

Determination of trace triazine and chloroacetamide herbicides in tile-fed drainage ditch water using solid-phase microextraction coupled with GC–MS

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Solid-phase microextraction methods were successfully developed to quantify low levels of herbicides in tile-fed drain water by gas chromatography–mass spectrometry.

Abstract

Solid-phase microextraction coupled with gas chromatography–mass spectrometry (SPME–GC–MS) was used to analyze two triazine (atrazine and simazine) and three chloroacetamide herbicides (acetochlor, alachlor, and metolachlor) in water samples from a midwest US agricultural drainage ditch for two growing seasons. The effects of salt concentration, sample volume, extraction time, and injection time on extraction efficiency using a 100- μm polydimethylsiloxane-coated fiber were investigated. By optimizing these parameters, ditch water detection limits of 0.5 $\mu\text{g L}^{-1}$ simazine and 0.25 $\mu\text{g L}^{-1}$ atrazine, acetochlor, alachlor, and metolachlor were achieved. The optimum salt concentration was found to be 83% NaCl, while sample volume (10 or 20 mL) negligibly affected analyte peak areas. The optimum extraction time was 40 min, and the optimum injection time was 15 min. Results indicated that atrazine levels in the ditch water exceeded the US maximum contaminant level for drinking water 12% of the time, and atrazine was the most frequently detected among studied analytes.

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1. Introduction

1.1. Solid-phase microextraction function

To most effectively predict and minimize negative off-target effects of herbicides to humans and the environment, it is necessary to monitor herbicide pollution in environmental matrices. In parts of the midwest US, herbicide transport occurs partly through a network of subsurface drainage tiles which drain into open channel ditches, producing sample matrices which have characteristics of both surface water and ground water, and may contain elevated levels of herbicides

transported primarily with surface runoff and herbicides transported primarily with subsurface drainage. Quantification of levels of herbicides in water at or below levels allowed in drinking water by regulatory agencies is necessary to protect human health. The USEPA has set the maximum contaminant levels (MCLs) for US municipal drinking water at 4, 3, and 2 $\mu\text{g L}^{-1}$ for simazine, atrazine, and alachlor, respectively. In order to achieve such low detection limits, it is usually necessary to employ analyte extraction and enrichment techniques prior to instrumental analysis. A traditional preconcentration technique, solid-phase extraction (SPE), is useful in achieving low detection limits (Balinova, 1993; Aguilar et al., 1997; Pichon and Hennion, 1994). However, SPE has the disadvantage that it requires organic solvents and a large sample volume.

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An alternative sample preparation technique, solid-phase microextraction (SPME), has been previously established (Arthur and Pawliszyn, 1990; Zhang et al., 1994). In the SPME method, a small piece of fused-silica fiber coated with a polymeric stationary phase is used to extract the analytes and to concentrate them on the fiber. The fiber/analyte is then transported to the analytical instrument for injection, separation and quantification. The SPME method has been successfully applied to the trace determination of pollutants such as pesticides (Dugay et al., 1998; Boyd-Boland and Pawliszyn, 1995; Aguilar et al., 1998; Natangelo et al., 1999; Hu et al., 2001; Hernandez et al., 2000). This technique offers several advantages over SPE, the more conventional extraction method, as it is solvent free, fast, simple to use, and requires a comparatively small volume of sample (Arthur and Pawliszyn, 1990).

Typical SPE followed by gas chromatography (GC) or GC–mass spectrometry (MS) methods requires sample volumes ranging from 200 to 1000 mL in order to detect low levels of triazine and chloroacetamide herbicides. For field and laboratory studies where volume of sample production is relatively low, or where desired time or flow resolution is high, a smaller sample volume requirement is necessary. SPME techniques followed by GC–MS allow pesticides to be quantified at low levels in aqueous samples using less than 10 mL of sample (Hu et al., 2001; Zamboni et al., 1998; Eisert and Levsen, 1995). The larger volume requirement of the SPE technique also increases the cost, time, and effort to preprocess and preserve the samples for analysis.

The SPME method has become particularly useful as a sampling method prior to GC or GC–MS analyses since it integrates sampling, extraction, concentration and sample introduction procedures into a single, rapid, sensitive, and simple solvent-free step. Since it is possible to automate SPME using readily available in-line equipment, significant labor savings can be achieved. Several factors such as fiber type, pH, ionic strength, and volume of sample, extraction and injection times and temperatures, and agitation can influence SPME efficiency. These parameters must be evaluated and adjusted during method development and are often matrix-specific.

While several different coatings are commercially accessible for SPME–GC, polydimethylsiloxane (PDMS) has been the most useful SPME coating material for volatile and semi-volatile organic chemicals (Riter et al., 2003; Krutz et al., 2003). A SPME fiber coated with 100 μm of polydimethylsiloxane has been previously shown to be effective in determining the chloroacetamide and triazine herbicide families (Krutz et al., 2003; Barnabas et al., 1995). Studies indicate that when pH is adjusted from neutral to base or to acid the extraction efficiencies of these herbicides decrease (Boyd-Boland and Pawliszyn, 1995; Ferrari et al., 1998; Nilsson et al., 1998). Salt addition is frequently used to adjust ionic strength and improve extraction efficiency and reduce the limit of detection (Eisert and Levsen, 1995; Yu et al., 2004; Dias-Cabral et al., 2003; Salleh et al., 2000), and it has been previously reported that rapid stirring of the sample proved essential to obtain acceptable equilibration times (Eisert and Levsen, 1995).

Optimal extraction times reported in the literature range from 15 to 180 min (Krutz et al., 2003), and the complete time for desorption/injection has been reported as 15 min for alachlor (Gonzalez-Barreiro et al., 2000), atrazine, and simazine (Barnabas et al., 1995). It is known that a higher extraction temperature can increase the diffusion coefficient of analytes in water, thus causing a reduction in extraction time (Yu et al., 2004).

1.2. SPME method application

The St. Joseph River Watershed, which has the primary land use of agriculture (79%), and drains 280,852 ha of land in northeast Indiana, northwest Ohio, and south central Michigan, serves as the drinking water supply for over 200,000 residents of Fort Wayne, IN. The sub-basins in the near upstream from Fort Wayne's Three Rivers Filtration Plant are largely tile-drained corn (*Zea mays*) and soybean (*Glycine max*) cropland. The Three Rivers Filtration Plant influent has a history of excessive atrazine contamination, and requires extensive treatment in order to meet the safe drinking water standard set forth by the USEPA. In order to evaluate the effects of agricultural management practices designed to minimize herbicide loading into the Fort Wayne drinking water supply, an automatic water sampling device was deployed along a second order tile-fed drainage ditch draining a 4415 ha basin to the largest tributary to the St. Joseph River, which outlets to the St. Joseph River in the near upstream of Three Rivers Filtration Plant. Samples were monitored for atrazine and other commonly used herbicides used on the predominant crops: corn and soybean in the watershed. Some typical application rates are given in Table 1. Because of high sample generation rate, especially during the early spring, short sample storage life, and limited available labor, a labor saving high throughput method of pre-concentration was required for analysis. The main objective of this work was to develop a method to determine trace amounts of commonly used corn-belt herbicides (atrazine, simazine, acetochlor, alachlor, and metolachlor) in tile-fed ditch water samples using SPME with polydimethylsiloxane-coated fiber and gas chromatography–mass spectrometry analysis.

2. Materials and methods

2.1. Reagents

Two separate standard mixtures of herbicides in methanol (mix 1 and mix 2, Crescent Chemical Co., Inc. (New York, USA), 10 $\mu\text{g mL}^{-1}$) were used in this

Table 1
Common herbicide application rates used in the study watershed

Herbicide	Typical application rate (kg/ha)	MCL ($\mu\text{g L}^{-1}$)
Atrazine	1.6	3
Simazine	1.5	4
Alachlor	1.5	2
Acetochlor	1.0	N/A
Metolachlor	2.7	N/A

study. The standard mixtures contained simazine, atrazine, acetochlor, alachlor, and metolachlor. These standards were stored at 4 °C and they were used to prepare dilute standard solutions to the required concentrations. In order to minimize inconsistent matrix effects between standards and field samples, a standard matrix designed to simulate the ditch water sample matrix was used to prepare dilute standard solution. For the standard matrix, ditch sediment was collected prior to spring herbicide applications and exposed to NANOpure water (Barnstead ultrapure water system) in 10-g 100 mL⁻¹ batches by shaking in uncovered beakers at STP for 24 h. The standards were then treated in the same manner as field samples. Blank analyses were performed to ensure that no herbicides were present in the standard matrix, laboratory reagents, or equipment.

2.2. Instrumentation

GC analyses were performed according to separation methods described within EPA method 525.2 (USEPA, 1995) using a Varian (Walnut Creek, CA, USA) CP3800 gas chromatograph equipped with a Saturn 2200 mass spectrometer. A split/splitless injector in the splitless mode was used and it was held isothermally at 270 °C. A merlin microseal high-pressure septum from Varian and an injecting port liner of 0.75 mm I.D. were used. Analytes were separated using a Varian CP5860 WCOT fused-silica capillary column of 30 m × 0.25 mm with a phase thickness of 0.25 µm, which was inserted directly into the ion trap of the mass spectrometer. The following temperature program was used: 50 °C, hold for 1 min (total time 1 min), 50–150 °C at 15 °C/min, hold for 0.5 min (total time 8.17 min), 150–250 °C at 4 °C/min, hold for 1 min (total run time 34.17 min). The gas carrier was Helium with a flow-rate of 1.0 mL min⁻¹.

The mass spectrometric detector conditions were as follows: transfer line temperature 40 °C; 70 eV electron impact; and mass range 80–300 *m/z* under full acquisition mode.

2.3. SPME procedure

The SPME auto-holder and fiber coated with 100 µm of polydimethylsiloxane were obtained from Supelco (Bellefonte, PA, USA). The fiber was conditioned prior to use as recommended by the manufacturer by heating it at 250 °C for 30 min in the GC injecting unit. The fiber was then exposed to the aqueous phase for an appropriate time period with agitation at 40 °C. After extraction, the fiber was directly exposed to the hot injector of the GC for analysis.

Because studies indicate that when pH is adjusted from neutral to base or to acid the extraction efficiencies of these chemicals decrease (Boyd-Boland and Pawliszyn, 1995; Ferrari et al., 1998; Nilsson et al., 1998) and because the unadjusted sample pH was generally neutral, neutral pH was chosen in this paper. The ionic strength of samples and standards was adjusted by adding 0.3 g mL⁻¹ sodium chloride AR-grade, purchased from Mallinckrodt Baker, Inc. (Paris, Kentucky). All standards and samples were filtered (0.45 µm) prior to analysis, and terbuthylazine (10 µg L⁻¹), purchased from Crescent Chemical Co., Inc. (New York, USA) was used as the internal standard. Both 7.5- and 20-mL samples were preliminarily analyzed in order to determine if the sample size has an impact on the response of the analytes (data not shown). The results indicated negligible effect on analyte peak areas when the sample volume was increased from 7.5 to 20 mL. Extractions were made from 7.5-mL aliquots of solutions in 10-mL glass vials sealed with hole-caps and Teflon lined septa.

The extraction time was studied by monitoring peak area counts as a function of fiber exposure time. The fiber was exposed to standard solutions with analyte concentration of 10 µg L⁻¹ and internal standard concentration of 10 µg L⁻¹ for time intervals ranging from 1 to 60 min. All extractions were performed in triplicate at a temperature of 40 °C with constant agitation. After extraction, the analytes were injected at 270 °C for 15 min.

Time required for injection was determined in triplicate by purging the fiber into the GC–MS system by thermal desorption into the GC split/splitless injector at 270 °C from 1 to 60 min. An extraction time of 40 min was used. For these experiments, we used standard solutions with analyte concentration of 5 µg L⁻¹ and internal standard concentration of 10 µg L⁻¹.

2.4. Tile-fed ditch water sampling

An automatic sampler was deployed at the outlet of the largest tile-fed drainage ditch which feeds the Cedar Creek, the largest tributary of the St. Joseph River. Daily composite samples were collected from April through October during 2004 and 2005. Fifty millilitres of ditch water was sampled every 4 h and composited into 300-mL daily samples. A 300-mL sample volume was used in order to provide enough sample for additional analysis for nutrients (not presented). Subsamples were filtered through a 45-µm filter and stored in pre-cleaned amber bottles at or below 4 °C until herbicide extraction and analysis. Water level and velocity data were collected every 10 min with a level gage and an area velocity sensor, respectively, and averaged daily to correspond with daily composite samples. Channel cross section surveys were also conducted in order to obtain flow data for calculation of flow-weighted average concentrations.

3. Results and discussion

3.1. Optimization of standard and sample preparation for SPME extraction

Matrix effects were tested by comparing analyte and internal standard peak areas from our prepared standards at 2 and 20 µg L⁻¹ with those from ditch water spiked to the same concentrations. The test analytes had been volatilized from the unspiked ditch water to a concentration below detection limit prior to spiking. Results indicate that internal standard peak areas were affected similarly to counts of most analytes, such that determined concentrations were not significantly different between matrices ($\alpha = 0.05$) (Figs. 1 and 2).

In order to test the effect of ionic strength on the SPME extraction efficiency for the analytes, preliminary tests were conducted by preparing the samples in 0–100% NaCl saturation solutions. Data from these experiments (not given) showed that addition of salt enhances the extraction for all analytes and the best effect was observed when 83% NaCl saturation (0.3 g mL⁻¹) was used. The most notable improvement was for simazine and atrazine. This result may be explained by differences in the hydrophobicity, which is lowest for simazine. Increasing the ionic strength will lower the aqueous solubility of the analyte in the solution, which consequently increases

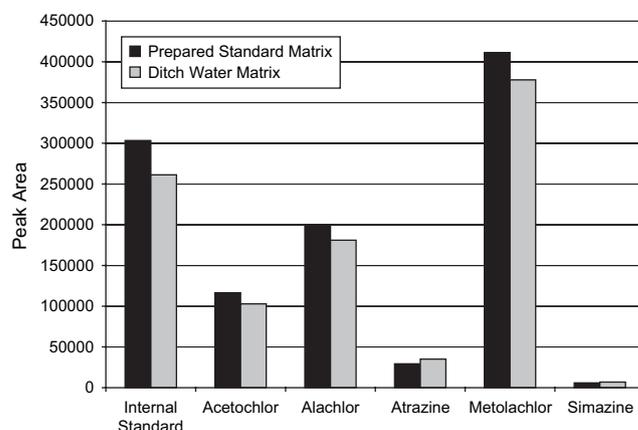


Fig. 1. Internal standard (terbuthylazine, 10 µg L⁻¹) and analyte peak areas from prepared standard matrix and ditch water matrix samples having analyte concentration = 2 µg L⁻¹.

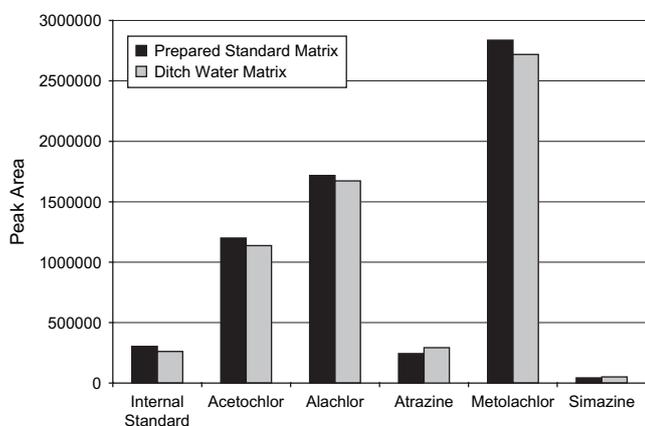


Fig. 2. Internal standard (terbutylazine, $10 \mu\text{g L}^{-1}$) and analyte peak areas from prepared standard matrix and ditch water matrix samples having analyte concentration = $20 \mu\text{g L}^{-1}$.

the partition coefficient of the SPME film. Salt addition is frequently used to improve extraction efficiency and reduce the limit of detection (Eisert and Levsen, 1995; Yu et al., 2004; Dias-Cabral et al., 2003; Salleh et al., 2000).

Increasing the sample volume was not found to result in increased peak area, so a sample volume of 7.5 mL was chosen as optimal. This volume allows SPME extraction from a 10-mL vial exposing the entire fiber, but none of the sheath to the sample.

3.2. Optimization of SPME parameters

The optimum extraction time was determined to be 40 min. The results for these tests are shown graphically in Fig. 3. It can be seen from the graph that the peak area increases with extraction time reaching a maximum at 40 min for atrazine, terbuthylazine, acetochlor, alachlor, and metolachlor, and the maximum peak area was observed at 45 min for simazine. Based on these results, an extraction time of 40 min was chosen for all compounds as the best time since it did not cause significant changes in the detection of simazine. In addition, the extraction time chosen is within the range of 15–180 min reported in the literature (Krutz et al., 2003). In contrast to the

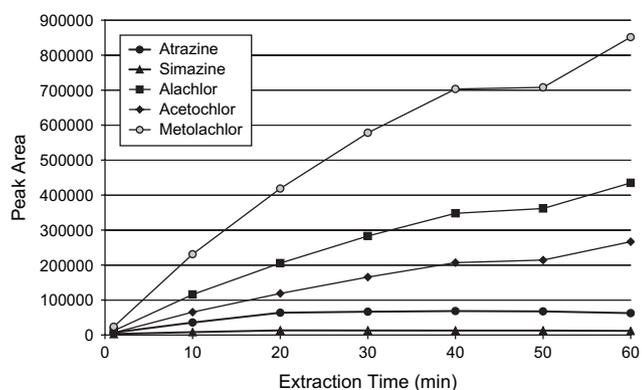


Fig. 3. Analyte peak area response to extraction time with injection time = 15 min.

finding of Ferrari et al. (1998) that increasing the extraction time only slightly improved the sensitivity of the method, we achieved greatly improved detection limits of the herbicides analyzed in this study by increasing extraction time.

After the extraction time had been optimized, the time to complete desorption of all analytes from the fiber was determined. The results of the tests are given in Fig. 4. These data indicate that the best injection time was 15 min for all compounds. These results are in agreement with the literature that reports 15 min as the complete time for desorption of alachlor (Gonzalez-Barreiro et al., 2000), atrazine, and simazine (Barnabas et al., 1995). A 1-min injection time yielded peak areas comparable to those of chromatograms gathered with an injection time of 15 min, but with much greater noise levels. In order to achieve greater signal to noise ratio, a 15-min injection time was selected as optimal.

3.3. Limits of determination

Measurements using a 40-min extraction time and a 15-min injection time with solutions ranging from 0.25 to $5.00 \mu\text{g L}^{-1}$ were performed. This concentration range was used because the US drinking water MCLs are 3, 4, and $2 \mu\text{g L}^{-1}$ for atrazine, simazine, and alachlor, respectively (Code of Federal Regulations, 2003).

The results showed that, except for simazine, all compounds were determined for solutions above $0.25 \mu\text{g L}^{-1}$. However, simazine could not be determined in the range 0.25 – $0.50 \mu\text{g L}^{-1}$.

Working with a 100- μm fiber and using an extraction time of 5 min and an injection time of 15 min, Barnabas et al. (1995) could not determine atrazine and simazine in concentrations below $1 \mu\text{g L}^{-1}$. It is believed that this was due to the short extraction time utilized in the analysis performed by these authors, which was not sufficient to extract these analytes.

3.4. Selected ion monitoring

The selected ion monitoring (SIM) mode was tested by the proposed method with an injection time of 15 min and an

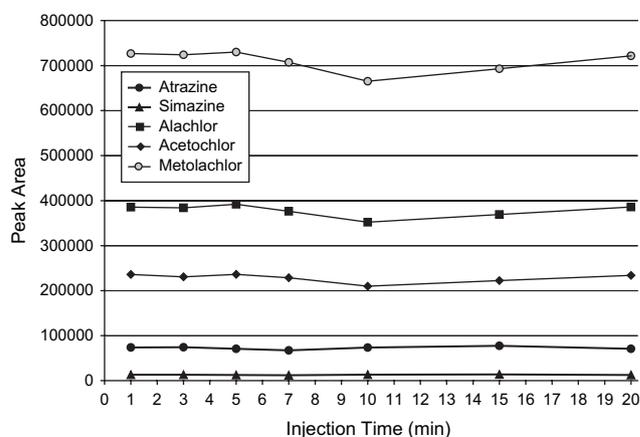


Fig. 4. Analyte peak area response to injection time with extraction time = 40 min.

Table 2
Daily composite herbicide levels in tile-fed ditch water during 2004–2005

Herbicide	Median ($\mu\text{g L}^{-1}$)	Maximum ($\mu\text{g L}^{-1}$)	Flow-weighted average ($\mu\text{g L}^{-1}$)	Time >MCL (% of total time in monitoring season)
Atrazine	0.4	49.3	3.1	12
Simazine	BDL	10.8	BDL	3
Alachlor	BDL	10.6	BDL	<1
Acetochlor	BDL	11.4	0.3	N/A
Metolachlor	0.4	22.2	1.1	N/A

BDL = below detection limit.

$n = 447$.

extraction time of 40 min. Measurements with the SIM mode on and off were made using solutions of $1 \mu\text{g L}^{-1}$ concentration for all compounds. The results showed that when the SIM mode was turned on it did not improve the results as expected.

3.5. Field herbicide findings

Levels of herbicides detected in tile-fed drainage ditch water are presented in Table 2. Most notably, flow-weighted average atrazine concentration was $3.1 \mu\text{g L}^{-1}$ and atrazine levels exceeded the MCL of $3 \mu\text{g L}^{-1}$ 12% of the time. Maximum concentrations of all herbicides having an established MCL were greater than the MCL. Atrazine concentrations as high as $49.3 \mu\text{g L}^{-1}$ were observed. Simazine concentrations exceeded the MCL of $4 \mu\text{g L}^{-1}$ 3% of the time, while alachlor concentrations rarely exceeded the MCL of $2 \mu\text{g L}^{-1}$. Relatively high concentrations of acetochlor and metolachlor were observed, although the USEPA has not yet established drinking water MCLs for these compounds. However, the lifetime metolachlor non-cancer health advisory level for a 70-kg adult is $70 \mu\text{g L}^{-1}$ (USEPA, 1999).

4. Conclusion

In this study, SPME coupled with GC–MS was used to determine triazine and chloroacetamides in aqueous samples. A fiber coated with $100 \mu\text{m}$ of polydimethylsiloxane was used and several parameters' effects on SPME were investigated. The results showed the optimized extraction conditions were: temperature 40°C , NaCl concentration 0.3 g L^{-1} , and extraction time 40 min. The optimum injection conditions of these herbicides are: temperature 270°C , time 15 min. The pH of the sample need not be adjusted before the extraction. Using these parameters, it is possible to detect $0.5 \mu\text{g L}^{-1}$ simazine and $0.25 \mu\text{g L}^{-1}$ atrazine, acetochlor, alachlor, and metolachlor.

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