Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Chromatography A, 1064 (2005) 219–226
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Determination of chloro-*s*-triazines including didealkylatrazine using solid-phase extraction coupled with gas chromatography–mass spectrometry

Hua Jiang[a], Craig D. Adams[a,*], Wayne Koffskey[b]

[a] *Environmental Research Center, Department of Civil, Architectural and Environmental Engineering, University of Missouri-Rolla, Rolla, MO 65409, USA*
[b] *Jefferson Parish Water Quality Laboratory, Jefferson, LA 70121, USA*

Received 8 June 2004; received in revised form 15 December 2004; accepted 16 December 2004
Available online 7 January 2005

Abstract

Chloro-*s*-triazines are a class of compounds comprising atrazine, simazine, propazine, cyanazine and their chlorinated metabolites. The US Environmental Protection Agency (EPA) has determined that selected chloro-*s*-triazines – atrazine, simazine, propazine, deethylatrazine, deisopropylatrazine, and didealkylatrazine – have a common mode of toxicity related to endocrine disruption. In this paper, a dual-resin solid-phase extraction (SPE) gas chromatography–mass spectrometry (GC–MS) method is reported that provides for each of these chloro-*s*-triazines including the polar metabolite, didealkylatrazine. The method utilizes deuterated internal standards for quantitation and terbuthylazine as a recovery standard. The limit-of-detection was 0.01 μg/L for simazine, deethylatrazine, deisopropylatrazine and didealkylatrazine, and 0.02 μg/L for atrazine and propazine in surface water. Mean recoveries for 0.5 and 3.0 μg/L spikes for atrazine, simazine, propazine, deethylatrazine, deisopropylatrazine and didealkylatrazine were 94, 104, 103, 110, 108 and 102%, respectively, in surface water. The method was also validated by matrix spikes into fourteen different raw and treated natural surface waters. This method is useful for monitoring "total chloro-*s*-triazines" in both raw and treated drinking waters.
© 2004 Elsevier B.V. All rights reserved.

Keywords: Chloro-*s*-triazines; Gas chromatography–mass spectrometry; Solid-phase extraction

1. Introduction

Atrazine (ATR; 2-chloro-4-ethylamino-6-isopropylamino-*s*-triazine; CAS 1912-24-9) is probably the most widely used herbicide in the world and one of the most common contaminates in ground and surface waters [1]. Atrazine is a restricted-use herbicide often used on crops including corn, sorghum and sugar cane to control broadleaf and grassy weeds worldwide. In the soil, atrazine and the related herbicides – simazine (SIM; 2-chloro-4,6-diethylamino-*s*-triazine; CAS 122-34-9) and propazine (PROP; 2-chloro-4,6-diisopropylamino-*s*-triazine; CAS 139-40-2) – degrade to deisopropylatrazine (DIA; 2-amino-4-chloro-6-ethylamino-*s*-triazine; CAS 1007-28-9) and deethylatrazine (DEA; 2-amino-4-chloro-6-isopropylamino-*s*-triazine; CAS 6190-65-4), respectively. DEA and DIA will further degrade to didealkylatrazine (DDA; 2-chloro-4,6-diamino-*s*-triazine; CAS 3397-62-4) in biologically mediated reactions in the soil and groundwater [2,3]. The current maximum contaminant level (MCL) for drinking water for atrazine and simazine are 3 and 4 μg/L, respectively. In 2002, the EPA released a document that detailed a common mode of toxicity for ATR, SIM, PROP, DEA, DIA and DDA based on endocrine disruption, specifically disruption of the hypothalamic-pituitary-gonadal (HPG) axis [4]. A new study conducted by a group of researchers suggested that atrazine induced hermaphroditism in frogs at concentrations of only 0.1 μg/L which is 30 times

* Corresponding author. Tel.: +1 573 341 4041; fax: +1 573 341 4729.
E-mail address: adams@umr.edu (C.D. Adams).

0021-9673/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.chroma.2004.12.047

lower than the current drinking water standard of 3 μg/L [5–7]. These studies, however, were suggested to be inconclusive by an EPA Scientific Advisory Panel in 2003 [8]. The EPA may promulgate a drinking water regulatory endpoint on total chloro-*s*-triazine that may trigger increased monitoring for drinking water utilities.

A variety of analytical methods are used to measure ATR, SIM and PROP using SPE combined with either GC–MS or liquid chromatography–mass spectrometry (LC–MS). Many of these methods may also be used for analysis of the mono-dealklyated metabolites DEA and DIA [3,9–15]. Few methods for drinking water, however, have been reported that allow simultaneous analysis of the parent chloro-*s*-triazines and its primary mono-dealkylated metabolites (DEA and DIA) along with the polar metabolite, DDA. One pesticide method using graphite/cation exchange mixed-mode solid-phase extraction for analysis of ATR, SIM, PROP, DEA, DIA and DDA was reported by Lin and Yokley [16]. Another method using C_{18} cation-exchange mixed-mode SPE for analysis of ATR, DEA, DIA and DDA was later reported by Huang et al. [17]. However, quantitation employed by both of these mixed-mode methods were based on external standard curves and did not contain internal standards with which to quantitate analyte concentrations. Another method reported by Carter [2] and Panshin et al. [18] uses SPE–chemical derivatization followed by GC–MS methods to analyze atrazine and three chlorinated metabolites—DEA, DIA and DDA. A liquid–liquid partitioning method followed by GC–MS was reported by Yokley and Cheung [19] that also included DDA determination. Unfortunately, both the chemical derivatization and liquid–liquid extraction of chloro-*s*-triazines can be problematic due to method complexity or waste generation considerations, respectively. A variety of other methods have also been developed for triazine analysis at low concentrations have been developed using, for example, LC–MS [20], immunoaffinity-based SPE [21], and molecularly imprinted polymers [22]. Another method has been reported that utilizes high-resolution mass spectrometry with SPE using a C_{18}-bonded cartridge [23] or a graphite–carbon cartridge [24]. While these methods allow determination of DDA, the methods use a high-resolution mass spectrometer that may not be available to many researchers. Thus, there is a need for a method that will allow simultaneous determination of ATR, SIM, PROP, DEA, DIA and DDA that uses the more traditional SPE–GC–MS approach. The purpose of this project was to develop such a method for the simultaneous analysis of ATR, SIM, PROP, DEA, DIA and DDA at sub-μg/L concentrations for natural water and treated drinking water matrices.

2. Experimental

2.1. Chemicals

Ammonium acetate and ammonium hydroxide (buffer), HPLC-grade methanol, methylene chloride and acetone were obtained from Fisher Scientific (Fair Lawn, NJ,

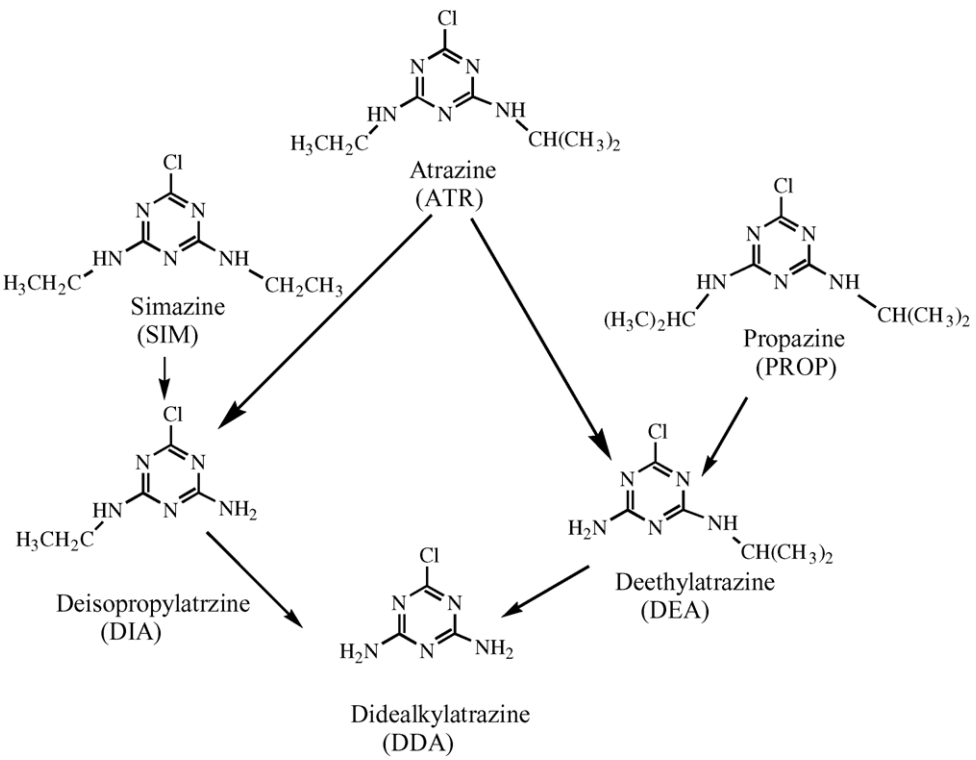

Fig. 1. Chemical structures and relative degradation pathways of study compounds.

USA). Standards of ATR, SIM, PROP, CYN, DEA, and DIA, terbuthylazine (TBUT) were obtained from Supelco (Bellefonte, PA, USA). Structures of these compounds are presented in Fig. 1. Deuterated standards – [$^2H_5$]ATR(ATR-d_5), [$^2H_6$]DEA(DEA-d_6), [$^2H_5$]SIM(SIM-d_5) and [$^2H_5$]DIA(DIA-d_5) – were obtained from EQ Labs. (Atlanta, GA, USA). Individual stock solutions of 500 mg/L ATR, PROP, TBUT, DEA, and DIA were prepared by dissolving 15.0 mg of each respective triazine in 30.0 mL of methanol. Individual stock solutions of 100 mg/L SIM and DDA were prepared for SIM and DDA by dissolving 10.0 mg of each compound into 100.0 mL of methanol. A mixed solution of deuterated triazines was prepared by diluting 100 mg/L stock solution in methanol to achieve a concentration of 9.8 mg/L of ATR-d_5 and 4.8 mg/L of other three deuterated triazines in mix solution. All stock solutions were stored in the dark at 4 °C except for the deuterated solutions which were stored at room temperature based on manufacturer's instruction.

SPE cartridges containing 150 mg of Oasis MCX were obtained from Waters (Milford, MA, USA). SPE cartridges containing 500 mg of ENVI-Carb graphite carbon black were obtained from Supelco (Bellefonte, PA, USA). Distilled (DI) water and HPLC-grade methanol were used for cartridge conditioning.

2.2. Samples

Stock solutions were used to prepare standard mixture samples in methanol with individual triazine concentrations of 0, 0.3, 0.5, 1, and 3 μg/L for the calibration curve. Raw and treated natural water samples from eight drinking water treatment plants in the United States were used to examine matrix recovery for each analyte. Each of the fourteen water samples was analyzed both unspiked and spiked with 0.5 or 2 μg/L of each of the triazines.

2.3. Solid-phase extraction

Prior to SPE, 120-mL samples were filtered using a 25-mm Whatman 0.45-μm nylon filter (Clifton, NJ, USA). After filtration, 6.0 mL of buffer was added to adjust the pH of the sample to approximately 10 immediately prior to analysis. To each sample, 50 μL of the deuterated standard stock mixed solution in methanol was added to achieve concentrations of 4 μg/L for ATR-d_5 and 2 μg/L of three other deuterated standards.

SPE was conducted using a VisiPrep 24-port manifold (Supelco, Bellefonte, PA, USA). The SPE cartridges were conditioned in tandem (MCX followed by ENVI-Carb) at a rate of approximately 60 drops per minute under a 500 mmHg vacuum (1 mmHg = 133.322 Pa) with 25 mL of methanol followed by 25 mL of DI water with care that the cartridges were not allowed to become dry. The 125-mL samples were the passed through the cartridges at a rate of approximately 60 drops per minute. After extraction of the entire sample, air was allowed to pass through the cartridges for 30 min to dry the cartridges. The cartridges were then separated and eluted individually. Both cartridges were eluted with 5 mL of methanol followed by 25 mL of methylene chloride at a rate of approximately 30 drops per minute. The extracts were combined into a 60-mL borosilicate centrifuge tube and then evaporated to dryness under a gentle nitrogen stream at 37 °C in a Zymark TurboVap (model LV Zymark; Hopkinton, MA, USA). To each vial, 200 μL of acetone and 50 μL of TBUT stock solution (as a recovery standard) were added followed by a 15-s vortex. The solution was then transferred to a 300-μL sylanized insert in a 2-mL amber vial for GC–MS analysis.

2.4. Gas chromatography–mass spectrometry

Analysis of concentrated samples was conducted using an Agilent 6893 gas chromatograph with a 5973 mass-selective detector and a 7673 autosampler (Palo Alto, CA, USA). The column used was a HP-5MS capillary column from Agilent (30 m × 0.25 mm I.D., film thickness = 0.25 μm) injected with 2 μL of sample in splitless injection mode with an injection temperature of 225 °C. High-purity helium from Airgas (Ozark, MO, USA) was used as the carrier gas at a rate of 1 mL/min. Column conditions were: inlet pressure of 84.1 kPa (101.3 kPa = 14.7 psi), total flow of 54.1 mL/min, injector purge flow of 50.0 mL/min at 0.3 min. The temper-

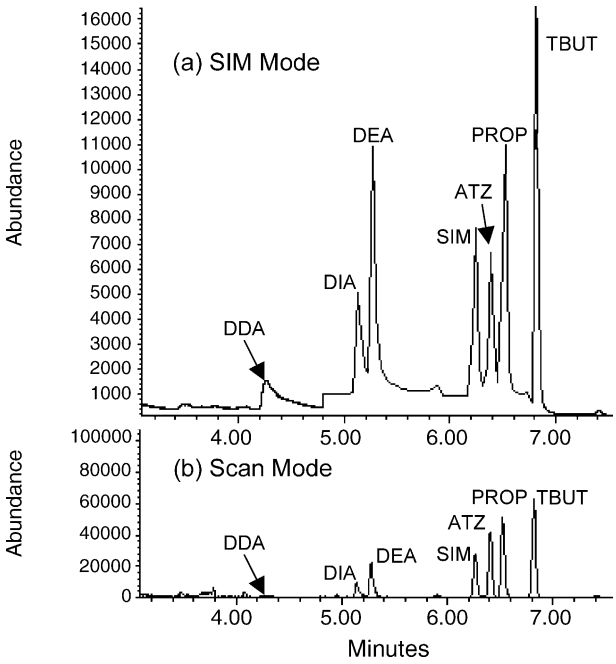

Fig. 2. Total ion chromatogram of mixture of ATR, SIM, PROP, DEA, DIA, and DDA. See Section 2.4 for GC–MS conditions. (a) Selected ion monitoring (SIM) peaks referenced in Table 1 on non-SPE sample containing 10 mg/L of each compound. (b) TIC in scan mode on non-SPE sample containing 10 mg/L of each compound.

Table 1
Gas chromatography retention times and mass spectral quantitation and confirmation ions

Compound	Code	M_r	GC–MS retention time (min)	Quantitation ions	Confirmation ions
Atrazine	ATZ	215.7	6.63	215.1	173.1, 217.1
Simazine	SIM	201.7	6.48	201.1	186.1, 188.0
Propazine	PROP	229.7	6.77	214.1	229.2, 216.1
Deethylatrazine	DEA	187.6	5.46	172.1	145, 187.1
Deisopropylatrazine	DIA	173.6	5.26	158	130.0, 147.0
Didealklyatrazine	DDA	147.5	4.31	145	110.0, 147.0
[$^2H_5$]Atrazine-d_5	ATZ-d_5	220.7	6.58	220.1	204.1, 222.1
[$^2H_5$]Simazine-d_5	SIM-d_5	206.7	6.44	206.1	191.1, 208.1
[$^2H_6$]Deethylatrazine-d_6	DEA-d_6	193.6	5.41	175.1	146, 193.1
[$^2H_5$]Deisopropylatrazine-d_5	DIA-d_5	178.6	5.26	178.1	160, 180.1

Table 2
Method detection limits (MDL) and method quantitation limits (MQL) for study compounds in DI water and filtered surface water

Compound		Method detection limit (μg/L)			Method quantitation limit (μg/L)		
		A	B	Mean	A	B	Mean
DI water							
Atrazine	ATR	0.02	0.01	0.02	0.06	0.05	0.05
Simazine	SIM	0.01	0.00	0.01	0.05	0.00	0.02
Propazine	PROP	0.00	0.01	0.01	0.00	0.05	0.02
Deethylatrazine	DEA	0.01	0.01	0.01	0.04	0.04	0.04
Deisopropylatrazine	DIA	0.02	0.01	0.02	0.07	0.04	0.05
Didealklyatrazine	DDA	0.03	0.03	0.03	0.11	0.11	0.11
Surface water							
Atrazine	ATR	0.02	0.02	0.02	0.06	0.05	0.06
Simazine	SIM	0.00	0.02	0.01	0.00	0.05	0.03
Propazine	PROP	0.02	0.02	0.02	0.05	0.05	0.05
Deethylatrazine	DEA	0.02	0.01	0.01	0.05	0.04	0.04
Deisopropylatrazine	DIA	0.02	0.01	0.01	0.05	0.05	0.05
Didealklyatrazine	DDA	0.01	0.01	0.01	0.04	0.04	0.04

A and B represent separate samples each injected as 0.1 μg/L of each compound.

ature gradient was: initial temperature of 100 °C, ramped at 40 °C/min to 170 °C, 3 °C/min to 185 °C, 10 °C/min to 220 °C, and 60 °C/min to 280 °C which was held for 1 min. MS quadrupole and source temperatures were 150 and 230 °C, respectively.

2.5. Quality assurance

The quality assurance protocol used included extraction of one blank and one check standard analyzed at the beginning and end of each GC–MS sample set. If the indi-

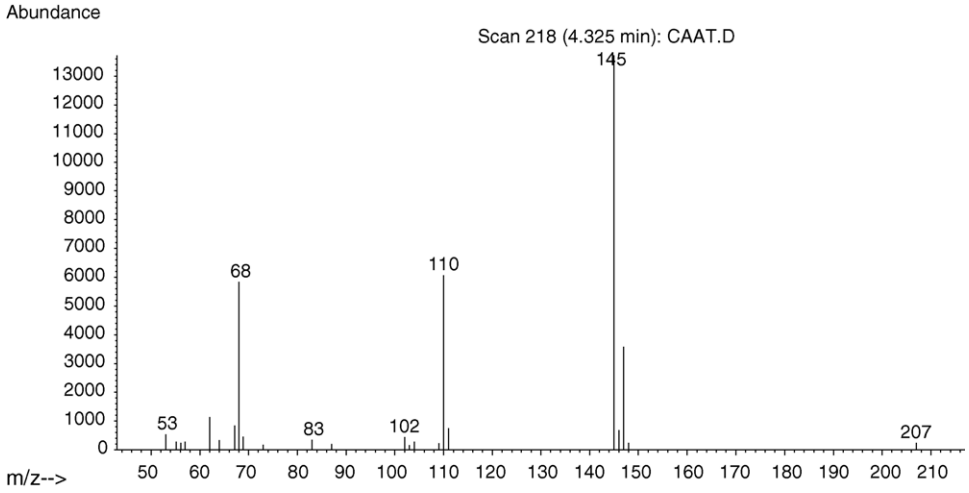

Fig. 3. Mass spectra for didealkylatrazine (DDA) acquired in SCAN mode.

cated concentration of the check sample varied more than 10%, the sample set was reinjected in its entirety. Sample mass recoveries were determined as discussed in Section 3.3. Spike recovery samples were assessed in selected sample sets. Finally, GC–MS system stability was monitored by tabulating the terbuthylazine peak response in each sample (which was added to each extract just prior to GC–MS analysis). Terbuthylazine is not used in the United States and, hence, has been used for at least 15 years in common US Geological Survey herbicide methods as an internal standard.

3. Results and discussion

3.1. Mass spectra and retention

A total ion chromatogram (TIC) conducted in scan mode on the GC–MS of a mixture containing 10 mg/L each of a chloro-*s*-triazine mixture is presented in Fig. 2b. This mixture was prepared directly from stock standards in methanol and was then analyzed without solid-phase extraction. A chromatogram of a 10-μg/L mixture concentrated using the SPE extraction method and analyzed in selected ion monitoring (SIM) mode is presented in Fig. 2a. A mass spectrum obtained in scan mode for DDA is presented in Fig. 3. The retention times, quantitation ion and confirmation ions used for

Table 3
Percent recovery of study compounds in distilled water and filtered Missouri River water based relative to TBUT recovery standard

Compound	Concentration (μg/L)	Percent mass recovery	
		DI water	Surface water
ATR	0.5	98	90
	3	94	99
SIM	0.5	99	99
	3	100	111
PROP	0.5	104	95
	3	102	112
DEA	0.5	103	110
	3	95	110
DIA	0.5	102	108
	3	96	108
DDA	0.5	72	95
	3	80	106
ATR-d_5	0.5	96	99
	3	90	106
SIM-d_5	0.5	103	91
	3	97	97
DEA-d_6	0.5	95	104
	3	90	104
DIA-d_5	0.5	91	104
	3	90	108

Table 4
Recoveries for raw surface waters spiked with 0.5 μg/L of each study compound

Compound	Smpl.									Mean delta (μg/L)	Mean recovery (%)
	RGC35005			RGC32004			RGC38009				
	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)		
ATZ	0.32	0.44	88	0.20	0.44	88	0.84	0.45	90	0.44	89
SIM	0.11	0.42	84	0.00	0.54	108	0.14	0.51	102	0.49	98
PROP	0.03	0.43	86	0.00	0.43	86	0.00	0.49	98	0.45	90
DEA	0.11	0.43	86	0.04	0.42	84	1.15	0.69	138	0.51	103
DIA	0.00	0.51	102	0.00	0.53	106	0.91	0.43	86	0.49	98
DDA	0.00	0.44	88	0.00	0.40	80	0.00	0.44	88	0.43	85

Table shows raw water concentration ($C_{unspiked}$), the difference between the spiked and unspiked concentrations ($C_{spiked} - C_{unspiked}$), the mean apparent loss between amount spiked and recovered, and the percent recovery.

Table 5
Recoveries for finished surface waters spiked with 0.5 μg/L of each study compound

Compound	Smpl.									Mean delta (μg/L)	Mean recovery (%)
	TGC01004			TGC11016			TGC37009				
	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)		
ATZ	0.05	0.44	88	0.75	0.43	86	1.80	0.55	110	0.47	95
SIM	0.00	0.50	100	0.00	0.50	100	0.07	0.55	110	0.52	103
PROP	0.00	0.43	86	0.00	0.45	90	0.03	0.59	118	0.49	98
DEA	0.01	0.44	88	0.14	0.39	78	0.33	0.58	116	0.47	94
DIA	0.00	0.53	106	0.00	0.52	104	0.00	0.58	116	0.54	109
DDA	0.00	0.54	108	0.00	0.51	102	0.00	0.52	104	0.52	105

Table shows raw water concentration ($C_{unspiked}$), the difference between the spiked and unspiked concentrations ($C_{spiked} - C_{unspiked}$), the mean apparent loss between amount spiked and recovered, and the percent recovery.

Table 6
Recoveries for raw surface waters spiked with 2.0 μg/L of each study compound

Compound	Smpl.												Mean delta (μg/L)	Mean recovery (%)
	R3210576			R1810542			R0910515			R4510611				
	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)		
ATZ	0.21	1.97	98	0.71	2.04	102	0.48	2.01	101	0.34	2.00	100	2.00	100
SIM	0.00	2.17	108	0.11	2.19	109	0.14	2.02	101	0.06	2.00	100	2.09	105
PROP	0.00	1.83	91	0.00	1.80	90	0.00	1.81	91	0.00	1.81	91	1.81	91
DEA	0.00	2.05	102	0.00	2.09	104	0.00	2.04	102	0.21	2.02	101	2.05	102
DIA	0.00	1.99	100	0.09	1.99	99	0.00	2.02	101	0.00	2.04	102	2.01	100
DDA	0.00	1.83	92	0.00	1.89	94	0.09	1.95	97	0.08	2.10	105	1.94	97

Table shows raw water concentration ($C_{unspiked}$), the difference between the spiked and unspiked concentrations ($C_{spiked} - C_{unspiked}$), the mean apparent loss between amount spiked and recovered, and the percent recovery.

Table 7
Recoveries for finished surface waters spiked with 2.0 μg/L of each study compound

Compound	Smpl.												Mean delta (μg/L)	Mean recovery (%)
	T3211502			T1811042			T0811015			T4511111				
	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)	$C_{unspiked}$ (μg/L)	$C_{spiked} - C_{unspiked}$ (μg/L)	Recovery (%)		
ATZ	0.00	2.13	107	0.13	1.97	99	0.28	1.93	96	0.33	2.11	106	2.03	102
SIM	0.00	2.14	107	0.08	2.17	109	0.10	1.93	96	0.06	1.99	99	2.05	103
PROP	0.00	1.88	94	0.00	1.83	91	0.00	1.73	87	0.00	2.03	102	1.87	93
DEA	0.00	2.03	101	0.01	2.07	103	0.01	1.97	98	0.20	2.07	104	2.03	102
DIA	0.00	1.96	98	0.00	1.97	99	0.00	1.94	97	0.00	2.02	101	1.97	99
DDA	0.00	1.83	92	0.00	1.87	94	0.09	1.97	98	0.08	1.92	96	1.90	95

Table shows raw water concentration ($C_{unspiked}$), the difference between the spiked and unspiked concentrations ($C_{spiked} - C_{unspiked}$), the mean apparent loss between amount spiked and recovered, and the percent recovery.

integration and data analysis are tabulated in Table 1. The 215 peak was used for quantitation rather than 200 peak due to a minor but observable interference with a ATR-d_5 215 peak.

3.2. Method detection and quantitation limits, and linearity

The method detection limit (MDL) (or instrument limit of detection) and method quantitation limit (MQL) were determined in both DI and surface water and were calculated based on the standard EPA protocol [25]. Specifically, two samples each containing 0.1 μg/L of each analyte was analyzed seven times via the GC–MS method. The quantification and confirmatory ion were observable at this concentration. The MDL is then calculated from a two-tailed *t*-test analysis of seven replicate samples ($\nu = 6$ degrees of freedom) as [25]:

$$\text{MDL}\,(\mu\text{g/L}) = 3s \tag{1}$$

where *s* is the sample standard deviation for the seven replicate analyses. Similarly, the MQL is calculated as [25]:

$$\text{MQL}\,(\mu\text{g/L}) = 10s \tag{2}$$

The individual MDL and MQL, and mean of two replicate MDL and MQL determinations, are tabulated in Table 2. The MDL and MQL for all analytes except DDA were equal to or less than 0.02 and 0.06 μg/L, respectively. The MDL and MQL for DDA were slightly higher, specifically, 0.03 and 0.11 μg/L, respectively (Table 2).

Internal standard calibration curves were constructed using the minimum sum of squares regression of standard concentration versus the ratio of the standard peak area to the equivalent deuterated standard peak area. For compounds for which deuterated standards were not available – PROP and DDA – DEA-d_6 was used for quantitation. Calibration curves were developed over the concentration range from 0 to 3 μg/L for each analyte. For each of twenty separate five-point standard curves, the regression coefficients (R^2) were all greater than 0.99 for each analyte.

3.3. Recovery

The mass recovery of each analyte on the SPE cartridges in both DI and filtered surface water was determined by dividing the analyte peak area (subjected to SPE) normalized to the recovery standard (TBUT) peak area (added after extraction) by the analyte peak area (added after extraction of a water sample containing no chloro-*s*-triazines) normalized to the recovery standard (TBUT), that is:

$$\text{Percent recovery} = \frac{\text{Analyte ratio with SPE}}{\text{Analyte ratio without SPE}} = \left(\frac{\text{peak area of analyte subjected to SPE/peak area of recovery standard (TBUT) added after SPE}}{\text{peak area of analyte added after SPE/peak area of recovery standard (TBUT) added after SPE}}\right) \tag{3}$$

The analyte ratio without SPE was developed by extracting either DI or filtered surface water containing no chloro-*s*-triazine, and adding the analyte after SPE. This was done to assess the effect, if any, of compounds that could leach from the SPE cartridge during an extraction causing potential interference.

Recoveries in DI water ranged from 72 to 104% (Table 3) for all analytes and deuterated standards. For DI, there was no significant difference between recoveries for 0.5 μg/L versus 3.0 μg/L samples ($\alpha = 0.05$) based on *t*-test analysis [26].

Recoveries in filtered surface water ranged from 90 to 112% (Table 3) for all analytes and deuterated standards. For surface water, the calculated recovery was slightly higher for the 3.0 μg/L samples ($\alpha = 0.05$) than for the 0.5 μg/L sample.

There was no significant difference between recoveries in DI versus surface water for the 0.5 μg/L samples ($\alpha = 0.05$). For the 3.0 μg/L samples, however, the calculated recoveries were slightly higher (6.9–13.4%; $\alpha = 0.05$) in surface water compared with DI. The recoveries for DDA were significantly lower (18–29%) than for the other analytes in DI water but not in surface waters ($\alpha = 0.05$) (Table 3).

3.4. Matrix spike experiments

Matrix spike experiments were conducted to assess the recovery of analyte in both raw and treated (finished) from different water treatment plants. Raw and finished waters from each plant were spiked with 0.5 or 2.0 μg/L of each analyte with the results presented in Tables 4–7. Each sample was analyzed using the SPE–GC–MS method both before and after spiking, so the difference in apparent concentration could be compared with the actual (spike) concentration. Similar experiments in DI water resulted in 100% recovery, and are, in fact, replicating samples used for development of calibration curves. For the raw and finished waters, the mean recoveries for ATR, SIM, PROP, DEA, DIA and DDA were 96, 102, 92, 100, 102 and 96%, respectively (Tables 4–7).

4. Conclusions

The analytical method described herein encompasses the use of co-extracted deuterated quantitation standards, dual-cartridge SPE, and GC–MS–SIM. The method has both high sensitivity and recovery in natural waters for the analysis of both parent chloro-*s*-triazine herbicides and their chloro-*s*-triazine metabolites. This method also provides a highly sensitive method for the chloro-*s*-triazine metabolite DDA, for which few analytical methods have been published.

References

[1] US Environmental Protection Agency, Fed. Reg. 59 (1994) 60412.
[2] D.S. Carter, US Geol. Survey Open-File Report 96-459, Indianapolis, IN, 1996.
[3] E.A. Scribner, E.M. Thurman, L.R. Zimmerman, Proceedings of the 29th Mississippi Water Resources Conference, Mississippi Water Resources Research Institute, Mississippi State University, 1999, p. 110.
[4] US Environmental Protection Agency website: http://www.epa.gov/pesticides/cumulative/other_cum_assessments.htm (accessed Sept. 04).
[5] T.B. Hayes, A. Collins, M. Lee, M. Mendoza, N. Noriega, A.A. Stuart, Proc. Natl. Acad. Sci. U.S.A. 99 (2002) 5476.
[6] T. Hayes, K. Haston, M. Tsui, A. Hoang, C. Haeffele, A. Vonk, Environ. Health Perspect. 111 (2003) 568.
[7] T. Hayes, K. Haston, M. Tsui, A. Hoang, C. Haeffele, A. Vonk, Nature 419 (2002) 895.
[8] US Environmental Protection Agency, Meeting minutes of the FIFRA Scientific Advisory Panel Meeting, 17–20 June 2003 (http://www.epa.gov/scipoly/sap/2003/june/junemeetingreport.pdf).
[9] C. Adams, T. Watson, J. Environ. Eng. 122 (1996) 327.
[10] C. Adams, S. Randtke, Environ. Sci. Technol. 26 (1992) 2218.
[11] E.M. Thurman, M. Meyer, M. Pomes, C.A. Perry, A.P. Schwab, Anal. Chem. 62 (1990) 2043.
[12] M. Berg, S.R. Muller, R.P. Schwarzenbach, Anal. Chem. 67 (1995) 1860.
[13] A. Corcia, C. Crescenzi, E. Guerriero, R. Sampel, Environ. Sci. Technol. 31 (1997) 1658.
[14] R. Franssanito, G.D. Socio, D. Laula, D. Rotilio, J. Agric. Food Chem. 44 (1996) 2282.
[15] R. Yokley, in: P. Lee, H. Aizawa, A. Barefoot, J. Murphy (Eds.), Handbook of Residue Analytical Methods for Agrochemicals, Wiley, New York, p. 412.
[16] Y. Lin, R.A. Yokley, Syngenta Method 2070-02, Syngenta Crop Protection, Greensboro, NC, 2002.
[17] S. Huang, J. Stanton, Y. Lin, R. Yokley, J. Agric. Food Chem. 51 (2003) 7252.
[18] S.Y. Panshin, D.S. Carter, E.R. Bayless, Environ. Sci. Technol. 34 (2000) 2131.
[19] R.A. Yokley, M.W. Cheung, J. Agric. Food Chem. 48 (2000) 4500.
[20] R. Koeber, C. Fleischer, F. Lanza, K. Boos, B. Sellergren, D. Barcelo, Anal. Chem. 73 (2001) 2437.
[21] J. Dalluge, T. Hankemeier, R. Vreuls, U. Brinkman, J. Chromatogr. A (1999) 377.
[22] F. Chapuis, V. Pichon, F. Lanza, B. Sellerfren, M. Hennion, J. Chromatogr. B (2004) 93.
[23] Z.W. Cai, V.M.S. Ramanujam, D.E. Giblin, M.L. Gross, R.F. Spalding, Anal. Chem. 65 (1993) 21.
[24] Z.W. Cai, M.L. Gross, R.F. Spalding, Anal. Chim. Acta 304 (1995) 67.
[25] US Environmental Protection Agency, EPA's Guidance for Data Usability in Risk Assessment (DURA) Part A (October, 1990), Section 3.2.4, 1990.
[26] P. Berthouex, L. Brown, Statistics for Environmental Engineers, Lewis Publ., Boca Raton, FL, 1994.