Presence of Organoarsenicals Used in Cotton Production in Agricultural Water and Soil of the Southern United States

A. J. Bednar,[†,‡] J. R. Garbarino,*[,‡] J. F. Ranville,[†] and T. R. Wildeman[†]

Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401, and National Water Quality Laboratory, U.S. Geological Survey, P.O. Box 25046, MS 407, Denver, Colorado 80225

Arsenicals have been used extensively in agriculture in the United States as insecticides and herbicides. Mono- and disodium methylarsonate and dimethylarsinic acid are organoarsenicals used to control weeds in cotton fields and as defoliation agents applied prior to cotton harvesting. Because the toxicity of most organoarsenicals is less than that of inorganic arsenic species, the introduction of these compounds into the environment might seem benign. However, biotic and abiotic degradation reactions can produce more problematic inorganic forms of arsenic, such as arsenite [As(III)] and arsenate [As(V)]. This study investigates the occurrences of these compounds in samples of soil and associated surface and groundwaters. Preliminary results show that surface water samples from cotton-producing areas have elevated concentrations of methylarsenic species (>10 μg of As/L) compared to background areas (<1 μg of As/L). Species transformations also occur between surface waters and adjacent soils and groundwaters, which also contain elevated arsenic. The data indicate that point sources of arsenic related to agriculture might be responsible for increased arsenic concentrations in local irrigation wells, although the elevated concentrations did not exceed the new (2002) arsenic maximum contaminant level of 10 μg/L in any of the wells sampled thus far.

KEYWORDS: **Organoarsenic herbicides; cotton; arsenic speciation; redox transformations**

INTRODUCTION

Arsenicals have been used in agriculture in the United States for more than 100 years (*1*). Inorganic arsenic compounds historically were used as pesticides, and today, methlyated arsenicals are used as herbicides for cotton production (*2, 3*). More complex organoarsenical species with substituted phenyl rings increasingly are being used to control intestinal parasites in poultry and swine (*4*). In addition to anthropogenic sources, microorganisms can further influence arsenic speciation in natural systems by redox reactions, methylation, and demethylation, as well as biosynthesis processes (*5, 6*). Abiotic redox reactions with natural organic matter (NOM) can occur in natural water, and photochemical reactions, which usually involve oxidation by a hydroxyl radical mechanism, also are known (*7*).

In the 1990s, it is estimated that >3000 metric tons per year of monosodium methylarsonate (MSMA) and disodium methylarsonate (DSMA) [sodium salts of monomethylarsonic acid (MMA)] was applied to cotton fields in the United States (*8, 9*). This total does not include the use of dimethylarsinic acid (DMA), which sometimes is used as a defoliant (use is ~35 metric tons arsenic/year) (*3, 8*). The usage numbers for MSMA

and DSMA alone translate into >1000 metric tons of arsenic being introduced into the environment each year as a result of the application of these herbicides. Structural formulas for the four common inorganic and organic arsenicals measured in this study are given in **Figure 1**. The localized and repeated use of organoarsenical herbicides results in the concentrated addition of arsenic on farmland (*10*). In addition, the sorptive properties of arsenical compounds in natural soil can cause them to persist in the environment long after application has ended (*11*).

A primary area of organoarsenical herbicide use in the United States includes the cotton-belt states of Alabama, Arkansas, Louisiana, Mississippi, and Texas, among others. The effects of residual organoarsenic herbicides on other crops that are rotated commonly with cotton production have been investigated previously (*12*). Rice, specifically, is a crop that can be rotated with cotton, and, therefore, can be adversely impacted by previous use of organoarsenic herbicides (*10*). Irrigation practices among these different crops vary greatly and will affect soil conditions, such as redox potential (Eh) and pH, as well as NOM concentration. Such drastically different soil conditions can result in interconversion and mobilization of arsenic species by biotic and abiotic means (*11, 12*). Mobilization of arsenite under reducing conditions caused by soil flooding during rice production might result in arsenic mobilization to surface water and leaching to groundwater. Preliminary data suggest that application of organoarsenic herbicides and subsequent leaching

* Author to whom correspondence should be addressed (e-mail jrgarb@usgs.gov).
† Colorado School of Mines.
‡ U.S. Geological Survey.

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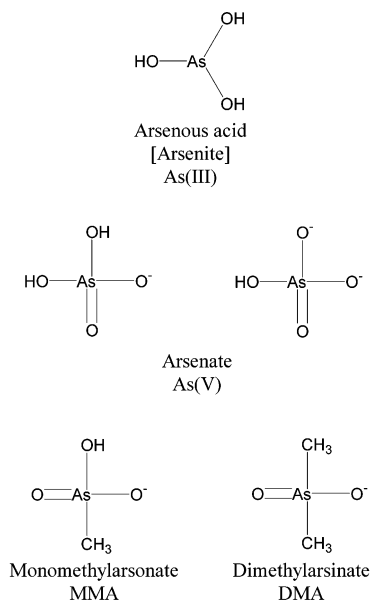*J. Agric. Food Chem.,* Vol. 50, No. 25, 2002 **7341**

Figure 1. Structural formulas for inorganic and organic arsenicals measured in surface and groundwater samples from Arkansas and Mississippi. As(III) is fully protonated, As(V) can be either protonated species shown, and MMA and DMA are also partially or fully deprotonated at environmentally relevant pH values (circumneutral). As(III) $pK_{a1} = 9.3$; As(V) $pK_{a1} = 2.2$, $pK_{a2} = 6.9$; MMA $pK_{a1} = 4.1$, $pK_{a2} = 8.7$; DMA $pK_a = 6.2$.

from the soil can be a long-term source of arsenic to the aquatic environment.

The purpose of this paper is to describe the presence and behavior of organoarsenic species in natural water and soil samples affected by agriculture, primarily cotton production. Samples collected from two major cotton-producing regions of the southeastern United States have been investigated. Results indicate the presence of four common arsenic species in surface water samples from these agricultural areas. Point sources, such as cropduster airstrips in particular, can elevate levels of arsenic in adjacent drainage ditches and nearby irrigation wells, yet natural dilution and sorptive remediation processes maintain dissolved arsenic levels in groundwater at less than the current drinking water maximum contaminant level (MCL) of 10 μg/L.

MATERIALS AND METHODS

All chemicals used for analyses in this study were of reagent grade or higher purity and used without further purification; the deionized water used had a resistivity of 18.3 MΩ·cm. Arsenic speciation in all samples was determined using two recently developed high-performance liquid chromatography inductively coupled plasma mass spectrometry (HPLC-ICP-MS) techniques (*13*). The first method uses a sodium phosphate mobile phase and a Hamilton PRP-X100 HPLC column with hydride generation sample introduction into the ICP-MS (Perkin-Elmer Elan 6100). The second method uses an ammonium malonate/acetate mobile phase on a short SAX HPLC column and nebulization sample introduction into the ICP-MS. Both methods have detection limits between 0.1 and 0.6 μg of arsenic/L for each species (*13*). Sample preservation of field samples used either freezing or chemical preservation with ethylenediaminetetraacetic acid (EDTA) and storage in opaque high-density polyethylene (HDPE) bottles (*13, 14*). Both preservation techniques have been shown to be effective in arsenic preservation, particularly for methylated species that are considered to be more stable than inorganic species in most sample matrices (*14, 15*). Details of the chromatographic speciation and EDTA preservation techniques have been described elsewhere (*13, 14*). Elemental concentrations in the water
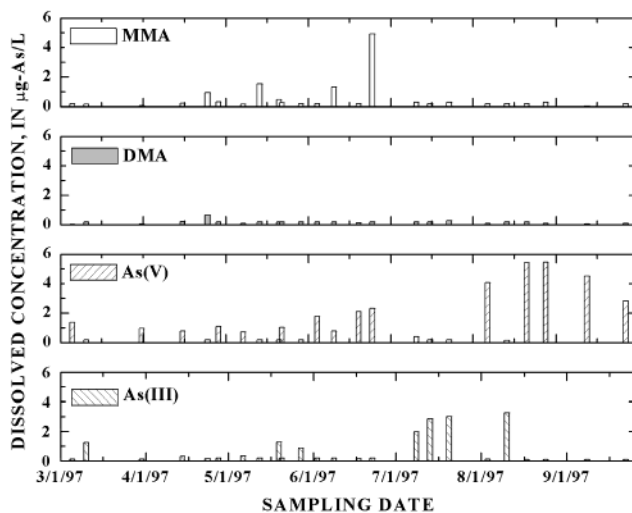

Figure 2. Arsenic species concentrations in surface water samples collected at the Mississippi Bogue Philia site from March through September 1997.

samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), and total arsenic concentrations were determined by ICP-MS or graphite furnace atomic absorption spectroscopy (GF-AAS).

Water samples were collected from multiple locations in two historically high-cotton-producing regions of the southeastern United States. Mississippi and Arkansas are ranked third and fourth, respectively, in annual acres of cotton planted in the United States (*16*). In Mississippi, 24 surface water samples were collected from two drainage basins (Bogue Philia and Yazoo) in agricultural areas where the herbicide MSMA was applied. In Arkansas, about 25 surface and groundwater samples were collected from drainage ditches and rivers, precipitation surface puddles, and irrigation wells in a cotton-, rice-, and soybean-producing region. Water samples also were collected from three cropduster airstrips in Arkansas. All water samples were filtered (0.45 μm), preserved, and analyzed for MMA, DMA, arsenite [As-(III)], and arsenate [As(V)] using HPLC separation and ICP-MS detection as described above. Samples were collected at different times of the year to determine seasonal variations in arsenic concentration and speciation.

In addition to water samples, soil samples were collected in Arkansas from a cropduster airstrip (abandoned airstrip 1) and three cotton fields to determine the effect of soils on the mobility, concentration, and speciation of arsenic in associated natural water. Soil extracts were prepared in the laboratory by shaking 1 g of dry soil, sieved to <150 μm, in 10 mL of deionized water, 50 mM sodium phosphate (monobasic salt, solution pH ~4.5), or 0.5% nitric acid for 1 h followed by filtration to 0.45 μm. These extraction solutions were chosen to encompass the extremes in water composition that might result from natural precipitation. The extracts were analyzed in the same manner as the water samples for arsenic speciation and total arsenic concentrations.

The Mississippi water samples were collected at 1- or 2-week intervals from early March through the middle of September 1997. MSMA normally is applied to the fields from May through July for weed control and from September to October on fallow or stale seedbeds and for defoliation prior to harvest (*17, 18*). The Arkansas water samples were collected twice each year (June and December) from 1999 to 2001 to differentiate background arsenic concentrations (December) from concentrations after herbicide application (June).

RESULTS AND DISCUSSION

Mississippi Samples. Dissolved arsenic species concentrations measured in the Mississippi samples are shown in **Figures 2** and **3**. The highest concentrations of MMA were measured in samples collected after the period when the application of MSMA was most likely and did not exceed 6 μg of As/L. Except
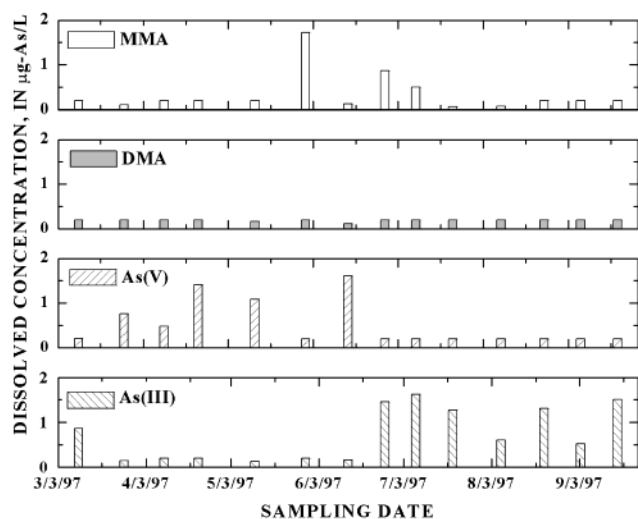
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Figure 3. Arsenic species concentrations in surface water samples collected at the Mississippi Yazoo site from March through September 1997.

Table 1. Arsenic Species and Total Arsenic Concentrations (in Micrograms of Arsenic per Liter) in Surface Water and Soil Samples Affected by Cropduster Airstrips

	[DMA]	[MMA]	[As(III)]	[As(V)]	[As(T)]
natural-water sample					
airstrip 1 surface puddle	8.4	25.0	3.2	0.3	36.9
ditch adjacent to airstrip 1	ND[a]	ND	ND	ND	10.7
airstrip 2 surface puddle	10.0	2.8	2.9	6.8	22.5
ditch adjacent to airstrip 2	0.6	0.4	0.5	12.8	14.3
ditch adjacent to airstrip 3	7.8	2.1	1.2	4.2	15.3
St. Francis River, Lake City, AR					
Dec 2000	0.2	0.3	0.4	3.0	3.9
July 2002	0.1	BDL[a]	0.7	2.0	2.8
background ditch					
Brookland, AR	ND	ND	ND	ND	1.3
Farville, AR	0.1	BDL	0.5	1.2	1.8
extracts of airstrip 1 soil					
DI water	0.3	0.4	0.6	4.3	5.6
phosphate	0.5	2.1	1.2	69.0	72.8
nitric acid	0.9	0.3	0.8	19.8	21.8

[a] ND, not determined; BDL, below detection limit ($\sim$0.1 μg of As/L).

for a single occurrence at the Bogue Philia site, all DMA concentrations were $\leq$0.2 μg of As/L. The data suggest that MMA and DMA either degrade quickly, are sorbed to soil components, or are simply diluted by the drainage systems.

Concentrations of As(III) and As(V) increased later in the summer in the Bogue Philia samples primarily, possibly indicating demethylation reactions or a secondary source of inorganic arsenic. As(III) predominates in samples collected at the Yazoo site for July, August, and September, possibly indicating a stagnant, low-dissolved oxygen, reducing hydrologic environment. Concentrations of As(III) and As(V) were 2−3 times higher in the Bogue Philia samples than in the Yazoo samples. Total dissolved arsenic never exceeded 6 μg/L at either site. Differences in land use between the two study sites could account for the observed differences in arsenic species concentrations because the Bogue Philia area is more agricultural.

Blind field blanks and blind duplicate samples were analyzed throughout the collection period for each site. All arsenic species concentrations were less than the method detection limits in field blanks. Blind duplicate results for total arsenic (relative difference of 7 $\pm$ 4%, $n = 9$) and arsenic species (relative difference for all species of 5 $\pm$ 4%, $n = 9$) compared favorably except for a Bogue Philia duplicate submitted on May 7, 1997 (110% at <3 μg/L total arsenic), and a Yazoo duplicate submitted on April 10, 1997 (80% at <1 μg/L total arsenic). The concentrations of MMA and DMA in nearly all of the duplicate samples were at the method detection limits, whereas inorganic species had concentrations high enough for accurate comparisons.

Arkansas Samples. The highest total dissolved arsenic concentration found in irrigation wells was <6 μg/L, whereas one surface water puddle contained 380 μg/L. Drainage ditches and streams generally had total arsenic concentrations of <5 μg/L, in agreement with the results from the Mississippi drainages. Speciation of surface water puddle samples at airstrips often showed substantial concentrations of all four arsenic species with concentrations of DMA and MMA of up to 10 and 103 μg of As/L, respectively. Such high DMA and MMA concentrations suggest that these species are desorbed from soil particles sequestering organoarsenicals from previous herbicide applications. In contrast, flowing water has lower arsenic concentrations as a result of dilution.

Speciation results for surface water collected at or near three cropduster airstrips, and the corresponding laboratory extractions of soil collected at airstrip 1, are listed in **Table 1**. MMA and DMA dominate the arsenic species distribution in most of the natural water samples, whereas the airstrip 1 soil extractions contain primarily inorganic arsenic. Speciation was not determined for the ditch samples near airstrip 1, yet total arsenic was greater than background levels (see Brookland and Farville ditch results in **Table 1**). Water samples from ditches adjacent to airstrips 2 and 3, however, show elevated DMA and MMA concentrations (compared to background sites), similar to the airstrip puddle samples. Samples from the St. Francis River, the major river draining the area, had a total arsenic concentration of $\sim$3 μg/L, primarily as As(III) and As(V), but with detectable concentrations of DMA and MMA. Also, it should be noted that airstrip 1 has been abandoned for more than 10 years except for occasional use as a takeoff point for fertilizer application, whereas airstrips 2 and 3 are being used for cotton, rice, soybean, and corn herbicide and fertilizer applications.

Extracts of the soil collected at airstrip 1 showed substantial concentrations of arsenic, primarily as As(III) and As(V). DMA and MMA were near detection limits in the deionized water and nitric acid extracts. Measurable concentrations were found in the phosphate extract, however. The airstrip 1 natural puddle and laboratory soil extract speciation results suggest that a transformation in the arsenic species distribution has occurred in the soil primarily involving demethylation reactions, whereas methylated species persist in the surface water samples. However, extraction differences between natural precipitation and the laboratory procedures are also likely to affect the arsenic species distribution.

High levels of phosphate (up to 24 mg of P/L—possibly from spilled fertilizer), which could affect arsenic desorption from the soil by competitive displacement (*19*, *20*), were found in some of the surface water samples collected near the airstrips. The airstrip 1 surface puddle sample had a total arsenic concentration near that of the laboratory soil extractions (**Tables 1** and **2**), yet the arsenic speciation was different. Organoarsenicals dominate in the natural surface puddle, whereas inorganic species dominate in the laboratory soil extracts. The speciation difference possibly reflects the different extraction processes because of other dissolved constituents in the natural puddle [e.g., natural organic matter (*21*)] rather than a species interconversion. Furthermore, irrigation wells <25 m away from

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Table 2. Arsenic Species Concentrations (in Micrograms of Arsenic per Liter) in Surface Water and Soil Samples Collected from Four Cotton Fields Where DMA, MSMA, DSMA, or All Three Historically Have Been Applied

	[DMA]	[MMA]	[As(III)]	[As(V)]	[As(T)]
water sample					
cotton field 4 irrigation puddle	1.4	5.1	0.5	2.6	9.6
ditch adjacent to cotton field 4	1.0	0.2	6.5	0.3	8.0
soil extractions					
DI water extract					
soil W	0.2	0.1	0.2	0.3	0.8
soil P	0.2	0.3	0.2	1.6	2.3
soil H	0.3	0.5	0.3	1.5	2.6
phosphate extract					
soil W	0.2	0.2	0.2	13.2	13.8
soil P	0.3	0.8	0.3	18.1	19.5
soil H	0.6	2.5	0.3	23.3	26.7
nitric acid extract					
soil W	0.2	0.1	0.2	1.5	2.0
soil P	0.3	0.9	0.3	14.6	16.1
soil H	0.6	2.3	0.3	11.4	14.6

airstrip 1 showed arsenic concentrations greater than background levels (~5 μg/L), yet only inorganic arsenic species were present. Such findings coincide more closely with the deionized water and nitric acid soil extracts than the precipitation surface puddle or the phosphate soil extract. These results possibly indicate complex sorption and/or transformation processes are involved in the natural systems that cannot be exactly duplicated in these simple laboratory experiments.

Extracts of soil samples collected from three Arkansas cotton fields where DMA or MMA or both have been applied historically were analyzed to further investigate the persistence of methylated species in soil. The arsenic species distributions in the cotton field soil extracts were similar to those measured in the extracts of the airstrip 1 soil (see **Table 2**). However, total arsenic concentrations in the extracts of the field soil were lower than those in the airstrip soil. As with the airstrip soil, inorganic arsenic species generally predominated over the methylated species except in soil H, in which a substantial amount of MMA was seen in the phosphate and nitric acid extracts. Soil W was collected from a field that has not grown cotton for more than 10 years and, therefore, could represent a location where natural leaching has lowered the anthropogenic arsenic concentration to near background levels (see **Table 2**). Additionally in **Table 2** are surface water samples collected from a fourth cotton field, again showing a predominance of organoarsenic species in natural waters.

Diffuse sources of arsenic from previous field application of DMA or MMA also can be seen in rice field drainages. An arsenic HPLC-ICP-MS chromatogram of a rice field overflow water is shown in **Figure 4**. The total arsenic concentration in this sample was ~2 μg/L. As(III) was the primary species present, with a trace amount of DMA, indicating the reducing environment of an NOM-rich rice field. The source of the DMA in this sample could either be desorption from soil particles from previous cotton production or in situ microbial methylation of the arsenic in the rice field irrigation water.

In addition to soil extractions and surface water, groundwater used for irrigation also was studied. Some irrigation wells in the area have iron concentrations >5 mg/L, a near neutral pH, and a slight odor of hydrogen sulfide, indicating a reducing environment. Within 5 m of most well discharges, the oxidation of the dissolved iron(II) is evident from the precipitation of iron-(III) oxyhydroxides. Notably, in these dynamic redox systems, measurable concentrations of As(III) and As(V) are found. This
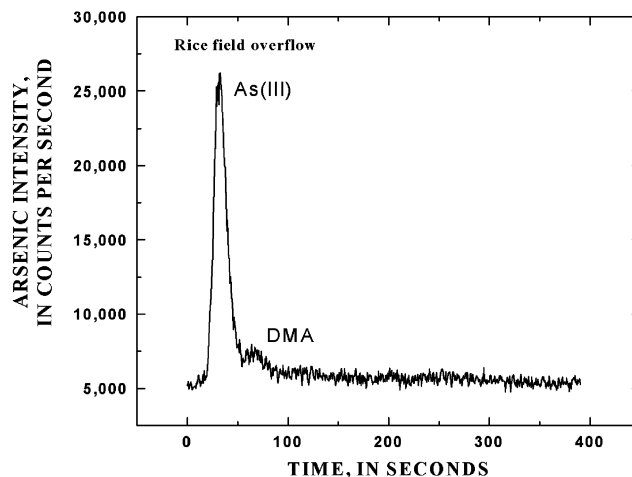

Figure 4. Arsenic HPLC-ICP-MS chromatogram of a rice field irrigation overflow water sample containing As(III) and DMA.

Table 3. Impact by a Point Source of Organoarsenic Herbicide on Total Dissolved Arsenic Concentration (in Micrograms of Arsenic per Liter) in Irrigation Groundwater as a Function of Distance (in Kilometers) from a Cropduster Airstrip

distance of well from airstrip 3	[As(T)]	distance of well from airstrip 3	[As(T)]
0.4	5.9	2.4	3.5
0.8	5.8	3.2	3.6
0.8	3.0	3.2	3.8
1.0	5.7	4.0	2.0
1.6	4.0	16.0	0.5

apparent inorganic arsenic speciation disequilibrium can be common in matrices in which a dominant redox couple does not exist or the reactions are kinetically slow (*22*). Variable As(III)/As(V) ratios, with most near 1, were found in reducing irrigation well water as well as NOM-rich, oxic surface water.

Methylated arsenicals were not found in groundwater samples, thereby suggesting that sorption or demethylation reactions in the soil affect the arsenic species during transport to groundwater. Despite the differences in arsenic speciation between the surface and groundwater samples, a direct correlation of total arsenic in groundwater can be made with distance from airstrip 3, where nearby surface water samples contain elevated arsenic concentrations, similar to airstrips 1 and 2 (see **Table 1**).

The concentration of arsenic in irrigation wells as a function of distance from airstrip 3 is listed in **Table 3**. Clearly, total dissolved arsenic concentration decreases with increased distance from airstrip 3. The total arsenic concentrations in irrigation and domestic wells not affected by cotton production range from 0.1 to 0.5 μg/L, suggesting the well at 16 km from the airstrip has a background concentration of arsenic. Land use around this well is residential and livestock pasture, which is consistent with no agricultural use of organoarsenicals. Although the arsenic concentration in some of the irrigation groundwater is greater than background levels, the concentrations are still less than the new U.S. Environmental Protection Agency MCL of 10 μg/L, suggesting that natural remediation processes are capable of controlling the anthropogenic sources of arsenic in these systems despite decades-long use of organoarsenical compounds.

This preliminary study demonstrates the impact of the agricultural use of organoarsenicals on arsenic concentration and speciation in the surrounding environment. Arsenical species

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can transform in soil systems, possibly resulting in cycling of arsenic to surface and groundwaters in close association with the soil. Results for both point sources (airstrips) and diffuse sources (field applications) indicate there is a substantial interaction among soil and surface and groundwaters that influence the fate of arsenic-containing herbicides. However, on the basis of the results presented here, the concentration of total dissolved arsenic in groundwater samples from this region has not exceeded the drinking water limit of 10 μg/L as the result of the agricultural use of organoarsenic compounds. In general, high arsenic concentrations were measured in surface water samples from both Mississippi and Arkansas during the summer months when application was most likely or dilution from precipitation least likely. Further studies involving more extensive sampling of wells, surface water, soil, and drainage ditch sediment are needed to better understand the cycling and fate of arsenic from agricultural sources.

ACKNOWLEDGMENT

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