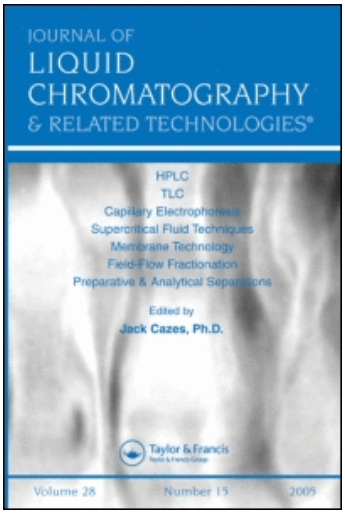

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AUTOMATED HOT SOLVENT EXTRACTION AND HPLC DETERMINATION OF ATRAZINE AND ITS DEGRADATION PRODUCTS IN SOIL

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AUTOMATED HOT SOLVENT EXTRACTION AND HPLC DETERMINATION OF ATRAZINE AND ITS DEGRADATION PRODUCTS IN SOIL

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ABSTRACT

Automated hot solvent extraction of atrazine (ATR), desethylatrazine (DEA), and desisopropylatrazine (DIA) from soil samples has been optimized and variation of recoveries with total organic carbon content (TOC) in soil has been studied.

Soil (20 g) was extracted for 30 min at an enhanced temperature with 120 mL of dichlormethane/acetone 65:35 v/v and, subsequently, rinsed 10 min with condensate. Extract was cleaned-up by gel permeation chromatography and an aliquot of triazine fraction was injected onto a narrow bore HPLC column packed with polymeric octadecyl phase. Mobile phase containing acetonitrile and 0.002 mol/L phosphate buffer of pH 6.8 was used for gradient elution.

Recoveries higher than 98%, 93%, and 81% can be attained for ATR, DEA, and DIA (1 μg/g level), respectively, by extracting soils with TOC ≤ 2.5%. With TOC increasing to 39% recovery,

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values decrease up to approx. 25%. Limits of detection based on a signal-to-noise ratio of 3 and calculated on a dry-weight basis were 4 ng/g ATR and 2 ng/g DEA or DIA. Relative standard deviation of the measurement was 3.4% for ATR, 1.1% for DEA, and 3.6% for DIA. The method has been used for determination of atrazine and its degradation products in soil from maize fields.

INTRODUCTION

Triazine herbicides have been widely applied for crop protection during the past four decades. Among them, atrazine (ATR), 2-chloro-4-(ethylamino)-6-(isopropylamino)-*s*-triazine, is one of the most used pesticides worldwide. Atrazine is introduced in a priority list of herbicides in Europe and in the USA and its application has been banned in some countries,[1] e.g., Germany and Italy. Besides ATR, the determination of its more polar, phytotoxic metabolites, desethylatrazine (DEA) and desisopropylatrazine (DIA), is of great interest, due to their high leaching and, thus, groundwater contamination potential.

Except environmental waters, most pollution with triazines occurs in soil. Triazine herbicides and their metabolites can persist for months in some soils and seasonal carry-over can cause phytotoxicity problems in crop rotation.[2] Monitoring of ATR, DIA, and DEA in soil is important from the point of view of correct atrazine dosing and is necessary for environmental fate studies. Similarly, detection of possible water contamination sources requires determination of these analytes in soil.

A comprehensive review on environmental sample preparation and chromatography of triazine herbicides and their metabolites can be found in the literature.[2,3-5] As shown in contemporary works [6-8] on determination of *s*-triazines in waters, an efficient separation and determination of nine up to eleven triazines and its metabolites differing substantially in polarities, can be attained by RP HPLC.

Works engaged in the analysis of triazines in soil are less numerous, and suggested procedures of sample preparation are usually time consuming and cumbersome and/or possessing low or variable recoveries. Sonication, shaking, and supercritical fluid extraction (SFE) are the mostly used extraction methods besides Soxhlet extraction.

Four methods of *s*-triazines extraction were evaluated using both field treated and laboratory fortified samples.[9] For ATR and two other *s*-triazines, the highest recoveries were attained after 1-hour shaking with methanol-water mixture. On the other hand, sonication in acetonitrile-water was shown as the most efficient method for extraction of dealkylated metabolites with recoveries > 60%. After shaking or sonication, extracts were cleaned up by solid phase extraction.

Supercritical fluid extraction (SFE) was found as efficient as sonication or shaking but its results were more variable. Some other studies[10,11] on SFE of triazines have also shown the variability of recoveries depending upon the soil matrix and analyte extracted. It was concluded, that the greater the polarity of triazine derivative, the greater is the effect of the carbon content upon extraction efficiency.[11]

While the ATR recoveries from sand or clay samples were in the range between 90% and 110%, great variation was observed for DEA (55% to 115 %) and DIA (25% to 92%) in dependence on organic carbon content (< 0.05% up to 4.8%).

Sonication was applied to consecutive isolation of ATR or DEA and DIA from soil by using different solvents.[12] Sample preparation was rather complex and cumbersome because several other preseparation and preconcentration steps followed after extraction. Recoveries were 61%-65% for ATR, 74%-83% for DEA, and 68%-83% for DIA. High sensitivity of the determination was reported (LOD 0.5 ng/g) but chromatograms of field samples were relatively complex. A promising approach was shown in the works[13,14] engaged in derivatization of triazines after their extraction from water, soil, or crops. It was shown, that derivatization can not only increase the sensitivity of detection but even replace cleanup and concentration processes.

Soils (TOC 0.88%-1.55%) were extracted with methanol in three subsequent 5-min sonications and joint extracts were dried by anhydrous Na_2SO_4 and evaporated. The residue was dissolved in benzene and, after derivatization, an aliquot was injected onto HPLC column without any further cleanup and/or preconcentration. Atrazine recoveries in the range from 90% to 95% and LOD of 1.1 ng/g were reported.

Triazine metabolites, DEA and DIA, were extracted from soil or aquifer sediments by twice repeated shaking with water-methanol mixture, 105 min each, 30 min at 75°C inclusive.[15] Extracts were evaporated down and cleaned up by automated SPE on a mixed mode bed. Recoveries of 75% and LOD of 0.1 ng/g were attained.

Percolation of the soil sample with acetone, and retention of triazines by salt formation on cation-exchange column, were successfully applied to non metabolized triazines.[16] The effect of soil type and, to a lesser extent, the effect of organic carbon content on atrazine recovery was discussed. Anomalies were found in one of the three soils investigated, i.e., in the sample with the lowest clay content and the largest amount of organic matter (TOC 4.2%). ATR recovery from the other two soils was > 90% and LOD was 1 ng/g.

The objectives of our work were to provide a rapid and simple method of determination of atrazine and its dealkylated metabolites, DEA and DIA in soil, and to gain some insight into the effect of organic matter content on sample

extraction. Hydroxyatrazine, a major degradation product,[1,17] was not chosen as a target because of its non-phytotoxic properties. The proposed method is based on an automated hot solvent extraction by using Büchi Extraction System enabling extraction of four samples simultaneously, a cleanup by gel permeation chromatography, and an RP HPLC determination.

EXPERIMENTAL

Reagents and Solutions

Standard solutions of atrazine in methanol (NSI Environmental Solutions, USA) and desethylatrazine in acetone (Absolute Standards, USA), both at 1 mg/mL, were stored in 1.5-mL Certan vials (Promochem, FRG). A stock standard solution of desisopropylatrazine (purity > 98.5%, Institute of Industrial Organic Chemistry, Poland), 1 mg/mL, was prepared by weighing and dissolving in acetonitrile. All working solutions were prepared in acetonitrile. Solutions were stored at -20°C.

Acetonitrile of HPLC gradient grade (J. T. Baker, The Netherlands) and ethyl acetate of HPLC grade (Scharlau, Spain) was used. Other solvents (J. T. Baker, The Netherlands or Scharlau, Spain) and reagents (Lachema, Czech Republic) were of analytical grade.

HPLC mobile phases were prepared in volume flasks by diluting a volume of acetonitrile with water or phosphate buffer. The buffer was prepared by neutralization of potassium dihydrogenphosphate solution with KOH to desired pH value and filtered through 0.45 μm pore size Nylon 66 membrane (Supelco, USA).

Apparatus

Soil samples in glass thimbles with sintered glass bottom were extracted in a model B-811 Universal Extraction System (Büchi, Switzerland) with 120 mL dichlormethane (65% or 75% v/v) mixed with acetone. Solvents in a boiling flask were heated at a level 9 of 20-level scale, those in an extraction chamber at level 1 or 2 of 10-level scale (the highest levels recommended for water).

Gel permeation chromatography (GPC) equipment comprised of an HPP5001 syringe pump (Laboratory Instruments Prague, CR) and LCI 30 injection valve. By using a stainless steel column 500 x 8 mm I.D. packed with Bio-Beads S-X3 with particle size 37-57 μm (column A purchased from Tessek, CR), 1 mL of sample in chloroform was injected and chloroform was delivered at 0.6 mL/min as a mobile phase. If column B, a PLgel column 300 x 7.5 mm I.D.

with 5-μm particles (Polymer Laboratories, USA), was used, 0.5 mL sample was injected and eluted with chloroform at 0.8 mL/min.

HPLC analyses were performed on an HP 1050 series chromatograph consisting of quaternary pump, programmable autosampler, diode-array detector, and HP ChemServer with 3D ChemStation software. The assembly was completed with a HP 1100 thermostatted column compartment (all Hewlett-Packard, FRG).

A sample volume of 3.6 μL was injected onto a Vydac 201TP52 column 250 x 2.1 mm I.D. packed with 5-μm polymeric octadecyl phase, with carbon load of 15.5-16% (Vydac, USA). An ODS-Hypersil cartridge 20 x 2.1 mm I.D., 5-μm particle size, (Hewlett-Packard, FRG) was used as a guard column. Columns were thermostatted at 25°C. Gradient separation was performed at a flow rate of 0.4 mL/min. The mobile phase contained acetonitrile and 0.002 mol/L phosphate buffer of pH 6.8.

Atrazine and its degradation products were quantified at a wavelength of 220 ± 2 nm and the reference signal was measured at 450 ± 25 nm. Spectral data were acquired between 200 and 365 nm. Detector response time was set to 2.6 s. Calibration was carried out by injecting standard solutions.

Acidity was measured by means of a model 526 pH-meter equipped with a SenTix 97T glass-Ag/AgCl combined electrode (WTW, FRG), calibrated by using standard buffers of pH 4.0 and pH 7.0 (Institute of Sera and Vaccines, CR).

Soil Samples

Field samples were collected from September 1999 to April 2000 in a rural area near to Zlín City, CR. The samples (approx. 1-kg) were taken from 15-cm thick surface layer in maize fields treated with Gesaprim 500 FW or Zeazine S 40 containing 500 g/L or 450 g/L atrazine, respectively. Soils were air-dried one to

Table 1. Blank Samples

Sample	Dry Weight (%)	TOC[a] (%)
S 99/484	98.5	1.33
S 99/479	98.4	1.91
S 98/278	96.9	4.73
S 99/483	95.0	11.6
S 98/293	93.9	20.0
S 98/294	92.3	39.1

[a]Total organic carbon content (Agema Ltd., Brno, CR).

three days at room temperature, ground, passed through a 2.0 mm sieve, and subsequently homogenized by thorough mixing by hand, and stored in a powder bottle at -20°C.

Five soils and an S 98/294 sample of humified needle-leaves, all of them originating from a background area at Košetice observatory, CR, were collected in the year 1998 or 1999, treated in identical manner as field samples, and archived at room temperature. The samples were analyzed by the method described in this work, and no evidence for ATR, DIA, and DEA presence was found. They were used as blank matrices, or spiked with analytes, by adding a standard solution to the their weighted amount prior to extraction.

RESULTS AND DISCUSSION

Extraction

Dichlormethane (DCM), acetone, ethyl acetate, 2-propanol, and five mixtures of DCM and acetone (95:5 to 50:50 v/v) were tested as possible extraction solvents by an 8-hour Soxhlet extraction of VS0999 field sample that was collected 1 day after herbicide application. Best results were attained when DCM-acetone mixtures with 10% to 50% v/v acetone were used. Dependence of atrazine extraction yield on the acetone content exhibited a flat maximum, positioned between 25% and 40% v/v acetone. About 70% of the yield attained at 25% v/v acetone was extracted with pure acetone and 50% with ethyl acetate or 2-propanol.

Consequently, S 99/479 blank soil (5 g) spiked with ATR, DIA, and DEA at 1 μg/g level was extracted with DCM/acetone 75:25 v/v and 65:35 v/v by using automated hot solvent extraction. The extraction chamber was heated at level 2 in the course of a 30-min extraction. After a 10-min rinsing of the sample with condensate, the extract in boiling flasks was evaporated to a volume of 5 mL. Concentrated extracts were dried under a gentle stream of nitrogen, their residues were redissolved in chloroform and injected onto GPC column A. Blow dried residues of triazine fractions were redissolved in 1 mL acetonitrile and analyzed by HPLC.

A blank matrix was treated in an identical manner and the absence of analytes at detectable concentrations, as well as the absence of interfering compounds, was verified by HPLC. As shown in Table 2, slightly higher recoveries of all analytes were attained and standard deviation values were lower at 35% v/v acetone in the mixture.

To investigate the effects of extraction time and heating level of extraction chamber on extraction yields, VS0999 field sample (5 g) fortified with 1 μg/g DIA and DEA, was extracted 10 to 60 min with DCM/acetone 75:25 v/v and then 20 min rinsed with condensate. Parallel experiments, in which the solvent in the extraction chamber was heated at level 2 or 1 and were performed by experimen-

Table 2. Effect of Acetone Content on Hot Solvent Extraction of Triazines

	DCM/Acetone 75:25 v/v		DCM/Acetone 65:35 v/v	
Analyte[a]	Recovery (%)[b]	s_n[c]	Recovery (%)[b]	s_n[c]
ATR	92.22	1.99	95.64	1.50
DIA	91.11	4.19	94.50	2.42
DEA	76.83	1.63	81.44	0.79

[a]Blank matrix spiked with analytes 1 μg/g each.
[b]Mean of 4 parallel determinations.
[c]Standard error of the mean.

tal conditions, were described in a previous paragraph. As follows from the curves in Figure 1, the highest yields can be attained after 30-min extraction with extractant heated at level 2. At a lower extractant temperature, extraction yields were lower, and in the case of DEA were practically identical.

Further, the time of rinsing with condensate was varied from 10 to 40 min in 10-min steps after 30-min extraction at heating level equal to 2. A moderate decrease of atrazine yields with prolonged rinsing time was observed, while the yields of DIA and DEA were practically independent of this parameter. Considering the usefulness of the rinsing step, extractions of S 99/479 blank matrix (5 g) spiked with analytes (1 μg/g each) were performed with and without 10-min rinsing, each in quadruplicate. The samples were extracted with DCM/acetone 65:35 v/v.

Without rinsing, the recovery values of DIA and ATR were 86.9% and 88.3%, respectively, while the values of 94.5% and 95.6% were attained after 10 min of rinsing. On the other hand, recovery of DEA was almost independent of the rinsing step, i.e., 82.5% without and 81.4% with rinsing. As a consequence, the rinsing time of 10 min was chosen as sufficient.

Variance of the yields with sample amount was verified by extraction of 5 to 20 g VS0999 field sample, fortified with DIA and DEA at 1 μg/g concentration. Extraction with 120 mL DCM/acetone 65:35 v/v proceeded at optimized conditions. To cleanup the extracts, GPC column B was used. Dry residues of triazine fractions were redissolved in 0.5 mL acetonitrile and analyzed by HPLC. The extraction yields were found to be independent of the sample amount in the range studied. RSD values of the mean concentrations determined for extraction of 5, 12.5, and 20 g of the sample were 4.67% for ATR (2.53μg/g), 4.07% for DIA (0.83 μg/g), and 3.87% for DEA (0.88 μg/g).

A detailed study of recovery variance with organic carbon content in the extracted soil has not been found in literature. To follow this effect, blank matrices (10 g) containing 1.33% up to 39.1% of organic carbon were spiked with

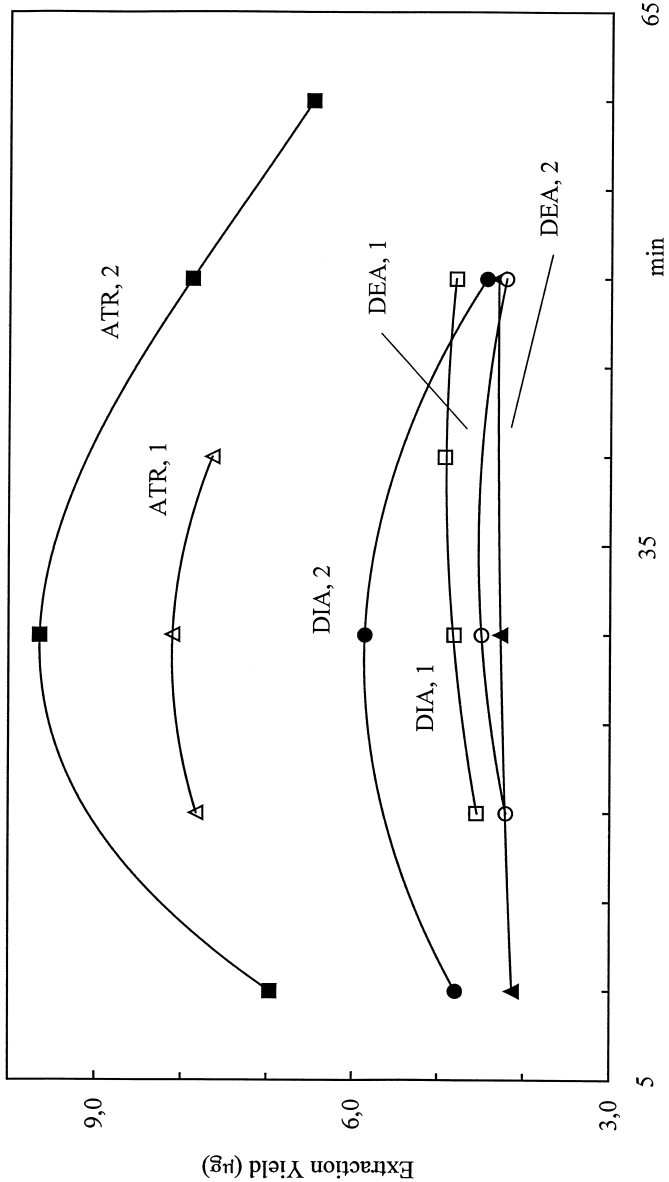

Figure 1. Variation of extraction yields with extraction time. VS0999 field sample (5 g) fortified with 1 µg/g DIA and DEA. Extracted with DCM/acetone 75:25 v/v at heating level 2 or 1 and 20 min rinsed with condensate.

1 μg/g ATR, DIA, and DEA, and analyzed by optimized experimental conditions. The measurements were performed in triplicate for each sample. To avoid influences of interferents co-extracted from the soils rich in organic matter, a chromatogram of each blank matrix was subtracted from a corresponding chromatogram of spiked sample prior to its integration. As shown in Figure 2, recovery was decreasing with increasing content of organic carbon and, consequently, TOC of 2.5% (98% ATR, 93% DEA, and 81% DIA recovered) was suggested as a reasonable limit for the method presented.

Maize is usually cultivated in soils with a lower content of organic matter and, thus, the limit mentioned seems to be high enough for samples collected in cornfields treated with atrazine. An observed variation of recoveries with TOC values is lower than was stated for SFE,[11] and recovery values are higher than by SFE,[9] sonication,[12] or shaking[15] with an organic solvent. At TOC values from 2.5% to approximately 10%, the addition of internal standard or estimation by using a standard addition method can be recommended.

Sample Cleanup

Elution curves of triazines obtained by using GPC column A and column B were compared. By using column A, the curves were broad (5 to 6 mL at the baseline) with their maxima positioned at 15.5 mL (ATR), 16.5 mL (DEA), and 17 mL (DIA). The triazine fraction had a total volume of 7 mL. Column B was preferred because the triazines were eluted earlier (elution curves maxima at 8 mL for ATR and 9 mL for DEA and DIA), width at the peak baseline was only about 2 mL, and the total volume of triazine fraction was 5 mL.

HPLC Determination

Separation was performed on a small-bore (2.1 mm I.D.) column. The phosphate buffer concentration of 2 mmol/L and pH value of 6.8 were found to be sufficiently high. The aqueous buffer was stabilized against bacteria growth by addition of 10% v/v acetonitrile. Because of a relatively low retention of DIA at initial composition of the mobile phase containing 19% v/v acetonitrile, the effect of lower initial acetonitrile concentration on separation was investigated; however, band broadening was observed for DIA and for DEA too.

To gain better separation of solutes with low retention, isocratic elution was applied before a gradient one. At the end of a chromatographic run, the column was flushed with acetonitrile/water 75:25 v/v and, afterwards, with acetonitrile to elute compounds with high retention. Separation conditions are summarized in Table 3. Results of HPLC separation are demonstrated on a chromatogram of spiked blank matrix in Fig. 3.

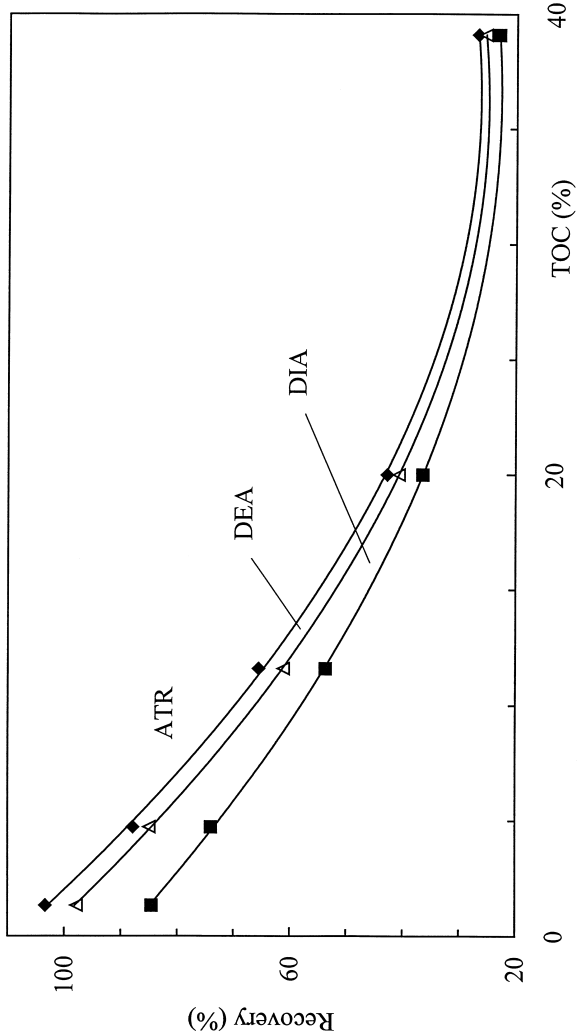

Figure 2. Variation of recovery with organic carbon content in soil. Blank matrices (10 g) spiked with ATR, DIA, and DEA, 1 µg/g each. Extracted 30 min with DCM/acetone 65:35 v/v at heating level of 2 and rinsed 10 min with condensate.

Table 3. Gradient Separation Conditions

min	% A	% B	% C
0	10	90	0
4	10	90	0
15	50	50	0
16	0	0	100
20	0	0	100
21	100	0	0
25	100	0	0
26	10	90	0

Solvent A - acetonitrile; B - 2 mmol/L KH_2PO_4, pH 6.80, 10% v/v CH_3CN; C - CH_3CN/water 75:25 v/v. Flow rate 0.4 mL/min, post-run equilibration with mobile phase 5 min.

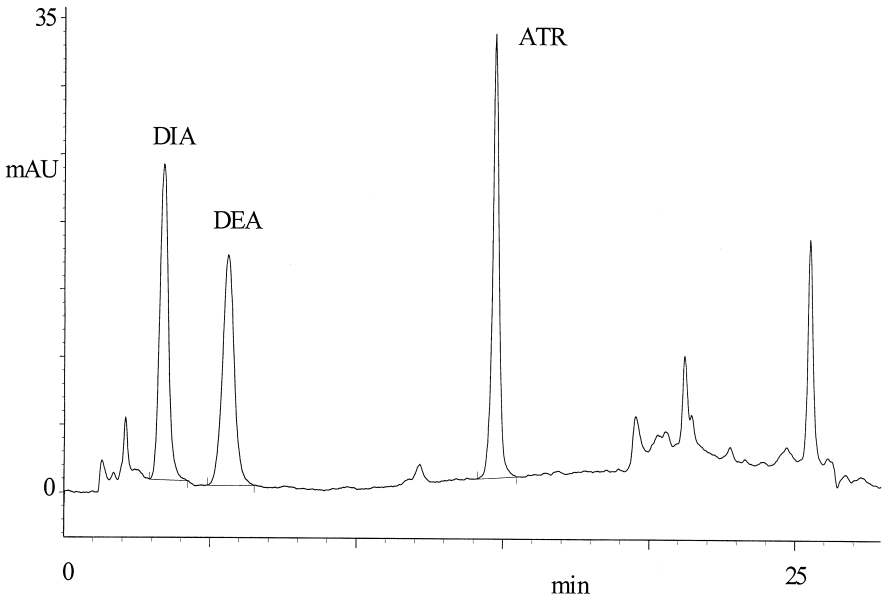

Figure 3. Analysis of S 99/479 blank matrix spiked with atrazine, desethylatrazine, and desisopropylatrazine at 1 μg/g level. Sample (10 g) 30 min extracted with 120 mL dichlormethane/acetone 65:35 v/v at heating level of 2 and 10 min rinsed with condensate. Extract cleaned up by GPC, column B, triazine fraction redissolved in 0.5 mL acetonitrile. HPLC separation as in Tab. 3, injected volume 3.6 μL. Solvent blank chromatogram subtracted.

Repeatability, Recovery, and LOD

Ten grams of S 99/479 blank matrix (TOC 1.91%) spiked with analytes at 1 μg/g level was analyzed at optimized experimental conditions. Standard deviations of 12.5 ng/g for ATR, 11.8 for DIA, and 4.2 ng/g for DEA were determined from seven parallel measurements. These values correspond to repeatability limits of 35 (ATR), 33 (DIA), and 11.8 ng/g (DEA) with a probability of 95%. ATR, DIA, and DEA were recovered at 98.1%, 87.5%, and 98.6%, respectively.

The highest sensitivity of determination was attained by extraction of 20-g samples. Limits of detection based on signal to noise ratio S/N=3 were found to be 2 ng/g for ATR and DIA and 4 ng/g for DEA.

Analyses of Field Samples

Samples (20 g) of surface layer of soil from maize fields treated with atrazine during May or at the end of September 1999 (VS locality only) were analyzed. As follows from the data presented in Tab. 4, the concentration of ATR in soil from VS locality decreased rapidly in a period of the first two months after

Table 4. Field Samples

Sample[a]	TOC[b] (%)	Period[c] (Days)	Found (mg/g Dry Weight) ATR	DIA	DEA
VS0999	0.77	1	2.874	0.023	0.012
VS1199	—	40	0.412	0.023	0.012
VS0400	—	195	0.116	< LOD	< LOD
ZE0999	1.25	126	0.002	0.014	< LOD
ZE0400	—	347	0.002	0.004	< LOD
TE0999	1.52	97	0.110	0.022	0.031
TE0300	—	290	< LOD	0.009	0.013
KL0999	1.86	121	0.070	0.026	< LOD
KL0400	—	342	< LOD	0.017	< LOD
PH0999	2.20	119	< LOD	< LOD	< LOD
PH0300	—	251	< LOD	< LOD	< LOD

[a]Denomination consisting of locality code, month and year of sampling.

[b]Total organic carbon content (Agema Ltd., Brno, CR).

[c]Time from treatment with herbicide to sampling date. VS locality treated with Zeazine S 40, the other ones with Gesaprim 500 FW. Locality code - ATR dose in mg/m^2: VS - 90, ZE - 50, TE - 75, KL - 75, PH - 100.

the treatment. However, a relatively high residue of ATR was found in soil from this locality in spring 2000, while in all other samples, ATR concentrations were lower than LOD value, or equal to it. Thus, after its autumn application, ATR can persist in the surface layer of soil till spring of the next year and contribute to phytotoxicity at the beginning of a new vegetative period.

Concentrations of more polar metabolites, DIA and DEA, were mostly several times lower than those of ATR and also decreased with time. DIA was shown as more persistent in the surface layer of soil than the other two phytotoxic analytes. DIA and DEA, found in a sample that was taken one day after treatment of VS locality, probably originates from the herbicide preparation used. It is of interest that their concentrations were not changed after 40 days. Unfortunately, processes influencing DIA and DEA concentrations in soil are too complex to explain this fact by a simple mean.

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