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Analysis and Detection of the Herbicides Dimethenamid and Flufenacet and Their Sulfonic and Oxanilic Acid Degradates in Natural Water

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Dimethenamid [2-chloro-*N*-(2,4-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl)acetamide] and flufenacet [*N*-(4-fluorophenyl)-*N*-(1-methylethyl)-2-(5-(trifluoromethyl)-1,3,4-thiadiazol-2-yl)oxy] were isolated by C-18 solid-phase extraction and separated from their ethanesulfonic acid (ESA) and oxanilic acid (OXA) degradates during their elution using ethyl acetate for the parent compound, followed by methanol for the polar degradates. The parent compounds were detected using gas chromatography−mass spectrometry in selected-ion mode. The ESA and OXA degradates were detected using high-performance liquid chromatography−electrospray mass spectrometry (HPLC-ESPMS) in negative-ion mode. The method detection limits for a 123-mL sample ranged from 0.01 to 0.07 μg/L. These methods are compatible with existing methods and thus allow for analysis of 17 commonly used herbicides and 18 of their degradation compounds with one extraction. In a study of herbicide transport near the mouth of the Mississippi River during 1999 and 2000, dimethenamid and its ESA and OXA degradates were detected in surface water samples during the annual spring flushes. For flufenacet, the only detections at the study site were for the ESA degradates in samples collected at the peak of the herbicide spring flush in 2000. The low frequency of detections in surface water likely is due to dimethenamid and flufenacet being relatively new herbicides. In addition, detectable amounts of the stable degradates have not been detected in ground water.

KEYWORDS: Acetamide; dimethenamid; flufenacet; degradation compounds; analysis; mass spectrometry

INTRODUCTION

The acetamide herbicides, including acetochlor, alachlor, dimethenamid, flufenacet, and metolachlor, are an important class of herbicides in the United States and in Europe. Together with the triazine compounds, acetamide herbicides comprise the majority of pesticides applied in the midwestern United States for control of weeds in corn, soybeans, and other row crops (*1*). Some acetamide herbicides, namely, alachlor and metolachlor, have been used extensively for more than 20 years, whereas acetochlor application is relatively recent, having been applied since 1994 (*2*). In Germany, the most used acetamide herbicides are metolachlor and metazachlor.

Dimethenamid (CAS Registry No. 87674-68-8) was registered in March 1993 by Sandoz Agro (now Syngenta) (Basel, Switzerland). It is now marketed by BASF. Dimethenamid-P, the *S*-isomer, was granted registration in March 2000 under the U.S. Environmental Protection Agency's Reduced-Risk Initiative. The isomeric mixture has a maximum application rate of 1.7 kg/ha. The formulation containing only the biologically active isomer has a maximum allowed application rate of 1.1 kg/ha. Dimethenamid is primarily used on field corn (*Zea mays*), but its use has been extended to a broad variety of crops including soybean (*Glycine max*), snapbean (*Phaseolus vulgaris*), cucumber (*Cucumis sativus*), squash (*Cucurbita maxima*), sweet potato (*Ipomoea batatas*), sunflower (*Helianthus annuus*), and even wheat (*Triticum aestivum*) together with a safener that enhances glutathione-mediated detoxification (*3*).

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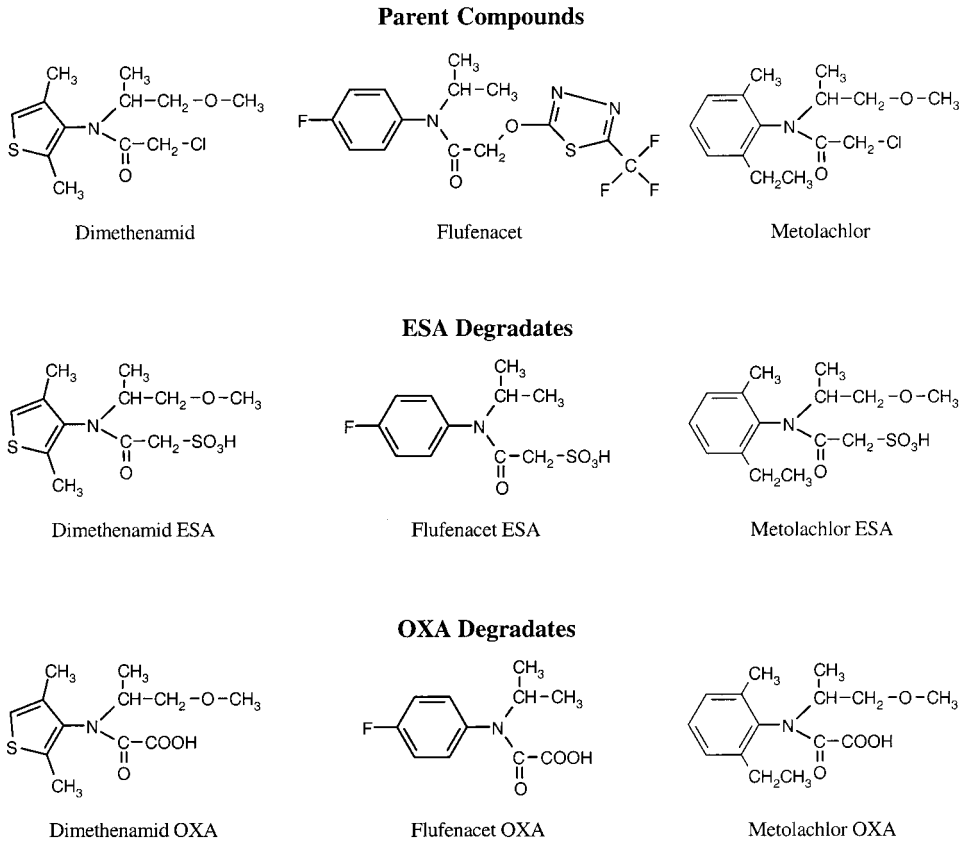

Figure 1. Chemical structures of three parent acetamide herbicides, their ethanesulfonic acid (ESA) degradates, and their oxanilic acid (OXA) degradates.

Dimethenamid use in U.S. corn production has been increasing, and during 1999 it ranked fourth in usage, behind atrazine, metolachlor, and acetochlor (*4*). Its chemical structure is closely related to that of metolachlor (**Figure 1**). Dimethenamid has a relatively high water solubility compared to other common corn herbicides. For instance, the water solubilities for acetochlor, atrazine, dimethenamid, and metolachlor are 223, 33, 1174, and 530 μg/mL, respectively (*5*). Flufenacet water solubility is 56 μg/mL (*6*). Therefore, because other herbicides with less aqueous solubility than dimethenamid are known to be mobile, dimethenamid has the potential to be mobile in the environment.

Flufenacet (CAS Registry No. 142459-58-3) received conditional registration by the U.S. EPA in April 1998 (*6*). Flufenacet is in the thiadiazole chemical family but is also an acetamide (see **Figure 1**). It is registered by Bayer Corp. (Pittsburgh, PA). The maximum use rate is 0.88 kg of flufenacet/ha per year. Flufenacet is classified as a "not likely" carcinogen on the basis of the lack of carcinogenicity in rats and mice. According to the U.S. EPA (*6*), flufenacet residues are not likely to degrade under anaerobic conditions; thus, it is possible that parent concentrations could be detected in ground water. However, Gupta et al. (*7*) reported that flufenacet is strongly adsorbed on alluvial soil and that the possibility of leaching to ground water is extremely low from laboratory studies. The U.S. EPA (*6*) also reported that data on flufenacet from surface water monitoring were lacking.

Much recent research has documented an alachlor degradation compound, alachlor ethanesulfonic acid, that commonly is found in both ground and surface water (*8*−*13*). The formation and presence of ethanesulfonic (ESA) and oxanilic acid (OXA) degradates of other acetamide herbicides, such as acetochlor and metolachlor, have been reported in studies as well (*2*, *13*−*18*). Kolpin et al. (*11*) found that degradate concentrations in ground water often exceeded parent compound concentrations for both chloroacetanilide (also acetamides) and triazine herbicides, whereas in surface water the parent compound concentrations were highest after application of herbicide in the spring and declined, relative to the concentrations of degradation compounds, throughout the growing season. By fall, the degradate concentrations exceeded concentrations of the parent compound unless fall applications were made. Kolpin et al. (*19*) reported that the ESA and OXA degradates of the acetamide herbicides alachlor and metolachlor were the four most commonly detected herbicides found in Iowa ground water from municipal wells, and Kalkhoff et al. (*17*) reported that individual ESA and OXA degradates were detected from 2 to >100 times more frequently than the parent compounds in Iowa streams. Phillips et al. (*18*) reported that concentrations of metolachlor ESA in ground water samples collected from tile drains exceeded 2−1800 times the concentrations of the parent compound and 1.5−5 times the concentrations of metolachlor OXA. The data from these studies clearly indicate that ESA and OXA are important degradation compounds of the acetamide herbicides and that the water solubility of these ionic compounds may contribute to their leaching to ground water, where the parent acetamide herbicides are rarely found.

A review by Field and Thurman (*20*) suggested that the sulfonated alachlor degradate may be the result of a glutathione conjugation process occurring in plants, algae, and terrestrial microorganisms. Additionally, it has been hypothesized that mobile sulfonated and nonsulfonated degradates of other chloroacetanilide herbicides may result from this glutathione conjugation pathway and occur in surface water (*13*).

Studies done by Heydens et al. (*21*) indicated that the ESA degradate of alachlor has negligible potential to produce adverse subchronic and developmental effects in humans. Compared to the parent compound, alachlor, the toxicity of alachlor ESA is substantially less. Alachlor ESA was not mutagenic in the Ames

assay (*22*). In a study of the oncogenic potential of alachlor ESA, Heydens et al. (*23*) concluded that their results support the judgment by the U.S. EPA Office of Pesticide Programs that alachlor ESA is not of toxicological concern. However, studies of degradates of parent herbicides are critical to understanding the fate and transport of herbicides applied to soil. For this reason, development of reliable and sensitive methods of analysis for degradates and their parent herbicides is important for studies of water quality.

To conduct a study on the distribution of dimethenamid, flufenacet, and their ESA and OXA degradates at a reasonable cost and time, simple and sensitive analytical methods are needed. There are a number of technologies that can be explored to alleviate the problems encountered in the analysis of these compounds. First is the use of solid-phase extraction (SPE) for sample preparation. SPE reduces the use of organic solvents, removes interferrents, and can be easily automated. Second is the use of liquid chromatography−mass spectrometry (LC-MS) for the mass spectral confirmation of the ESA and OXA compounds that cannot be obtained by high-performance liquid chromatography (HPLC) with diode array detection. Likewise, gas chromatography−mass spectrometry (GC-MS) can be used to obtain clean chromatograms with mass spectral confirmation for the parent compounds.

The objective of this paper is to describe the development of analytical methods for the simultaneous enrichment of parent herbicides (dimethenamid and flufenacet) and their ESA and OXA degradates and the quantification of each of these compounds in ground and surface water in a concentration range of a few nanograms per liter to micrograms per liter. This paper describes the quantification of the parent compounds by GC-MS and of the ESA and OXA degradates by LC-MS. To date, very limited research has been published on the fate of dimethenamid and flufenacet, so it is important to have robust analytical methods available for studies of their fate, particularly methods that can simultaneously detect other common herbicides and degradation products. A final objective seeks to determine if widespread ESA and OXA occurrence in water extends to the newer acetamide herbicides, dimethenamid and flufenacet.

MATERIALS AND METHODS

Reagents, Sampling, and Sample Preparation. ACS grade ethyl acetate and HPLC grade methanol were purchased from Burdick and Jackson (Muskegon, MI). Glacial acetic acid was purchased from Fisher Scientific (Pittsburgh, PA). The analyte standards for dimethenamid, dimethenamid ESA, and dimethenamid OXA were obtained from BASF (Research Triangle Park, NC). The standards for flufenacet, flufenacet ESA, and flufenacet OXA were obtained from Bayer Corp. (Stillwell, KS). A stock solution containing a suite of 24 parent herbicides and 17 degradation products was prepared in methanol. The additional herbicides and degradation products in the stock solution are included so that compounds from other classes (triazine, phenyl urea, thiocarbamate, pyridazinone, and dinitroaniline) can be performed from a single extraction.

Samples were collected in 1999 and 2000 at a site on the Mississippi River at Baton Rouge, LA. At this site, the Mississippi River drains ~41% of the conterminous United States (drainage area is 3,208,700 km^2), which includes the major corn- and soybean-growing regions. The samples were collected from the upper 6 m of the water column at the end of a pier extending ~45 m from shore. Previous work by Goolsby et al. (*24*) indicates that dissolved solutes in the Mississippi River at this Baton Rouge site are well mixed vertically and laterally, so a sample taken here should be representative of the entire cross section of the river and a composited sample, in which samples taken from the entire cross section of the river are combined, is not required. Samples were collected at least once a month between April and December of both years and more often during the times believed to correspond to the spring flush of herbicides (*25*).

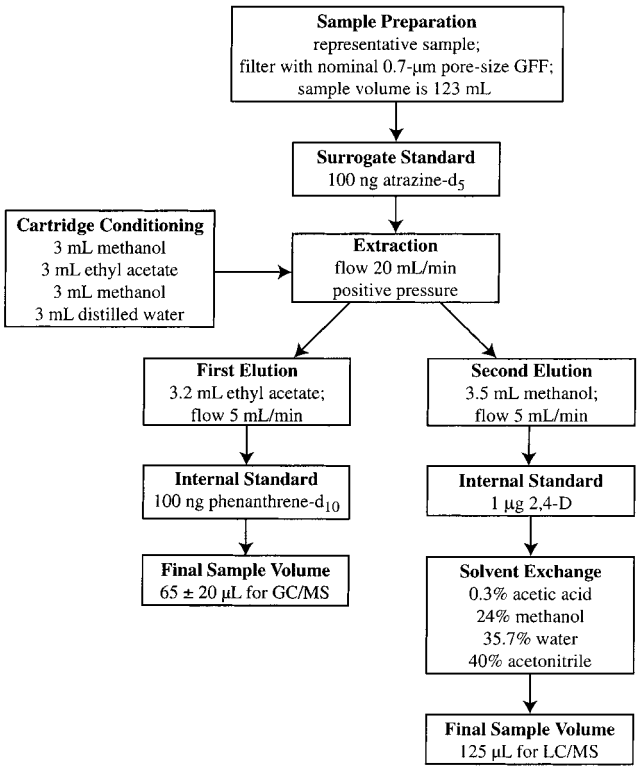

Figure 2. Schematic diagram of solid-phase extraction (SPE) procedure.

Samples were collected in glass or Teflon containers and filtered into 4 oz (123 mL) glass bottles. Glass-fiber filters (GFF) with nominal 0.7-μm pore diameters are used to remove suspended particulate matter; thus, only herbicides and degradation products that are in solution are analyzed. The samples were chilled immediately and shipped to the laboratory within 3 days of collection. At the laboratory, samples were refrigerated at 4 °C until extracted.

Sample Concentration and Preseparation by SPE. The SPE procedure is automated using a Tekmar six-position AutoTrace (Tekmar-Dohrmann, Cincinnati, OH) for conditioning the SPE cartridge, loading the sample onto the cartridge, and eluting the compounds into test tubes. The SPE cartridges (Vac C-18 6 mL) used to extract samples are obtained from Waters Corp. (Milford, MA). These vacuum cartridges contain 500 mg of endcapped, 55−105-μm, monofunctional C-18 bonded to silica.

The SPE procedure is described schematically in **Figure 2**. Each sample is fortified with a surrogate standard, atrazine-d_5, for GC-MS analysis of the parent compounds. Control samples are buffered with a 0.1 M, pH 7.0, phosphate buffer. The AutoTrace conditions each SPE cartridge by sequentially passing 3 mL of methanol, 3 mL of ethyl acetate, 3 mL of methanol, and 3 mL of distilled water through each cartridge at a flow rate of 20 mL/min by positive pressure. Then 123 mL of sample is passed through the preconditioned cartridges at a flow rate of 20 mL/min. Both the parent compounds and the anionic degradate compounds are eluted from the same SPE cartridge. In the first elution, the parent compounds and other compounds that may interfere with the LC-MS analysis are eluted with 3.2 mL of ethyl acetate. In the second elution, the ESAs and OXAs are eluted with 3.5 mL of methanol. Both elutions are performed at a flow rate of 5 mL/min. Each fraction is collected in a new 10-mL disposable, glass centrifuge tube that has been spiked with internal standard for quantitation. The first elution fraction, containing the parent compounds dimethenamid and flufenacet, uses 500 μL of 0.2 ng/μL phenanthrene-d_{10} in ethyl acetate as the internal standard, and the second fraction, containing the ESA and OXA degradates, uses 500 μL of 2.0 ng/μL 2,4-dichlorophenoxyacetic acid (2,4-D) in methanol. The internal standards are used to normalize injection volume variation, as a retention time reference, and for quantitation.

Table 1. Molecular Weights and Retention Times of the Internal Standards, Surrogate Standard, and Analytes

compound	molecular weight			retention time (min)			acquired ions (*m/z*)[a]		
	parent compound	OXA	ESA	parent compound	OXA	ESA	parent compound[a]	OXA[a]	ESA
2,4-dichlorophenoxyacetic acid (internal)	221.0			21.28			**219**, 161		
atrazine-d_5 (surrogate)	220.7			19.27			**205**, 220		
phenanthrene-d_{10} (internal)	188.2			19.55			**188**		
dimethenamid (analyte)	275.8	271.4	321.4	21.50	38.14	64.88	**154**, 230, 203	**198**, 270	**320**
flufenacet (analyte)	363.3	224.3	275.3	23.72	34.15	40.98	**151**, 211, 123	**152**, 224	**274**

[a] Bold numbers are ions used for quantification.

The first elution, containing parent compounds, is prepared for GC-MS analysis by transferring the ethyl acetate from the residual water using a disposable Pasteur pipet. Then the ethyl acetate fraction is concentrated by evaporating the solvent with a gentle nitrogen stream at 50 °C to a volume of 65 ± 20 μL. The second elution is evaporated to dryness under nitrogen in a water bath at 50 °C. The extract is reconstituted in 125 μL of a solution containing 0.3% acetic acid, 24% methanol, 35.7% water, and 40% acetonitrile and transferred to an autosampler vial containing a 0.1 mL insert for LC-MS analysis.

Separation and Detection of Parent Compounds with GC-MS. The analysis of dimethenamid and flufenacet is performed by GC-MS. The instrumental setup consists of a model 5890A GC with autosampler and a 5970A mass selective detector (MSD), all from Hewlett-Packard (now Agilent Technologies) (Palo Alto, CA). Two microliters of extract is injected in the 210 °C injector with a split time of 1 min. All compounds are separated on an HP-2 capillary column of (5%) diphenyl−(95%) dimethyl siloxane copolymer (DB5 equivalent, 12 m, 0.2 mm i.d, 0.33 μm film thickness) (Agilent) and a deactivated precolumn (5 m, 0.18-mm i.d.) (Restek, Bellefonte, PA) with the following temperature program: initial temperature of 60 °C for 1 min; temperature gradient of 5 °C/min to 210 °C, which is held for 2 min, followed by a gradient of 30 °C/min to 250 °C, which is held for 1 min. Full-scan spectra are acquired to select two or three major ions per compound for single-ion monitoring. After it is established that there are no overlapping peaks or matrix effects from natural water samples, the ion with the highest abundance (base peak) for each compound is used for identification and quantification with the detector operating in selected-ion monitoring mode (see **Table 1**).

The source of the mass spectrometer is held at 250 °C. The emission current is 70 eV. The electron multiplier is set at 400 V above autotune. The filament and multiplier are turned on at 4 min into the analysis. A dwell time of 25 ms is used while as many as 11 selected ions are monitored. An autotune using perfluorotributylamine is performed daily prior to the analysis of samples.

A calibration curve is prepared on the basis of the ratio of the base peak's area relative to the area of the 188 (amu) ion of phenanthrene-d_{10}, the internal standard. Confirmation of dimethenamid and flufenacet is based on the presence of the confirming ions and the ratio of area of the major confirming ions (see **Table 1**) to base peak ions within ±20% and a retention time match of ±0.2% relative to phenanthrene-d_{10}. Recovery of the surrogate compounds must be within ±10% relative to the average recovery determined in the three control samples that are run with each sample set for acceptable recovery. In addition, a duplicate sample is run with each sample set (approximately eight samples) for quality assurance.

Separation and Detection of ESA and OXA Degradation Compounds with LC-MS. The analysis of dimethenamid and flufenacet ESA and OXA is performed on an LC-MS. The instrumental setup consists of a model 1100A GC HPLC with autoinjector and MS detector, all from Hewlett-Packard (now Agilent Technologies) (Palo Alto, CA). A 10 μL injection of sample extract is made. The LC uses two Phenomenex (Torrance, CA) 5 μm, 250 × 3 mm, C-18 columns coupled to one Phenomenex 3 μm, 150 × 2.0 mm, C-18 column to separate the degradation products. The column compartment is held at a constant 65 °C. The mobile phase solution of 0.3% acetic acid, 24% methanol, 35.7% distilled water, and 40% acetonitrile solution is delivered at a flow rate of 0.37 mL/min.

The mass selective detector is operated in electrospray (ES) in negative-ion mode. The drying gas temperature is 300 °C, and its flow is set at 9 L/min. The nebulizer gas pressure is set at 207 kPa, the fragmentor voltage is set at 70 V, and the capillary voltage is set at 3100 V. Compounds eluting from the liquid chromatograph are identified by comparing the retention times of the mass spectral signals against the measurement of standards and control samples analyzed using the same conditions. Compounds are identified further by selected fragment ions for compounds that produce fragment ions. The concentration of each identified compound is measured by relating the mass selective detector response produced by that compound to the MS response produced by the internal standard to primary standards analyzed using the same method. The linear quantitation range is 0.02−5.0 μg/L.

Calibration. For the data presented in this paper, linear calibration curves for GC-MS were developed using a stock solution containing 41 herbicides and degradation products prepared in methanol each at a concentration of 1.23 ng/μL. A similar stock solution was made for analysis by LC-MS with 10 degradates at 1.23 ng/μL in methanol. An internal calibration curve in distilled water and an external standard curve were used for GC-MS and LC-MS, respectively, and analyzed interspersed with the samples. A range of concentrations equivalent to 0.05−5.0 μg/L of starting water sample (prior to SPE) was used.

Determination of Extraction Recoveries and Method Detection Limits. For the determination of extraction recovery for the parent compounds, solvent extracts derived with and without SPE were compared. Five replicate samples of buffered distilled water fortified at 1.0 μg/L were analyzed with SPE/GC-MS. The ratio of compound to internal standard was made for each replicate sample and the mean determined. Similarly, five replicate samples of a solvent solution fortified with the same mass of parent compounds were prepared and analyzed by direct injection into the GC-MS. The ratio of compound to internal standard was made for each replicate sample and the mean determined. Finally, the mean value determined with SPE/GC-MS was divided by the mean value determined by direct injection into the GC-MS to calculate extraction recovery.

For the determination of extraction recoveries for the degradation compounds, eight replicate samples of buffered distilled water fortified at 1.0 μg/L were analyzed using the SPE/LC-MS method described and calculated against an external standard curve.

For the determination of method detection limits (MDLs), eight buffered distilled water samples were spiked at 0.05 μg/L with a stock solution containing the entire set of 24 parent herbicides and 17 degradation products prepared in methanol. These fortified samples then were extracted and analyzed using the methods described. The mean and standard deviations of the concentrations detected were used to calculate MDLs. These were calculated using the method described by the U.S. EPA (*26*).

RESULTS AND DISCUSSION

Solid-Phase Extraction. The sequential elution used to separate parent compounds from their polar degradation compounds described here is an improved version of that first described by Aga et al. (*9*). The improvements consist of (1) the addition of four new parent compounds (acetochlor, dimethenamid, flufenacet, and metolachlor) and nine additional degradation compounds (acetochlor ESA, acetochlor OXA, alachlor OXA, dimethenamid ESA, dimethenamid OXA, flufenacet ESA, flufenacet OXA, metolachlor ESA, and metolachlor

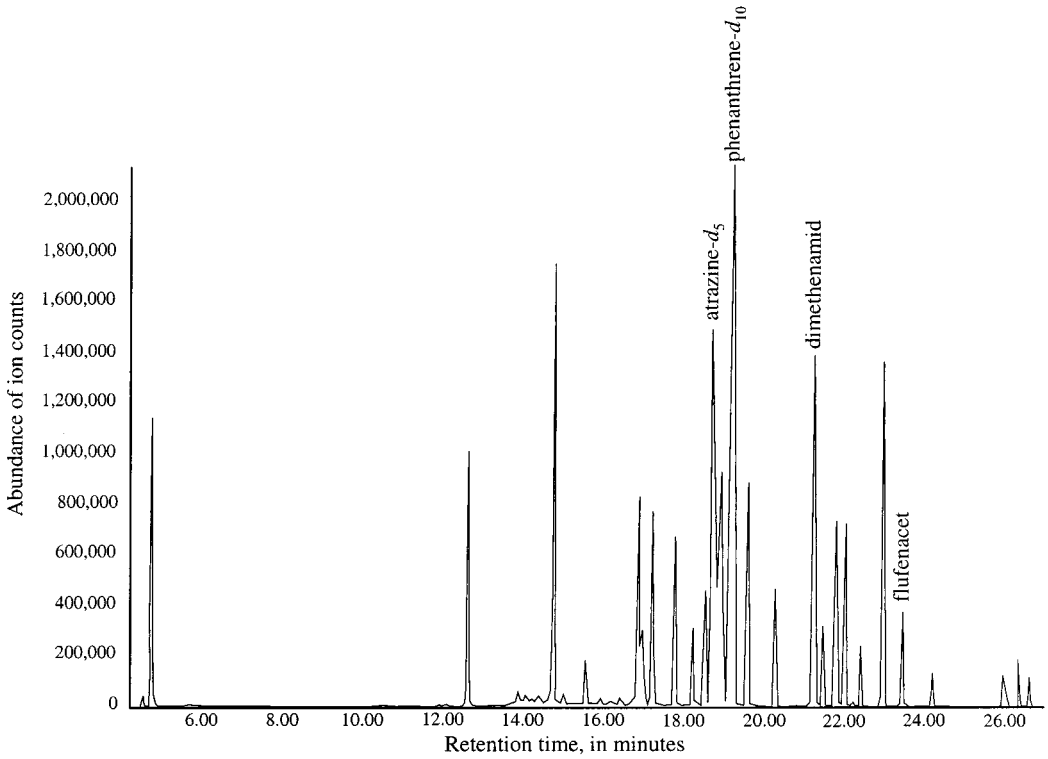

Figure 3. Example total-ion chromatogram of a 1.0 μg/L fortified surface-water sample. The large unlabeled peaks are the other 15 parent herbicides and 8 degradation products in the standard stock solution as determined by the SPE/GC-MS method.

OXA), (2) automation using an AutoTrace, and (3) the addition of buffer to the control samples (deionized water).

The SPE automation using an AutoTrace decreases the opportunity for technician error and exposure to solvents. The addition of 0.5 mL of 0.1 M phosphate buffer, pH 7.0, to the control samples (deionized water) increases the reproducibility and recovery of flufenacet ESA and OXA during the extraction procedure. This step either improves recoveries or has no effect on the recoveries of the other analytes and better represents the matrix of surface and ground water samples.

The SPE method described allows for the isolation of a parent compound fraction as well as a degradate fraction from one water sample. The trace enrichment, from 123 mL to ~75 μL, enables low-level detection. Finally, the sequencing of eluates in this SPE method contributes to the removal of interferences that would otherwise shorten the life of both the GC and LC or, worse, interfere with analyte identification. Chlorinated solvents, such as methylene chloride, are not used in this procedure as it is in other methods (*27*) that fractionate the parent compound, ESA degradate, and OXA degradate from one sample.

Analysis of Parent Compounds by SPE/GC-MS. Figure 3 shows a total-ion chromatogram of fortified surface water that was acquired using the method described herein. The large unlabeled peaks are the other 15 parent herbicides and 8 degradation products in the standard stock solution that were determined using SPE/GC-MS. The acquired ions for quantification and confirmation of dimethenamid and flufenacet and the corresponding retention times are given in **Table 1**. These ions were determined from scans of individual standards of each compound and represent the most abundant ions with an m/z >100. Where there are coeluting peaks, there is complete separation of the ions acquired by the mass spectrometer detector (data not shown). The use of SPE/GC-MS for analysis of parent herbicides is adapted from that originally described by Thurman et al. (*28*). The current (2001) method appears in Kish et al. (*29*).

Analysis of Degradation Products by HPLC-ES/MS in Negative-Ion Mode. Figure 4 is a total-ion chromatogram of a ground water sample fortified with 10 acetamide degradates and acquired using HPLC-ES/MS following SPE. A surface water sample's total-ion chromatogram is similar (data not shown) because the ions are acquired in selected-ion mode and because the color of the relatively clear SPE extracts indicates that some of the natural organic compounds from the sample have been removed by the successive elutions. A ground water sample is used in **Figure 4** because ground water is the matrix most commonly analyzed for ESA and OXA degradation products. Where there are coeluting peaks, there is separation of the ions acquired by the mass spectrometer detector (data not shown).

In each case, the base peak ion for the ESA degradation compound is the deprotonated molecular ion [$(M - H)^-$] (see **Table 1**). This agrees with the work by Ferrer et al. (*30*) and Vargo (*31*), who showed analogous base peak ions for the ESA degradates of other amide herbicides. Two ions are monitored for each of the OXA degradates. In the case of dimethenamid OXA, the base peak ion comes from the fragmentation that occurs between the alkyl side chain and the amide nitrogen, giving the base peak of mass 198. This is analogous to the metolachlor OXA base peak (*30*). For flufenacet OXA, the fragmentation giving rise to the base peak ion is between the oxoacetic acid group and the amide nitrogen, resulting in a mass of 152. The confirming ions for both dimethenamid OXA and flufenacet OXA are the molecular ions. Use of SPE/HPLC-ESP/MS for the analysis of dimethenamid and flufenacet ESA and OXA is adapted from that originally described by Hostetler and Thurman (*32*). The current (2001) method appears in Lee et al. (*33*).

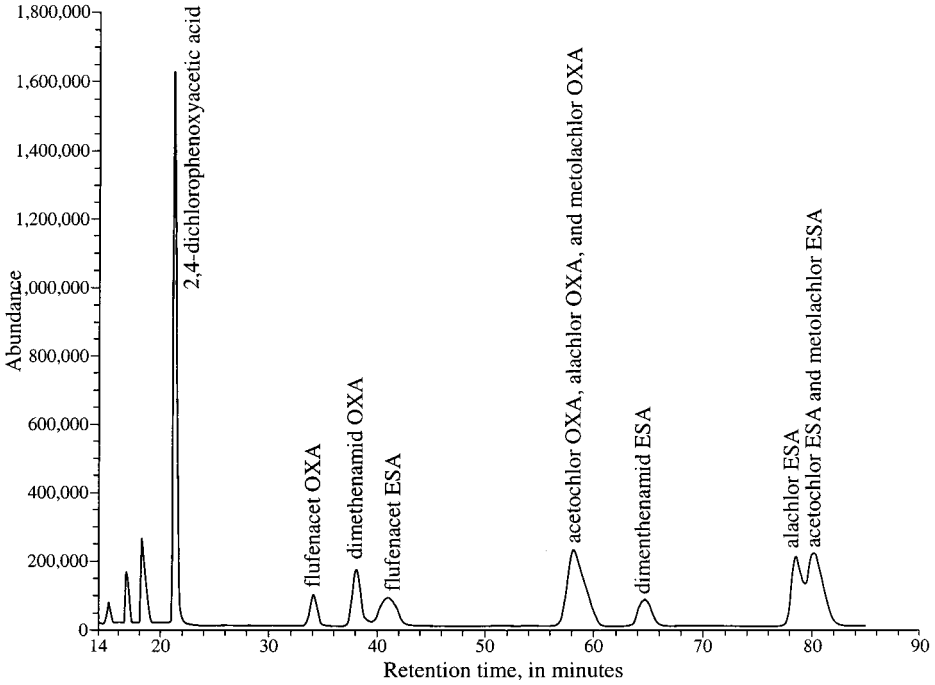

Figure 4. Total-ion chromatogram of a ground-water sample fortified with 1.0 μg/L of degradation products and analyzed using the SPE/LC-MS method.

Table 2. Mean Extraction Recoveries from Reagent Water

compound	mean extraction recovery (%)	compound	mean extraction recovery (%)
dimethenamid	107	flufenacet	103
dimethenamid ESA	97	flufenacet ESA	95
dimethenamid OXA	98	flufenacet OXA	76

Table 3. Method Detection Limits (MDL) Based on Eight Replicate Samples of Buffered Reagent Water Fortified at 0.05 μg/L

compound	mean obsd concn (μg/L)	SD	MDL (μg/L)
dimethenamid	0.05	0.01	0.02
dimethenamid ESA	0.05	0.01	0.03
dimethenamid OXA	0.06	0.01	0.02
flufenacet	0.05	0.01	0.04
flufenacet ESA	0.06	0.00	0.01
flufenacet OXA	0.05	0.02	0.07

Extraction Recoveries and Method Detection Limits. The mean recovery of dimethenamid was 107%, and the mean recovery of flufenacet was 103% (**Table 2**). All four degradates had recoveries $\geq$95% except for flufenacet OXA, which had a mean recovery of only 76% (**Table 2**). All compounds had low MDLs (**Table 3**), with flufenacet OXA having the highest MDL (0.072 μg/L).

Results from Surface and Ground Water Samples. Forty samples collected from the Mississippi River at Baton Rouge, LA, between April 1999 and December 2000 were analyzed by the SPE/GC-MS method described. However, only 35 samples were analyzed for the degradates using the SPE/LC-MS method described because the method for the degradation compounds had not been developed before the sample was depleted. Fifty-three percent of the samples contained dimethenamid concentrations greater than the MDL (0.016 μg/L), and 28% of the samples contained concentrations greater than the method reporting limit (MRL, 0.05 μg/L) (**Figure 5**). For comparison, metolachlor, the most extensively used amide herbicide, was detected in 50% of the same samples at a concentration greater than the MRL (0.05 μg/L). The highest concentrations were found in samples collected in May through August. This seasonal pattern has been observed in many streams of the Mississippi River Basin and is known as the spring flush (*25*). Flufenacet was not detected in any of the samples from the Mississippi River at Baton Rouge, LA.

Dimethenamid ESA and OXA were detected in 11 and 14% of the samples, respectively, at concentrations greater than the MRL (0.05 μg/L). If all detections greater than the MDLs were considered, the rate of detection would be 29% for both compounds. Flufenacet ESA and OXA were never detected at concentrations greater than the MRL. However, two samples (6%) contained flufenacet ESA concentrations greater than the MDL. For comparison, metolachlor ESA and OXA were detected in 100 and 94% of the samples, respectively, at concentrations greater than the MRL (0.05 μg/L).

Median concentrations of dimethenamid, dimethenamid ESA, and dimethenamid OXA were 0.05, 0.04, and 0.05 μg/L, respectively. Median concentrations of flufenacet, flufenacet ESA, and flufenacet OXA were nondetected, 0.03 μg/L, and nondetected, respectively. Median concentrations of metolachlor, metolachlor ESA, and metolachlor OXA were 0.23, 0.34, and 0.17 μg/L, respectively.

Data provided by the National Agricultural Statistics Service (NASS) of the U.S. Department of Agriculture (*4*) were used to determine dimethenamid usage on corn (by weight) as a percentage of metolachlor's usage. There were four states that had data for both herbicides. These were Iowa, Illinois, Indiana, and Minnesota. There were no data available in the NASS report for flufenacet. From the USDA data (*4*), it was determined that dimethenamid usage was 31% of metolachlor's by weight. Despite being used about one-third as much and having a water solubility more than twice metolachlor's, dimethenamid was detected about half as often as metolachlor and at $\sim$25% the mean concentration.

The SPE/GC-MS and SPE/LC-MS methods described herein are compatible with existing methods and provide for the simultaneous enrichment of parent herbicides (dimethenamid and flufenacet) and their ESA and OXA degradates from one

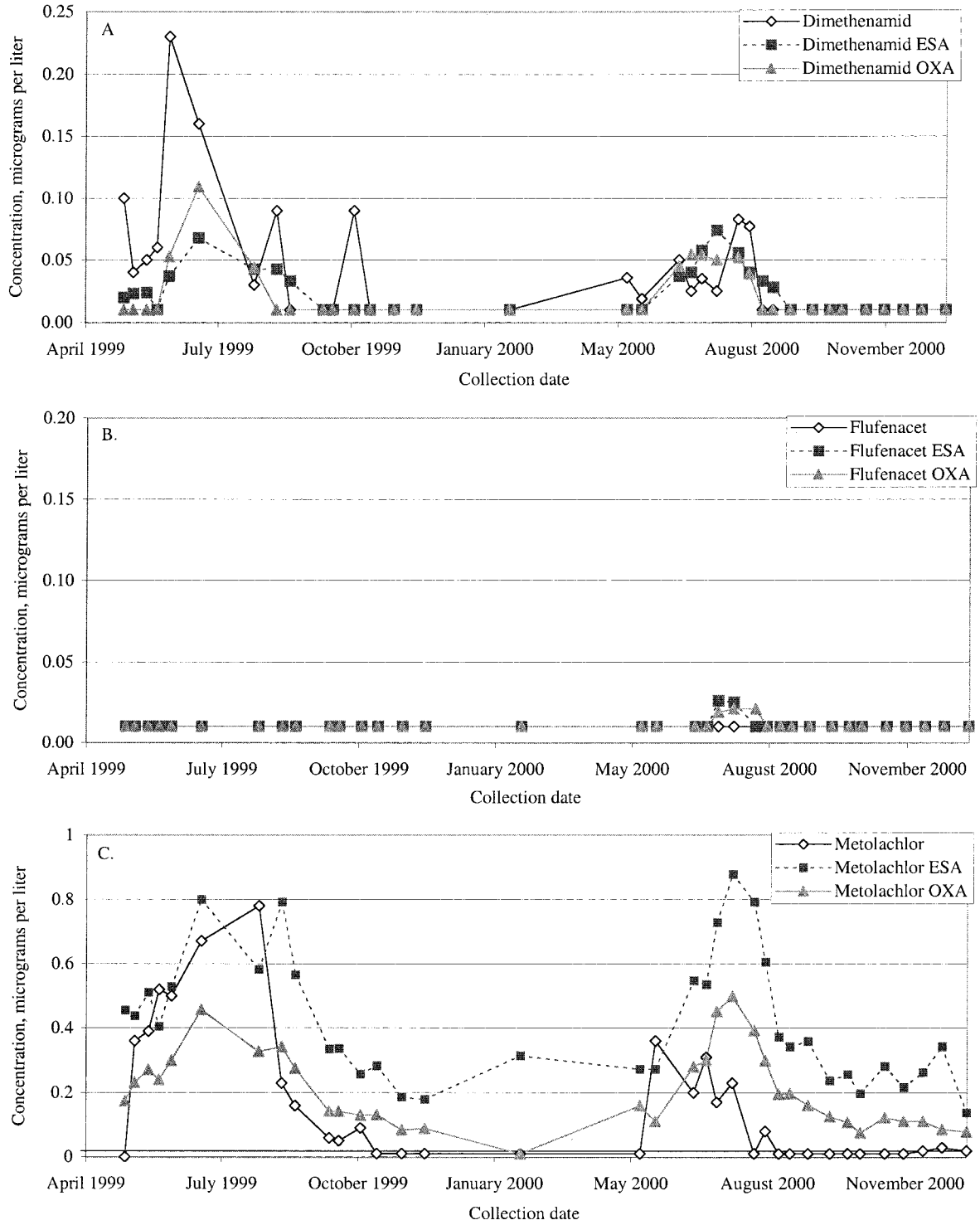

Figure 5. Graphs of surface-water concentrations detected at Baton Rouge, LA, for (A) dimethenamid, dimethenamid ESA, and dimethenamid OXA; (B) flufenacet, flufenacet ESA, and flufenacet OXA; and (C) metolachlor, metolachlor ESA, and metolachlor OXA.

sample along with other common herbicides and degradation products. Initial data from Mississippi River samples indicate that MDLs at low levels are suitable for fate and water-quality studies of natural water. Finally, ESA and OXA degradates of the relatively new acetamide herbicide, dimethenamid, were detected, but only a trace of flufenacet or its degradates was detected.

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