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Analytical Method for the Determination of Metolachlor, Acetochlor, Alachlor, Dimethenamid, and Their Corresponding Ethanesulfonic and Oxanillic Acid Degradates in Water Using SPE and LC/ESI-MS/MS

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A Good Laboratory Practices (GLP) validated, multiresidue analytical method is presented for the determination of the chloroacetanilide herbicides metolachlor, acetochlor, and alachlor, the chloroacetamide herbicide dimethenamid, and their respective ethanesulfonic (ESA) and oxanillic (OA) acid degradates in ground and surface water. A 50-mL water sample is subjected to purification using a C-18 SPE column. The four parent components and their eight ESA and OA degradates are isolated using 80/20 methanol/water (v/v) for elution. The eluate is reduced to <1.0 mL and reconstituted in 10/90 acetonitrile/water (v/v) to the desired final fraction volume. Final analysis is accomplished using liquid chromatography/electrospray ionization-mass spectrometry/mass spectrometry in the + (parent compounds) and − (ESA and OA degradates) ion modes by monitoring appropriate precursor/product ion pairs for each of the 12 analytes. The method limit of quantification is 0.10 ppb and the limit of detection is 0.125 ng injected for each analyte. Average procedural recovery data range from 95 to 105% for fortification levels of 0.10−100 ppb. The method validation study was performed following GLP guidelines.

Metolachlor, acetochlor, and alachlor (chloroacetanilides) and dimethenamid (chloroacetamide) are important herbicides used on farmland for the control of broadleaf weeds and annual grasses in row crops: primarily corn, soybean, and sorghum. They undergo transformation in the environment to form the corresponding ethanesulfonic (ESA) acids, oxanillic (OA) acids, and other degradates.[1,2] There is some evidence that these compounds might migrate into ground and surface waters due to their solubility and mobility,[3−5] and their detection in water samples[6−11] is addressed in several recent reports. Several studies have been done with certain ESA and OA degradates that show differential toxicity between the acids and their parent compounds.[12] Their chemical names and CAS numbers are listed in Table 1, and their chemical structures are shown in Figure 1.

To conduct comprehensive water-monitoring studies, a Good Laboratory Practice (GLP) validated analytical method is needed that provides accurate quantification and reliable identification of these 12 compounds in ground and surface water samples at the sub-ppb concentration level. Previously reported methods lack the required selectivity,[13,14] do not include the parent or OA degradates in the analysis,[15] or rely on derivitization for GC/MS analysis.[16] Nor does the GC/MS method include dimethenamid and its degradates. Immunoassay techniques are single-analyte procedures that are hindered by cross-reactivity issues and lack mass spectral confirmatory evidence for analyte identification.[17] Method validation following GLP guidelines[18] is not mentioned in any of these reports.

In this GLP method validation study, ground (well), surface (lake), and laboratory-deionized water samples were fortified with the 12 analytes at concentrations ranging from 0.10 to 100 ppb and subjected to purification using C-18 solid-phase extraction (SPE) columns. Final analysis was accomplished using liquid

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Table 1. Common and CAS Names and CAS Registry Numbers

common name	CAS name	CAS no.
metolachlor	2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)-acetamide	51218−45−2
metolachlor ESA	2-[(2-ethyl-6-methylphenyl)(2-methox-1-methylethyl)amino]-2-oxoethanesulfonic acid	171118−09−5
metolachlor OA	2-[(2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl)amino]-2-oxoacetic acid	152019−73−3
acetochlor	2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide	34256−82−1
acetochlor ESA	2-[(ethoxymethyl)(2-ethyl-6-methylphenyl)amino-2-oxoethanesulfonic acid	187022−11−3
acetochlor OA	[(ethoxymethyl)(2-ethyl-6-methylphenyl)amino]-2-oxo-acetic acid	194992−44−4
alachlor	2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide	15972−60−8
alachlor ESA	2-[(2,6-diethylphenyl)(methoxymethyl)amino]-2-oxoethanesulfonic acid	142363−53−9
alachlor OA	[(2,6-diethylphenyl)(methoxymethyl)amino]oxoacetic acid	171262−17−2
dimethenamid	2-chloro-*N*-(2,4-dimethyl-3-thienyl)-*N*-(2-methoxy-1-methylethyl)acetamide	163515−14−8
dimethenamid ESA	2-[(2,4-dimethyl-3-thienyl)(2-methoxy-1-methylethyl)amino]-2-oxo-ethanesulfonic acid	205939−58−8
dimethenamid OA	[(2,4-dimethyl-3-theinyl)(2-methoxy-1-methylethyl)amino]oxo-acetic acid	not assigned

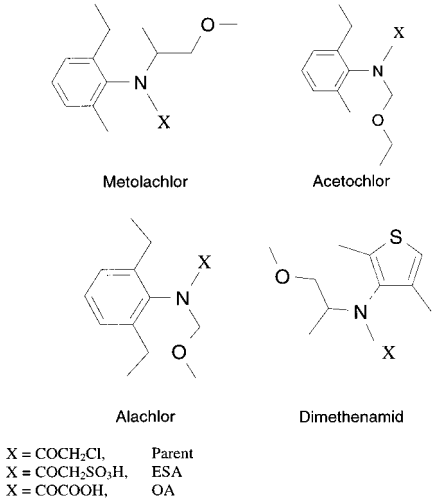

Figure 1. Chemical structures of the parent compounds and their ESA and OA degradates.

chromatography/ electrospray ionization-mass spectrometry/mass spectrometry (LC/ESI-MS/MS) by monitoring appropriate precursor/product ion pairs for each of the 12 analytes.

EXPERIMENTAL SECTION

Standards. All the parent compounds and the acetochlor ESA and alachlor ESA standards were supplied by the Analytical and Product Chemistry Department of Syngenta Crop Protection, Inc. (SCP). The metolachlor ESA, metolachlor OA, acetochlor OA, and alachlor OA standards were synthesized by the Chemistry Group of the Health Assessment and Environmental Safety Resources Department of SCP. The dimethenamid ESA and OA standards were supplied by BASF Corp., Research Triangle Park, NC. Stock solutions of the 12 compounds were prepared separately by dissolving 10.0 mg (corrected for percent purity) of standard into 100 mL of methanol. A 1.0 μg/mL mixed standard was prepared by transferring 2.5 mL of each stock solution into a 250-mL volumetric flask followed by dilution to the mark with HPLC grade water. Serial dilutions of the mixed standard were prepared in acetonitrile/water (10/90, v/v) to obtain analytical and fortification standards at the desired concentrations.

Solvents and Reagents. HPLC grade methanol (Catalog No. A452-4), acetonitrile (Catalog No. A998-4), water (Catalog No. W7-4), Certified ACS Plus phosphoric acid, 85% (Catalog No. A242-4), and acetic acid (Catalog No. A38-212) were all obtained from Fisher Scientific. All solutions were prepared on a volume/volume basis.

Solid-Phase Extraction Columns. The 500 mg/6 cm^3 capacity C-18 SPE columns were obtained from Varian (Catalog No. 1210-2052).

Water Sample Sources. The ground water was obtained from a private residence in Forsyth County, NC, utilizing well water (containing ~25 ppm hardness as $CaCO_3$), and the surface water was obtained from Lake Higgins, located in Guilford County, NC. The laboratory deionized water was obtained from a Picopure water purification system located in the laboratories of SCP, Greensboro, NC.

Sample Preparation Procedure. The C-18 SPE column was conditioned with 5 mL of methanol and then 5 mL of 0.50% phosphoric acid. A volume of 0.10 mL (2 drops) of concentrated phosphoric acid was added to a 50-mL aliquot portion of water sample (fortification at the appropriate concentration level could be done at this time, if desired, for procedural recovery purposes). The water sample was loaded onto the SPE column, initially under gravity, followed by low vacuum until a flow rate of ~3 mL/min was obtained. When all but ~1 mL of the sample had entered the SPE column, the concentration tube previously containing the water sample was rinsed with 5 mL of DI water which was then added to the SPE column. After the sample had completely entered the sorbent bed of the SPE column, the column was dried under vacuum for a minimum of 10 min. The analytes were eluted with three 2-mL portions of 80/20 methanol/water (v/v) and the eluate was collected in a 10-mL test tube. This fraction was transferred to a 50-mL concentration tube (Fisher Catalog No. 05-538-35C or equivalent) using 2-mL of methanol to rinse the 10-mL test tube. The concentration tube was precalibrated at the 1.0-mL mark. The eluate was subjected to rotary evaporation at a water bath temperature of 30 °C until the volume was reduced to ~0.50 mL (only water remaining). The sample was reconstituted to an appropriate volume using 10% acetonitrile/90% water (note that the volume required to establish the method limit of quantification (LOQ) is 1.0 mL). Caution: do not allow the sample to go to dryness. If dryness is inadvertently attained, reconstitute the residues in 1−2 mL of methanol, strongly vortex and mix, and repeat the concentration step.

Table 2. MS/MS Operating Parameters

compound	t_R[a]	MRM transition[b]	alternative product ions[c]	cone voltage	collision energy (eV)	MW
metolachlor	8.0	284.0 > 175.5	252	25	25	283.8
acetochlor	8.1	270.0 > 147.5	224	15	20	269.8
alachlor	8.1	270.0 > 161.5	238	15	20	269.8
dimethenamid	7.8	276.0 > 167.5	244	25	20	275.8
metolachlor ESA	6.7	328.0 > 79.0	121	45	30	329.1
acetochlor ESA	6.7	313.9 > 79.0	162	50	30	315.1
alachlor ESA	6.7	313.9 > 120.0	176	40	25	315.1
dimethenamid ESA	6.5	319.8 > 79.5	121	45	25	321.1
metolachlor OA	6.9	277.9 > 205.5		25	25	279.3
acetochlor OA	6.7	263.8 > 145.0		20	10	265.3
alachlor OA	6.7	263.8 > 159.5		20	10	265.3
dimethenamid OA	6.5	269.8 > 197.4		20	10	270.3

[a] This will vary slightly due to small changes in the column used and other operating parameters. [b] These are the optimized masses recorded for these ions while infusing standards of each compound during this study. The exact ion masses from instrument to instrument may vary slightly due to varying degrees of instrumental mass calibration. [c] Alternative product ions available if interferences are encountered.

Method Optimization. LC/MS/MS Instrumentation. Analysis of the final fractions was accomplished using a Micromass (Beverly, MA) Quattro II tandem mass spectrometer with a Z-Spray electrospray ionization (ESI) source and MassLynx software version 3.1. The instrumental operating parameters were as follows: capillary voltage, 3.0 kV; source temperature, 80 °C; desolvation temperature, 250 °C. Pressures: analyzer, 3.5×10^{-5} mbar; inlet, 2.5×10^{-2} mbar; collision cell, $1.5-2.0 \times 10^{-3}$ mbar (argon gas). The cone voltages, collision energies, precursor/product ion pairs, etc., for the 12 analytes are listed in Table 2. These parameters were determined during the infusion of individual 5 ng/μL standard solutions of each analyte into the ESI source at a flow rate of ~42 μL/min. Various source and mass spectrometer operating parameters were adjusted while the precursor and product ion abundances were monitored in real time. The values shown in Table 2 were selected because they were either the optimum or best compromise values to obtain the overall highest product ion abundances for each of the 12 analytes. Alternate product ions can be used by judicious choice of cone voltage and collision energy if interferences are encountered using the ions recommended here. The ESI+ mode was used for the parent compounds, and the ESI− mode was used for the ESA and OA degradates. Scanning was alternated between the + and − ion modes from 4 to 10 min during each analysis using dwell times ranging from 0.2 to 0.4 s for specific analytes.

An Agilent (Wilmington, DE) Series 1100 LC system equipped with a 2.1 × 50 mm Zorbax SB C-8 column, 5-μm particle size (Agilent Technologies, 860975-906) was used for the separation. The flow rate was 0.20 mL/min. and the column was maintained at 25 °C. Switching valves were used to route 100% of the column effluent to waste until 2 min before elution of the first analyte through 1 min after elution of the last analyte. In the interim, the column effluent was directed to the ESI source. The column effluent was not split prior to being directed to the source of the mass spectrometer since the LC flow rate was near optimum for ESI. The mobile phases were as follows: mobile phase A, 0.10% acetic acid/99.9% water; mobile phase B, 0.10% acetic acid/99.9% acetonitrile. (Note that formic acid is not routinely used in our laboratory when another acid can be suitably substituted—formic acid can inflict severe burns in a very short period of time when in contact with skin.) The LC gradient used was 10−90% B in 2 min, hold 90% B for 7 min, ramp back to 10% B in 1 min, followed by a reequilibration time period of 2 min. The injection volume was 50 μL and the t_R were typically 6.4−8.0 min for all 12 analytes (see Table 2).

Quantification. Seven analytical standards were injected at concentration levels of 0.0025−0.20 ng/μL to create a calibration plot of 0.125−10 ng injected for each analyte. The calibration standards were evenly dispersed among the samples and quality control sample injections in each analytical set sequence. The first and last injection of each set was always a calibration standard. The quality control injections were simply standards that were quantified as if they were samples but were not used in the construction of the calibration plot.

Method Validation. The samples to be analyzed for GLP protocol-driven method validation purposes were divided into six sets. Two sets of analyses each were performed for ground, surface, and deionized water. Each set consisted of a reagent blank, a water control, and fortified water control samples at the 0.10 (3), 1.0 (2), 10 (2), and 100 (2) ppb concentration levels. The nine procedural recovery samples resulted in 108 recovery values for the 12 analytes per set. Thus, a total of 648 recovery values were available from the six sets of analyses for method performance evaluation.

RESULTS AND DISCUSSION

Mass Spectrometry. The parent compounds form protonated molecular ions $(M + H)^+$ in the + ion mode and the ESA and OA degradates form deprotonated molecular ions $(M - H)^-$ in the − ion mode. These modes were selected because they produced the higher precursor ion abundances for parent and degradate compounds (e.g., the precursor ion abundance was much lower for the parent compounds when analyzed in the − ion mode). Once the operating conditions were optimized for the precursor ions, the cone voltages and collision energies were adjusted to optimize the abundance of one of the respective product ions. This high degree of selectivity negated the need to attain chromatographic resolution. If interferences are encountered using the precursor/product ion pairs recommended here, one can use alternate product ions for monitoring purposes by

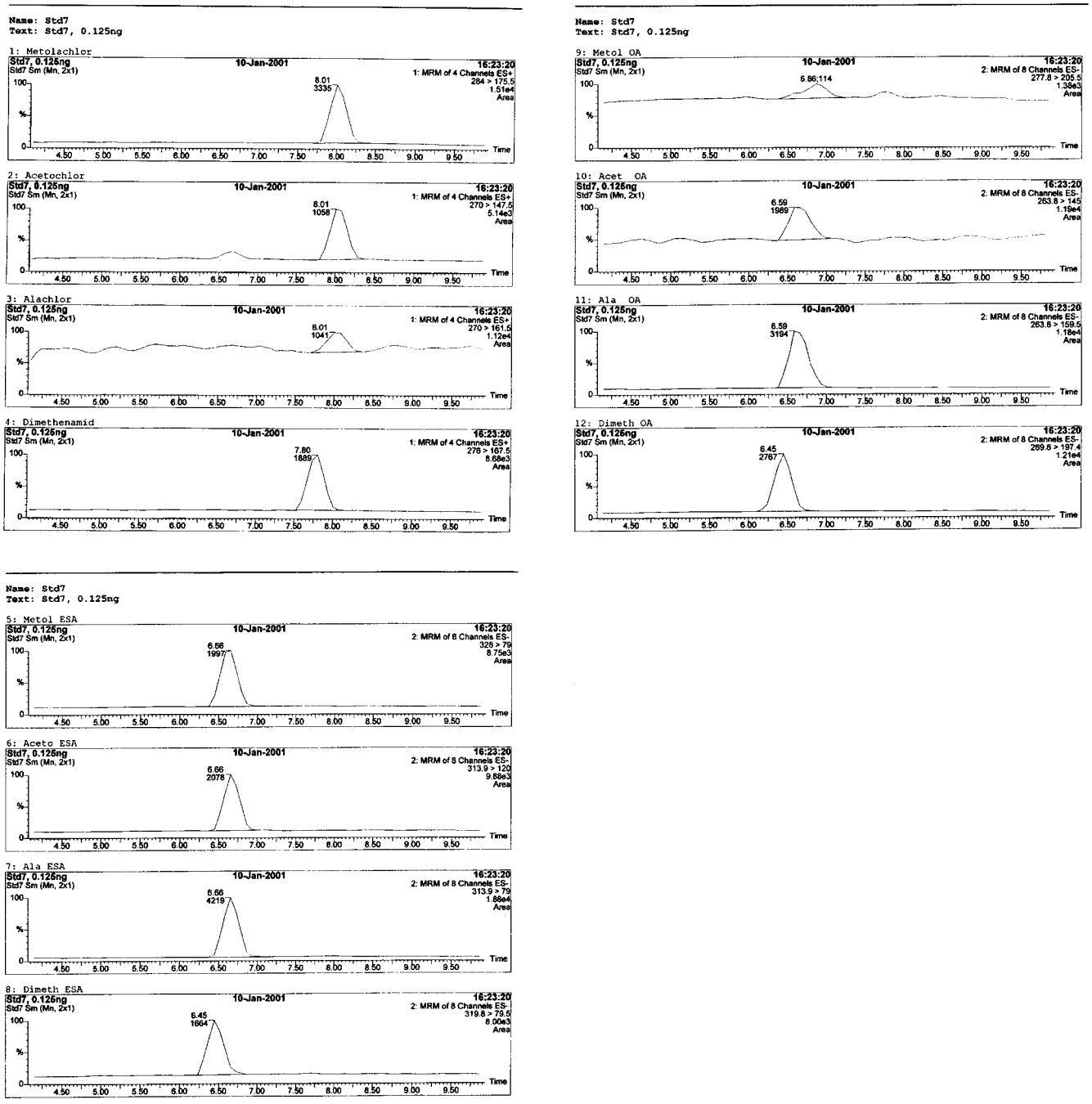

Figure 2. Representative multiple reaction monitoring chromatograms for a 0.125-ng standard injection of each analyte.

judicious choice of cone voltage and collision energy. For example, the product ion scans for the ESA degradates of acetochlor and alachlor contain both the m/z 120 and 79 ions. The unique cone voltage and collision energy for each analyte allows the analyst to maximize the abundance of ion m/z 79 for acetochlor ESA while minimizing the abundance for ion m/z 120 and, conversely, maximize the abundance of ion m/z 120 for alachlor ESA while minimizing the abundance for ion m/z 79. However, in real world samples, a sample containing a high concentration of either acetochlor ESA or alachlor ESA could result in a false-positive, low-concentration detection for the other compound. Thus, if a high concentration of one of these two analytes is detected in addition to a low-level positive detection of the other analyte, the low-level detection should be confirmed by reinjection of the sample while monitoring for the alternate product ions listed in Table 2.

Chromatography. Representative multiple reaction monitoring (MRM) chromatograms of the lowest concentration of standard injected (0.125 ng) are shown in Figure 2. Note in Figure 1 that these molecules contain chiral centers. Thus, they are composed of *R* and *S* isomers that can result in peak splitting when using long LC columns or longer t_R (the *S* form of metolachlor contains the majority of the herbicidal activity). Peak splitting was significantly suppressed in this work for all the analytes except metolachlor OA by using a relatively short 50-mm LC column. Quantification of the analytes is improved when integrating

Table 3. Summary of Procedural Recovery Data for Each Analyte at Each Fortification Level

		0.10 ppb	1.0 ppb	10.0 ppb	100 ppb
metolachlor	mean	106	99	105	98
	SD	16.2	9.9	9.1	10.5
	n	18	12	12	12
acetochlor	mean	100	94	106	93
	SD	16.4	9.0	8.7	7.6
	n	18	12	12	12
alachlor	mean	94	95	104	93
	SD	17.0	12.1	9.3	8.7
	n	18	12	12	12
dimethenamid	mean	103	102	106	99
	SD	13.0	12.7	10.4	9.2
	n	18	11	12	12
metolachlor ESA	mean	104	94	99	97
	SD	11.0	12.4	9.3	7.4
	n	18	12	12	12
acetochlor ESA	mean	97	95	101	99
	SD	16.5	15.1	8.1	9.2
	n	18	12	12	12
alachlor ESA	mean	101	95	100	97
	SD	11.5	13.5	7.5	8.0
	n	18	12	12	12
dimethenamid ESA	mean	101	96	105	100
	SD	11.7	9.8	8.5	11.8
	n	18	11	12	12
metolachlor OA	mean	101	85	94	97
	SD	19.8	10.6	8.4	13.2
	n	18	12	12	12
acetochlor OA	mean	98	98	106	104
	SD	18.6	16.3	8.2	9.5
	n	18	12	12	12
alachlor OA	mean	101	101	112	108
	SD	21.5	17.9	8.8	11.2
	n	18	12	12	12
dimethenamid OA	mean	96	94	105	103
	SD	20.3	20.1	8.1	8.6
	n	17	11	12	12

Table 4. Statistical Summary of All Procedural Recovery Data for Each Compound

		all recovery levels	minimum	maximum
metolachlor	mean	102	66	126
	SD	12.5		
	n	54		
acetochlor	mean	98	72	133
	SD	12.4		
	n	54		
alachlor	mean	96	69	132
	SD	13.3		
	n	54		
dimethenamid	mean	103	78	127
	SD	11.5		
	n	53		
metolachlor ESA	mean	99	72	128
	SD	10.8		
	n	54		
acetochlor ESA	mean	98	70	122
	SD	13.0		
	n	54		
alachlor ESA	mean	99	73	123
	SD	10.6		
	n	54		
dimethenamid ESA	mean	100	73	121
	SD	10.8		
	n	53		
metolachlor OA	mean	95	72	147
	SD	15.4		
	n	54		
acetochlor OA	mean	101	70	137
	SD	14.5		
	n	54		
alachlor OA	mean	105	57	141
	SD	16.7		
	n	54		
dimethenamid OA	mean	99	60	128
	SD	16.1		
	n	52		

symmetrical peaks. At this lowest concentration injected level, the peaks are symmetrical (except metolachlor OA) and the signal/noise ratio is >10 for all the analytes.

The parent compounds elute ~1.1 min after the more polar ESA and OA degradates, and there is essentially no separation between the ESA and OA compounds. Chromatographic resolution is not required due to the high selectivity of the MS/MS measurement. Small peaks were occasionally detected in 12 of the 72 control samples, but these were always ≪0.10 ppb and were, in most cases, barely sufficient in area for integration.

An acetonitrile/water/acetic acid mobile phase was used because the Zorbax SB-C8 column to column chromatography was very reproducible (similar peak shape and R_t). A mobile phase using methanol was also employed in the early part of this work because the R_t between the parent compounds and the ESA and OA degradates could be sufficiently increased to allow solely + ion or − ion monitoring. This increased the sensitivity of the measurement. However, the column-to-column reproducibility was very poor and method ruggedness suffered. Interestingly, the less polar parent compounds eluted from the Zorbax SB-C8 column before the more polar ESA and OA compounds when a methanol mobile phase was used. We speculate that the parent compounds interacted with the methanol in a manner that increased their polarity by forming some type of charge complex.

The calibration plots were linear and the correlation coefficients (R^2) were almost always >0.99.

Method Performance. A summary of the procedural recovery data obtained for each analyte at each fortification level is shown in Table 3. The standard deviations for each fortification level generally decreased as the fortification level concentration increased, and the mean recovery for each analyte appears to be independent of the fortification level. A summary of the procedural recovery data for each analyte at all fortification levels is shown in Table 4. The average procedural recoveries at all fortification levels ranged from 95 to 105% and the standard deviations ranged from 10.6 to 16.7%. Note that, in a GLP method validation, procedural recovery values obtained outside the usual acceptable range of 70−120% cannot be rejected unless a condition exists to explain and reject the unacceptable value (e.g., a power outage in the middle of an analysis set). In this study, 4 of the 648 recovery values were rejected due to apparent and known instrumental hardware issues. Of the 644 obtained recovery values, 49 (7.6%) were outside the range of 70−120% (the lowest was 57% for alachlor OA and the highest was 147% for metolachlor OA). Of these 49 recoveries, 11 were <70% and 38 were >120%. Thus, 92.4% of the 644 recovery values obtained in this study were between 70 and 120% with standard deviations ranging from 10.6 to 16.7% for each of the 12 analytes. This indicates a considerable degree of method accuracy and ruggedness when one considers

the analysis of 12 analytes simultaneously at a LOQ of 0.10 ppb. The recovery data obtained from the deionized, ground, and surface water samples analyzed in this study were virtually indistinguishable. Thus, matrix enhancement (or suppression) does not appear to be an issue with regard to the type of water sample[19] as was reported when more complex sample matrixes were analyzed.[20] Note that for the purposes of this study the LOQ is simply defined as the lowest fortification level studied (0.10 ppb). The limit of detection (LOD) is defined as the lowest concentration of standard injected (0.125 ng) and was used in the construction of the calibration plot. Obviously, if one chose to use more stringent definitions, the LOQ and LOD of this method could be lowered.

We now routinely add 0.5 mL of a 5% phosphoric acid solution to the water sample rather than adding 2 drops (~0.10 mL) of concentrated phosphoric acid. This increases the reproducibility of the acid addition step and avoids the possibility of unintentionally decreasing the pH to too low a value. The recoveries for the parent compounds during routine sample analysis can be adversely affected when the sample pH is adjusted to 1 or lower and appears to be due to damage to the surface of the C-18 packing material in the SPE cartridge.

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CONCLUSION

The analytical method described in this report is a valid, accurate, and rugged procedure for the determination of metolachlor, acetochlor, alachlor, dimethenamid, and their corresponding ESA and OA degradates in water at a LOQ of 0.10 ppb. An analyst can prepare a set of 10 samples in ~3 h while injection can be performed overnight. Compared to previously published procedures, this is the only reported GLP-validated analytical method applicable to the simultaneous analysis of all 12 analytes in water.

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