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Determination of Triazine and Chloroacetanilide Herbicides in Soils by Microwave-Assisted Extraction (MAE) Coupled to Gas Chromatographic Analysis with Either GC−NPD or GC−MS

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A simple and rapid method based on microwave-assisted extraction (MAE) coupled to gas chromatographic analysis was developed for the analysis of triazine (atrazine, cyanazine, metribuzine, simazine and deethylatrazine, and deisopropylatrazine) and chloroacetanilide (acetochlor, alachlor, and metolachlor) herbicide residues in soils. Soil samples are processed by MAE for 5 min at 80 °C in the presence of acetonitrile (20 mL/sample). Mean recovery values of most solutes are >80% in the 10 to 500 μg/kg fortification range with respective RSDs (relative standard deviations) < 20%. The limits of quantification (LOQ) and limits of detection (LOD) are 10 and 1 to 5 μg/kg, respectively. The method was validated with two types of soils containing 1.5 and 3.0% organic matter content, respectively; no statistically significant differences were found between solute recovery values from the two types of soils. The solute mean recovery values from freshly spiked (24 h aging) and spiked samples stored refrigerated for one week before processed were also not statistically different. Residue levels determined in field weathered soils were higher when soils were processed by MAE than with a comparison method based on flask-shaking of soil suspensions overnight. Extracts were analyzed by a gas chromatographic system equipped either with a thermionic (GC−NPD) or a mass spectrometric detector (GC−MS).

KEYWORDS: Triazines; chloroacetanilides; herbicides; microwave-assisted extraction (MAE); gas chromatographic analysis; GC−NPD; GC−MS; soil residues

INTRODUCTION

Simple, rapid, and inexpensive methods producing minimum amounts of wastes, preferably wastes free of toxic organic solvents, are needed in environmental analysis. In recent years, sample preparation attracted special attention and as a result different instrumental techniques such as supercritical fluid extraction (SFE), sonication, and microwave-assisted extraction (MAE) are gaining increased preference over the traditional laborious techniques of blending and shaking or refluxing (Soxhlet) substrates with organic solvents. In fact, among these instrumental techniques, MAE is becoming particularly popular because of its simplicity, low cost of operation in terms of required materials and manpower, and rapidity while it is as accurate as SFE and sonication and superior in terms of precision (*1*). Thus, applications of MAE, especially in the area of environmental organic analysis, are increasing rapidly (*2*, *3*); however, the main body of applications is devoted so far to the extraction of persistent hydrocarbons from marine sediments, soils, and solid wastes (*1*, *3*−*5*). Applications of MAE for the extraction of a few chemical groups of pesticides from soil (*4*, *6*−*9*) and plant matrixes (*10*−*12*) have been reported so far. Stability problems under MAE conditions for some thermally labile organophosphorus pesticides have been also reported (*13*).

The purpose of this study was to investigate the feasibility of using microwave energy for the efficient extraction from soils of triazine and chloroacetanilide herbicides and develop a simple and rapid method that can be used in soil pollution monitoring programs as well monitoring pesticide residues on farm or off farm contaminated sites (sites of rinsing and filling of spraying equipment and accidental spill sites). Triazine and chloroacetanilide herbicides are widely used worldwide and their environmental behavior, especially in the soil environment where they are applied or spilled, is of great concern because these are among the most frequently found pesticides contaminating surface and groundwater aquatic systems (*14*−*16*), atmospheric air (*17*), and rainwater (*17*, *18*).

EXPERIMENTAL SECTION

Materials. Acetonitrile, methanol, and ethyl acetate of pro-analysis grade and Lichrolut EN 500 mg cartridges were purchased from Merck (Darmstadt, Germany). Analytical standards of atrazine [6-chloro-*N*-ethyl-*N*′-(1-methylethyl)-1,3,5-trazine-2,4-diamine] of 98% purity, deethylatrazine [DEA: 2-amino-4-chloro-6-isopropylamino-*s*-triazine] of 92% purity, deisopropylatrazine [DIA: 2-amino-4-chloro-6-(ethylamino)-*s*-triazine] of 92% purity and metolachlor [2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl)acetamide] of 98% purity

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Table 1. MAE Operational Conditions

magnetron power	90% (900 W)
time to reach settings	1.5 min
extraction temperature	80 °C
extraction duration	5 min
solvent	acetonitrile
solvent volume	20 mL
sample weight	10 ± 0.1 g of air-dried soil
maximum vessel pressure cutoff	100 psi

were donated by Syngenta (Basil, Switzerland). Simazine [6-chloro-*N*,*N*′-diethyl-1,3,5-trazine-2,4-diamine] of 99.8% purity, acetochlor [2-chloro-*N*-(ethoxymethyl)-*N*-(2-ethyl-6-methylphenyl)acetamide] of 99.5% purity, alachlor [2-chloro-*N*-(2,6-diethylphenyl)-*N*-(methoxymethyl)acetamide] of 99% purity and cyanazine [2-[[4-chloro-6-(ethylamine)-1,3,5-trazin-2-yl]amino]-2-methylpropanenitrile] of 99% purity analytical standards were obtained from Promochem (Wesel, Germany), and metribuzin [4-amino-6-(1,1-dimethylethyl)-3-(methylthio)-1,2,4-trazin-5(4H)-one] of 99.3% purity was donated by Bayer (Monheim, Germany).

Stock solutions of individual analytes at 1 mg/mL were made in ethyl acetate; mixed standard stock solutions made were serially diluted with ethyl acetate to produce a series of working standard solutions of 0.1 to 100 μg/mL. The latter solutions were used for the construction of calibration curves and the preparation of the fortified soil samples. Stock solutions were stored in deep freeze (−23 °C), while the working standard solutions were stored refrigerated and renewed at bimonthly intervals.

Apparatuses and Respective Operational Parameters. The MSP 1000 laboratory microwave system (CEM, Matthews, NC) equipped with 12 vessel carousel operated in the closed mode was used for the microwave-assisted solvent extraction (MASE) of soils. PTFE-lined extraction vessels were used. During operation, both temperature and pressure were monitored in a single vessel and a sensor monitoring the solvent leaks in the interior of the microwave oven was also in use. The operational parameters of the microwave-assisted extraction apparatus are shown in **Table 1**.

For separation and quantification of solutes a Hewlett-Packard, model 5890, gas chromatograph equipped with a thermionic detector (NPD) and an on-column injector was used. Gas chromatography (GC) was carried out on a HP-1 megabore column (10 m, 0.53 mm, 2.65 μm film thickness). The detector and injector temperatures were at 300 and 220 °C, respectively. Helium was used as carrier gas at a constant flow rate of 4 mL/min by use of EPC (electronic pressure control). For operation of the NPD the hydrogen flow was set at 4 mL/min and the air at 100 mL/min. Helium was used as the detector makeup gas at 30 mL/min. The oven was operated under temperature gradient with initial temperature set at 80 °C (hold for 2 min), increase to 190 °C at the rate of 3 °C/min (hold 3 min), increase to 265 °C at the rate of 30 °C/min (hold 2 min) and return to initial conditions in 10 min. Total run time 46.2 min. Two microliter injections were made by use of an autosampler (model HP6890). The GC−NPD system was controlled and data were acquired and processed by use of the Chemstation software (Hewlett-Packard).

A gas chromatographic-ion trap mass spectrometric system (GC−ITMS) can be also used for residue determination and/or confirmation only. A GC−MS ion trap system, model GCQ (TSP, Austin, TX) was used. The system was equipped with a Restek RTX 5MS 30 m × 0.25 mm and 0.25 μm film thickness column (Bellefonte, PA). The oven column was operated under the following temperature gradient: 80 °C (initial, hold 1 min), 25 °C/min to 150 °C, 4 °C /min to 200 °C (hold 2 min), 15 °C /min to 230 °C (hold time zero), 22.5 °C/min to 275 °C (hold time 5 min) and return to initial temperature (total run time 26 min with 20 min acquisition period). Injections of 1 μL were made by use a AS2000 autosampler (TSP); a Split/Splitless injector (Split ratio 50 mL/min) thermostated at 250 °C and operated in splitless mode under surge pressure of 13.3 psi for 1 min was used. Helium was used as carrier gas set under constant flow (1 mL/min). The MS system was operated under the following conditions: source and transfer line temperatures at 200 and 280 °C, respectively; full scan mode in the 50−500 *m*/*z* range, and quantification at 172 (DEA), 173 (DIA), 215 (atrazine), 188 (alachlor), and 238 (metolachlor) *m*/*z*.

Table 2. Mechanical Texture and Organic Matter (OM) Content of Soils Used for Method Development and Validation

soils/origin	% clay	% silt	% sand	% OM	soil category
typical soil[a]	12.8	33.7	49.7	1.5	sandy silt loam
corn field A	16.5	67.4	21.3	2.97	silt loam
corn field B	27.3	20.9	48.1	0.81	clay loam

[a] This is a typical Mediterranean soil.

In both GC systems, quantification was made by use of external standard calibration curves made by use of the mixed standard working solutions (0.1 to 10 μg/mL for the GC−NPD system and 1−100 μg/mL for the GC−MS system).

Microwave-Assisted Extraction (MAE). Soils were air-dried, mixed, and sieved through a 2-mm sieve; portions of 10 ± 0.1 g of air-dried soils were processed by MAE. All experiments for method development were carried out in triplicate using a typical Mediterranean soil, a sandy silt loam soil with 1.5% organic matter content (**Table 2**); the moisture of the air-dried soil was 1.4%. Soil samples transferred into the MAE vessels were suspended into 20-mL portions of acetonitrile and the vessels closed gastight were shaken vigorously by hand for 30 s; sets of 12 vessels were microwave extracted according to the operational program shown in **Table 1**. The vessels, before being removed from the microwave oven, were allowed to stand for about 10 min to cool to 38−40 °C. The vessels removed from the oven were shaken by hand for 10 s and the samples transferred into 50-mL centrifuge tubes were centrifuged at 4500 rpm for 5 min. Aliquots of 10 mL removed from the supernatants were concentrated to dryness, by use of a nitrogen stream, and the residues redissolved in 0.2-mL aliquots of ethyl acetate were taken for GC analysis.

Comparison of Soil Extraction Techniques. For comparison reasons a previously used and validated method based on the traditional flask-shaking extraction technique was compared to the MAE-based method. Portions of 10 ± 0.1 g of air-dried soil dispersed in 60 mL of methanol/water (80:20) were shaken overnight (18 h) by use of a planar mechanical shaker operated under ambient conditions. Samples were centrifuged for 5 min at 4500 rpm and while the supernatants were transferred into round-bottom flasks, the pellets resuspended into an additional 60 mL of the extraction mixture were shaken for an additional 1 h, the shaker thermostated at 50 °C. After centrifugation, as above, the supernatants combined into the same round-bottom flasks were concentrated to a small volume (20−30 mL) by use of a rotary evaporator operated under reduced pressure. The aqueous concentrates were diluted by addition of distilled water and after filtration through 0.5 μm membrane filters the respective volumes were adjusted to 100 mL. These aqueous extracts were subsequently processed by solid-phase extraction (SPE) using Lichrolut EN cartridges of 500 mg. SPE cartridges were conditioned with methanol (6 mL) and water (6 mL) before use. After sample loading solutes were eluted with 5 mL of methanol followed by 1 mL of ethyl acetate. The eluates collected into the same centrifuge tube were concentrated to dryness by use of a nitrogen stream and the residues redissolved in aliquots of 200 μL of ethyl acetate were taken for GC analysis. Recovery values of all solutes were >80%, while LOD and LOQ levels were the same as those of the MAE-based method.

Method Validation. The method was validated with the analysis of fortified soil samples spiked at 500, 100, 50, 10, and 5 μg/kg of soil air-dried weight. Fortified samples were processed at 24 h (fresh residues) and one week storage (aged residues) after spiking, respectively. After spiking, all samples were allowed to stand for 1 h at ambient conditions for the evaporation of the spiking solvent and then were stored for the specified period under refrigerated conditions (4−6 °C). The method was also validated with the analysis of fortified soil samples which were artificially enriched in organic matter (3%) by addition of peat. Finally, the method was validated with the analysis of field treated soils sampled from the plough (0−10 cm) layer of two corn fields. The same set of samples were also processed by the

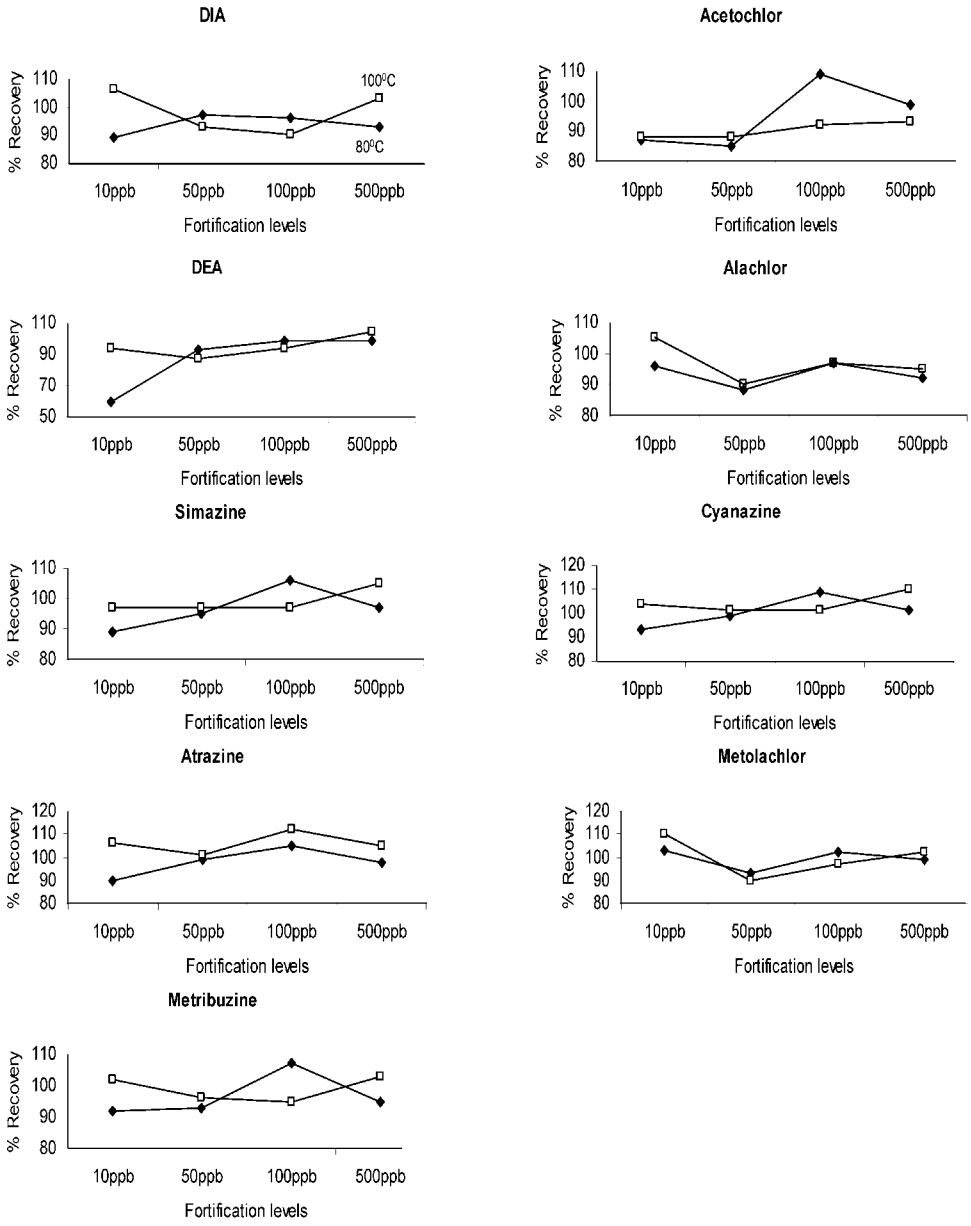

Figure 1. Analyte recoveries vs fortification levels when soil samples were processed by MAE at 80 and 100 °C, respectively, while all other parameters were set as shown in Table 1.

comparison flask-shaking extraction technique. Soil extracts derived from both extraction techniques analyzed by GC−ITMS were compared.

Determination of the Detection and Quantification Limits. For the GC−NPD based method, the limit of detection (LOD, μg/kg) of each solute was determined as the lowest concentration giving a response of three times the standard deviation of the baseline noise defined from the analysis of three control (untreated) samples. For the GC−ITMS based method, the respective LOD (μg/kg) was based on full-scan spectrum identification at a signal-to-noise ratio of 3. The limit of quantification (LOQ, μg/kg) in both cases was determined as the lowest concentration of a given compound giving a response that could be quantified with a relative standard deviation (RSD) lower than 20%.

RESULTS AND DISCUSSION

General Considerations. A series of preliminary experiments were conducted in selecting the optimum operation conditions of the microwave oven (**Table 1**). Many experimental variables such as temperature and duration of extraction, amount of sample and extraction solvent, and respective volume needed to be optimized. For this optimization process, the factorial design approach has been adopted in some recently reported MAE-based methods (*9*, *19*). Among the parameters included in **Table 1**, the magnetron power setting of 90% (900 W) was selected arbitrarily. A sample weight of 10 ± 0.1 g (air-dried soil) was also selected without further consideration since this is the amount of sample normally needed in residue methods based on modern instrumental chromatographic systems associated with either selective or mass spectrometric detectors.

Acetonitrile was also selected a priori as the extraction solvent because most pesticides have good solubility in acetonitrile and an acetonitrile−water mixture was previously found to be appropriate (recovery values > 80%) for the extraction of soil residues of many chemical groups of pesticides including also those of triazine and chloroacetanilide herbicides (*20*). However, in the latter method solutes were extracted by shaking the soil suspensions overnight (16 h) and the presence of water in the extraction medium was found necessary to efficiently desorb

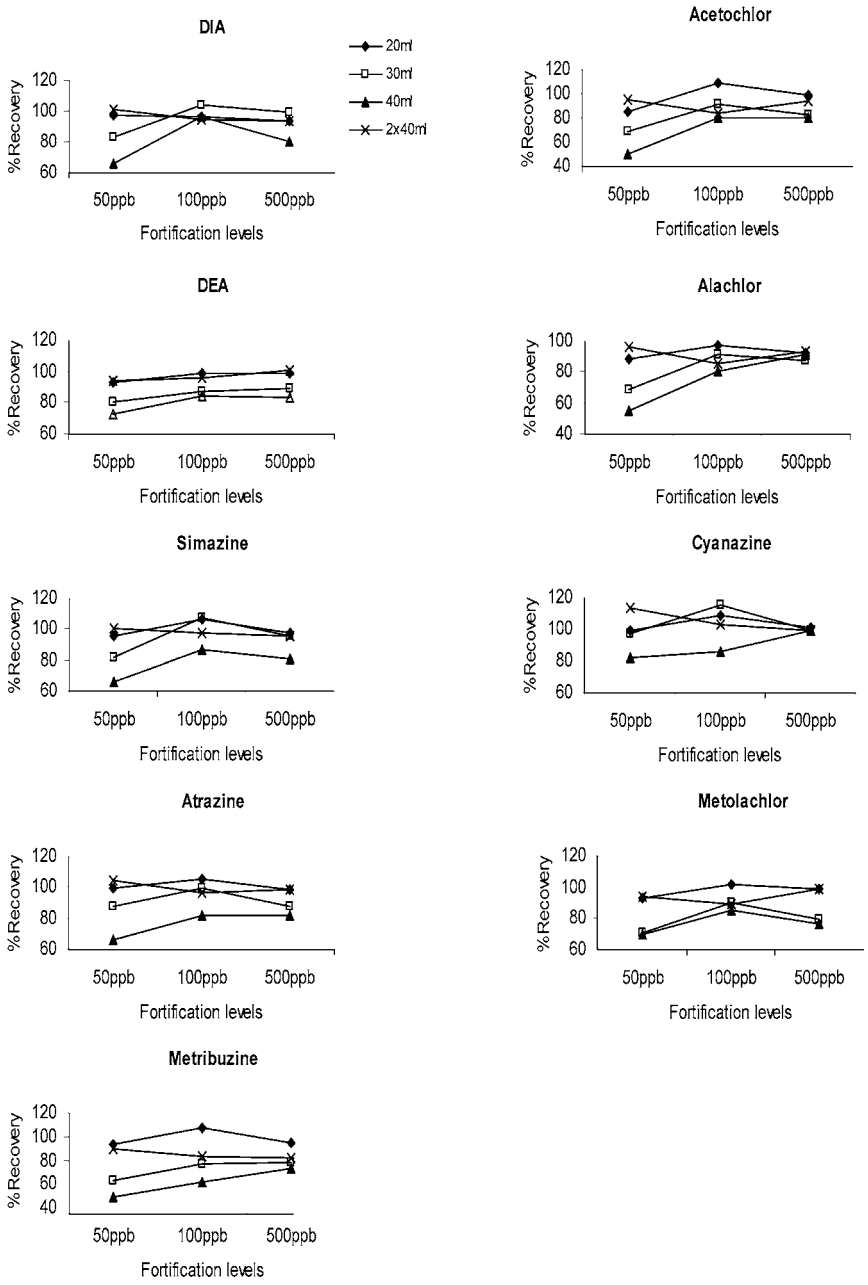

Figure 2. Analyte recoveries vs fortification levels when soil samples were processed by MAE and the solvent (acetonitrile) volume was set at 20, 30, 40, and 2 × 40 mL, respectively, while all other parameters were set as shown in Table 1.

pesticides from the soil matrix. The addition of water was found unnecessary in the MAE operated method since acceptable recovery values were also obtained in the absence of water. Moreover, due to the absence of water from the extraction medium, a liquid−liquid partition or solid phase extraction step, otherwise needed to transfer solutes from the aqueous medium into a water immiscible GC-amenable organic solvent, was made redundant. Furthermore, the use of pure acetonitrile, as the extraction solvent, was considered as an improvement over another MAE-based method reported for the analysis of triazine residues in soils (*6*); in the latter method, MAE was carried out in the presence of dichloromethane−methanol mixtures. The use of dichloromethane and of other halogenated solvents is slowly phasing out from analytical methods especially those intended to be used for reasons of environmental protection.

In conclusion, among the main parameters affecting the efficiency of a microwave-assisted extraction (*2*, *3*), the extraction temperature and duration and the solvent volume were the only ones experimentally optimized. An upper limit of 100 psi pressure was also set for operator safety precautionary reasons even though the pressure in MAE vessels never exceeded 10 psi.

Optimization of Solvent Volume and Extraction Temperature. Preliminary experiments of MAE with spiked soils were carried out at 80 and 100 °C, respectively. A higher extraction temperature was excluded to avoid solute degradation. Analyte recovery data derived from these experiments are shown in **Figure 1**. Mean recovery values for all solutes except for DEA were higher than 90% with respective RSDs less than 20% obtained at both temperature settings and at all fortification levels (10 to 500 μg/kg); the recovery of DEA was 60% at 80 °C of samples spiked at 10 μg/kg. Furthermore, the mean recovery values obtained at the two temperature settings were found to have a nonstatistically significant difference for most analytes except for DIA and DEA; for the latter two compounds, mean recovery values from soils spiked at 10 μg/kg were

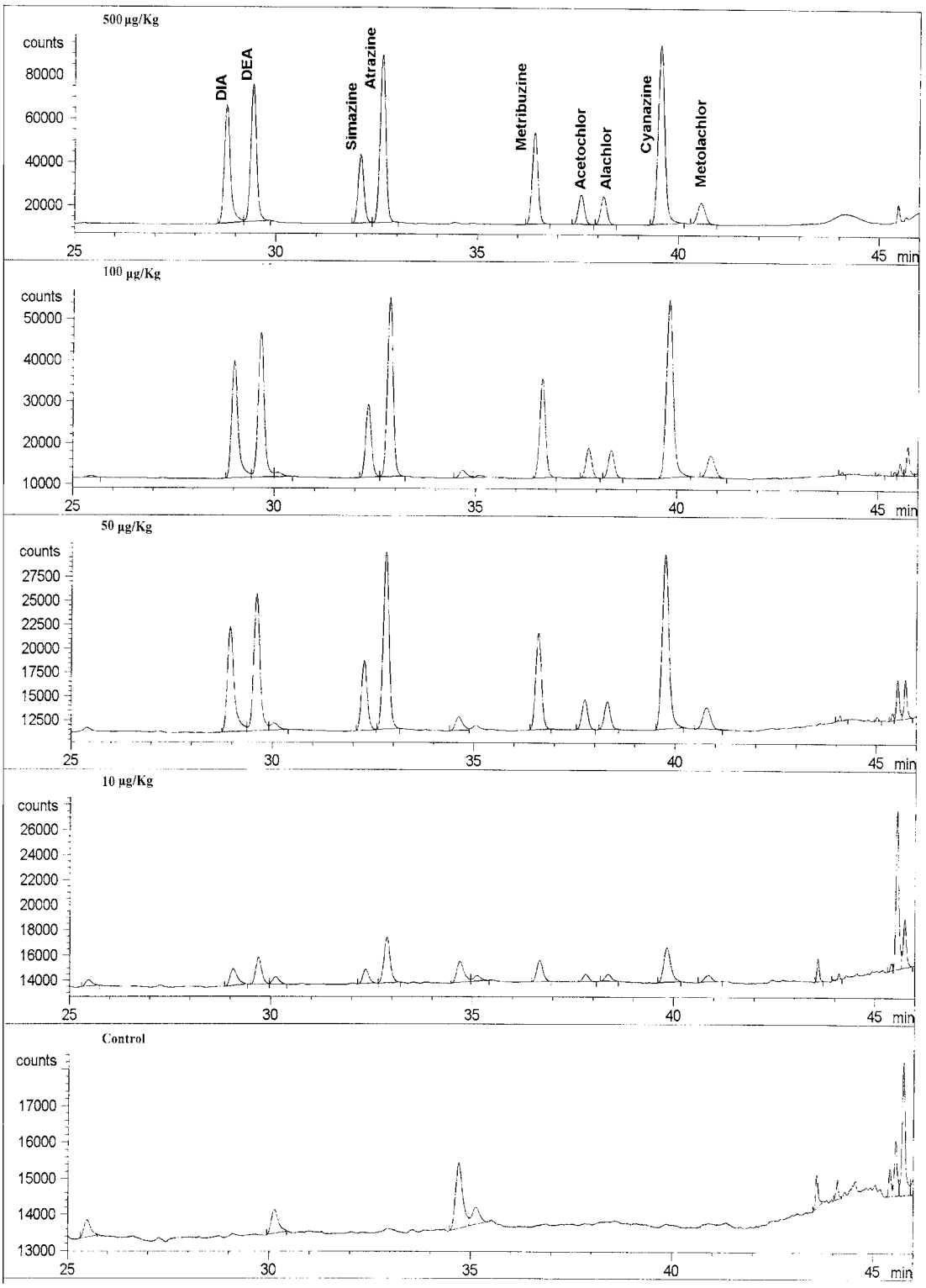

Figure 3. Sample chromatograms from the analysis by GC–NPD of extracts of fortified soil samples processed by MAE operated under the selected conditions (Table 1). After concentration of the acetonitrile extracts, residues were taken for GC analysis dissolved in 500 μL for the 500 μg/kg fortification level and in 200 μL of ethyl acetate for the rest. Gas chromatographic and other experimental conditions are as given in the Experimental Section.

significantly higher when extraction was carried out at 100 than 80 °C. Nevertheless, despite the lower recoveries of DIA and DEA at the 10 μg/kg level, the 80 °C setting was selected as the extraction temperature since at this temperature extracts were much cleaner of co-extractives. The significance of the recovery differences between the two sets of mean recovery values derived from experiments carried out at 80 and 100 °C, respectively, was evaluated by the least significant difference test (LSD at $a = 0.05$) (data are not shown).

The influence of the extractant volume on the efficiency of the MAE was evaluated by processing soils spiked at 50−500 μg/kg with the solvent volume ranging from 20 to 40 mL (**Figure 2**). The mean recoveries of all solutes increased as the solvent volume decreased from 40 to 20 mL. These recovery increases were found to be statistically significant when evaluated by the Duncan's test at $a = 0.05$ (data are not shown). Furthermore, the mean recovery values of metribuzin and acetochlor were also significantly higher when soils were

Table 3. Mean (%) Recoveries[a] and Respective (RSDs) of Target Analytes from Fortified Soils Processed by MAE[b] 24 h (Fresh Residues) and 168 h (Aged Residues) after Spiking and Combined (Fresh and Aged Residue) Recovery Data and Respective RPDs (Relative Percent Differences)

	fortification levels								
	50 μg/kg			100 μg/kg			500 μg/kg		
compound	24 h	168 h	mean (%RPD)	24 h	168 h	mean (%RPD)	24 h	168 h	mean (%RPD)
DIA	97(2)a	96(1)b	97(1)	96(7)a	101(2)a	99(5)	93(10)a	94(6)a	94(1)
DEA	93(2)a	87(6)a	90(7)	99(6)a	95(2)a	97(4)	99(7)a	97(6)a	98(2)
simazine	95(2)a	98(2)a	97(3)	106(6)a	104(3)a	105(2)	97(7)a	96(5)a	97(1)
atrazine	99(0)a	96(3)a	98(3)	105(5)a	102(5)a	104(3)	98(8)a	93(4)a	96(5)
metribuzine	93(3)a	100(2)a	97(7)	107(6)a	105(4)a	106(2)	95(7)a	95(5)a	95(0)
acetochlor	85(6)a	94(3)a	90(10)	109(8)a	100(4)a	105(9)	99(7)a	83(4)a	91(18)
alachlor	88(6)a	95(3)b	92(8)	97(7)a	103(5)a	100(6)	92(7)a	83(2)a	88(10)
cyanazine	99(1)a	104(0)a	102(5)	109(9)a	105(6)a	107(4)	101(12)a	98(9)a	100(3)
metolachlor	93(5)a	86(6)a	90(8)	102(5)a	97(3)a	100(5)	99(4)a	85(3)a	92(15)

[a] Recovery values in the same row and at the same fortification level designated by different letters are statistically different (comparisons of means, LSD, at 0.05). [b] Other MAE operational conditions are those shown in Table 1.

extracted by MAE with 20 than 2 × 40 mL of acetonitrile; recovery differences were not significantly higher for the rest of the target analytes. Consequently, the volume of the extraction solvent was set at 20 mL. In preliminary experiments, lower volumes of the extraction solvent were also evaluated. Recovery values increased as the solvent volume decreased up to 10 mL; however, by decreasing the solvent volume beyond 20 mL the precision of the method decreased (RSDs of mean recovery values >20%) (data are not shown). The increase of solute recovery values as the extractant volume decreased was also reported in other MAE-based methods (*2*), and it was assigned to a better stirring of sample suspensions by microwaves energy as the extractant volume decreased. Apparently, the same reasoning can be also applied for the efficacy equivalence or even superiority (metribuzin and acetochlor) of 1 × 20 mL than 2 × 40 mL partition steps reported above.

All the above experiments were carried out at 5 min extraction period, and since this short extraction period was found adequate for the quantitative recovery of all solutes no further reduction of the extraction period was investigated.

Chromatographic Analysis, Calibration, and Linearity. Sample data derived from the analysis by GC−NPD of MAE extracts of spiked soils are shown in **Figure 3**. The chromatograms of all samples are clean of co-extractives and solutes are eluted well resolved. A long oven temperature gradient was selected (run time 46.2 min) to improve the chromatographic resolution since among the target analytes of this method certain pairs of solutes such as DIA/DEA, atrazine/simazine, and acetochlor/alachlor are difficult to resolve under many chromatographic conditions. A shorter chromatographic run time (26 min) was possible with the GC−ITMS system taking advantage of the higher resolution and solute confirmatory power of the MS. Calibration for quantification was carried out by use of external standard calibration curves; calibration curves were linear in the 0.2−20 ng range (GC−NPD) and 1−100 ng range (GC−ITMS) with respective correlation coefficients being better than 0.999 for all the solutes.

Method Validation. The mean recovery values of solutes from soils spiked at 50−500 μg/kg and the MAE operational parameters set as selected above (**Table 1**) are shown in **Table 3**. The accuracy and precision of the method, as depicted by the % mean recovery values and respective RSDs, are acceptable since recovery values are >80% and respective RSDs are <20% for all solutes and at all fortification levels. Recovery values for all solutes, except for DEA, were also as good at the 10 μg/kg fortification level (**Figure 1**); the respective mean recovery value for DEA at the 10 μg/kg level was 60%.

The proposed method was also validated by analyzing fortified soil samples stored, before processed, for one week (168 h) at 4−5 °C, to simulate conditions of field weathered soil residues (**Table 3**). The mean recovery values of all solutes and at all fortification levels were not significantly different from the respective recoveries of fresh residues (24 h weathering period). The differences between mean recovery values were evaluated by use of the least significant difference test at $a = 0.05$. Thus, by use of the MAE technique aged residues of the sought analytes can be desorbed from soils as effectively as those of fresh residues. For these experiments, residues were aged under low-temperature conditions (4−5 °C) to diminish solute chemical and microbial degradation as well evaporation losses. Apparently, microwave energy does not operate only as a sole internal heating source of the processed matrix; the fact that in MAE heating is generated by ionic conduction and dipole rotation the solute release from the matrix and partition into the liquid phase is highly facilitated and thus desorption of both fresh and aged residues is equally effective.

Since the % mean recoveries of fresh and aged residues of all solutes were not significantly different, these two sets of data were also used to assess the reproducibility of the overall method. Thus, for each solute and at each fortification level a mean recovery value and the respective RPD (relative percent difference) was calculated (**Table 3**). Obviously, since the RPDs for all solutes and at all fortification levels are < 20% the reproducibility of the method is acceptable.

All optimization experiments were performed with a sandy silt loam soil with 1.5% organic matter content, which is a typical soil of the Mediterranean region. Given that all target analytes of this method are mainly adsorbed onto the soil organic matter, it was expected that the desorption efficiency of MAE will deviate depending upon the organic matter content of the processed soils. Therefore, the method was also evaluated by analyzing spiked samples prepared with a batch of the above typical soil artificially enriched in organic matter (OM) by addition of peat (10%, w/w). These recovery data are presented in **Figure 4**. In the same figure, for reasons of comparison, the recovery data derived from the analysis of spiked soils containing 1.5% OM are also included. The mean recovery values of solutes were equal or slightly lower from the soils with 3% OM than from 1.5% OM; however, for most solutes the differences between the recovery values from the two types of

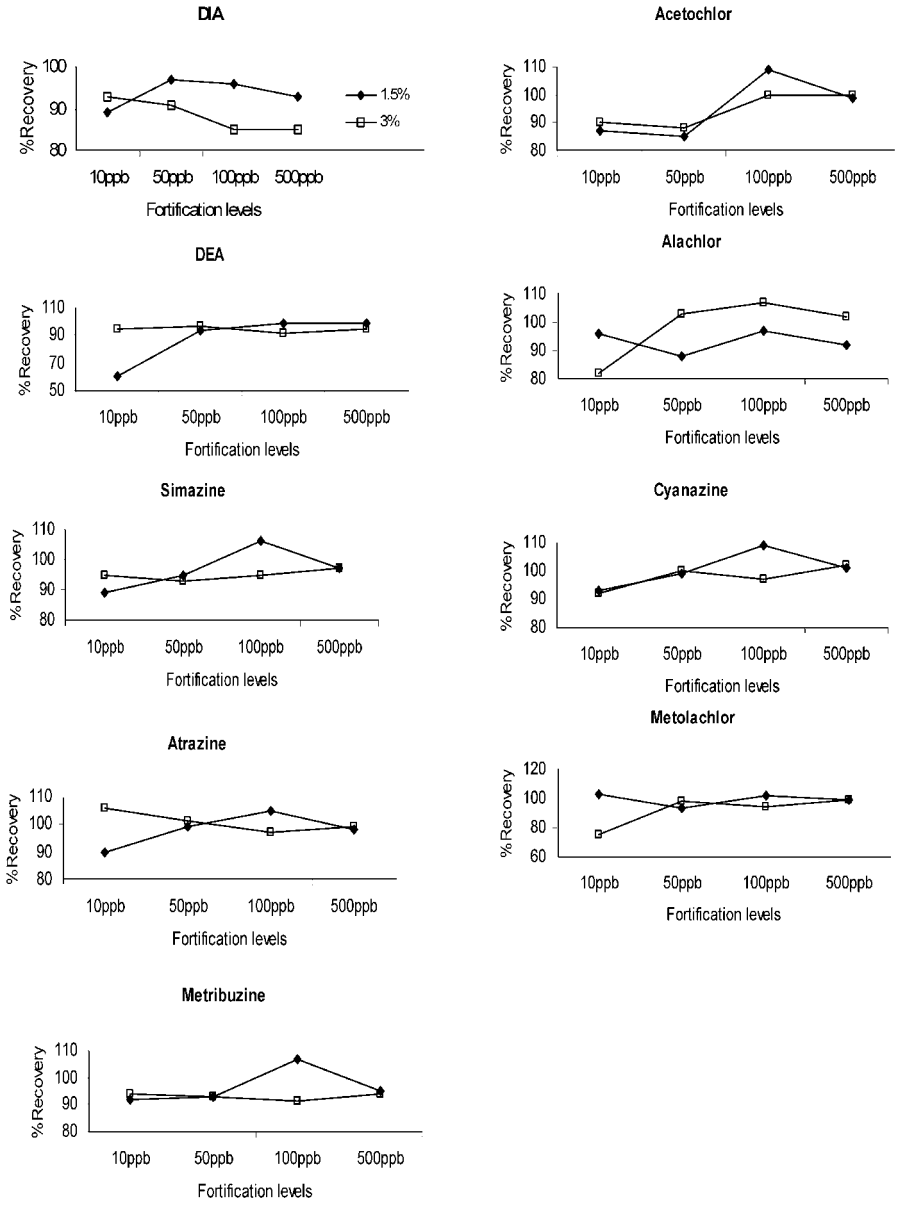

Figure 4. Analyte recoveries vs fortification levels of fortified soil samples containing 1.5 and 3% OM, respectively, and all other extraction parameters set as shown in Table 1.

Table 4. Residues[a] (mg/kg) of Some Target Analytes in the Plough Layer (0–10 cm) of Treated Corn Fields Processed by Microwave-Assisted Extraction (MAE) and Flask-Shaking (FS) Techniques, Respectively[b]

	field A sampling date				field B sampling date			
	04/15/2001		05/16/2001		04/15/2001		05/16/2001	
compd	MAE	FS	MAE	FS	MAE	FS	MAE	FS
alachlor	0.068a[c]	0.054b	nd	nd	0.014a	0.007b	0.009a	0.006b
atrazine	3.800a	4.099a	0.199a	0.130b	2.659a	2.107b	0.076a	0.033b
DEA	nd[d]	nd	nd	nd			0.006	nd
DIA	nd	nd	nd	nd			nd	nd
metoachlor	4.013a	4.252a	0.703a	0.450b	3.753a	2.709b	0.717a	0.401b

[a] These are mean residue levels derived from the analysis of triplicate laboratory samples. [b] Residues in both types of extracts were determined by gas chromatography ion trap mass spectrometry (GC–ITMS). [c] For each field and at each sampling date, pairs of residue values on the same row designated by the same letter are not statistically different (one-way ANOVA, significance level 0.05). [d] Denotes nondetectable (<LOD).

soils were not significant. (Significance was assessed by comparisons based on LSD at $a = 0.05$, data are not shown.) Consequently, the proposed MAE technique is equally efficient for extracting residues of the target compounds present in organic soils (3% OM) as for those present in soils of low organic matter content (1.5%). Certainly in other regions of the world contaminated soils might have higher than 3% organic matter content, and residue methods should be also validated for these types of soils. In the absence of a natural soil with organic matter higher than 3%, no further evaluation was made

because preliminary experiments contacted with soils enriched with peat at >3% OM (i.e., 5, 7, and 10% OM) resulted in erroneous results mainly due to difficulties in dispersing the peat mass into the soil matrix to produce a homogeneous batch of soil. Nevertheless, since the recovery values of most target analytes from soils containing 3% OM were not statistically different from respective values derived from soils with 1.5% OM content, it is expected that residues with acceptable accuracy (recoveries > 80%), precision (RSD < 25%), and reproducibility (RPD < 15%) can be also measured in soils with higher OM content. In addition, since MAE extracts of soils were relatively clean, as judged from the amount of solid residue left after the evaporation of 10 mL of acetonitrile extract corresponding to 5 g of soil, and the fact that there was no background interference in either GC-selective detection (NPD) or GC−ITMS analysis of extracts, it is expected that this method will be free of interferences and equally precise when soils with >3% OM content are also analyzed. Nevertheless, it has been reported that MAE extracts of soils with OM content >5% when a methanol/dichloromethane mixture was used as extractant required a cleanup step before GC−NPD analysis (*21*).

The LOQ and LOD levels for all solutes and for both types of soils, on the basis of the data included in **Figure 1**, were set at 10 and 1−5 μg/kg (atrazine and cyanazine at 1, metribuzin at 3, and the rest at 5 μg/kg), respectively.

The MAE technique was also validated with the analysis of field weathered residues present in soil samples collected from the plough layer of two corn fields (fields A and B) 3 h after application and after one month of weathering period. These same samples were also processed by the comparison flask-shaking (FS) extraction technique, as described in the Experimental Section. In this comparison exercise extracts of soils derived from both MAE and FS techniques were also analyzed by GC−ITMS, and these data are presented in **Table 4**. The residue levels in samples processed by MAE were found to be slightly higher than in those processed by the FS comparison technique, except for the residue levels of atrazine and metolachlor found in soils of field A on 04/15/2001; in the latter case, the residue levels of atrazine and metolachlor found in samples processed by MAE were slightly lower than those found in samples processed by FS; however, these differences were not statistically significant (the significance of difference evaluated by one-way ANOVA at $a = 0.05$).

CONCLUSIONS

The proposed method combining MAE and gas chromatographic analysis is a simple and rapid approach for the accurate determination of commonly used triazine and chloroacetanilide herbicides in soils. The method is simple and rapid because 12 samples can be processed simultaneously by MAE ready for GC analysis within 30 min. The overall method is also environmentally friendly because very low volumes of an organic solvent (20 mL of acetonitrile/sample) are utilized and thus minimum quantities of laboratory wastes are produced. The method, in terms of accuracy, precision, and reproducibility is acceptable and favorably compared to a more laborious and costly method based on the flask-shaking extraction technique requiring a solid-phase extraction or liquid−liquid partition step of solutes before extracts become GC-amenable.

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