Occurrence of Sulfonylurea, Sulfonamide, Imidazolinone, and other Herbicides in Midwestern Rivers, Reservoirs, and Ground Water, 1998

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ABSTRACT

Sulfonylurea (SU), sulfonamide (SA), and imidazolinone (IMI) herbicides are relatively new classes of chemical compounds that function by inhibiting the action of a plant enzyme, stopping plant growth, and eventually killing the plant. These compounds generally have low mammalian toxicity, but plants demonstrate a wide range in sensitivity to SUs, SAs, and IMIs with over a 10,000-fold difference in observed toxicity levels for some compounds. SUs, SAs, and IMIs are applied either pre- or post-emergence to crops commonly at 1/50th or less of the rate of other herbicides. Little is known about their occurrence, fate, or transport in surface water or ground water in the United States.

To obtain information on the occurrence of SU, SA, and IMI herbicides in the Midwestern United States, 212 water samples were collected from 75 surface-water and 25 ground-water sites in 1998. These samples were analyzed for 16 SU, SA, and IMI herbicides by USGS Methods Research and Development Program staff using high-performance liquid chromatography/mass spectrometry. Samples were also analyzed for 47 pesticides or pesticide degradation products. At least one of the 16 SUs, SAs or IMIs was detected above the method reporting limit (MRL) of 0.01 micrograms per liter (µg/L) in 83% of 130 stream samples. Imazethapyr was detected most frequently (71% of samples) followed by flumetsulam (63% of samples) and nicosulfuron (52% of samples). The sum of SU, SA, and IMI concentrations exceeded 0.5 µg/L in less than 10% of stream samples. At least one SU, SA, or IMI herbicide was detected above the MRL in 24% of 25 ground-water samples and 86% of 7 reservoir samples.

INTRODUCTION

During the last 20 years, low application rate herbicides have been developed that act by inhibiting the action of a key plant enzyme, which stops plant growth and eventually causes plant death. Sulfonylurea (SU), sulfonamide (SA), and imidazolinone (IMI) herbicides are three classes of compounds that share this mode of action (Meister, 1997).

Herbicide use

Crops that can be treated with SU, SA, and IMI herbicides include barley, corn, cotton, durum wheat, rice, canola, peanuts, soybeans, sugar beets, spring wheat, and winter wheat. Some compounds are also approved for use on Conservation Reserve Program acreage and for noncropland weed control.

The amount of cropland treated with SU, SA, and IMI herbicides has nearly tripled since 1990. The total corn, soybean, and wheat acreage on which 9 SUs, 1 SA and 2 IMIs were applied in eleven Midwestern States (Iowa, Illinois, Indiana, Kansas, Kentucky, Minnesota, Missouri, Nebraska, Ohio, South Dakota, and Wisconsin) from 1990 through 1997 is shown in figure 1 (U.S. Department of Agriculture, 1991-98). In 1997, more than 66 million acres were treated with one of the 12 herbicides. For comparison, atrazine, a triazine herbicide, was used on 41 million acres of corn and metolachlor, a chloracetanilide herbicide, was used on 23 million acres of corn and soybeans in the same 11-State area.

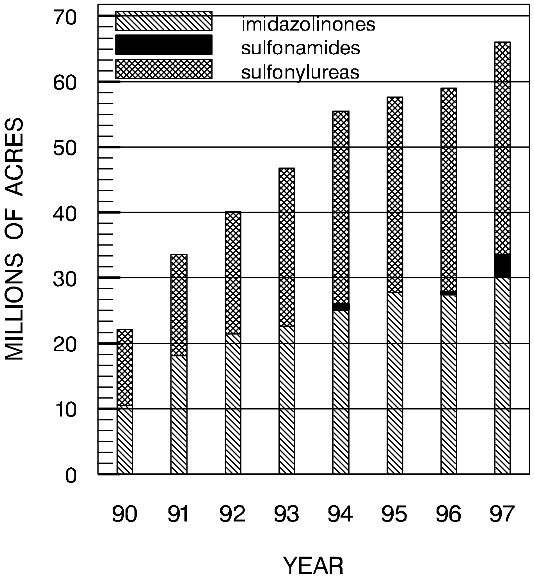

Figure 1. Estimated acres of corn, soybeans, and wheat treated with selected SU, SA, and IMI herbicides, 1990-97, in Midwestern States.

Although applied over comparable areas, SU, SA, and IMI herbicides are frequently applied after crops have emerged, and at low rates (typically less than 25 grams active ingredient/hectare). These application rates are commonly 1/50th or less of the rates for triazine or chloracetanilide herbicides (typically more than 1,200 grams/hectare). Hence, the overall use amount for SU, SA, and IMI herbicides is relatively small. For example, in 1997 in the 11-State area, an estimated 20,300 metric tons (tonnes) of atrazine and 21,500 tonnes of metolachlor were applied to cropland, while the total estimated use of the 9 SUs, 1 SA, and 2 IMIs was only 1,090 tonnes (U.S. Department of Agriculture, 1998).

Herbicide Chemistry

The soil half-life of SUs, SAs, and IMIs generally ranges from 1 to 25 weeks depending on soil pH and temperature. Their water solubilities range from 6 to 40,000 part per million. The water solubility of SUs are dependent on water pH. SUs degrade by chemical hydrolysis and microbial activity. SUs degrade faster in warm, moist, low organic, low pH soils (DuPont, 1998). IMIs degrade by microbial activity and photolysis. IMIs degradate faster in warm, moist, low organic soils (Goetz and others, 1990).

Herbicide Toxicity

SUs, SAs, and IMIs act upon a specific plant enzyme (acetolactate synthase) that is not found in mammals or other animals and are reported to have very low toxicities in animals (Brown, 1990; Meister, 1997). Plants demonstrate a wide range in sensitivity to SUs, SAs, and IMIs (Peterson and others, 1994) with over a 10,000-fold difference in observed toxicity levels for some compounds. EC50 concentrations are measures of compound toxicity. An EC50 is the concentration in water of a compound that causes a 50% reduction in a chosen plant characteristic for which a toxicity endpoint exists. For example, EC50s for algae can be calculated from laboratory tests measuring biomass development in the presence of varying compound concentrations. EC50 values for selected SU, SA, IMI, and other herbicides on 5 aquatic plants are shown on figure 2 (Fahl and others, 1995; U.S. Environmental Protection Agency, 1997; Sabater and Carrasco, 1997; Fairchild and others, 1997; Wei and others, 1998; C. J. Peter, DuPont Agricultural Products, written commun., 1999). The EC50 values plotted are for green algae (Selenastrum capricornutum), duckweed (Lemna gibba), blue-green algae (Anabaena flos-aquae), freshwater algae (Scenedesmus costatum), and freshwater diatom (Navicula pelliculosa). In some cases, EC50 values from more than one test on the same plant species are included. EC50 values for several herbicides range over 3 orders of magnitude. The EC50 data plotted on figure 2 support the hypothesis that a concentration of 0.1 µg/L in water is the baseline for non-target aquatic plant toxicity.

SUs, SAs, and IMIs are active at very low concentrations and can cause a problem with plant vigor in some crop rotations even when only 1 percent or less of the originally applied material remains. Some of these herbicides have demonstrated residual phytotoxicity to rotation crops such as corn, sunflowers, sugar beets, and dry beans (Anderson and Humburg, 1987; Curran and others, 1991). The labels of some of these herbicides restrict the planting of certain rotational crops. Fletcher and others (1993) indicated that spray drift containing SUs at concentrations less than 1 percent of the recommended application rate may adversely impact fruit tree yields. Felsot and others (1996) suggested that the appearance of chlorotic spots on crops in south central Washington is a result of exposure to low levels of SU herbicides in precipitation and not from direct spray drift. However, Obrigawitch and others (1998) questioned the validity of Fletcher's findings and the results of other studies that based their findings on short-term plant-response assessments. Obrigawitch and others (1998) found that a treatment rate of 0.1 gram of the most active SU ingredient per hectare (0.00009 pound per acre) represents a "threshold dose" and would be unlikely to reduce the yields of even the most sensitive non-target plants.

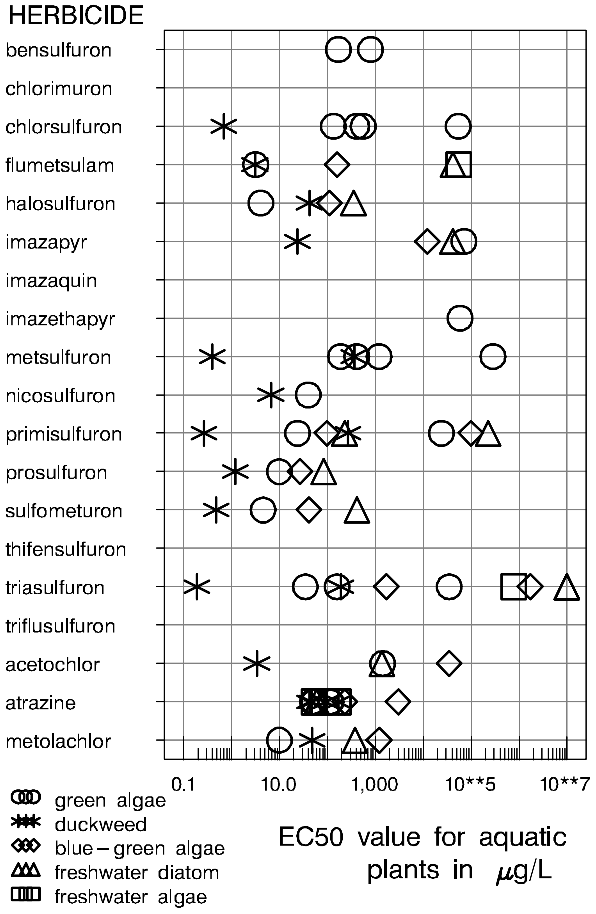

Figure 2. EC50 concentrations in micrograms per liter for 5 aquatic plants for selected SU, SA, IMI, and other herbicides.

Herbicide Occurrence

Detections of SUs, SAs, and IMIs in water collected from environmental settings have been rare and the few reported detections have been at nanogram per liter concentrations (Bergstrom, 1990; Michael and Neary, 1993; D'Ascenzo and others, 1998; Steinheimer and others, 1998; Okamoto and others, 1998). However, several studies indicate that some SUs, SAs, and IMIs herbicides may leach beyond the active root zone and enter ground-water or surface-water systems (Anderson and Humburg, 1987; Bergstrom, 1990; Flury and others, 1995; Veeh and others, 1994). Once in ground water or surface water, some SUs, SAs, and IMIs will tend to persist as the parent compound while others will tend to hydrolyze (Dinelli and others, 1997; Harvey and others, 1985). A study by Afyuni and others, (1997) indicated that between 1.1 and 2.3% of an applied SU was lost in runoff during a simulated rainfall event 24 hours after herbicide application.

Because of their low application rates and low overall use amounts, concentrations of SUs, SAs, and IMIs are expected to be low in most water resources. One can also assume based upon their chemical characteristics, application rates, and acres treated that individual SUs, SAs, and IMIs herbicides would be expected to occur in surface or ground water at 1 to 0.1 percent or less of the concentration of common triazine herbicides. Thus, one could expect to observe SUs, SAs, and IMIs herbicides in Midwestern rivers during post-application runoff events at concentrations ranging from 0.001 to 0.1 μg/L. Further, one could expect maximum concentrations of SUs, SAs, and IMIs herbicides to range from 0.01 to 1.0 μg/L (Battaglin and others, 1998a). In ground water, one would expect SU, SA, and IMI concentrations to seldom exceed 0.01 μg/L.

OBJECTIVES AND METHODS

Purpose and Scope

Currently, little is known about the occurrence, fate, or transport of SUs, SAs, and IMIs in the hydrologic system in the United States. The overall objective of this project is to determine if and at what concentrations selected SUs, SAs, and

IMIs occur in surface- and ground-water resources of the Midwestern United States. Specific objectives include:

- Develop an analytical method for selected SUs, SAs, and IMIs.
- Conduct a reconnaissance to determine the environmental occurrence of SUs, SAs, and IMIs herbicides in surface water and ground water in the Midwestern United States.
- Determine the frequency of detection and concentration distributions of SUs, SAs, and IMIs herbicides relative to those of selected other herbicides in Midwestern surface water and ground water.

A Cooperative Research and Development Agreement (CRADA) between the U.S. Geological Survey (USGS) and DuPont Agricultural Products was developed to accomplish the objectives of this project in a unbiased, yet economical manner (Battaglin and others, 1998b).

The data collected in this study are only adequate to identify the occurrence of selected SU, SA, and IMI herbicides during post-application runoff events in Midwestern streams and in ground water in parts of Iowa and Illinois. The data are not adequate to determine annual mean concentrations of detected herbicides or whether non-detected herbicide are present at other times of the year.

Plan of Study

The study involved collection of 212 samples during a 1998 reconnaissance. Samples were collected from streams, large rivers, reservoir outflows, and wells, sometimes in conjunction with USGS National Stream Quality Accounting Network (NASQAN) (Hooper and others, 1997) and National Water Quality Assessment (NAWQA) (Leahy and Thompson, 1994) activities. All reconnaissance samples were analyzed for 16 SU, SA, and IMI herbicides (table 1) using high performance liquid chromatography coupled with mass spectrometry. This custom analytical method has a method reporting limit (MRL) of 0.01 μg/L for all analytes and is fully described in Furlong and others (1999).

Sampling Sites

Samples were collected from 75 surface-water sites in the Upper Mississippi, Missouri, and Ohio River basins (figure 3). Fifty-two of the surface-water sites have been studied in previous Mid-continent Herbicide Initiative (MHI) investigations (Thurman and others, 1992; Goolsby and others, 1994; Scribner and others, 1998). These sites were selected out of the set of 150 sites sampled in 1989 using a stratified random method (Scribner and others, 1993). It is important to note that the sampling strategy used was not designed to produce an unbiased estimate of herbicide occurrence in all Midwestern streams. Rather the intent was to target higher risk areas while still capturing the variability of the entire population. Samples also were collected at selected NASQAN and NAWQA sites and just downstream from five reservoirs at locations that had been sampled in a previous investigation (Coupe and others, 1995; Scribner and others, 1996).

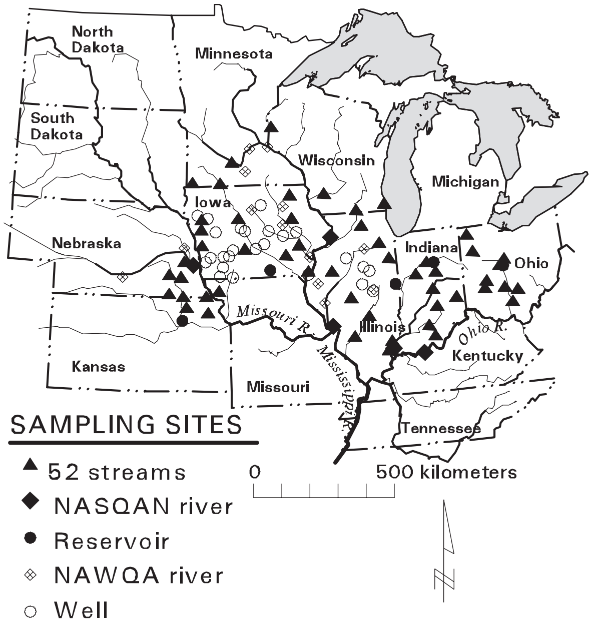

Figure 3. Location and type of sites sampled in 1998 herbicide reconnaissance.

Twenty ground-water samples were collected from a network of municipal wells in Iowa that are part of the Iowa Ground water Monitoring (IGWM) program (Detroy and others, 1988; Kolpin and others, 1997). Wells from this network have been sampled systematically since 1982. The depths to the top of the well screen for the sampled wells, ranged from 6 to 83 meters and most were less than 30 meters. Five samples also were collected from observation wells in the Lower Illinois NAWQA study unit (Warner and Schmidt, 1994). These wells were all less than 8 meters deep.

Sampling Schedule and Procedure

Two samples were collected at each surface-water and reservoir site, and one sample was collected at each ground water site in 1998. The first surface-water samples were collected after pre-emergence herbicides were applied (May or June) and following a precipitation event that produced a significant increase in streamflow. The second surface-water samples were collected after post-emergence herbicides were applied (June or July) again following a precipitation event that produced runoff and an increase in streamflow. The first NASQAN and reservoir samples were collected 2-3 weeks after the first surface-water samples were collected from nearby sites. The second NASQAN and reservoir samples were collected 2-3 weeks after the second surface-water samples were collected from nearby sites. Ground-water samples were collected in June, July, or August.

Samples were collected using protocols that are identical to those used for the collection of samples for low levels of other dissolved organic compounds (Shelton, 1994). The equal-width-increment sampling method was used in all cases except on some large rivers where equal-discharge-increment sampling was used (Edwards and Glysson, 1988).

All equipment was precleaned with a Liquinox/tap-water solution, rinsed with tap water, deionized water, and then methanol, and air dried. All samples were filtered through 0.7-µm pore-size heat-cleaned glass-fiber filters using an aluminum-plate filter holder and a ceramic-piston fluid-metering pump with all Teflon tubing into precleaned 1-liter or 125-ml amber glass bottles. Samples were immediately chilled and shipped on ice from the field to the USGS National Water Quality Laboratory (NWQL) within two days of collection.

Analytical Methods

An analytical method was developed that is an extension and improvement of the high-performance liquid chromatography/mass spectrometry (HPLC/MS) method by Rodriguez and Orescan (1998). Briefly, the method consists of isolation of the analytes of interest from approximately 1 liter of water (precisely measured) using two stacked solid-phase extraction cartridges. After isolation, the second cartridge is dried and the analytes are eluted using acidified acetone. The analytes are then concentrated and solvent exchanged into 1 mL of 10% acetonitrile and 90% water.

HPLC/MS analysis is performed using a Hewlett Packard 1100 series HPLC, coupled to a Hewlett Packard LC/MSD. Electrospray ionization, operated in the positive ion mode, is used to ionize the analytes. Selected-ion monitoring is used to maximize sensitivity. A calibration curve is developed using external standards and the linear range of the method is from 0.005 to 0.5 µg/L. Three ions (1 quantitation, 2 confirmation) are monitored for each compound. For confirmed identification of analytes, the relative ion abundances for the detection must be within 20% of average response for standards, as well as have the correct relative retention time (within 0.1 min). Detected analytes that don’t meet one criterion are reported as estimates, as are all detections below the MRL of 0.01 µg/L. Details of this analytical methods are provided elsewhere in this volume by Furlong and others (1999).

In addition, all samples were analyzed for several other classes of pesticides. Samples were analyzed for 41 pesticides and pesticide metabolites by GC/MS with selected-ion monitoring using methods described by Zaugg and others (1995). This method has MRLs that range from 0.001 to 0.018 µg/L.

RESULTS AND DISCUSSION

Sample collection began in May and was completed in August, 1998. Two hundred twelve samples were submitted to Methods Research and Development Program staff at the NWQL. Of these, 177 are from surface-water sites and 29 are from ground water sites (results from 6 samples collected from 2 tile drains in New York State are not discussed here). These numbers include QA samples. One hundred fifty surface-water samples and 25 ground-water samples were submitted to the NWQL for analysis of 47 pesticides or pesticide degradation products.

Occurrence in Surface Water

SU, SA, and IMI Herbicides

Results from 130 stream and river samples are summarized in table 1. At least one of the 16

SU, SA or IMI herbicides was detected in 83% of stream samples. Imazethapyr was the most frequently detected compound (71% of samples) followed by flumetsulam (63%), nicosulfuron (52%), imazaquin and chlorimuron ethyl (32%). Chlorsulfuron, halosulfuron methyl, imazapyr, prosulfuron, sulfometuron methyl, and thifensulfuron methyl were detected in 5 percent or less of samples. The detection frequencies reported are for samples with concentrations at or above the method reporting limit (MRL), currently 0.01 µg/L. Bensulfuron methyl, metsulfuron methyl, primisulfuron methyl, triasulfuron, and triflusulfuron methyl were not detected above the MRL.

The distributions of concentrations of the target analytes in 130 samples are summarized in figure 4. In some cases, estimated concentrations are reported that are below the MRL. These concentrations are not counted as detections above the MRL (numbers to the right of the boxplots in figure 4), but are used in the calculation of summary statistics (the boxplots themselves). The sum of SU, SA, and IMI concentrations exceeded 0.5 ug/L in less than 10% of stream samples.

At least one of the 16 SU, SA or IMI herbicides was detected above the MRL in 6 of 7 (86%) of reservoir samples. Flumetsulam, imazethapyr, imazaquin, and nicosulfuron were each detected in 4 samples. The sum of SU, SA, and IMI concentrations did not exceeded 0.5 ug/L in any reservoir sample.

Other Herbicides

The results of analysis for selected other herbicides in 129 stream or river samples are also included on table 1. Acetochlor, alachlor, atrazine, cyanazine, and metolachlor were all detected in 90% or more of the stream samples. Atrazine had the highest median concentration (3.97 µg/L), followed by metolachlor (1.73 µg/L), and acetochlor (0.411 µg/L). The sum of the 5 other herbicides included in table 1 exceeded 50 µg/L in about 10% of the samples. This sum was expected to be at least 100 times greater than the sum of the SU, SA, and IMI herbicide concentrations.

Table 1. Statistical summary of SU, SA, IMI, herbicide concentrations in 130 samples and selected other herbicide concentrations in 129 water samples from Midwestern streams and rivers, 1998 (in µg/L)

Herbicide	Detections above MRL	median	maximum
SU, SA, and IMI herbicides			
bensulfuron methyl	0	<0.01	<0.01
chlorimuron ethyl	41	<0.01	0.304
chlorsulfuron	1	<0.01	0.013
flumetsulam	82	0.020	2.11
halosulfuron methyl	7	<0.01	0.067
imazapyr	5	<0.01	0.072
imazaquin	41	<0.01	1.11
imazethapyr	92	0.031	0.689
metsulfuron methyl	0	<0.01	<0.01
nicosulfuron	67	0.010	0.266
primisulfuron methyl	0	<0.01	<0.01
prosulfuron	6	<0.01	0.036
sulfometuron methyl	2	<0.01	0.018
thifensulfuron methyl	1	<0.01	0.015
triasulfuron	0	<0.01	<0.01
triflusulfuron methyl	0	<0.01	<0.01
sum of 16 SUs, SAs, and IMIs	108	0.137	2.23
Other herbicides			
acetochlor	124	0.411	25.1
alachlor	116	0.045	17.2
atrazine	129	3.97	224.
cyanazine	119	0.326	14.0
metolachlor	129	1.73	143.
sum of 5 other herbicides	129	6.90	385.

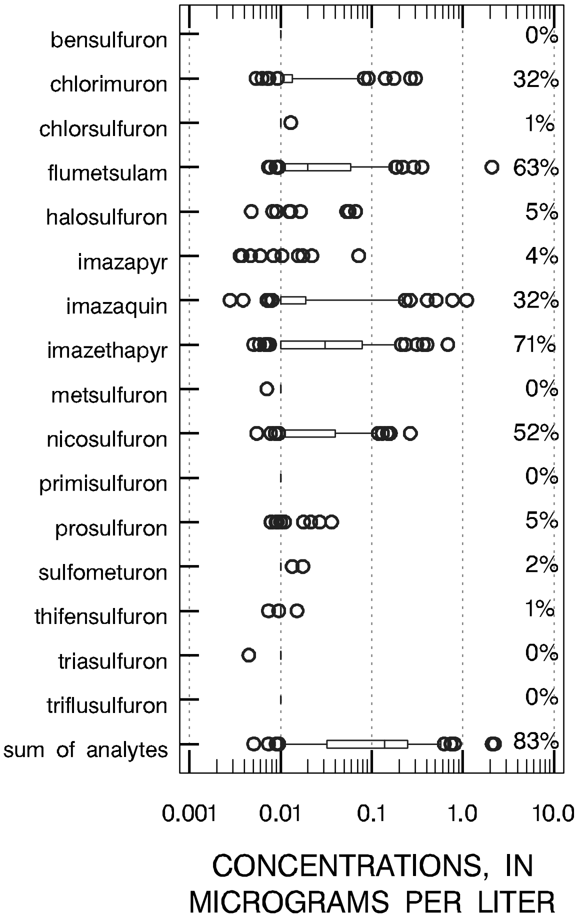

Figure 4. Boxplots of SU, SA, and IMI herbicide concentrations and percent detections above the MRL (0.01 micrograms per liter) in 130 samples from midwestern streams, 1998. The boxes show the 25th, 50th (median) and 75th percentiles, the wiskers extend to the 5th and 95th percentiles, and outliers less than the 5th or greater than the 95th percentiles are shown as circles.

Occurrence in Groundwater

SU, SA, and IMI Herbicides

Results from 25 groundwater samples are summarized in table 2. At least one of the 16 SU’s, SA’s or IMI’s was detected in 24% of groundwater samples. Imazethapyr was the most frequently detected compound (16% of samples) followed by flumetsulam (12%), and nicosulfuron and imazaquin (8%). The sum of SU, SA, and IMI concentrations exceeded 0.01 ug/L in 6 samples.

Other Herbicides

The results of analysis for selected other herbicides are also included on table 2. Atrazine and metolachlor were detected in about one-half of the samples. The sum of the concentrations of the 5 herbicides did not exceeded 1.0 µg/L in any sample. This sum was also expected to be at least 100 times greater than the sum of the SU, SA, and IMI herbicide concentrations.

Concentrations of SUs, SAs, and IMIs Relative to other Herbicides

Because they have similar chemical properties, but much lower application rates, SU, SA, and IMI herbicides were expected to occur at fraction (1/100th or less) of the concentrations of other herbicides such as atrazine (Battaglin and others, 1998). In figures 5a, 5b, and 5c, the concentrations in streams of imazethapyr, flumetsulam, and nicosulfuron, the three most frequently detected target analytes, are plotted versus atrazine concentration. The lines crossing these plots show the 1:10, 1:100, and 1:1,000 ratios of concentration. The data plotted on figure 5 suggest that in about half the samples imazethapyr, flumetsulam, and nicosulfuron occur at 1/100th or less of the concentration of atrazine.

The observed range and maximum concentrations of SU, SA, and IMI herbicide in samples collected from Midwestern streams during post-application runoff events in 1998 was very close to what we expected. The majority of SU, SA, and IMI detections were at concentrations less than 0.1 µg/L. These concentrations are not likely to be toxic to non-target aquatic plants. The maximum concentrations of SU, SA, and IMI herbicide in samples collected from Midwestern ground water in 1998 were slightly higher than expected.

Table 2. Statistical summary of SU, SA, IMI, and selected other herbicide concentrations in 25 samples of Midwestern ground water, 1998 (in µg/L)

Herbicide	Detections above MRL	median	maximum
SU, SA, and IMI herbicides			
bensulfuron methyl	0	<0.01	<0.01
chlorimuron ethyl	0	<0.01	<0.01
chlorsulfuron	0	<0.01	<0.01
flumetsulam	3	<0.01	0.035
halosulfuron methyl	0	<0.01	<0.01
imazapyr	0	<0.01	<0.01
imazaquin	2	<0.01	0.024
imazethapyr	4	<0.01	0.059
metsulfuron methyl	0	<0.01	<0.01
nicosulfuron	2	<0.01	0.016
primisulfuron methyl	0	<0.01	<0.01
prosulfuron	0	<0.01	<0.01
sulfometuron methyl	0	<0.01	<0.01
thifensulfuron	0	<0.01	<0.01
triasulfuron	0	<0.01	<0.01
triflusulfuron methyl	0	<0.01	<0.01
Sum of 16 SUs, SAs, and IMIs	6	<0.01	0.110
Other herbicides			
acetochlor	1	<0.002	0.004
alachlor	1	<0.002	0.016
atrazine	14	0.010	0.410
cyanazine	1	<0.004	0.007
metolachlor	12	<0.002	0.557
sum of 5 other herbicides	14	0.014	0.703

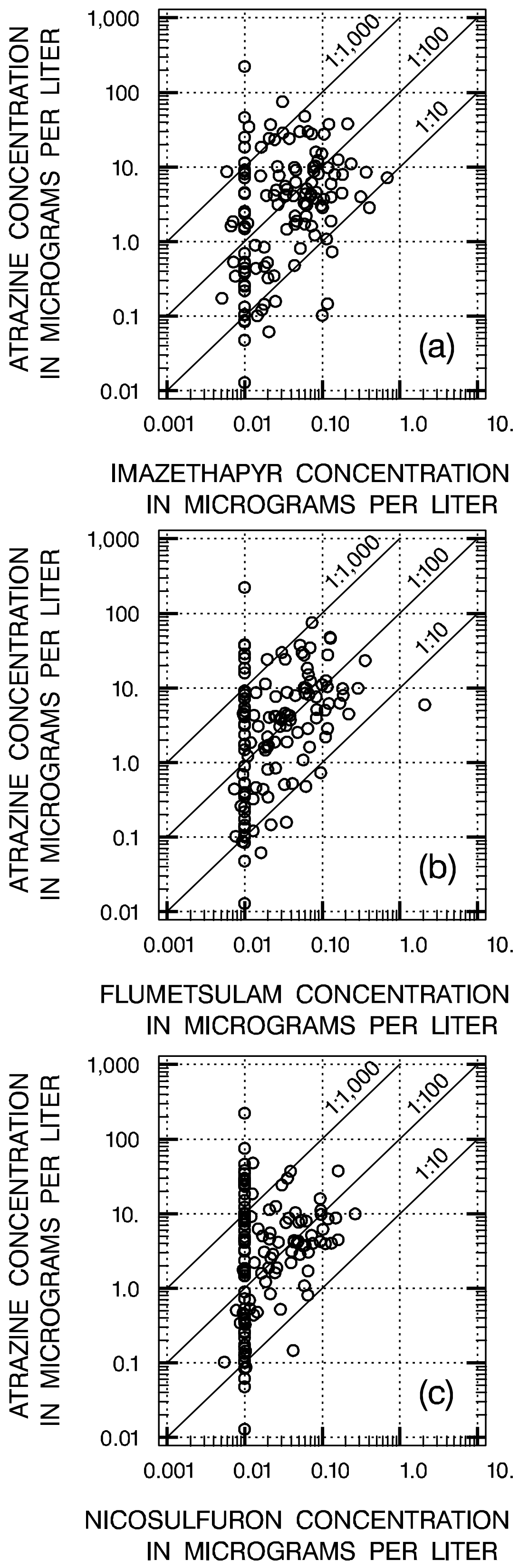

Figure 5. Concentrations of atrazine versus (a) imazethapyr, (b) flumesulam, and (c) nicosulfuron, in 130 samples collected from Midwestern streams in 1998.

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