JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY
ARTICLE

Simultaneous Screening of Herbicide Degradation Byproducts in Water Treatment Plants Using High Performance Liquid Chromatography−Tandem Mass Spectrometry

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Currently, herbicides are widely used in various combinations at many stages of cultivation and during postharvest storage. There are increasing concerns about the public health impact of herbicide degradation byproducts that may be present in water bodies used either as drinking water or for recreational purposes. This work investigated the sulfonic acid and oxanilic acid degradation products of metolachlor, alachlor, acetochlor, and propachlor in a variety of water bodies. The objective was to develop a fast, accurate, and easy method for quantitative analysis of herbicide degradation products using liquid chromatography with tandem mass spectrometry without solid phase extraction, but performing levels of detection lower than those obtained in previous studies with solid phase extraction. This research also screened 68 water samples, both untreated source water and treated water, from 34 water treatment plants in Missouri. Finally, it examined seasonal trends in levels of those degradation products by collecting and testing samples monthly. This highly sensitive method can analyze these degradation products to low ng/L levels. The method limit of quantification ranges from 0.04 to 0.05 ppb for each analyte; and quantitative analyses show a precision with RSDs of around 0.6% to 3% in treated water and 2% to 19% in untreated source water. Concentrations of alachlor ESA, acetochlor OA, metolachlor OA, and metolachlor ESA were detected from the Missouri River and the Mississippi River water bodies in summer time. Occurrences of these compounds in treated water samples are all lower than those in the untreated source water samples.

KEYWORDS: Herbicide degradation byproduct; mass spectrometry; occurrence

INTRODUCTION

Herbicides are introduced into the environment intentionally to control certain broadleaf weed species and annual grassy weeds, barnyard grass, crabgrass, foxtails, and so on (*1*). They are primarily used on corn, soybean, peanuts, sorghum, potatoes, cotton, safflower, and woody ornamentals. The herbicides most commonly used in the State of Missouri include acetochlor, alachlor, propachlor and metolachlor, belonging to members of the chloroacetanilide herbicide chemical family. These herbicides were developed to be toxic to the target weed species or pests, but at certain levels they may also be harmful to humans, animals, or other organisms because they share a common mechanism of toxicity due to their ability to cause nasal turbinate tumors (*2*). Their high mobility in water promotes leaching from agricultural fields into ground and surface water. The transportation of herbicides in the environment depends on several factors such as application rate, rainfall, and climate (*3*). Herbicides in soil are subject to sorption as well as to several biological and chemical degradation mechanisms, and they can be transported to different parts of an environment by wind, runoff erosion, and leaching. Transport by runoff and leaching may cause contamination of surface and ground water.

Undergoing certain degradation processes, herbicides generate a complex pattern of degradation products that can be transported to ground water and streams. Aerobic microorganisms facilitate herbicide degradation in the soil, and sulfonic acid (ESA) and oxanilic acid (OA) are the two most common herbicide degradation products. Barbash (*4*) has suggested that the transformation of metolachlor to its primary degradation product (metolachlor ESA) by soil microorganisms occurs because the chlorine atom of the parent compound is displayed by glutathione and followed by the formation of ESA degradation product after different enzymatic pathways.

Both ESA and OA degradation products of herbicides have been detected more frequently and at higher concentrations than their parent compounds in surface water (*5, 6*) and ground water (*7*). These findings highlight the importance of analyzing

degradation compounds of herbicides to assess the occurrence and environmental fate of herbicides in hydrologic systems. A study of degradations in tile drain discharge from agricultural fields in central New York indicated that ESA and OA degradations can persist in agricultural soils for three or more years after application (*8*). A series of studies and reports (*9−15*) have showed that ESA and OA degradation products were more persistent and mobile than their parent compounds. These properties can lead to frequent detection and increased concentration in ground and surface water. The United States Environmental Protection Agency (U.S. EPA) Office of Drinking Water has defined drinking water quality guidelines for many parent herbicides, but guidelines for ESA and OA degradations are relatively uncommon. Only minimum reporting levels are indicated in the Unregulated Contaminant Monitoring Regulation (UCMR) published by the U.S. EPA (*16*). Studies (*17*) have shown that in the Midwest ESA and OA degradation products of herbicides were present in some ground water and were generally present more frequently than the parent compounds. Their results demonstrate that ESA and OA degradations have enormous potential to contaminate ground water since they are relatively mobile and persistent in soil.

Liquid chromatography−tandem mass spectrometry (LC/MS/MS) and gas chromatography−tandem mass spectrometry (GC/MS/MS) have become the most commonly used methods for the analysis of target herbicide degradation byproducts (HDBs) (*18−20*). To detect low-concentration HDBs, water samples are typically extracted using solid-phase extraction (SPE) before injection (*21*, *22*). However, both LC/MS/MS−SPE and GC/MS/MS−SPE are time-consuming, require high solvent volumes, and usually have low recovery rates than those methods in which no SPE is involved. The objective of the present study was to develop a fast, accurate, and easy method for quantitative analysis of herbicide degradation byproducts using LC/MS/

MS, but performing levels of detection lower than those obtained in previous studies with SPE. This research also screened 68 water samples, both untreated source water and treated water, from 34 water treatment plants in Missouri during both winter and summer. Finally, seasonal trends were examined in levels of those byproducts by collecting and testing samples monthly.

MATERIALS AND METHODS

General Reagents. All chemicals and reagents used in this study were analytical grade or better unless otherwise stated. ESA and OA degradations of metolachlor, alachlor, acetochlor, and propachlor standards were purchased from Sigma-Aldrich (St. Louis, MO). Stock solutions were prepared with methanol, and solutions of other concentrations were prepared by diluting with Milli-Q water produced with a Millipore Simplicity 185 water system (Billerica, MA). Butachlor ESA (Sigma-Aldrich, St. Louis, MO) was used as an internal standard (IS).

Standard Solutions and Quality-Control Samples. Stock solution of all HDB standards were prepared at a concentration of 10 μg/mL in Milli-Q water, and working solutions were made up at concentrations in the range from 0.1 to 500 μg/L. All standard solutions were stored at −20 °C until required, and all were stable for a minimum of 3 months. Samples used for calibration and quality-control purposes were freshly prepared prior to analysis.

LC/MS/MS Analysis. Analysis of HDBs was performed using a triple quadrupole mass spectrometer (API 4000Q TRAP) equipped with an Agilent 1100 series LC system composed of a 1100 series pump and autosampler. An automated switching valve was used between the HPLC and mass spectrometer (MS) to direct the mobile phase to the waste or MS. Amber glass sampler vials were used for all samples. The tubing used is PEEK material. The analytical column was an Agilent Hypersil ODS 2.0 × 125 mm 5 μm. The elution flow rate was 300 μL min^{-1}, and the injection volume was 10 μL. Both the autosampler and column were kept at room tempreture (∼25 °C). Separation was achieved by a gradient elution programmed as follows: 10% B for 1 min; increased to 25% B over 3 min and maintained for 6 min; then decreased to 20% B over 0.1 min and maintained for 2 min; increased to 55% B over 9 min, increased to 95% B over 0.5 min, decreased to 92% B over 1.5 min, decreased to 10% B over 0.1 min and equilibrated at 10% B for 7 min, prior to the next injection, the total running time was 30 min. Analyst 1.4 software was used to control the LC/MS/MS systems and for data analysis.

Negative electrospray ionization combined with the multiple reaction monitoring (MRM) mode was used. To select the MS/MS parameters, standards of each HDB were injected in direct-infusion mode using a syringe pump, and the declustering potential, collision energy, and collision cell exit potential were optimized for each transition. The curtain and collision gas flows were 25 L h^{-1} and medium level, and the ion spray voltage was operated at 3000 V with a source temperature of 450 °C. A dwell time of 120 ms was used per ion pair monitored. Nitrogen for the curtain and collision gas was generated by a Peak Scientific N_2 generator. Tables **2** and **3** summarize the instrumental conditions and method parameters.

Sampling Location and Schedule. Water samples were collected across the state of Missouri. Winter water samples were collected between

Table 1. Studied Compounds and Minimum Reporting Levels in UCMR by U.S. EPA

compound	CAS registry no.	MW	MRL[a] (μg/L)
metolachlor OA	152019-73-3	279.33	2.0
metolachlor ESA	171118-09-5	329.42	1.0
acetochlor OA	184992-44-4	265.30	2.0
acetochlor ESA	187022-11-3	315.39	1.0
alachlor OA	171262-17-2	265.30	2.0
alachlor ESA	142363-53-9	315.39	1.0
propachlor OA	70628-36-3	207.23	n/a
propachlor ESA	947601-88-9	257.31	n/a
butachlor ESA	n/a	357.45	n/a

[a] Minimum reporting level in UCMR by U.S. EPA.

Table 2. MS Parameters for Determination of HDBs and IS in MRM Mode

MS parameter	propachlor ESA	propachlor OA	acetochlor ESA	acetochlor OA	alachlor ESA	alachlor OA	metolachlor ESA	metolachlor OA	butachlor ESA
ion transitions	256/80	206/134	314/120	264/146	264/160	314/80	328/80	278/206	356/80
collision gas (1 h^{-1})	medium	medium	medium	medium	medium	medium	medium	medium	medium
polarity	negative	negative	negative	negative	negative	negative	negative	negative	negative
curtain gas (1 h^{-1})	25	25	25	25	25	25	25	25	25
dwell time (ms)	120	120	120	120	120	120	120	120	120
ion spay voltage (V)	−3000	−3000	−3000	−3000	−3000	−3000	−3000	−3000	−3000
heater temp (°C)	450	450	450	450	450	450	450	450	450
declustering potential (V)	−100	−10	−125	−60	−55	−60	−130	−65	−95
collision cell exit potential (V)	−5	−9	−7	−7	−5	−9	−5	−5	−13
entrance potential (V)	−10	−10	−10	−10	−10	−10	−10	−10	−10
collision energy (V)	−52	−12	−32	−16	−56	−18	−62	−16	−13

4590 *J. Agric. Food Chem.,* Vol. 58, No. 8, 2010

Cheng et al.

Table 3. LC Gradient Program for Screening Method

| time (min)	flow rate (μL min^{-1})	eluent	
		A: H$_2$O, 5 mM ammonium acetate	B: methanol, 5 mM ammonium acetate
0	300	90	10
1	300	90	10
4	300	75	25
10	300	75	25
10.1	300	80	20
12	300	80	20
21	300	45	55
21.5	300	5	95
23	300	8	92
23.1	300	90	10
30	300	90	10

February and March 2009, and summer water samples were collected between June and July 2009. A total of 68 water samples were collected from a variety of water resources, including the Missouri River, the Mississippi River, and various lake water, reservoir water, and underground wells. Both untreated source and treated water samples from each water treatment plant were analyzed. To determine whether there are seasonal trends, three river water samples were collected and analyzed monthly from February to July 2009.

Sample Collection and Storage. Water samples were collected in precleaned amber glass bottles. For tap water collection, any aerator was removed, the tap was opened, and the water was allowed to flow for about 5 min. Sample bottles were filled to just overflowing so that there was no headspace in the bottle. For river water, a large precleaned wide mouth bottle or beaker was used to collect water at a representative area. Sample bottles were filled from the container to just overflowing, sealed and placed in a cooler with ice for overnight shipment to the lab. The samples were filtered through a 0.45 μm nylon membrane filter and stored in a refrigerator until analysis at 4 °C. The analysis was completed within a week after collection (*18*).

RESULTS AND DISCUSSION

LC/MS/MS Method Validation. A total of eight HDBs were separated and detected within 30 min using this method. **Table 1** shows studied compounds, molecular mass, and minimum reporting levels (MRL). A representative MRM LC/MS/MS chromatogram of HDB standards in reagent water is shown in **Figure 1**. The first compound eluted at ~6.5 min, and the last one eluted at 24.4 min. Because alachlor OA and acetochlor OA have very similar chemical structures, it is hard to separate them at high resolution meanwhile keeping the method also working for other analytes; the same phenomenon happened for alachlor ESA and acetochlor ESA. However, the coeluting compounds can be easily differentiated by different MRM transitions and quantitations of their levels were not affected. Other HDBs were well separated chromatographically, and the peak showed very good symmetry. The precursor ion detected was the [M − H]$^-$ ion for all HDBs and the internal standard. The most abundant transition of each compound was used for quantitation. The calibration and quantification was performed on the basis of analyte/IS area ratio versus concentrations. The concentration of IS used was 5 μg/L.

In this study, the limit of detection (LOD) for each HDB was determined following the U.S. EPA standard method. Specifically, seven spike replicates were analyzed at a concentration of 2−5 times the estimated instrument detection limit, with LOD calculated as the product of the standard deviation(s) and Student's *t* (α = 0.01, df = 6). However, because the instrument is sensitive and stable, this calculated LOD was too low to achieve. Thereafter, LOD for each HDB was determined as the lowest injected standard that gave a signal-to-noise (S/N) ratio between 3 and 5. The S/N ratio was calculated by measuring the peak
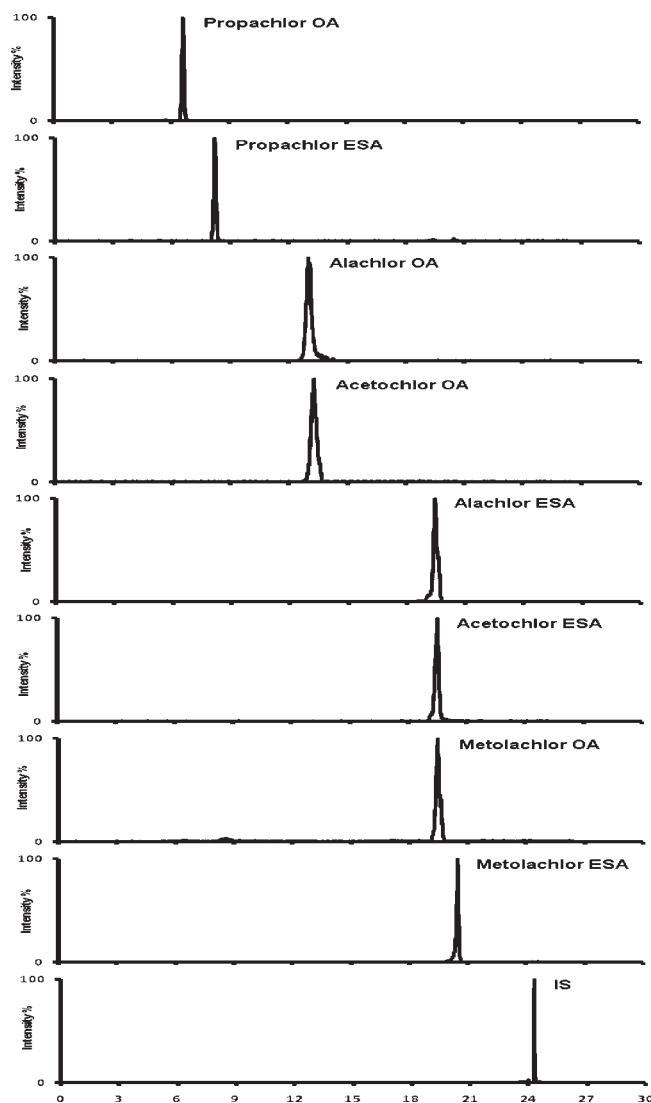
Figure 1. MRM LC/MS/MS chromatogram of HDBs in reagent water.

Table 4. The Validation Results of the Overall Method

compound	LOD (μg/L)	LOQ (μg/L)	linearity	
			range (μg/L)	R
acetochlor ESA	0.009	0.05	0.05−100	0.9978
acetochlor OA	0.009	0.05	0.05−100	1
alachlor ESA	0.007	0.04	0.05−100	0.9973
alachlor OA	0.009	0.05	0.05−100	0.9998
metolachlor ESA	0.007	0.04	0.05−100	0.9978
metolachlor OA	0.009	0.05	0.05−100	1
propachlor ESA	0.009	0.05	0.05−100	0.9995
propachlor OA	0.007	0.04	0.05−100	0.9997

height to averaged background noise ratio. The background noise was based on the peak-to-peak baseline near the analyte peak. The method LODs for this group of HDBs were between 0.007 and 0.009 μg/L in reagent water which were greatly improved compared with the LODs obtained in previous methods with SPE in which method LODs ranged from 0.008 to 0.043 μg/L (*18*). Similarly, limit of quantification (LOQ) for each HDB was obtained as the lowest injected standards that gave S/N ratio greater than 10, the method LOQ for each analyte was 0.04 or 0.05 μg/L, which are lower than those obtained by previous method with SPE in which LOQ was reported at 0.1 ppb for
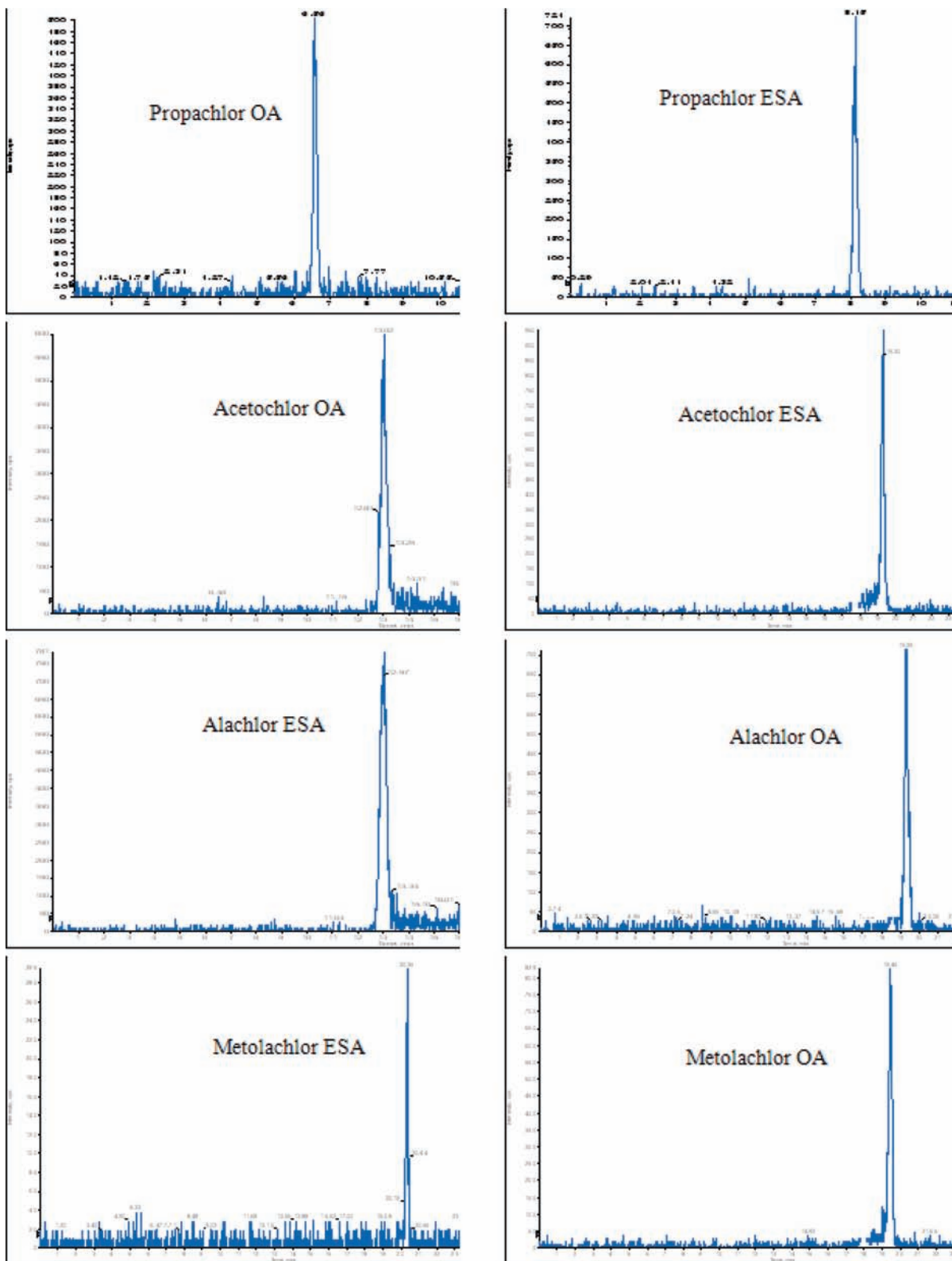
Article

J. Agric. Food Chem., Vol. 58, No. 8, 2010   **4591**

Figure 2. MRM LC/MS/MS chromatogram at a spiking concentration of 0.1 μg/L in reagent water.

those studied compounds (*19*). A six-point standard calibration curve, in concentration ranges of 0.05−100 μg/L, exhibited good linearity. The validation results of the overall method are listed in **Table 4**.

The precision of the method was evaluated by determining the relative standard deviation (RSD) of spiked samples. The RSDs were obtained from multiple (*n* = 4) analyses. For analyte-free reagent water spiked with 0.1 μg/L and 10 μg/L HDBs standards,

respectively, RSD ranged from 1.3% to 8%, with a median of 5.6%. For filtered tap water spiked with 10 μg/L HDBs standard, RSD ranged from 23.6% to 28%, with a median of 26.1%. **Figure 2** shows the MRM LC/MS/MS chromatogram at a spiking concentration of 0.1 μg/L HDBs in reagent water.

To test the method accuracy, spike recoveries for different levels of analyte spikes were conducted. The recoveries were obtained from multiple (*n* = 4) analyses. For analyte-free reagent

water spiked with 0.1 μg/L and 10 μg/L HDBs standards, respectively, spiked recoveries ranged from 92% to 103%. For filtered tap water spiked with 10 μg/L HDBs standards, spiked recoveries ranged from 77.4% to 121.9%. These recoveries are well within the commonly accepted range of 70−130% indicated in the U.S. EPA method (*18*).

Quality Assurance/Quality Control (QA/QC). To ensure precision in qualitative screening, replicate of 16% of all samples were measured. For those water samples in which HDBs were not detectable, 0.1 μg/L mixture standards was spiked in and used to calculate the RSD. Analytical accuracy for the measurements was tested by spike recoveries; 16% of all samples, containing both treated and untreated source water samples, were spiked with 0.1 μg/L HDBs standards. The recoveries indicated that the

matrix effects were acceptable. The QA/QC results in screening are listed in **Table 5**.

Occurrence Data in the Winter 2009. HDBs were not detected in all water samples collected in the winter. Analysis results showed that the concentrations in the water samples were all below limit of quantification for compounds of our interest. These results were expected, because HDBs are used primarily for agricultural purposes and thus applied in later winter or early spring. The water bodies most likely to contain HDBs were frozen in the winter time, and HDBs may not be transported to large rivers or reservoirs. Since no HDBs were detected in the winter season, 0.1 μg/L spiked samples were used to calculate the RSD and recovery. The QA/QC data in **Table 5** assured that the data was valid.

Occurrence Data in the Summer 2009. Compared with results for winter samples, some HDBs were detected in river water samples collected in the summer 2009. The HDB concentrations detected in the water samples ranged up to 0.06 μg/L; these concentrations were much lower than those indicated in UCMR. **Table 6** shows the concentrations of HDBs detected in water samples taken from June to July 2009. In untreated source water samples, the Missouri River was found containing the most kinds of HDBs, including alachlor OA (0.059 μg/L), alachlor ESA (0.04 μg/L), metolachlor ESA (0.043 μg/L), and acetochlor OA (0.055 μg/L). For the water samples collected from the Mississippi River, only acetochlor OA (0.06 μg/L) and Metolachlor ESA

Table 5. QA/QC Results in Qualitative Screening (Winter and Summer 2009)

water type	% RSD ($n = 3$)	% recovery
	February to March	
treated	0.63−3.28	91.2−121.83
untreated source	1.66−4.17	95−134.1
	June to July	
treated	0.67−2.41	104−121
untreated source	1.99−19.5	78−131

Table 6. HDB Concentrations (μg/L) Detected in Water Samples (Summer 2009)

			propachlor				alachlor				acetochlor				metolachlor			
			OA		ESA		OA		ESA		OA		ESA		OA		ESA	
ID no.	water type	treatment	T[a]	U[b]	T	U	T	U	T	U	T	U	T	U	T	U	T	U
1	Mississippi River	free chlorine	−[c]	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
2	Mississippi River	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
3	Missouri River	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
4	Missouri River	chloramines	−	−	−	−	−	0.059	−	0.04	−	0.055	−	−	−	−	−	0.043
5	ground water	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
6	ground water	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
7	deep rock wells	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
8	deep rock wells	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
9	reservoirs	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
10	reservoirs	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
11	Missouri River	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
12	Mississippi River	free chlorine	−	−	−	−	−	−	−	−	−	0.060	−	−	−	−	−	0.049
13	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
14	lake	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
15	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
16	lake	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
17	lake	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
18	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
19	deep well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
20	deep well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
21	deep well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
22	deep well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
23	unconsolidated well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
24	unconsolidated well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
25	unconsolidated well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
26	unconsolidated well	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
27	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
28	lake	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
29	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
30	reservoir	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
31	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
32	river	chloramines	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
33	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−
34	lake	free chlorine	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−	−

[a] Treated water sample. [b] Untreated source water sample. [c] Below LOQ.

Article

J. Agric. Food Chem., Vol. 58, No. 8, 2010   **4593**

(0.049 μg/L) were detected. Propachlor OA, propachlor ESA, metolachlor OA and acetochlor ESA were detected, but they were below limit of quantification. In treated water samples, concentrations of HDB compounds of our interest were all below limit of quantification, indicating that the current disinfection processes currently used in water treatment plants are effective to remove these compounds. From all of the water sample analyses, the Missouri River and Mississippi River were the two major water bodies containing HDBs. Two kinds of HDBs, acetochlor OA and metolachlor ESA, were detected in untreated source water samples from both the Missouri and Mississippi Rivers. No HDBs were detected in other water sources including deep well, reservoirs and ground water. In addition, different water treatment plants, even though the source water is the same, present different HDB occurrences because of different disinfection processes used in water treatment.

Monthly Monitoring Results. To determine whether there are seasonal patterns in the occurrence of HDBs, samples from reservoir and the Missouri and Mississippi Rivers were monitored monthly from February to June 2009. Both untreated source and treated water samples were analyzed. Analysis results showed that HDBs were detected only in water samples that collected in June 2009. The HDB concentrations in the water samples that collected in other months were all below limit of quantification for the compounds of our interests.

Conclusions. This study developed a fast and easy method for HDB analysis using LC/MS/MS with no SPE. It also screened 68 water samples, both untreated source water and treated, from 34 different water treatment plants across Missouri for HDBs. Samples were collected from several water resources, including the Missouri River, the Mississippi River, ground water, lakes, reservoirs, and wells. To study the seasonal patterns in HDB concentrations, water samples were collected and analyzed in both winter and summer. No HDBs were detected in either untreated source or treated water collected in winter (below limit of quantification). In water samples collected during the summer, concentrations of alachlor ESA, acetochlor OA, metolachlor OA, and metolachlor ESA were detected in the Missouri River and the Mississippi River. Concentrations of these compounds in treated water samples are consistently lower than those in the untreated source water samples. The seasonal monitoring data showed that alachlor ESA, acetochlor OA, metolachlor OA, and metolachlor ESA were detectable only in untreated source water samples collected in June from the Missouri River and the Mississippi River; no HDBs were detected in any water samples before summer.

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