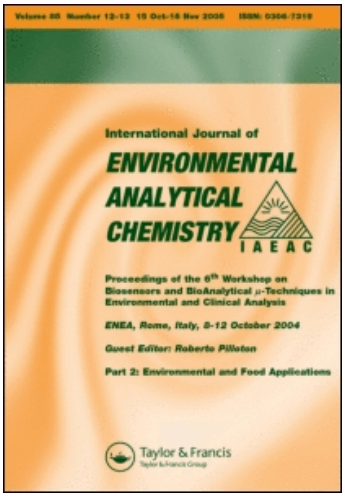

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LC–UV determination of atrazine and its principal conversion products in soil after combined microwave-assisted and solid-phase extraction

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A multiresidue method developed for the analysis of atrazine and its principal conversion products, deisopropylatrazine (DIA), deethylatrazine (DEA) and hydroxyatrazine (HA), in soil is presented. The method is based on the microwave-assisted extraction (MAE) of soil with aqueous methanol followed by solid-phase extraction (SPE) of the extracts and subsequent analysis by LC–UV with a diode array detector. MAE operational parameters (extraction solvent, extractant volume) were optimized with respect to extraction efficiency of the target compounds from soils with 2.5% organic matter (OM) content. Recoveries above 80% were obtained for all solutes. Soil OM content did not affect analyte recoveries. Recoveries from fresh and aged residues, the latter weathered under cold storage conditions, were not statistically different. Finally, MAE was found to be superior in terms of extraction efficiency, sample throughput, and solvent consumption to conventional flask-shaking extraction.

Keywords: Atrazine; Hydroxyatrazine; MAE; Soils

1. Introduction

Atrazine is a pre- and post-emergent herbicide belonging to the chemical class of S-triazines, used to control annual grasses and broad-leaved weeds in some vegetable and cereal crops, vines, fruit orchards, grassland, and forestry. It inhibits the growth of the target weeds by interfering with the normal function of photosynthesis [1]. Because of its extended use, the parent compound and some of its conversion products have often been found in surface and ground waters, especially in the USA and in Europe, raising concerns about its impact on the environment [2–7].

Atrazine can be degraded in soil via biotic or abiotic processes. N-dealkylation by soil bacteria can yield deethylatrazine (DEA) and deisopropylatrazine (DIA), whereas dechlorination yields hydroxyatrazine (HA). The latter, although it is thought to be

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a chemical hydrolysis procedure, can take place by the action of some bacteria as well [8]. The rate of atrazine degradation and the formation of its conversion products depend mainly on soil pH, organic matter, temperature, initial concentration, and soil micro-organisms [9–12].

Many methods have been reported for analysing atrazine and its conversion products, based on Soxhlet, ultrasonic, and flask-shaking techniques, where the soil is extracted using pure organic solvents or aqueous : organic mixtures in various proportions [13–17]. Quite often, these methods require the use of large amounts of organic solvents and are laborious and difficult to automate.

Microwave ovens, initially used for sample digestion, have also been used for extraction, offering advantages like improved efficiencies, reduced extraction time, low solvent consumption, and high level of automation compared with conventional extraction techniques [18, 19]. In MAE, microwave energy is absorbed by the extractant, which in turn transfers it to the sample in the form of heat. The partitioning of the analytes from the sample matrix to the extractant depends mainly on the temperature and nature of the extractant. Unlike classical heating, microwaves heat the entire sample simultaneously [20]. Microwave-assisted extraction (MAE) has been mainly used for extracting persistent organic pollutants like PCBs and PAHs from a variety of matrices, whereas in the field of pesticide residue analysis, methods for the extraction of triazines [21–27], phenylureas [28], sulphonylureas [29], phenoxyalkanoic acids [30, 31], chloroacetanilides [26], and EBDCs [32] have been reported. None of the aforementioned methods for the determination of triazines has incorporated HA in its target compound list. Recently, the determination of various triazines and some of atrazine's conversion products, including HA, based on the MAE concept has been reported [33]. However, the method was validated with only freshly spiked soil samples and only at a very high fortification level (15 μg/g), and because of the absence of a cleanup/pre-concentration step before HPLC analysis of extracts, LOD values are quite high (0.4–0.75 μg/g), precluding the use of the method when more realistic and/or trace levels of those compounds are to be determined. In fact, it is reported by the authors of this method that they had deliberately chosen to work with soils spiked at the 15 μg/g level in order to monitor only the recoveries of the extraction step by directly analysing crude soil extracts. Therefore, this method in its present form is not yet applicable to environmental monitoring of the target compounds.

The aim of this study was to provide an efficient method for the trace analysis of atrazine and its major conversion products DIA, DEA, and HA in agricultural soil, with subsequent cleanup/preconcentration utilizing solid-phase extraction (SPE) to enable the trace analysis of all compounds of interest in the μg/kg range.

2. Experimental

2.1. *Reagents*

Methanol, K_2HPO_4, H_3PO_4, and KH_2PO_4 for analysis grade, acetonitrile of HPLC grade and SPE Lichrolut EN cartridges (200 mg) were purchased from Merck (Darmstadt, Germany). Supelclean ENVI-Carb (250 mg) cartridges were purchased from Supelco (Bellefonte, PA). Water used in HPLC for mobile phase was

laboratory-distilled and filtered through 0.2 μm membrane filters (Millipore, Bedford, MA). Analytical standards of atrazine (2-chloro-4-ethylamino-6-isopropyl-amino-S-triazine), deisopropylatrazine (2-chloro-4-ethylamino-6-amino-S-triazine), deethylatrazine (2-chloro-4-amino-6-isopropylamino-S-triazine), and hydroxyatrazine (2-hydroxy-4-ethylamino-6-isopropylamino-S-triazine) were donated by Syngenta (Basel, Switzerland). Stock solutions of the above analytes at 1 mg/mL were made in methanol; working standard solutions containing each analyte at 0.5–50 μg/mL were also prepared in methanol. These solutions were used for the construction of calibration curves and the preparation of fortified soil samples. Stock solutions of individual compounds were stored in aluminium/Teflon-lined capped vials at −23°C; working standards solutions were also stored at −23°C.

2.2. *Instrumentation*

The MSP 1000 laboratory Microwave System (CEM, Matthews, NC) equipped with a 12-vessel carousel operated in the closed-vessel mode was used for the microwave-assisted extraction step. PTFE-lined extraction vessels were used, and during the operation both temperature and pressure were monitored in a single vessel; a sensor monitoring the solvent leaks in the interior of the microwave oven was also in use. The magnetron power was set at 100% (950 W).

The liquid chromatographic (LC) analysis was carried out on a TSP Spectra System (Thermo Separation Products, Austin, TX), which consisted of an in-line TSP degasser, a P4000 tertiary solvent pump, an AS3000 autosampler equipped with a 20 μL loop and a UV6000LP diode array detector. Chromatography was carried out on a Nucleosil 100–5 C18, 150 × 4.6 mm column (Macherey-Nagel, Düren, Germany) with a 7.5 mm Nucleosil guard column (Alltech Associates Inc., Deerfield, IL). Chromatographic data were monitored and processed by ChromQuest (TSP).

The mobile phase of the HPLC system consisted of a binary gradient mixture of a 10 mM KH_2PO_4 solution (solvent A) and a 90% acetonitrile : 10% water mixture (solvent B). The gradient programme was as follows: solvent A, initial 6%, then to 28% in 10 min followed by a gradient to 54% in 8 min and then to 80% in 7 min (hold for 5 min); then back to 6% B in 5 min. A linear ramp was always used. The mobile phase flow rate was set at 1 mL/min. The injection volume was 10 μL.

2.3. *Soil matrix*

All initial experiments (method optimization) were conducted using a sandy silt soil (33.7% silt, 12.8% clay, 49.7% sand) with 2.5% organic matter (OM) content and pH 7.4. The soil was air-dried and sieved through a 2 mm sieve before use.

Fortified samples were prepared by adding 1 mL portions of the appropriate stock solution to 10 g portions of soil. After thorough mixing, samples were left to stand overnight (freshly spiked samples).

For the preparation of soil samples with aged residues, fortification was done as in the case of freshly spiked samples. After an overnight standing, the samples were stored for a period of 6 months under refrigerated conditions (4–6°C) in order to minimize losses because of analyte degradation by soil micro-organisms.

2.4. *Sample preparation*

Ten-gram portions of soil samples were transferred into microwave extraction vessels and suspended in 40 mL of a 100 mM K_2HPO_4 (pH 7) : methanol (50 : 50, v/v) mixture. Extraction was carried out at 100°C for 20 min. After the extraction, the vessels were allowed to cool at a temperature below 40°C. The samples were centrifuged at 4500 rpm for 10 min, and then aliquots of 20 mL were withdrawn from the clear supernatants and diluted to 200 mL by the addition of the appropriate volume of distilled water. The samples were filtered through 0.45 μm membrane filters and then subjected to SPE.

SPE was performed on Lichrolut EN cartridges. Before use, the cartridges were preconditioned with 4 mL of methanol followed by 4 mL of distilled water. Extracts were loaded on the SPE cartridges at a rate of 5 mL/min. After sample application, and before air was drawn through the cartridges, the sample containers were washed with 10 mL of distilled water, which were loaded on the same cartridges. Finally, another 5 mL of distilled water was loaded onto the cartridges to wash away polar impurities. Subsequently, the cartridges were air-dried by pumping air for 15 min, and the retained solutes were eluted with 7 mL of methanol followed by 3 mL of ethyl acetate. The combined eluates were evaporated to dryness, and the residue was redissolved in 500 μL of methanol, filtered through a 0.45 μm membrane filter, and taken for HPLC analysis.

2.5. *Quantification and method validation*

Acquisition for quantitative measurements was made at 220 (atrazine, DIA, DEA) and 240 (HA) nm, while detection and identification were based on UV spectra scanned in the 200–350 nm range and compared with respective library stored spectra. Quantitative measurements were made by use of external standard calibration curves, which were linear in the range of 5–200 ng with $r^2 > 0.999$ for all compounds.

The method was validated by analysing freshly spiked soil samples with an OM content of 2.5% at the 50, 100, and 500 μg/kg fortification levels and soil samples with 1 and 5.6% OM content spiked at the 500 μg/kg fortification level. Also, soil samples with a 2.5% OM content spiked at the 500 μg/kg fortification level and stored at 4°C for a period of 6 months (aged residues) were also processed to assess the influence of aging on extraction efficiency. Finally, soil samples originating from two cornfields were processed by both the proposed MAE method and a conventional one based on the flask-shaking technique.

3. Results and discussion

3.1. *Selection of operational parameters*

Preliminary experiments were conducted in order to choose the best experimental parameters. A sample size of 10 g was selected without further consideration, since this represents a sample size providing adequate sensitivity for pesticide residue analysis. An extraction time of 20 min was selected based on initial experiments (data not shown). Although temperature is a key factor in the efficiency of the MAE methods, literature data indicated that the optimum extraction temperature for

triazines lies in the 100–115°C range [22, 25–27]. Thus, a temperature of 100°C was selected for all experiments.

It is generally accepted that the choice of the extraction medium is the most critical parameter in developing a MAE method. Thus, several extraction systems were evaluated for their efficiency to extract the target analytes, also taking into account the amount of co-extractive substances. Results are presented in figure 1. Recoveries for the dichloromethane : methanol (90 : 10) mixture were very high and in the same range as reported elsewhere for atrazine and its dealkylated conversion products using the same extractant [22]. However, HA was not extracted at all. Methanol and methanol : water (80 : 20) yielded recoveries above 80% for all analytes except for HA where recoveries were 25 and 58%, respectively. These extractants used widely in pesticide-degradation studies have often been shown to be inefficient for the adequate extraction of atrazine's hydroxylated conversion products [34]. The 100 mM buffer efficiently extracted DIA and DEA, which are the most water-soluble analytes, whereas atrazine and HA yielded recoveries of 75 and 64%, respectively. Recovery values for atrazine using an aqueous extractant have been reported to be 55% (21), 86% (27), and 91% (24), whereas for DIA and DEA, recoveries were >80% [21]. The 100 mM buffer : methanol (50 : 50) extractant yielded similar recoveries with the exception of HA where the use of the later yielded significantly higher recoveries (85%) (LSD test, $a = 0.05$). The MAE of atrazine, DIA, DEA, and HA using a 50 : 50 methanol : water extractant has been reported to yield recoveries similar to this study [33].

In view of these data, the 100 mM K_2HPO_4 (pH 7) : methanol (50 : 50) was selected. We also tested the effect of the buffer concentration (25, 50, and 100 mM) of the

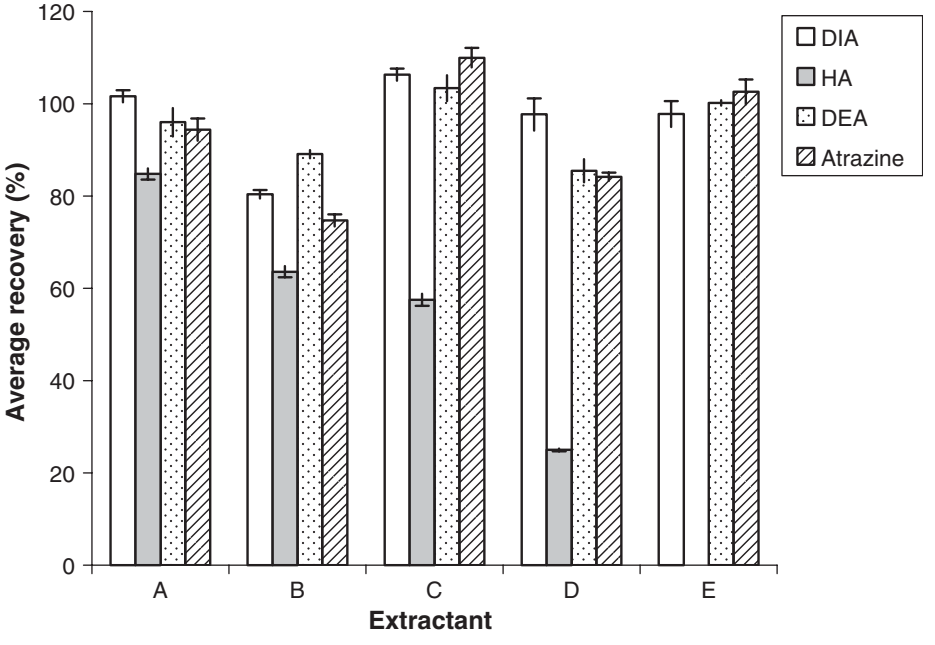

Figure 1. Effect of extractant on recoveries (A = 100 mM K_2HPO_4 (pH 7): methanol 50 : 50 (v/v), B = 100 mM K_2HPO_4 (pH 7), C = methanol : water 80 : 20 (v/v), D = methanol, E = dichloromethane : methanol 90 : 10 (v/v). Error bars represent the standard error.

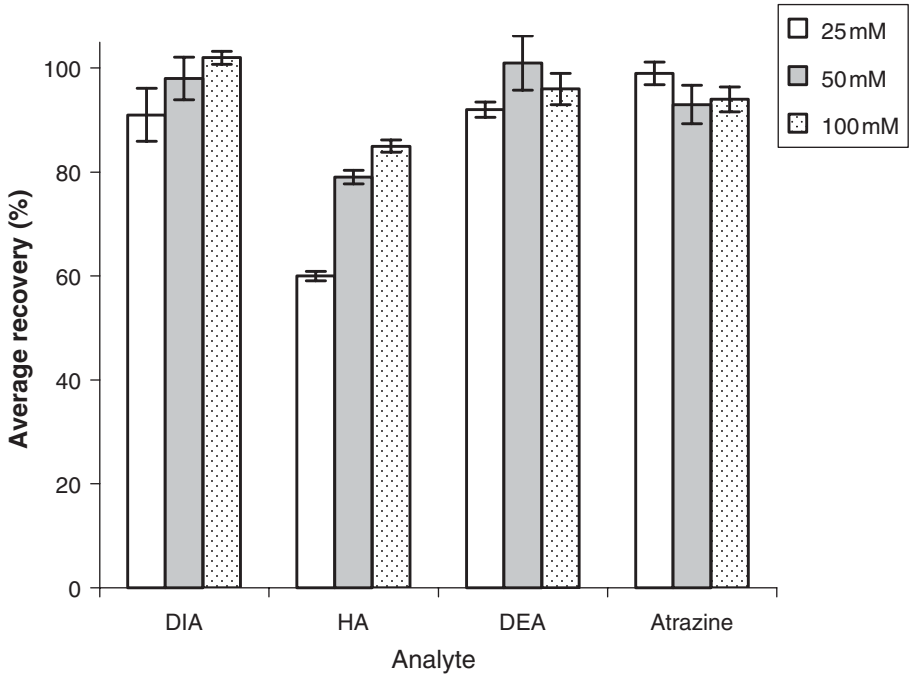

Figure 2. Effect of the buffer concentration of the extraction mixture on recoveries. Error bars represent the standard error.

selected extraction mixture on recoveries. Results are presented in figure 2. Although buffer concentration had no effect on the recoveries of atrazine, DIA, and DEA, it exerted significant effects (LSD test, $a = 0.05$) in the case of HA, with the 100 mM concentration giving the best.

The effect of the extractant volume on recoveries was also tested by performing extractions with 30, 40, and 50 mL of the selected extractant. No significant change in recoveries was observed, with the exception of HA, where there was a significant increase from 73 to 85% when the extractant volume was increased from 30 to 40 mL. No further increase was observed upon going to 50 mL (LSD test, $a = 0.05$).

3.2. *Optimization of the SPE procedure*

The conditions for the SPE pre-concentration step of the extracts were selected after preliminary experiments carried out to determine the breakthrough volumes of the target analytes on both Lichrolut EN and ENVI-Carb cartridges. The former is based on an ethylvinylbenzene–divinylbenzene copolymer with a large specific area ($\sim$1200 m^2/g), whereas the latter is based on a graphitized carbon black (GCB) material. Both cartridges have been employed successfully in the extraction of triazine herbicides and their polar degradation products from surface and ground waters [6, 35].

Although the usual approach in the case of aqueous organic solutions is to evaporate the organic solvent prior to SPE, we investigated the possibility of avoiding this time-consuming step by diluting the extracts with distilled water so as to obtain solutions with a low methanol content which could be directly processed by SPE.

Initial experiments were conducted using aqueous solutions containing 0 and 5% methanol, spiked with known amounts of each analyte. In each case, no breakthrough of the target analytes in the range of 50–400 mL was observed for both cartridges. In order to test the efficiency of the cartridges in the presence of sample matrix, the above procedure was repeated by processing blank soil samples by the MAE method, spiking the soil extracts with the target analytes and processing them as described before. Although recoveries for DIA, DEA, and atrazine were unaffected by the matrix in both cartridges, the Lichrolut EN cartridges yielded good recoveries only for HA. It has been reported that in the presence of large amounts of organic matter, low recoveries of polar analytes have been obtained from the GCB cartridges because of saturation phenomena [36]. However, in the present study, no further work has been done to ascertain the reason of HA's low recovery values. In light of these results, the use of the ENVI-Carb cartridges was discontinued, and the Lichrolut EN cartridges were selected for use. For the elution of the target analytes from the Lichrolut EN cartridges, the use of 3 mL of ethyl acetate in addition to 7 mL of methanol was found to be necessary, since it resulted in the better desorption of atrazine by 5–7%.

3.3. *Method validation*

The method was validated by analysing freshly spiked soil samples at the 50, 100, and 500 μg/kg fortification levels (table 1). Recovery values were in the range of 85–105%, while the RSDs were $<6\%$, except in the case of DIA at the 50 μg/kg fortification level (12%). LOQ values were found to be 50 μg/kg for every compound, thus facilitating the determination of those analytes at the residue levels found commonly in the environment. Sample chromatographic data are presented in figure 3.

The method was also tested by analysing freshly spiked soil samples with 1 and 5.6% OM content. It has been reported that atrazine sorption to soil is highly dependent on the soil's organic matter. Atrazine can interact with soil OM via electrostatic forces, hydrogen bonding, and hydrophobic partitioning [37], thus making extraction more difficult when increased amounts of OM are present. The results on the effect of the soil OM on recoveries are presented in figure 4. Recovery yield was not affected by soil OM for atrazine, DIA, and DEA, whereas for HA, recovery was higher in the 1% OM soil.

In addition to the analysis of the freshly spiked soil samples, soil samples with aged residues at the 500 μg/kg fortification level have been analysed, since the extractability

Table 1. Recoveries and RSDs of test analytes from 2.5% OM soil (a) freshly spiked (50–500 μg/kg) and (b) containing aged residues.

	Fresh residues						Aged residues	
	50 μg/kg		100 μg/kg		500 μg/kg		500 μg/kg	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
DIA	103	12	99	4	102	2	99	4
HA	98	1	92	4	85	2	85	5
DEA	101	3	102	1	96	6	90	3
Atrazine	105	2	103	1	94	4	89	1

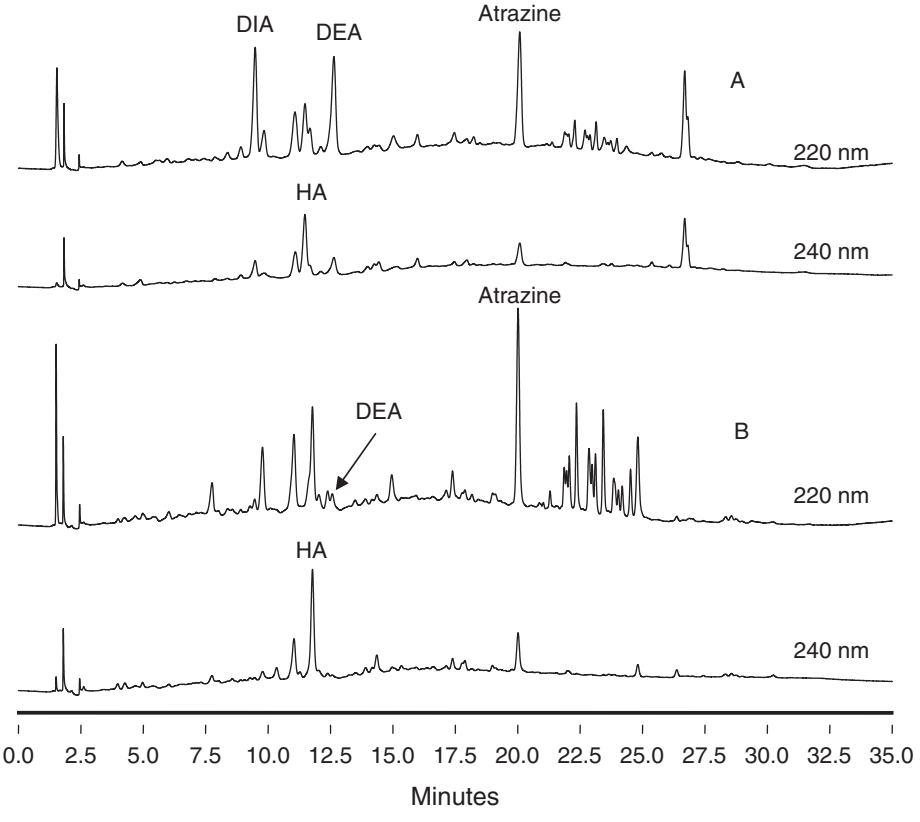

Figure 3. Sample chromatograms from the analysis of atrazine, HA, DEA, and DIA in soil extracts: A = fortified soil sample (2.5% OM) at the 500 μg/kg level; B = soil sample from Field B.

of atrazine and HA residues has been shown to be diminishing as a function of time [34]. Results are presented in table 1. The extraction efficiency of the method was not diminished in spite of the aging process (Student's *t*-test, $a = 0.05$), and recoveries were no different from those obtained from the freshly spiked samples, for every analyte. In another study employing an aqueous extractant, recoveries were lower for atrazine, simazine, propazine, and prometryn when a soil with aged residues was analysed [26]. However, recoveries for aged (300 days) residues of atrazine, simazine, DIA, and DEA were similar to fresh residues when the extraction was carried out with a dichloromethane : methanol (90 : 10) solution [21].

The proposed MAE method was also validated with the analysis of field soil samples from the plough layer (0–10 cm) of two fields cultivated with corn collected a month after the application of atrazine. For comparison reasons, the same soil samples were also processed with a method based on the conventional flask-shaking technique. Briefly, a 10 g portion of soil was extracted twice with 2×60 mL of a methanol : water (80 : 20, v/v) solution using a planar shaker (first extraction overnight; second for 1 h). After each extraction, the soil suspension was filtered through filter paper. The combined filtrates were concentrated using a rotary evaporator, diluted to 100 mL with distilled water, and processed by SPE (previously described). The performance of this method was checked by analysing freshly spiked soil samples with 2.5% OM at the

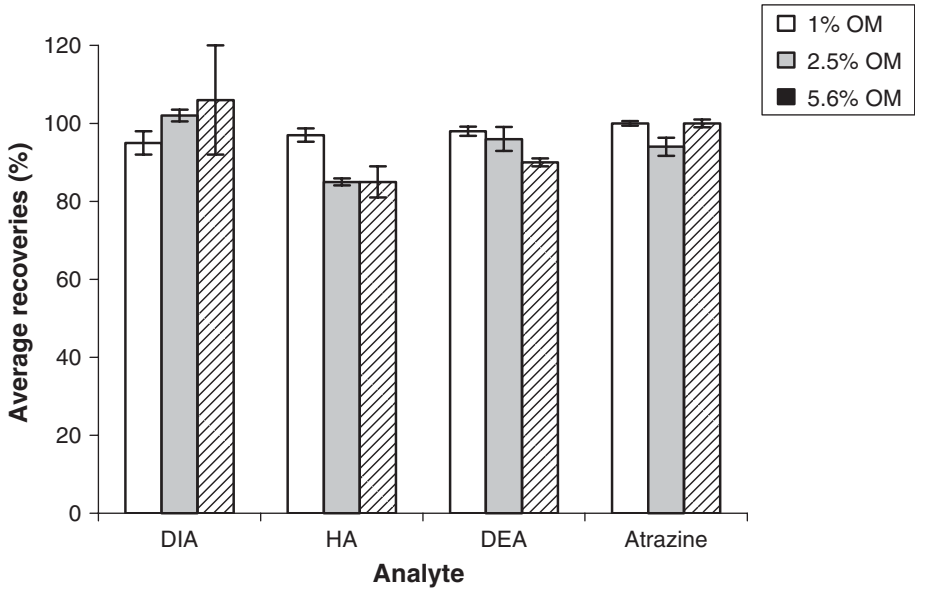

Figure 4. Effect of the soil OM content on recoveries. Error bars represent the standard error.

Table 2. Average concentrations ($n = 3$) in mg/kg and standard deviations of target analytes from two cornfield soil samples processed by the MAE and FSE methods.

	Field A		Field B	
	MAE	FSE	MAE	FSE
DIA	n.d.	n.d.	n.d.	n.d.
HA	1.19 (0.14)	0.25 (0.02)	0.66 (0.01)	0.18 (0.01)
DEA	0.06 (0.01)	n.d.	0.07 (0.01)	n.d.
Atrazine	1.23 (0.03)	0.82 (0.03)	0.72 (0.03)	0.49 (0.03)

50, 100, and 500 μg/kg fortification levels. Recoveries were >80% for all the target analytes.

Results are presented in table 2. It is clear that the MAE method was much more efficient for the extraction of atrazine, DEA, and HA from both samples. DIA was not detected in either case. Especially in the case of HA, the amount extracted using the MAE method was more than four times the respective amount extracted using the conventional method. Overall, even though the two methods exhibited similar extraction efficiencies for freshly spiked soil samples, when soil samples with incurred residues were analysed the conventional method was unable to efficiently extract the target analytes.

4. Conclusions

A method for the determination of atrazine, DIA, HA and DEA based on the MAE technique was developed. The recoveries of the proposed method were >80% for all

solutes in both freshly spiked and aged soils. Also, soil organic matter content had no effect on recoveries in the range of 1–5.6%. Moreover, the MAE method was more efficient than the method based on the conventional flask-shaking technique. Compared with the later, organic solvent consumption was reduced to 1/5, whereas the sample throughput was 1.5–2 higher.

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