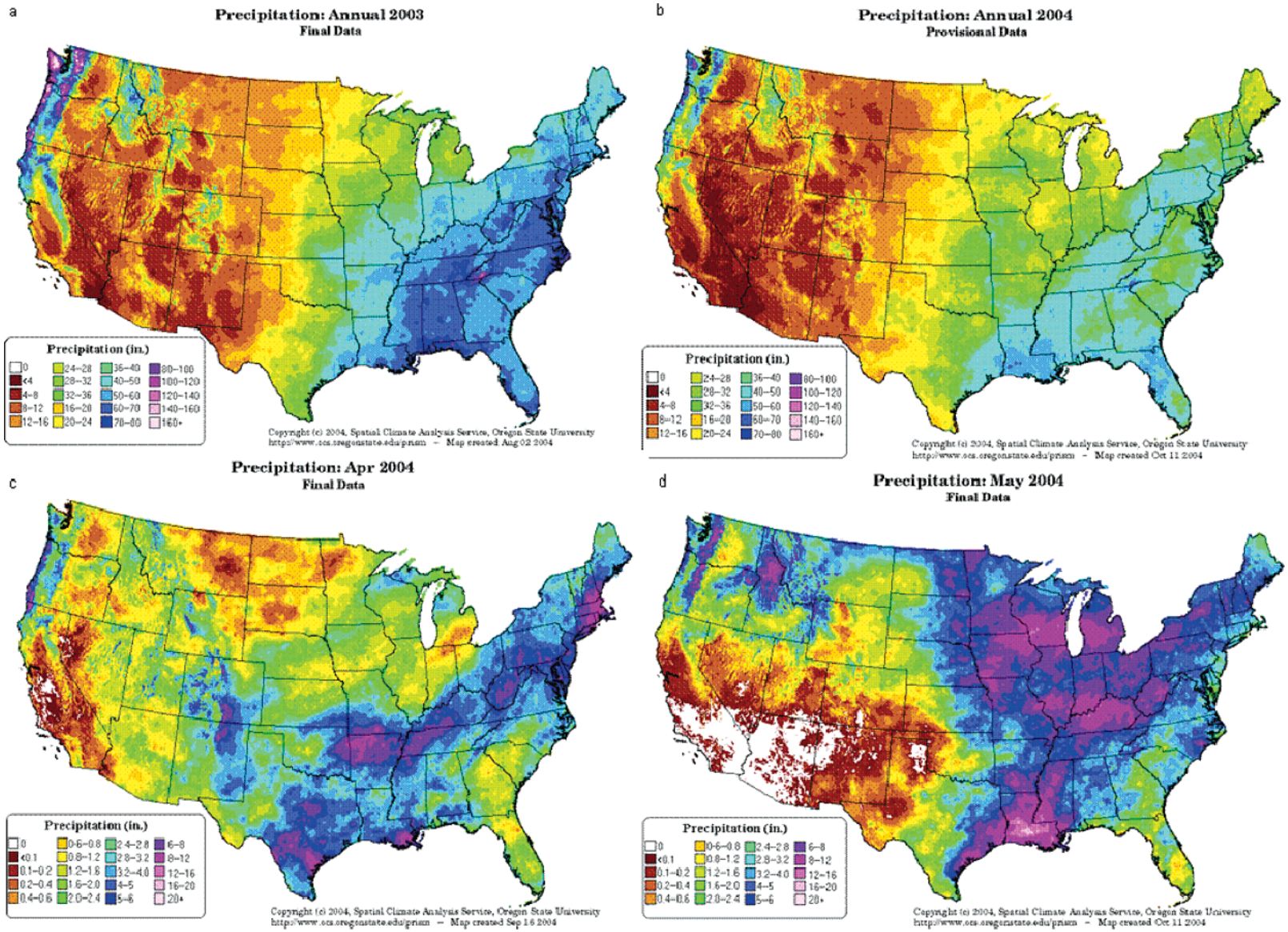

FIGURE 5. Yearly (2003 (a) and 2004 (b)) and monthly (April (c) and May (d) 2004) precipitation trends for sampled utilities. Reprinted with permission. Copyright 2004, Spatial Climate Analysis Service, Oregon State University, http://www.ocs.oregonstate.edu/prism/.

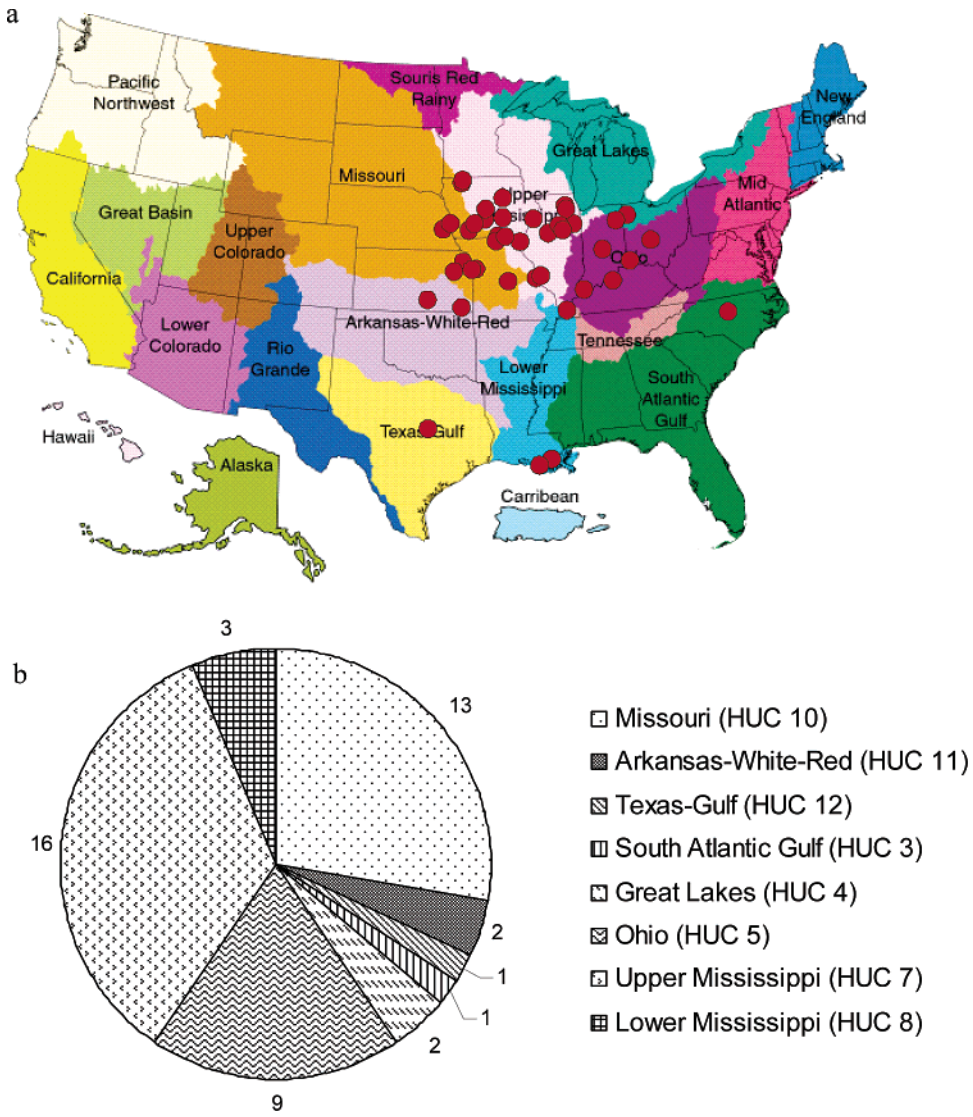

FIGURE 6. Participating treatment plants by major watershed according to the USGS hydrologic unit code.

HP-5MS capillary column, which had an atrazine detection limit of <0.2 μg/L.

A statistical software analysis program—Statistica version 5.5—was used to generate box-and-whisker (B&W) plots showing the 25th-, 50th-, and 75th-percentiles as well as the minimum and maximum values. The software determined if certain samples were either outliers or extremes based on the following equation:

Outlier defined as:

$$\text{UBV} + \text{oc}(\text{UBV} - \text{LBV}) \textit{ or } \text{LBV} - \text{oc}(\text{UBV} - \text{LBV})$$

Extreme defined as:

$$\text{UBV} + 1.5\text{oc}(\text{UBV} - \text{LBV}) \textit{ or } \text{LBV} - 1.5\text{oc}(\text{UBV} - \text{LBV})$$

where UBV = 75th percentile, LBV = 25th percentile, and oc = outlier coefficient (default in Statistica is 1.5).

Abraxis ELISA Method. ELISA kits were purchased from Abraxis (Warminster, PA). Samples were analyzed according to the instructions included in the test kit. Briefly, each sample was placed into a disposable 13-mm tube with the enzyme conjugate and paramagnetic particles attached with polyclonal antibodies specific to atrazine. Atrazine in the sample, along with the enzyme conjugate, was bound to the magnetic particles. After 15 min, a magnetic field was applied to the tubes to retain the magnetic particles while the unbound reagent solution was decanted. The tubes were then rinsed several times. A "color solution" containing the enzyme substrate was then added to the tubes and allowed to react for 20 min. Finally, an acid solution was added to quench the reaction and change the complex from blue to yellow for subsequent spectrophotometric analysis at a wavelength of 450 nm. The reported detection limit of the Abraxis ELISA kit was 0.05 μg/L.

Results and Discussion

Evaluation of the Abraxis Test Kit. Atrazine monitoring data collected in 2004 using the Abraxis ELISA test kit was first evaluated for both precision (i.e., spread in the data set) and accuracy (i.e., closeness to the true value). To evaluate the precision of the data set, the relative percent difference (RPD) was calculated for the 10% of samples that had duplicate samples. As shown in Figure 3a, the median RPD for the entire dataset was 10%. On the basis of this value, it was concluded that the Abraxis test kit was precise.

Accuracy was tested with both matrix-spiked samples and with comparison of ELISA samples results with results generated using the GC/MS method proposed by Adams et al. (*14*). For the first test of accuracy, 10% of all samples were split and spiked with 1 μg/L of atrazine using a certified atrazine stock solution. For each spiked sample set, the percent recovery was calculated. Overall, the median spike recovery for all of samples was 114% (Figure 3b). Raw water

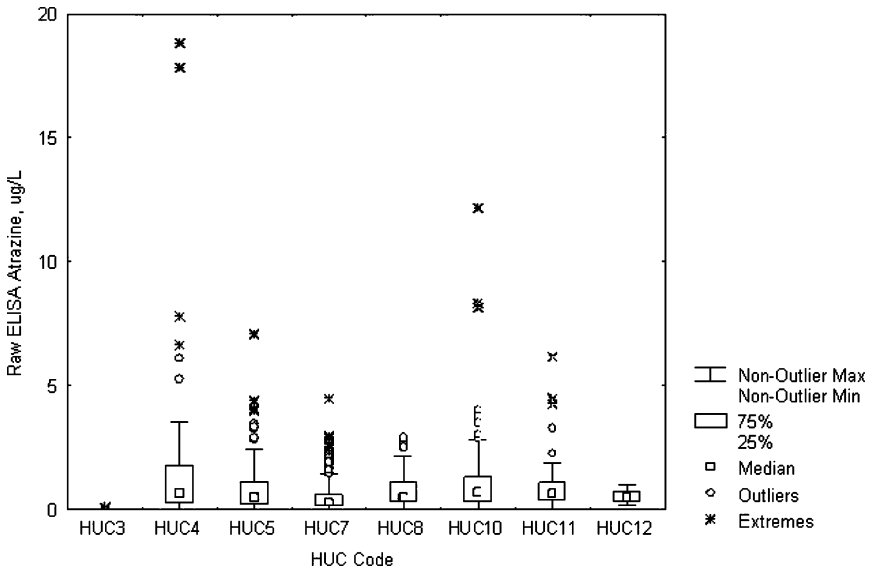

FIGURE 7. Raw water atrazine occurrence categorized by watershed.

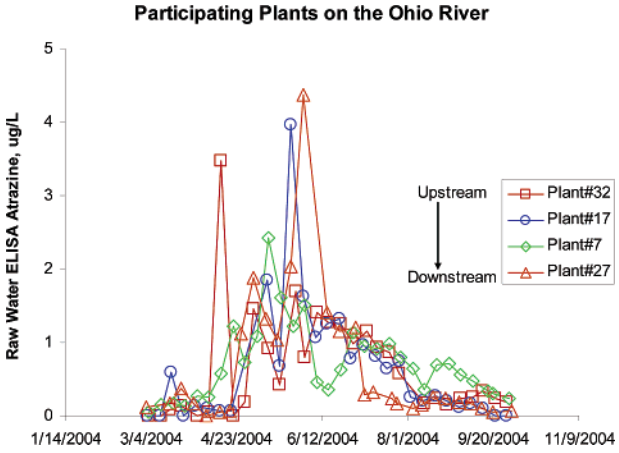

FIGURE 8. Raw water atrazine occurrence for four plants along the Ohio River.

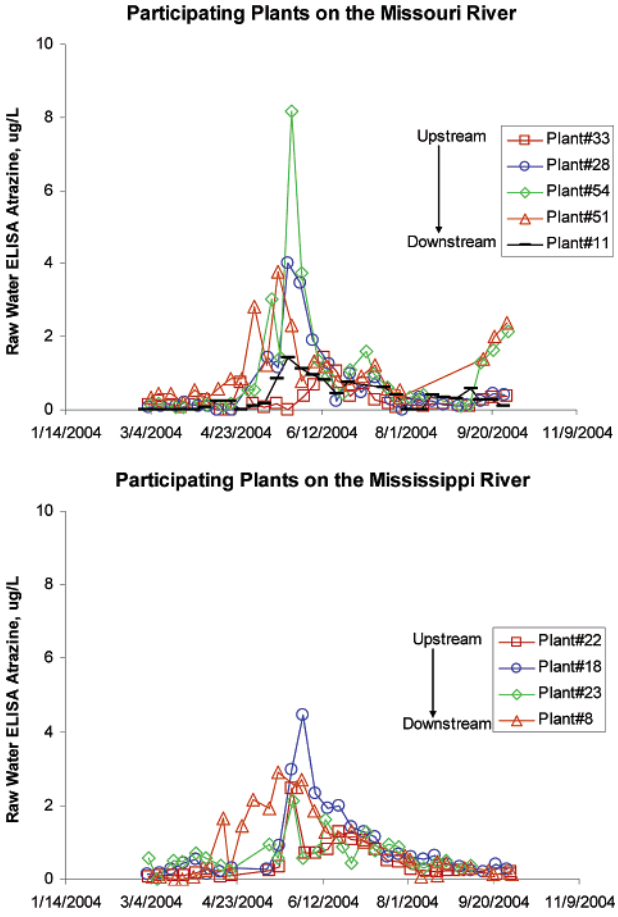

FIGURE 9. Raw water atrazine occurrence for plants along the Mississippi River and the Missouri River.

samples had a median spike recovery of 115% and finished water samples had a median recovery of 111%.

Another 10% of the ELISA samples were split and analyzed for atrazine using the GC/MS method as another check of accuracy for the ELISA method. Paired GC/MS results were correlated with ELISA results for both raw and finished water samples. While raw water atrazine concentrations samples were overestimated by only 11%, finished water values were observed to be overestimated by 49%. This same phenomenon was observed when Adams et al. (2004) investigated how well several different manufacturers' ELISA test kits performed in various drinking water matrixes. On the basis of the data reported by Adams (*13*), it was hypothesized that the greater overestimation of atrazine in finished water compared to raw water might be due to the effects of oxidants in the finished water even when a dechlorinating agent was included in the bottles.

On the basis of the RPD, matrix spike recovery data, and ELISA and GC/MS comparison data, the Abraxis ELISA test kit was determined to be precise and accurate for raw water samples but not accurate for all finished waters. Since oxidants may result in higher positive atrazine concentrations than the actual concentrations for finished water samples, the atrazine ELISA test kit is more suitable as a screening method for atrazine in raw water to obtain inexpensive estimates of atrazine occurrence that leads to the rapid employment of treatment and ensures removal by drinking water treatment processes.

Atrazine Occurrence. *Temporal Patterns.* A number of factors can impact atrazine's introduction into drinking water supplies, including application time periods, cultivation techniques, and precipitation events. Many studies have found correlations between peak herbicide occurrence and hydrologic conditions; specifically that pesticide occurrence

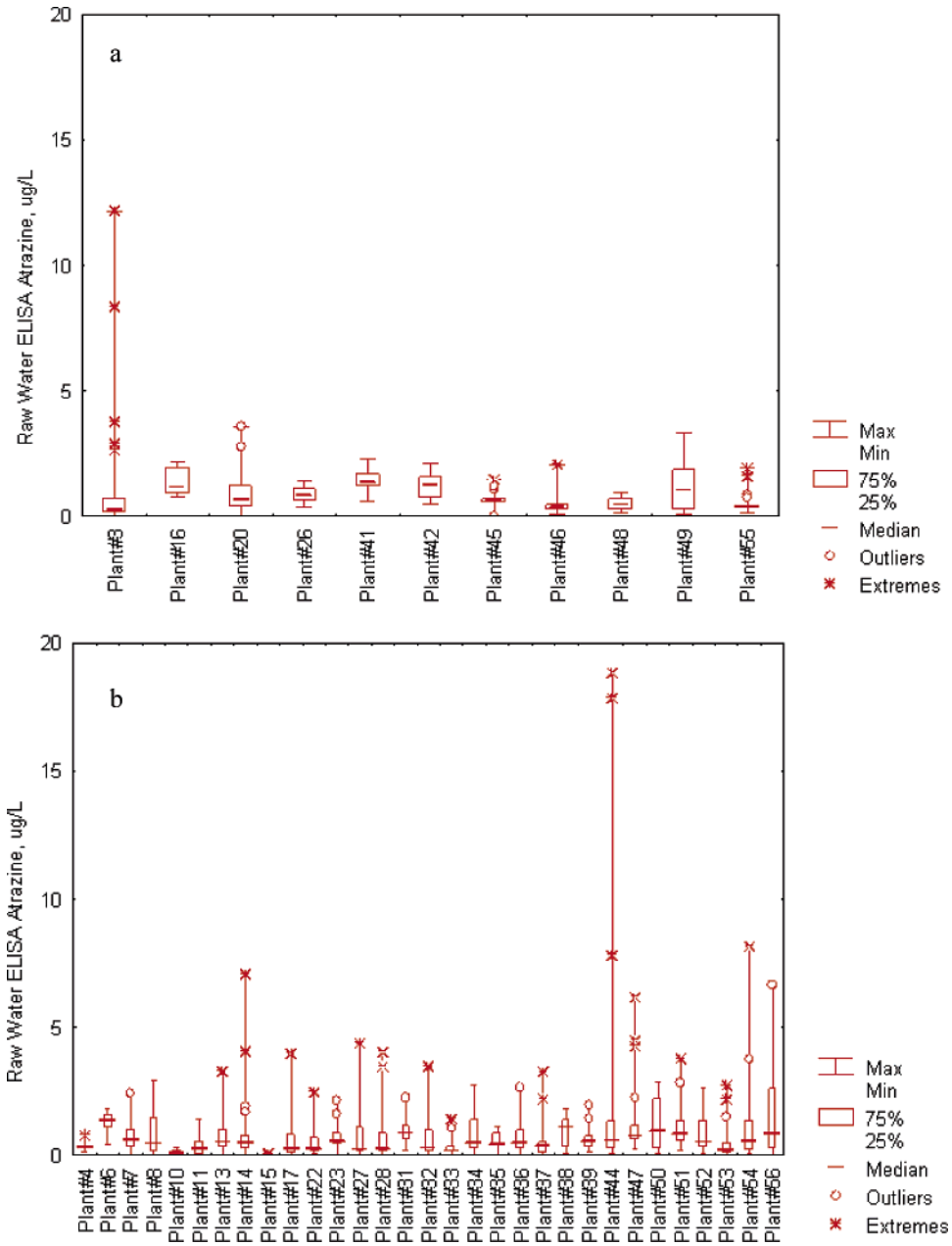

FIGURE 10. Box-and-whisker plots for plants drawing their raw water from (a) lakes or reservoirs or (b) rivers or streams.

was generally higher with the first storm following application than with subsequent storms (*16*−*20*). (This phenomenon is also referred to a "flush", with peak atrazine concentrations in surface waters typically occurring in the spring and summer following the spring/early-summer rains (*16*)).

Figure 4 presents atrazine occurrence for all of the raw and finished water samples for this study from March through September 2004. In agreement with previous studies (*21*−*22*), raw water atrazine concentrations were the lowest during March and April prior to atrazine crop application. During this study, significant precipitation occurred during May in the Midwest (Figure 5) compared to April, and the highest monthly raw water atrazine averages were experienced for almost all of the study participants. The "peaking" of raw water atrazine concentrations in May coincides with conditions likely to produce atrazine "flush" events (i.e., high precipitation and runoff following atrazine application).

While atrazine typically enters source water supplies as a component of runoff from fields near surface waters, atrazine can also leach through the soil into groundwater sources. For this reason, four utilities using groundwater as their primary water source participated in this study. All four of the utilities had samples that tested positive for atrazine. However, the atrazine concentrations found at these plants were less than 0.40 μg/L and no temporal trends were observed.

Because atrazine varies temporally, compliance sampling may be affected. Currently, utilities are required to monitor for atrazine on a quarterly basis. Based on this data set, there are two problems associated with this type of sampling. First, if samples are only collected once a quarter, high atrazine peaks may be missed since atrazine occurs in a relatively small time span even within a quarter. The other problem associated with quarterly sampling is that samples collected in quarters where there is little or no atrazine may dilute the final average. Logically, little or no atrazine is found in drinking water sources in the fall or winter quarter. Even if high atrazine values were measured in the spring and summer, results from the fall and winter samples may dilute the overall average.

Watershed Trends. Atrazine occurrence was also investigated as a function of major watershed (USGS-defined hydrological unit codes (HUCs)) to determine if utilities in some watersheds were more likely to be affected by atrazine than others. Participants represented 8 of the 21 major watersheds in the United States (Figure 6a). As illustrated in Figure 6b, a majority of the study participants were located within the Upper Mississippi watershed (HUC 7) (34%), the Missouri watershed (HUC 10) (28%), and the Ohio watershed (HUC 5) (19%) due to the widespread use of atrazine in those watersheds.

Statistical analyses of atrazine concentrations were performed to evaluate trends on the basis of HUC regions. Figure 7 shows B&W plots for raw water samples. In addition to illustrating the median, 25th-, and 75th-percentile concentrations, outlier and extreme atrazine results are shown. This analysis indicated that, on average, all watersheds were similarly impacted, which was anticipated since these watersheds are all located within high atrazine use areas. Outlier and extreme data, however, showed that some areas experienced sharp peaks in raw water atrazine concentrations.

These data conflict with data from the 2003 study where atrazine occurrence varied by watershed (*12*). In 2003, some drainage basins experienced higher concentrations of atrazine on the whole, such as the Ohio, Mississippi (Lower greater than Upper), and Missouri basins, corresponding to large river system supply sources draining the regions of highest atrazine use (*12*). The difference may be attributed to many factors, including atrazine application and precipitation. Unfortunately, precipitation at each of the participating utilities was not tracked. However, based on results in Figure 5a and b, it appears that the lower Midwest experienced more precipitation in 2003 compared to 2004. More precipitation may have flushed atrazine into the source waters. Application rate may be another contributing factor between the two years. However, this could not be evaluated. Normally, the USDA publishes atrazine application rates by state on an annual basis. Unfortunately, the 2004 report did not include any data on atrazine and therefore it is unknown if atrazine application rates between the two years varied.

River/Stream vs Lake/Reservoir Trends. Using the 2004 data set, atrazine variation within major rivers was also evaluated. Four participants in the Ohio watershed (HUC 5) used the Ohio River as their primary source. Figure 8 illustrates the temporal variation in each of these four raw water sources along the Ohio River. Excluding the first spring "flush" peak for plant 32, the other 4 plants shared similar profiles in pattern and amplitude with the highest concentrations generally in May. These data show that atrazine concentrations remain elevated above background values (e.g., March concentrations) throughout the summer. Weekly sampling captured discreet peaks that might not otherwise have been observed using a quarterly sampling frequency. Similar trends were observed for plants using the Mississippi or Missouri Rivers as their primary raw water sources. Figure 9 shows that these surface waters experienced elevated atrazine concentrations primarily in May 2004. No trend of atrazine concentration magnification or dilution through the river systems was discernible from these data sets.

Variation between plants withdrawing source water from lakes/reservoirs or river/streams was investigated. Figure 10a and b show a moderate dampening of atrazine outlier and extreme concentrations for the lake and reservoir systems. Median raw water atrazine concentrations for plants drawing their water from lake/reservoir systems ranged from 0.40 to 1.4 μg/L (Figure 10a). The 25th percentile values ranged from 0.1 to 1.2 μg/L and the 75th percentile ranged from 0.4 to 1.9 μg/L, demonstrating little variability compared to plants drawing their water from river and streams. Excluding Plant 3, the maximum raw water atrazine concentration for lake or reservoir systems was 3.6 μg/L. Upon further examination, it was discovered that Plant 3 was an "atypical" lake/reservoir system. This plant, located in Iowa, was located on a small, narrow naturally formed lake with no tributaries and was surrounded by cornfields. After atrazine was applied in the early spring, atrazine was flushed into the reservoir by precipitation/runoff events. This system resulted in a high atrazine peak occurring in June, after which concentrations decreased rapidly over time (Figure 11).

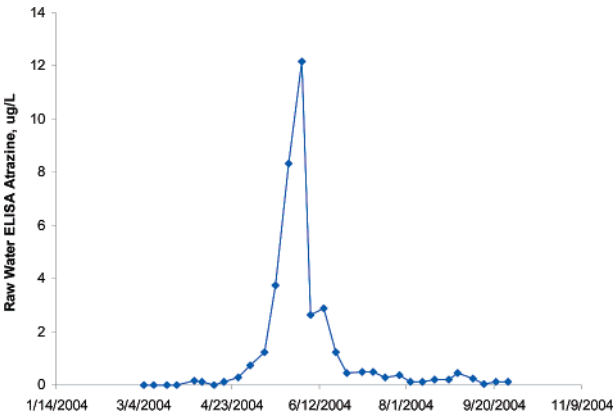

FIGURE 11. Raw water atrazine profile for Plant 3.

In contrast to the lake/reservoir systems, Figure 10b shows that river/stream systems experienced higher outlier and extreme raw water atrazine concentrations. Median and interquartile (25th- and 75th-percentile) values were similar for lake/reservoir and river systems. Median raw water atrazine concentrations ranged from less than 0.2 μg/L to 2.2 μg/L; the 25th-percentile values ranged from less than 0.2 to 1.1 μg/L, and the 75th-percentile values ranged from less than 0.2 to 2.6 μg/L. Ten plants on rivers and streams had maximum atrazine concentrations greater than 3 μg/L.

Acknowledgments

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