Determination of Atrazine and Its Major Degradation Products in Soil Pore Water by Solid-Phase Extraction, Chemical Derivatization, and Gas Chromatography/ Mass Spectrometry

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To Obtain
kilo-electron volts (KeV)	1.602×10^{-16}	joule
meter (m)	3.281	foot
micrometer (μm)	3.937×10^{-5}	inch
millimeter (mm)	3.937×10^{-2}	inch
liter (L)	2.642×10^{-1}	gallon
milliliter (mL)	3.382×10^{-2}	ounce
microliter (μL)	3.382×10^{-5}	ounce
gram (g)	3.527×10^{-2}	ounce
milligram (mg)	3.527×10^{-5}	ounce
microgram (μg)	3.527×10^{-8}	ounce
pound (lb)	4.536×10^{-1}	kilogram
pound-force per square inch (lbf/in^2)	6.895	kilopascal
torr	1.333×10^{-2}	pascal

Temperature is given in degrees Celsius (°C), which may be converted to degrees Fahrenheit (°F) as follows:

$$°F = 1.8 \times °C + 32$$

CONVERSION FACTORS AND ABBREVIATIONS—CONTINUED

The following abbreviations are used in this report:

Abbreviation	Description
amu	atomic mass unit
min	minute
µg/L	microgram per liter
µg/mL	microgram per milliliter
L/min	liter per minute
mL/min	milliliter per minute
°C	degrees Celsius
°C/min	degrees Celsius per minute
%	percent
GC	gas chromatography
GC/MS	gas chromatography/mass spectrometry
EIMS	electron impact mass spectrometry
ELISA	enzyme-linked immunosorbent assay
HPLC	high-performance liquid chromatography
SPE	solid-phase extraction
RF	response factor
MDL's	method detection limits
USGS	U.S. Geological Survey
ATR	atrazine
DEA	desethylatrazine
DIA	deisopropylatrazine
DAA	didealkylatrazine
HYA	hydroxyatrazine
MTBSTFA	N-methyl-N-(*tert*-butyldimethylsilyl)-trifluoroacetamide
PFTBA	perfluorotributylamine

DETERMINATION OF ATRAZINE AND ITS MAJOR DEGRADATION PRODUCTS IN SOIL PORE WATER BY SOLID-PHASE EXTRACTION, CHEMICAL DERIVATIZATION, AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY

By Donna S. Carter

Abstract

This report describes a method for the determination of atrazine, desethylatrazine, deisopropylatrazine, didealkylatrazine, and hydroxyatrazine from soil pore waters by use of solid-phase extraction followed by chemical derivatization and gas chromatography/mass spectrometry. The analytes are isolated from the pore-water matrix by extraction onto a graphitized carbon-black cartridge. The cartridge is dried under vacuum, and adsorbed analytes are removed by elution with ethyl acetate followed by dichloromethane/methanol (7:3, volume/volume). Water is removed from the ethyl acetate fraction on an anhydrous sodium sulfate column. The combined fractions are solvent exchanged into acetonitrile, evaporated by use of a nitrogen stream, and derivatized by use of N-methyl-N-(*tert*-butyldimethylsilyl)-trifluoroacetamide. The derivatized extracts are analyzed by capillary-column gas chromatography/electron-impact mass spectrometry in the scan mode. Estimated method detection limits range from 0.03 to 0.07 µg/L (microgram per liter). The mean recoveries of all analytes and surrogates determined at 0.74 to 0.82 µg/L in reagent water and in soil pore water were 94 percent and 98 percent, respectively. The mean recoveries of all analytes and surrogates determined at 7.4 to 8.2 µg/L in reagent water and in soil pore water were 96 percent and 97 percent, respectively. Recoveries were 90 percent or higher, regardless of analyte concentration or matrix composition, for all compounds except hydroxyatrazine, whose recoveries were slightly lower (77 percent) at the low concentration.

INTRODUCTION

The triazine herbicide atrazine (2-chloro-4-[ethylamino]-6-[isopropylamino]-1,3,5-triazine) has been one of the most heavily used herbicides in the United States since the mid-1960's. In 1988, atrazine accounted for 14 percent of the mass of all agricultural herbicides used in the nation, a total use of about 65 million lb (Gianessi and Puffer, 1990). In the Midwestern Corn Belt of the United States, the percentage use of atrazine is even higher. For example, in the White River Basin in central Indiana, atrazine accounted for 24 percent of all agricultural herbicides during the period 1992-94 (Anderson and Gianessi, 1995). Atrazine breaks down into four major

degradation products, as shown in figure 1. Because atrazine and these degradation products are somewhat water soluble, they have the potential to leach into ground water and run off to surface water. Thus, it is important to have analytical methods available for determination of these compounds in water matrices. Many analytical methods using gas chromatography/mass spectrometry (GC/MS), high-performance liquid chromatography (HPLC), and enzyme-linked immunosorbent assay (ELISA) have been developed for atrazine in water (Vermeulen and others, 1982; Thurman and others, 1990; Rubio and others, 1991). However, little work has been done on developing a method for the simultaneous determination of atrazine and all its major degradation products. Such a method would facilitate studies on the degradation and environmental fate of atrazine.

Recently, multi-residue methods using graphitized carbon-black solid-phase extraction (SPE) have been described for the determination of polar pesticides in water (Di Corcia and Marchetti, 1991, 1992). Graphitized carbon-black packings have been shown to sorb polar compounds such as desethylatrazine (DEA) and deisopropylatrazine (DIA) more efficiently than the commonly used octadecyl (C-18) silica packings (Di Corcia and others, 1993). In most analytical methods using graphitized carbon-black SPE, reversed-phase HPLC with ultraviolet detection is used to quantify analytes. Although HPLC is suited to direct determination of many polar compounds in SPE extracts, the chromatographic resolution of HPLC cannot compare to that of GC. HPLC also is hampered by the absence of a sensitive, selective, universal detection system, such as electron-impact mass spectrometry (EIMS), which allows definitive identification and quantitation of trace constituents in complex environmental matrices. Because of analytical considerations relating to sample compatibility, EIMS is much more easily interfaced to GC than to HPLC. However, GC is not suited to direct determination of many polar compounds. This shortcoming often can be circumvented by chemical derivatization of polar analytes to produce thermally stable, nonpolar derivatives suitable for GC separation followed by EIMS detection.

N-methyl-N-(*tert*-butyldimethylsilyl)-trifluoroacetamide (MTBSTFA) is an excellent derivatizing agent because it reacts quantitatively with atrazine degradation products under mild conditions. The resultant derivatives are 10,000 times more stable to hydrolysis than conventional trimethylsilyl derivatives (Early, 1987). The reaction byproduct and unused derivatizing agent are compatible with GC analysis, so the derivatized sample mixture can be analyzed without further modification.

This report describes a method for determining atrazine (ATR) and its four major degradation products, DEA, DIA, didealkylatrazine (DAA), and hydroxyatrazine (HYA) in soil pore waters. The method was developed by the U.S. Geological Survey (USGS) for use in a study by the National Water-Quality Assessment's White River Basin study unit, which operates out of the USGS office in Indianapolis, Ind. The method incorporates graphitized carbon-black SPE for removal of the analytes from water samples, silylation for derivatization of polar analytes, and GC/MS analysis in the scan mode for selective identification and quantitation of analytes. This report provides a description of all aspects of the method from sample preparation through calculation of results. Precision and accuracy data and estimated method detection limits for all analytes are presented.

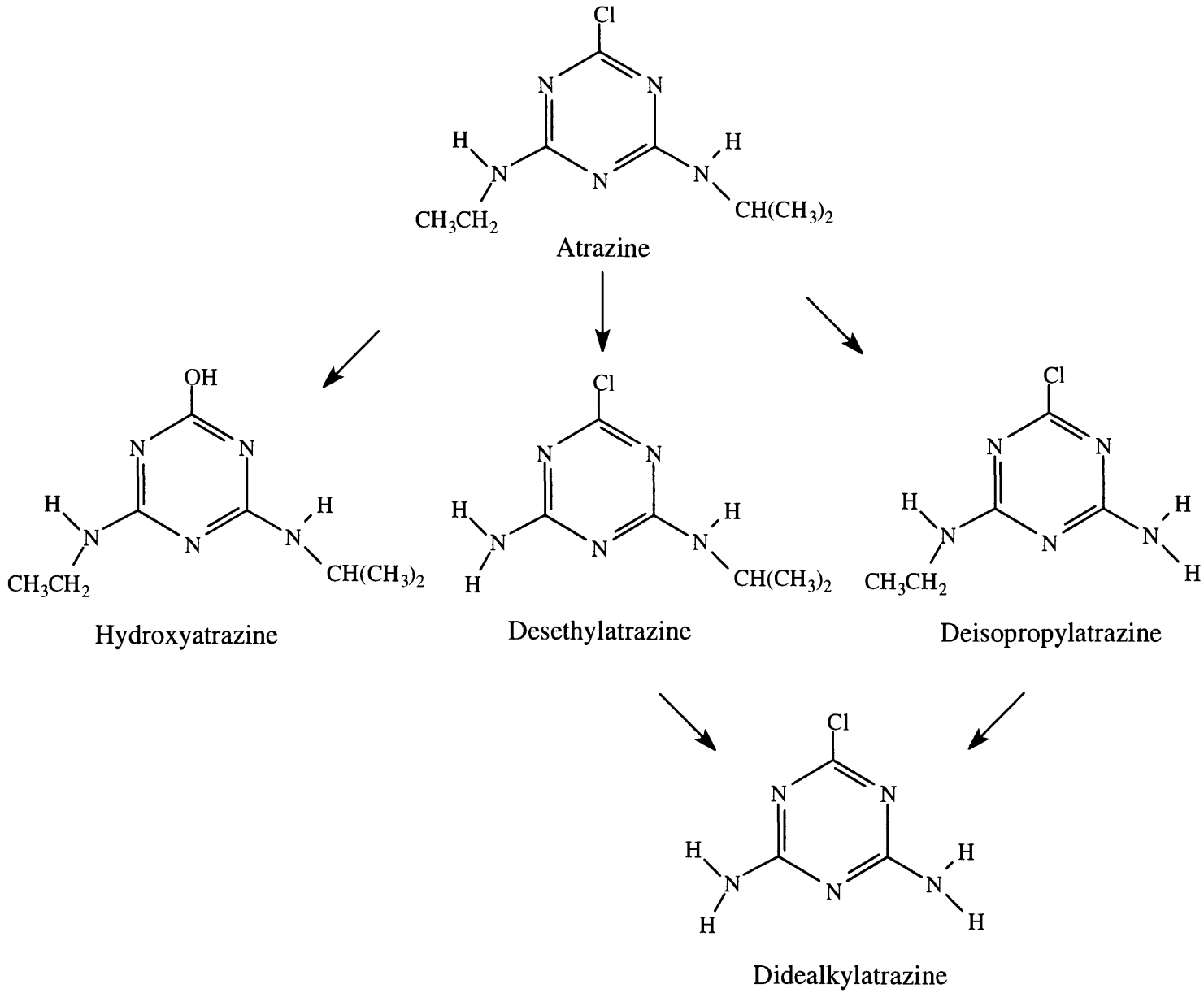

Figure 1. Structures and production pathways of four atrazine degradation products.

DETERMINATION OF ATRAZINE AND ITS MAJOR DEGRADATION PRODUCTS

Scope and Application

This method is suitable for the determination of the triazine herbicide ATR and its major degradation products DEA, DIA, DAA, and HYA in soil pore-water samples. The method is applicable to compounds that are (1) efficiently partitioned from the water phase onto a solid graphitized carbon-black organic phase and (2) sufficiently volatile and thermally stable for GC/MS or amenable to quantitative reaction with MTBSTFA to yield *tert*-butyldimethylsilyl derivatives that are suitable for GC/MS. Suspended particulate matter clogs the SPE cartridges, so this method is suitable only for dissolved analytes. Analyte concentrations from detection limit to 10.0 µg/L each can be determined quantitatively in 100 mL of the soil pore-water matrices used for this study; instrument response was found to be linear over the concentration range, and no chemical interferences (compounds with the same GC retention times and masses as analytes) were found. Development of the method included optimization of SPE conditions to obtain quantitative extraction of the analytes from water and optimization of derivatization conditions to obtain quantitative yields for all analytes.

Reagent Preparation

All solvents used in the method are pesticide- or HPLC-grade reagents, and all glassware is baked at 450°C for at least 5 hours before use.

Stock standard solutions of each analyte, surrogate, and internal standard are prepared from pure materials obtained from commercial vendors (Crescent Chemical; Ciba Geigy)[1]. A stock solution of each chemical (except hydroxyatrazine) is made by dissolving approximately 4.0 mg of the neat chemical into 100 mL of acetonitrile. The hydroxyatrazine stock is made by diluting 1 mL of a 100 µg/mL HYA solution (Crescent Chemical) with acetonitrile/methanol (1:1, volume/volume) to give a final volume of 10 mL. The standard solutions used in this method all are made from appropriate dilution of these stock solutions.

The surrogate solution is made by combining 1.0 mL each of terbuthylazine and deethylterbuthylazine stock solutions and diluting to 10.0 mL with methanol. The internal standard solution is made by diluting 5.0 mL of phenanthrene-d_{10} solution to 20 mL with acetonitrile. The solution for daily calibration of the GC/MS is made by combining 1.0 mL each of ATR, DEA, DIA, DAA, terbuthylazine, deethylterbuthylazine, and phenanthrene-d_{10} with 4.0 mL of HYA and diluting to 20 mL with acetonitrile. Calibration solutions for initial calibration of the GC/MS are made in the same way as the calibration solution above, but concentrations are varied to cover the entire range expected in sample analysis.

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[1] Use of brand names in this report is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

Sample Preparation

All samples and daily-calibration solutions are prepared and analyzed by means of the following procedure.

Solid-Phase Extraction

A soil pore-water sample (100 to 175 mL) is weighed to determine the volume, and 50 µL of a surrogate solution containing 4.0 µg/mL each of terbuthylazine and deethylterbuthylazine in methanol is added. The sample-pumping apparatus, consisting of a model QSY-CKC ceramic-piston, valveless metering pump (Fluid Metering, Inc.) and Teflon tubing and connectors, is pre-washed before use with 50 mL each of 0.1 percent liquinox soap solution, deionized water, pesticide grade methanol, and finally, HPLC reagent water. Immediately before sample extraction, a Supelclean ENVI-Carb SPE cartridge (Supelco) containing 0.25 g graphitized carbon black is conditioned sequentially with 6 mL each of dichloromethane, dichloromethane/methanol (7:3, volume/volume), methanol, and HPLC-grade water drained through the cartridge by gravity. The 100- to 175-mL water sample is pumped through the conditioned cartridge at a rate of 2 to 3 mL/min. The cartridge must be kept from going dry during the column conditioning and sample-extraction steps. After sample extraction is completed, interstitial water in the cartridge is removed using a vacuum aspirator (approximately 6 L/min for 3 to 5 min).

In order to avoid irreversible sorption to the solid-phase packing, analytes are eluted immediately from the dried cartridge by gravity draining of 3 mL ethyl acetate (fraction 1), followed by 8 mL dichloromethane/methanol (7:3, volume/volume) (fraction 2). A syringe is used to force any remaining solvent out of the cartridge. Residual water is removed from fraction 1 by elution through a disposable glass pipet containing approximately 1 g of pre-cleaned anhydrous sodium sulfate. The sodium sulfate column is then rinsed with three column-volumes of ethyl acetate, which are added to the rest of fraction 1. Sample extract fractions 1 and 2 can be stored in amber glass vials at 4°C for at least 1 month.

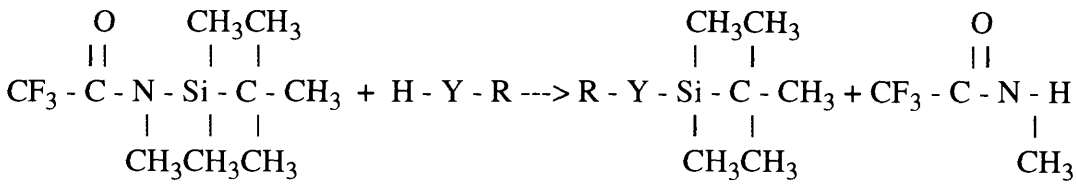
Sample Concentration and Solvent Exchange

Fractions 1 and 2 are combined and concentrated to approximately 150 µL under a gentle stream of 99.999 percent pure nitrogen (Air Products). The sample is solvent exchanged into acetonitrile by bringing the sample volume up to 1 mL with acetonitrile and concentrating to 100 µL under a gentle stream of nitrogen. The solvent-exchange procedure is repeated twice to ensure the removal of residual methanol, which interferes with the derivatization procedure. A 50-µL volume of 10.0 µg/mL phenanthrene-d_{10} (Ultra Scientific) in acetonitrile is added as an internal standard.

Derivatization

The 100-µL concentrated sample extracts are derivatized by the addition of 80 µL MTBSTFA (Pierce Chemical). The mixture is heated in a sealed glass reaction vial at 65°C for 45 minutes. Under these conditions, the derivatizing agent reacts quantitatively with any hydroxy and primary

amine functional groups present on the analytes and surrogates according to the reaction scheme below,



where Y = NH or O.

Thus HYA, DEA, DIA, and deethylterbuthylazine acquire one *tert*-butyldimethylsilyl group, DAA acquires two *tert*-butyldimethylsilyl groups; ATR, phenanthrene-d_{10}, and terbuthylazine remain unreacted (these compounds do not require derivatization for GC/MS analysis).

Sample Analysis

Instrumentation

All sample analyses are done on a Hewlett Packard GC/MS system consisting of a 5971A quadrupole mass spectrometer that is directly interfaced to a 5890 Series II capillary gas chromatograph with splitless injection. The interface is maintained at 280°C, the injection port at 250°C. The GC is equipped with a 30-m x 0.25-mm inside diameter x 0.25-µm film thickness poly (5 percent-diphenyl, 95 percent-dimethylsiloxane) capillary column and is maintained at a constant head pressure of 12 lbf/in^2 with chromatographic-grade helium (Air Products). The mass spectrometer is maintained in the electron impact mode at a source pressure of approximately 2 x 10^{-5} torr and at ionizing voltage of 70 keV.

Tuning and Calibration

The mass spectrometer is tuned daily by use of the procedure and standard software (autotune) supplied by the manufacturer. Parameters in the tuning software optimize instrument resolution and sensitivity with reference to masses 69, 219, and 502 in the spectrum of perfluorotributylamine (PFTBA). Tuning results are examined to ensure proper functioning of the mass spectrometer. Water and the components of air should not be detected. The mass axis should be accurate within 0.2 atomic mass units (amu). Peak shape should be symmetrical, with width at half height not exceeding 0.65 amu. Acceptable relative abundances of the tune masses and ratios of the isotope masses to the tune masses (isotope ratios) for PFTBA are listed in table 1. All tuning criteria must be met before the instrument is used.

Initial calibration data are acquired by use of calibration solutions prepared every 3 months as described in the "Reagent Preparation" section. The calibration solutions should cover the entire concentration range expected in sample analysis. The initial calibration data are acceptable if the relative standard deviation is less than 25 percent for response factors calculated (as shown below) across the concentration range. If this criterion cannot be met, all the calibration solutions must be analyzed (as described for the single calibration solution below) before the analysis of

each batch of derivatized samples. The response factor calculated from the calibration solution most closely corresponding to each sample analyte concentration then is used for data evaluation.

Table 1. Acceptable ranges for relative ion abundances and mass + 1 isotope ratios during mass spectrometer tuning with perfluorotributylamine

[amu, atomic mass unit; %, percent; >, greater than]

Mass (amu)	Relative ion abundance (%)	mass + 1 isotope ratio (%)
69.0	100	0.54 - 1.6
219.0	>35	3.2 - 5.4
502.0	>1	8.0 - 12

If the above initial calibration criterion is met, then the GC/MS is calibrated by use of a single daily calibration solution, as described in the "Reagent Preparation" section, before analysis of each batch of derivatized samples. A 100-µL aliquot of the above calibration solution(s) is solvent exchanged and derivatized at the same time and in the same manner as samples; it is analyzed with each batch of samples by use of the analytical method described below. A response factor (RF) relative to phenanthrene-d_{10} is calculated for each compound in the derivatized calibration solution(s) as follows:

$$RF = \frac{A_a \times C_i}{C_a \times A_i}, \quad (1)$$

where A_a is GC peak area of the analyte quantitation ion;
C_i is concentration of the internal standard, in micrograms per milliliter;
C_a is concentration of the analyte, in micrograms per milliliter; and
A_i is GC peak area of the internal standard quantitation ion.

Response factors for each sample batch must agree to within 25 percent of average values from previous batches; if this is not the case, then quantitative determinations of analytes in the batch are flagged as estimates.

Analytical Method

A 0.8- to 1.0-µL aliquot of sample is injected manually into the GC. The GC oven temperature is held at 50°C for 1 minute, ramped at 6°C/min to 280°C, and held for 5.67 minutes for a total run time of 45 minutes. After an 18-minute solvent delay, the mass spectrometer scans from mass 40 to 500 every 0.625 second.

Data Evaluation

The retention times of analytes in samples must match those in the calibration standard to within 0.05 minutes, and the full-scan mass spectra must match in order to be positively identified. For each analyte, the mass spectrum is examined, and the peaks from the quantitation ion (base peak) and the confirmation ion are integrated from ion mass chromatograms. Ions used for each compound are given in table 2. The ion ratio is calculated by dividing the confirmation ion peak area by the quantitation ion peak area and multiplying by 100. Positive identification of the analyte requires that the ion ratio fall in the range given in table 2. From the peak areas of the quantitation ions, analyte concentrations are calculated as follows:

$$C_a = \frac{Q_i \times A_a}{RF_a \times A_i \times V}, \qquad (2)$$

where C_a is concentration of analyte in the sample, in micrograms per liter;
Q_i is quantity of internal standard added to the sample, in micrograms;
A_a is GC peak area of the analyte quantitation ion;
RF_a is response factor of the analyte calculated during calibration;
A_i is GC peak area of the internal standard quantitation ion; and
V is volume of original water sample, in liters.

The percent recovery of surrogates is calculated as follows:

$$R = \frac{Q_i \times A_s}{RF_s \times A_i \times Q_s} \times 100, \qquad (3)$$

where R is percent recovery of the surrogate;
Q_i is quantity of internal standard added to the sample, in micrograms;
A_s is GC peak area of the surrogate quantitation ion;
RF_s is response factor of the surrogate calculated during calibration;
A_i is GC peak area of the internal standard quantitation ion; and
Q_s is quantity of surrogate added to the sample, in micrograms.

If surrogate recoveries are less than 75 percent, quantitative determinations of analytes are flagged as estimates. Quantitation of derivatized analytes is affected by the efficiency of the derivatization reaction. This efficiency is checked by examining the analytical results for DAA and HYA. DAA is the most difficult analyte to derivatize completely, and HYA is the easiest to overderivatize (it begins to acquire additional *tert*-butyldimethylsilyl groups). If more than 25 percent of the DAA or HYA signal is the result of underderivitization or overderivatization, then quantitative determinations of analytes are flagged as estimates.

Table 2. Quantitation ion, confirmation ion, and estimated method detection limits of analytes in soil pore waters for a 100-milliliter sample

[ion ratio is the peak area of the confirmation ion divided by the peak area of the quantitation ion times 100; amu, atomic mass units; %, percent; µg/L, microgram per liter; n.a., not applicable]

Compound	Quantitation ion (amu)	Confirmation ion (amu)	Ion ratio (%)	Estimated method detection limit (µg/L)
Atrazine	200	215	57 to 69	0.07
Desethylatrazine	244	246	34 to 42	.04
Deisopropylatrazine	230	232	33 to 39	.03
Didealkylatrazine	316	99	16 to 42	.03
Hydroxyatrazine	254	255	8 to 14	.04
Phenanthrene-d_{10} (internal standard)	188	184	8 to 14	n.a.
Terbuthylazine (surrogate standard)	214	216	26 to 34	n.a.
Deethylterbuthylazine (surrogate standard)	258	202	76 to 108	n.a.

METHOD PERFORMANCE

Reagent-water rinses of sampling equipment (blanks), fortified reagent water (reagent spikes), and fortified soil pore-water samples collected at a study site in New Palestine, Ind. (matrix spikes) were used to test the method performance. Reagent-water rinses of sampling equipment were obtained by collecting samples of laboratory reagent water through the sampling equipment before installation at the study site; two 100-mL samples were obtained. Two 100-mL laboratory reagent spike samples were fortified with known amounts of each analyte and surrogate to obtain concentrations in the range of 7.4 to 8.2 µg/L, and two were fortified to a range of 0.74 to 0.82 µg/L. Four 100-mL matrix spike samples were fortified in the same way as the reagent spikes described above, and one matrix sample was left unfortified to allow correction for analytes present in the matrix before fortification. All method performance samples were treated in the same way as regular samples and were analyzed at the Indianapolis office of the USGS by use of the same GC/MS.

Estimated method detection limits (MDL's) are listed in table 2. MDL's were set at concentrations where the analyte signal was three times that of background noise in soil pore-water matrix spikes. MDL's vary according to the analyte, sample volume and matrix, and instrumental conditions.

Mean recoveries and log-percent differences for duplicate analyses at two different analyte concentrations are reported in table 3 for organic-free reagent water and for soil pore-water matrices. Mean recovery is a measure of method accuracy. The mean recoveries of all analytes and surrogates determined at 0.74 to 0.82 µg/L in reagent water and in soil pore water were 94 percent and 98 percent, respectively. The mean recoveries of all analytes and surrogates determined at 7.4 to 8.2 µg/L in reagent water and in soil pore water were 96 percent and 97 percent, respectively. Recoveries were 90 percent or higher, regardless of analyte concentration or matrix composition, for all compounds except hydroxyatrazine, whose recoveries were slightly lower (77 percent) at the low concentration. If the accuracy of trace hydroxyatrazine determinations in each sample must be known, then an isotope-labeled analog such as ^{15}N- or ^{13}C-hydroxyatrazine (Ciba Geigy) can be used in addition to the terbuthylazine and deethylterbuthylazine surrogates described in the "Sample Preparation" section.

Log-percent difference was used as the measure of relative difference (precision) between two replicate analyses, x and y; it is defined as $100 \ln(y/x)$ (Tornqvist and others, 1985). Unlike the conventional percent difference, this measure of relative difference has the advantage of being symmetric (the log-percent difference between two items is the same regardless of which is used as a point of comparison—only the sign changes). The magnitude of the log-percent difference is roughly equivalent to the average of the absolute deviation of the 2 possible traditional percent differences between two numbers. For example, the traditional percent difference between replicate concentrations of 0.68 and 0.89 µg/L is either -23.6 percent or 30.9 percent, depending on which of the two numbers is used as the basis for comparison. The log-percent difference between the two numbers is either -26.9 log percent or 26.9 log percent, depending on which number is used as the basis for comparison.

The mean log-percent differences of all analytes and surrogates determined at 0.74 to 0.82 µg/L in reagent water and in soil pore water were 10 and 12, respectively. The mean log-percent differences of all analytes and surrogates determined at 7.4 to 8.2 µg/L in reagent water and in soil pore water were 6.2 and 4.4, respectively. The method precision is analyte-concentration dependent. In general, method precision decreases with analyte concentration, as is typical in the determination of trace organic compounds. From the data presented, SPE followed by chemical derivatization and GC/MS is an efficient and accurate method for analysis of atrazine and its major degradation products in soil pore waters.

Table 3. Accuracy and precision data from duplicate determinations of analytes and surrogates at 0.74 to 0.82 micrograms per liter and 7.4 to 8.2 micrograms per liter in organic-free reagent water and soil pore-water matrices

[µg/L; micrograms per liter; %, percent]

Compound	Matrix	Concentration spiked (µg/L)	Concentration measured (µg/L)		Log % difference between replicates	Mean recovery (%)
			Replicate 1	Replicate 2		
Atrazine	Reagent water	0.80	0.68	0.89	27	98
		8.0	7.12	7.76	8.6	93
	Soil pore water	.80	.74	.84	13	99
		8.0	8.08	7.52	7.2	98
Desethylatrazine	Reagent water	.82	.74	.74	0	90
		8.2	8.36	7.87	6.0	99
	Soil pore water	.82	.94	.81	15	107
		8.2	7.95	7.71	3.1	95
Deisopropylatrazine	Reagent water	.80	.79	.72	9.3	94
		8.0	7.52	7.84	4.2	96
	Soil pore water	.80	.78	.86	9.8	103
		8.0	7.92	7.84	1.0	99
Didealkylatrazine	Reagent water	.80	.84	.79	6.1	102
		8.0	7.52	7.60	1.1	95
	Soil pore water	.80	.93	.78	18	107
		8.0	7.92	7.76	2.0	98
Hydroxyatrazine	Reagent water	.80	.66	.58	13	78
		8.0	7.68	7.20	6.5	93
	Soil pore water	.80	.62	.61	1.6	77
		8.0	7.52	7.44	1.1	94
Terbuthylazine	Reagent water	.80	.74	.85	14	99
		8.0	6.96	8.16	16	95
	Soil pore water	.80	.77	.81	5.1	99
		8.0	8.40	7.60	10	100
Deethylterbuthylazine	Reagent water	.74	.75	.73	2.7	100
		7.4	7.25	7.18	1.0	98
	Soil pore water	.74	.63	.78	21	95
		7.4	7.40	6.96	6.1	97

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