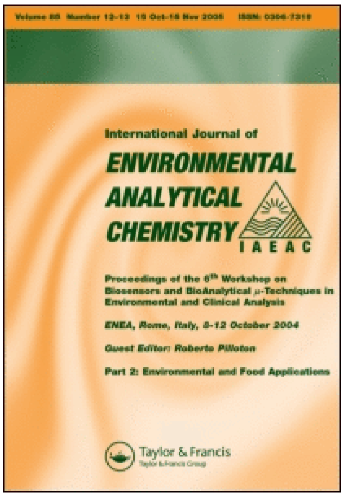

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Hernandez, Felix , Beltran, Joaquin , Forcada, Maria , Lopez, Francisco J. and Morell, Ignacio(1998) 'Experimental Approach for Pesticide Mobility Studies in the Unsaturated Zone', International Journal of Environmental Analytical Chemistry, 71: 1, 87 — 103

To link to this Article: DOI: 10.1080/03067319808032619

URL: http://dx.doi.org/10.1080/03067319808032619

Intern. J. Environ. Anal. Chem., Vol. 71(1), pp. 87-103
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EXPERIMENTAL APPROACH FOR PESTICIDE MOBILITY STUDIES IN THE UNSATURATED ZONE

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(Received 30 April 1997; In final form 25 August 1997)

An experimental approach for pesticide mobility studies in the soil environment has been developed, based on three main aspects: 1) the development of analytical procedures suitable for unsaturated zone pesticide monitoring; 2) adsorption studies; 3) controlled application of pesticides to two experimental sites and subsequent analysis of soil and water samples. Four pesticides have been selected to perform this study: two herbicides (atrazine and metribuzin) and two organophosphorus insecticides (fenamiphos and chlorpyrifos).

Soil and water samples spiked at different levels with pesticides were used to validate the analytical procedures by obtaining recoveries and coefficients of variation. Extraction procedures for water samples included: liquid-liquid extraction (conventional and micro scale) and solid phase extraction using C_{18} cartridges and elution with ethyl acetate. Detection limits for water sample extraction using either liquid-liquid extraction or solid phase extraction were similar and ranged between 0.02 and 0.3 $\mu g\ l^{-1}$, while for the liquid-liquid microextraction minimum detectable concentration was in the range of 1–10 $\mu g\ l^{-1}$, Extraction of soil samples was carried out with acetone, followed by two different clean-up procedures based on liquid-liquid partition and solid phase extraction with C_{18} cartridges (detection limits between 0.3 and 0.6 $ng\ g^{-1}$).

Results obtained for adsorption studies predicted that atrazine and metribuzin were probable leachers while the organophosphorus pesticides studied should be considered as improbable leachers. This agreed completely with the mobility results obtained in experimental plot experiments.

Keywords: Pesticides; gas chromatography; pesticide mobility; monitoring studies; soil adsorption

INTRODUCTION

In recent years an increasing interest has been devoted to the pollution of ground and surface waters in the European Union, as a result of the monitoring surveys

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carried out that showed frequent pollution by pesticides above the EU specification in several countries [1]. This situation is due to the extensive use of pesticides in agricultural practices, as the European Union is considered the largest user of agrochemicals and five of the individual countries are within the top 10 users [2].

Most of the efforts have to be directed to the monitoring of groundwater pollution as well as to the development of analytical methods allowing the rapid and accurate determination pesticides (mainly those with high leaching potential). However, to carry out an overall study on groundwater pollution by pesticides, many other aspects should be considered: data on pesticide levels at the unsaturated zone after controlled application to experimental plots, mathematical models to describe the movement of pesticides and predict the risk involved in the application of pesticides, adsorption studies on soils, persistence and degradation studies in the soil environment, etc. These studies are complex, expensive and time consuming as they should include laboratory experiments and field work as well as the analysis of several samples from experimental sites where controlled application of pesticides takes place.

One of the main problems one has to face is the need for applying several analytical procedures to a variety of water samples of different origin (groundwater, surface water and soil-solution) with different concentration levels (much higher in soil-solution samples) and available volumes. This forces to develop different analytical procedures, which include conventional and micro liquid-liquid extraction or solid phase extraction [3,4]. Besides, in a complete study it is highly advisable to analyse soil samples which again requires the application of extraction (using organic solvents as acetone or mixtures acetone/hexane) and clean-up procedures (mainly by liquid-liquid partition of solid phase extraction) [3,5].

As stated above, in order to achieve a global knowledge on the behaviour of pesticides in the soil environment and to predict the potential of contamination it would be very helpful to carry out adsorption studies to obtain the particular characteristics of the pesticides studied in different soil profiles. The most commonly used technique in adsorption studies is the batch equilibration method which conducts to the calculation of K_d (distribution coefficient) or K_{oc} (organic carbon related adsorption constant) [6–10]. The application of batch experiments requires the measurement of pesticide concentration in several water solutions (usually at high $\mu g.l^{-1}$ concentration level).

The aim of the present paper is to provide an experimental approach to be applied in pesticide mobility studies, based mainly on analytical aspects involved in this type of work. Several analytical procedures including liquid-liquid extraction (conventional and micro) and solid phase extraction have been optimised for different types of samples involved in leaching studies (groundwater, soil moisture and soil samples). Developed methods have been applied subsequently to the analysis of real samples from two experimental sites after controlled application of pesticides. Besides, adsorption experiments have been performed using soil samples from those experimental sites in order to gain insight into the knowledge of the pesticide behaviour in the soil environment. Selection of pesticides studied was carried out taking into account their extensive use in the areas where the experimental plots were located (Girona and Gran Canaria).

EXPERIMENTAL

Apparatus and reagents

Vac Elut solid-phase extraction system (Analytichem) equipped with 500 mg solid-phase extraction cartridges C_{18} was used.

Atrazine, metribuzin, fenamiphos and chlorpyrifos standards were purchased from Dr. Ehrenstorfer (Promochem, Wesel, Germany). Stock solutions (around 500 $\mu g\ ml^{-1}$) were prepared in acetone and stored at −18°C. Working solutions were prepared by dilution with acetone or hexane.

Organic solvents of pesticide residue analysis grade (methanol, ethyl acetate, dichloromethane, acetone and hexane) were purchased from Scharlau (Spain).

Sodium sulphate anhydrous of pesticide residue analysis grade (J.T. Baker) and sodium chloride of analytical reagent grade (Panreac) were purified by heating at 350°C overnight.

Sampling

Soils samples (used in adsorption and recovery studies) were obtained from the 0–10 cm horizon in four experimental fields located in Canary Islands (Gran Canaria, soil A, and Tenerife, soil B) and Catalonia (Girona, soil C, and Maresme, soil D). Soil samples were dried at ambient temperature and sieved through a 2 mm opening sieve, then sealed in a glass bottle until used. Their physical-chemical properties (Table I) were determined according to literature [11].

Soil-solution samples were collected at different depths from the experimental fields using ceramic cup samplers, previously tested.

TABLE I Soil properties

	Soil A[a]	*Soil B*[b]	*Soil C*[c]	*Soil D*[d]
Depth (cm)	10	10	10	10
pH	7.2	6.4	7.6	8.2
Organic matter (%)	2.7	2.4	2.8	1.1
Moisture (%)	na*	23.6	11.4	2.9
Sand (%)	50	22	65	81.6
Silt (%)	21	33.3	17	11.4
Clay (%)	29	44.7	18	7.0

* not available.
[a] soil from Gran Canaria experimental site.
[b] soil from Tenerife experimental site.
[c] soil from Girona experimental site.
[d] soil from Maresme experimental site.

Extraction of water samples

Liquid-liquid extraction (LLE)

500 ml of water sample containing 10 % NaCl were extracted twice with 50 ml of dichloromethane. The combined extracts were dried with sodium sulphate and concentrated in a Kuderna-Danish apparatus. Finally, the extract was evaporated to dryness under a gentle stream of nitrogen. The residue was dissolved in 500 μl of hexane prior to GC injection.

Liquid-liquid extraction of water samples was also carried out using a modified procedure based on mechanical shaking of water sample (50 ml) with dichloromethane (25 ml) for 30 minutes. Once the organic phase was separated, it was dried and evaporated as indicated before, and the final volume adjusted to 500 μl with hexane.

Micro liquid-liquid extraction (MLLE)

A volume of 1–2 ml of water was extracted with 1 ml of ethyl acetate (shaking manually for 1 minute). The organic phase was dried over sodium sulphate. 2 ml of hexane were added and evaporated until volume was below 0.5 ml. The final volume was adjusted to 1 ml with hexane.

Solid-phase extraction (SPE)

Solid phase extraction cartridges (C_{18}) were conditioned by passing two cartridge volumes of each methanol, ethyl acetate, methanol and distilled water. The cartridges were not allowed to run dry and the sample (100 ml of water containing 10% NaCl) was passed through the cartridge at 6–10 ml min^{-1} under vacuum. After drying the cartridge by passing air for 20 min, pesticides were eluted by gravity flow with 2 ml of ethyl acetate. The extract was evaporated and the final volume adjusted as indicated before to 500 μl of hexane.

Methods described above were applied to different types of water samples (groundwater and soil-solutions) from the experimental fields.

Extraction of soil samples

50 g of dried soil were wetted with 10–15 ml water, extracted twice with 50 ml acetone (containing 1 ml of ammonium acetate 1 M) by shaking mechanically for 15 min and then, sonicated for 5 min. The slurry was centrifuged and the supernatant was separated and filtered over paper filter. The extract was diluted with distilled water and then submitted to either liquid-liquid partition with dichloromethane or solid phase extraction using C_{18} cartridges as indicated above. Finally, the organic extract was evaporated to dryness and the volume adjusted to 500 μl with hexane.

Soil adsorption experiments

Batch-type adsorption experiments were used to generate adsorption data. Thus, 10 g of the soil sample were treated with 50 ml of a 5 10^{-4} M $CaCl_2$ aqueous solution containing different concentrations of the pesticide mixture (100, 300 and 1000 μg l^{-1}), shaken mechanically for 24 h, and then centrifuged at 2000 rpm during 15 min. Supernatant was separated, filtered through 0.45 μm pore filter and submitted to liquid-liquid micro-extraction with ethyl acetate. Subsequently, the organic layer was dried, the solvent exchanged to hexane and analysed by gas chromatography.

Gas chromatographic conditions

A gas chromatograph Hewlett-Packard 5890 series II, equipped with nitrogen-phosphorus detector, HP 7673 autosampler and HP Ultra 2 capillary column (cross linked 5% methyl-silicone, 25 m × 0.20 mm i.d., 0.33 μm film) was used. The operating conditions were: injector temperature 250°C; NPD 270°C, He 30 ml min^{-1}, hydrogen 3 ml min^{-1}, air 100 ml min^{-1}; column temperature program: 90°C (1 min), at 30°C min^{-1} to 180°C, at 4°C min^{-1} to 270°C (5 min); He carrier gas 0.5 ml min^{-1}. Injection: 2 μl using autosampler and splitless mode. Quantitation was made by external standard method.

A gas chromatograph HP 5890, equipped with MSD 5971, was used for confirmation of pesticide residues in field sample. The operating conditions were: injector temperature 250°C ; transfer line temperature 280°C; column temperature program: 90°C (1 min), at 30°C min^{-1} to 180°C, at 4°C min^{-1} to 270°C (5 min); He carrier gas 0.5 ml min^{-1}. Injection: 2 µl using autosampler and splitless mode. Quantitation was made by external standard method.

RESULTS AND DISCUSSION

Extraction of water samples

The three liquid-liquid extraction procedures previously described were applied to groundwater samples fortified at different levels by triplicate. Recoveries obtained at all fortification levels (1 and 10 µg l^{-1} for conventional LLE; and 100 and 1000 µg l^{-1} for micro LLE) were good for the pesticides studied, ranging from 83 % to 123 % with coefficients of variation lower than 10%, except for MLLE at 100 µg l^{-1} level, that exhibit values ranging from 9 to 19 %. Detection limits were calculated from chromatograms corresponding to the lowest fortification levels in each case as three times the background noise (see Table II). As it should be expected, the lowest detection limits correspond to the conventional liquid-liquid extraction procedure because it uses the largest sample volume and a concentration factor of 1000-fold. The time required for extraction, laboratory glassware as well as the amount of solvent used is different for each extraction procedure tested, corresponding the best conditions to the liquid-liquid microextraction that uses only 1 ml of organic solvent per sample.

TABLE II Detection limits (µg l^{-1} for water samples and ng g^{-1} for soil samples) obtained for the selected pesticides in groundwater and soil samples after different extraction procedures

	Water samples				*Soil samples*	
	LLE	*LLE**	*MLLE*	*SPE*	*LL partition clean-up*	*SPE clean-up*
Atrazine	0.02	–	2	0.1	0.5	0.3
Metribuzin	0.1	0.3	4	0.2	1	0.6
Chlorpyrifos	0.04	0.1	3	0.1	0.6	0.3
Fenamiphos	0.15	0.4	12	0.3	2	0.6

* liquid-liquid extraction by mechanical shaking.

In this work, we have also applied a SPE procedure, previously developed [12] to groundwater samples spiked at 1 and 10 μg l^{-1} levels. Satisfactory recoveries were obtained at the two concentration levels except for fenamiphos (around 60%), which showed poor retention in the cartridges. Detection limits for the procedure described ranged from 0.1 (chlorpyrifos) to 0.3 μg.l^{-1} (fenamiphos) (Table II).

SPE procedures can easily be applied to groundwater or soil-solution samples and low detection limits can be achieved with only 100 ml of sample. This procedure shows clear advantages over LLE as stated in many papers [4,5,13]. A special feature of this procedure is the capability of carrying sample extraction "in situ" just by passing the water sample through the cartridge using a syringe, avoiding transport and storage of water samples in the laboratory.

The study of different extraction procedures responds to the need for optimising the extraction of pesticides in the different sample types involved in leaching and unsaturated zone studies. For water samples the main requirement is concentration level. Taking into account the detection limits calculated it is evident that when dealing with very low concentration of pesticides (usually groundwater samples) only liquid-liquid and solid-phase extraction methods are feasible (below 0.1 μg.l^{-1}). Nevertheless, in unsaturated zone studies is also necessary to analyse soil solution samples obtained from experimental fields where pesticides have been applied to study transport behaviour and aqueous solutions derived from adsorption studies. In these cases, one should deal with low volume samples (soil-solution samples are usually obtained with suction cups, and their volume is often below 100 ml) and relatively high concentrations, above 1 μg l^{-1} in soil solution samples as described in many papers [6,14], and even higher in adsorption studies. Such a situation strongly recommends the use of extraction procedures less time and solvent consuming such as liquid-liquid microextraction despite of its lower sensitivity. If necessary, the use of micro-extraction methods can be applied for the analysis of more diluted samples when combined with more sensitive chromatographic techniques, such as large volume injection-GC which allows a drastic reduction in detection limits [15].

Thus, it is clear that when approaching a pesticide leaching/unsaturated zone project it is necessary to develop/optimise at least two extraction procedures for aqueous samples: a large sample volume procedure (such as conventional liquid-liquid or solid-phase extraction) for groundwater samples, and a micro-extraction procedure to manage low volume and high concentration samples (soil solution or adsorption studies). We selected the solid-phase extraction procedure for the analysis of groundwater and soil solution samples, and liquid-liquid micro-extraction for the adsorption study.

Extraction of soil samples

Two different approaches were applied for soil sample preparation using acetone as extractant, which is one of the most used solvents for the determination of medium polarity pesticides [5]. The extract obtained was concentrated, diluted with water and submitted either to liquid-liquid partition with dichloromethane or solid phase extraction using C_{18} cartridges, in order to compare the efficiency of the clean-up step.

Figure 1 shows the GC-NPD chromatograms obtained after application of the two extraction procedures to a soil sample containing 10 ng g^{-1} of each pesticide.

Mean recoveries obtained for soil samples spiked at 10 and 50 ng g^{-1} levels were over 80% for all pesticides studied in both extraction methods, with coefficients of variation between 5 and 13 % (n=3). Limits of detection obtained are slightly lower by using solid phase extraction as clean-up step, with values between 0.3 and 0.6 ng g^{-1}(Table II). This is a consequence of the more effective clean-up obtained by SPE in comparison with liquid-liquid partition, which leads to cleaner chromatograms. Consequently, this SPE clean-up based extraction procedure was selected to analyse experimental site soil samples in mobility studies.

Adsorption behaviour studies

Studies related with leaching of pesticides in soils would not be complete without data relative to the adsorption behaviour. These data allow to predict the future behaviour of a pesticide in soil under leaching conditions. In fact, adsorption of pesticides on the soil surface is one of the main processes taking place during the fate of the pollutants in soils [16,17].

There is a simple approach to obtain adsorption characteristics based on batch-type experiments, where soil is suspended using an aqueous solution of pesticides. Determination of supernatant concentration of pesticides conduces to the corresponding distribution coefficients (Kd) or Freundlich constants (K_F) depending on the mathematical approach used to fit experimental data [18].

In the present paper, equilibrium concentrations in soil and supernatant, obtained after the batch adsorption experiments described before, were fitted to linear and Freundlich isotherm equations. The related distribution coefficients (Kd), adsorption constant corrected to organic carbon (K_{oc}) and Freundlich coefficient (K_F) for atrazine, metribuzin, chlorpyrifos and fenamiphos were calculated (Table III) for four soils obtained from the experimental sites.

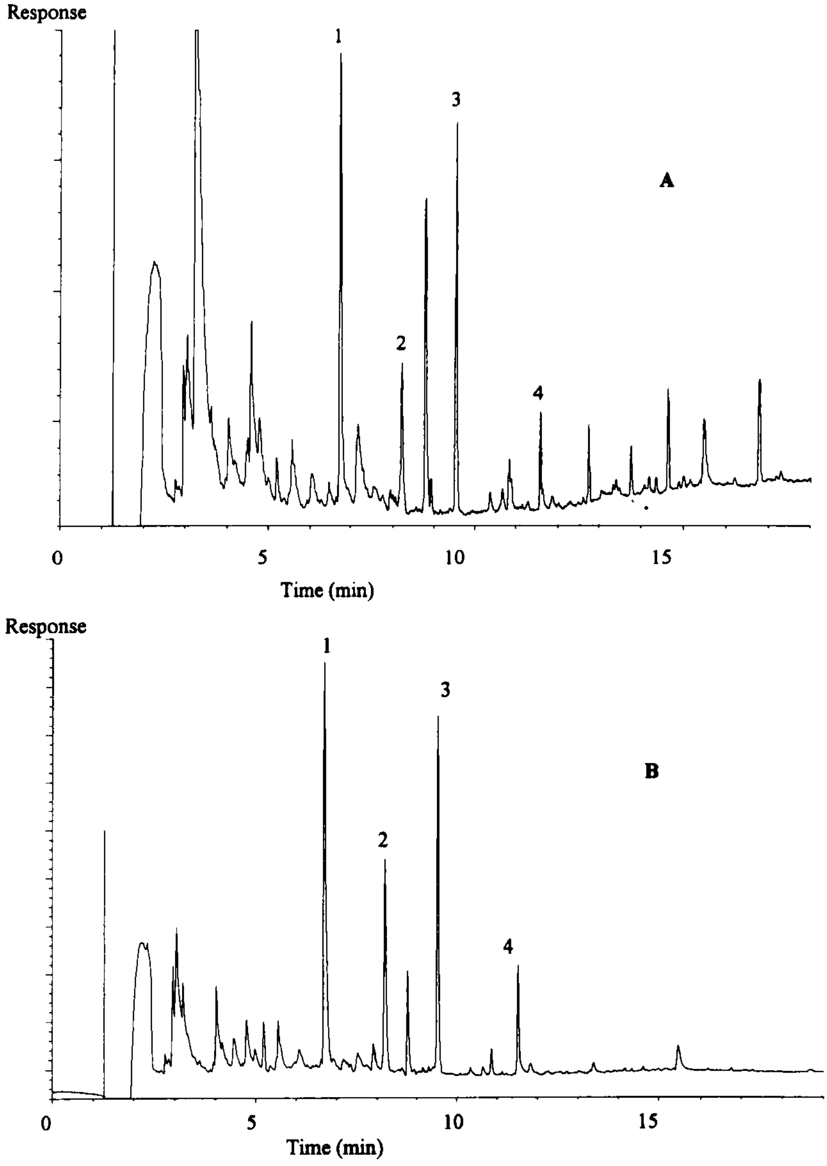

FIGURE 1 GC-NPD chromatograms of a soil sample fortified at 10 ng g^{-1}after extraction with acetone and clean-up by (A) liquid-liquid partition or (B) solid phase extraction with C_{18} cartridges 1. Atrazine, 2. Metribuzin, 3. Chlorpyrifos, 4. Fenamiphos

TABLE III Soil sorption coefficients (K_d), soil sorption constants (K_{oc}), Freundlich constants (K_F) and GUS index of pesticides in selected soils

	Soil A				*Soil B*				*Soil C*				*Soil D*			
	K_d	K_{oc}	K_F	*GUS*	K_d	K_{oc}	K_F	*GUS*	K_d	K_{oc}	K_F	*GUS*	K_d	K_{oc}	K_F	*GUS*
Atrazine (64)[a]	1.2	77	22.2	3.6	1.0	72	11.2	3.6	1.9	117	3.4	3.3	2.0	313	8.5	2.6
Metribuzin (10)[a]	1.0	64	0.5	3.4	1.2	86	0.8	3.2	1.4	86	6.4	3.2	1.4	219	4.0	2.6
Fenamiphos(37)[a]	72.5	4629	—	0.4	32.0	2299	—	0.8	56.2	3460	—	0.6	13.7	2147	—	0.8

[a] half-life time in days, after Jury et al. [20].

Adsorption results for the four pesticides studied allowed us to distinguish mainly between the two herbicides, with low K_d values (between 1.0 and 2.0), and the two organophosphorus insecticides, with higher Kd values. Chlorpyrifos behaviour was the same as for fenamiphos, the results showing complete adsorption (disappearing from water solution) on the soils studied in the actual conditions assayed (24 h shaking; concentration range 100–1000 ng ml^{-1}). The low K_d values obtained for atrazine and metribuzin led to the conclusion that they can be very mobile in the soils tested, so the possibilities for groundwater pollution after application of these herbicides are considered to be high.

TABLE IV Results obtained for atrazine and deethylatrazine (DEA) after analysis of soil (ng g^{-1}) and soil-solution ($\mu g\ l^{-1}$) samples obtained from Girona experimental field

Sampling date	*Soil samples*			*Soil-solution samples*		
	Depth (cm)	*Atrazine*	*DEA*	*Depth (cm)*	*Atrazine*	*DEA*
24 February 94	20	2	—			
	40	0.8	0.7			
	80	—	—	100	—	0.3
	160	2	—	150	0.2	0.2
	200	—	—	200	—	—
Atrazine application in the experimental field (15 May 94)						
22 May 94	20	61	3.7			
	40	8.4	—			
	80	2.5	—	100	12.6	—
	160	0.8	—	150	67	0.2
	200	3.2	—	200	0.2	—
29 May 94	20	42	4.4			
	40	14	1.2			
	80	19.7	1.7	100	—	—
	160	2.8	0.5	150	5.7	0.2
	200	5.6	0.6	200	1.2	—
7 June 94	20	26	3.9			
	40	14.8	2.7			
	80	2.5	0.7	100	0.2	0.4
	160	5.6	1.3	150	8.2	0.3
	200	0.6	—	200	—	—

The GUS index (a simple approach for assessing pesticide leachability, proposed by Gustafson [19]) for the pesticides studied were calculated using half-life times obtained from the literature [20]. The results obtained (Table III) indicate that the herbicides (atrazine and metribuzin) can be classified as probable leachers (GUS>2.8) while fenamiphos (and even more chlorpyrifos) is considered unlikely leacher (GUS<1.8).

These results, easily obtained at the laboratory, are of great help when designing field studies, as no relevant data should be obtained when studying pesticides considered non potential leachers. In addition, these data can be used to restrict the use of certain compounds in areas were aquifer recharge is taking place, mainly if the unsaturated zone is thin or when soil characteristics led to weak adsorption.

Thus, taking into account the estimated mobilities, only atrazine am metribuzin (considered probable leachers according to the calculated GUS index) were selected to carry out the unsaturated zone mobility studies.

Analysis of samples from experimental sites

In order to check the applicability of the analytical procedures developed and to obtain real data on pesticide behaviour in the unsaturated zone, application of pesticides in two separate experimental fields located in Gran Canaria Island (metribuzin) and Girona (atrazine) was made.

Samples taken from the experimental plots included soil, groundwater and soil-solution samples, that were analysed applying the procedures optimised previously (solid phase extraction for groundwater and soil-solution, and acetone extraction followed by solid phase extraction clean-up for soil samples).

Results obtained for atrazine in soil and soil-solution samples at different depths over a period of three weeks after pesticide application are shown in Table IV. The behaviour of this pesticide is in good accordance with what should be expected from the adsorption data available (K_d). Thus, atrazine shows a high degree of mobility through the unsaturated zone, reaching depths below 200 cm in concentrations of up to 5 ng g^{-1}in soil (Table IV). Results corresponding to soil-solution samples followed the same leaching pattern as for soil samples (see Table IV). The soil and water extracts were analysed by GC-MSD in order to confirm the presence of atrazine in the real samples. Positive identification of atrazine was achieved and, even more, the main transformation product of atrazine (deethyl atrazine) was detected in relatively high concentrations (Table IV). Additional experiments on recovery of deethyl atrazine (DEA) in soil and water samples, using the procedures applied to real samples, were carried out, leading to good recoveries for this compound with coefficients of variation lower than 10%. Detection limits for DEA in soils and in soil-solution samples were found to be 0.5 ng $g^{-1}$and 0.2 μg l^{-1}, respectively.

Figure 2 shows the GC-MSD chromatogram corresponding to a soil sample extract (0–20 cm depth) as well as the spectra of atrazine and deethyl atrazine found in this sample.

TABLE V Results obtained for metribuzin after analysis of soil (ng g^{-1}) and soil-solution (μg l^{-1}) samples obtained from Gran Canaria experimental field

Sampling date	*Soil samples*		*Soil-solution samples*	
	Depth (cm)	*Metribuzin*	*Depth (cm)*	*Metribuzin*
21 April 95	15	5.6	15	—
	30	1.7	30	—
	60	1.7	60	—
Metribuzine application in the experimental field (8 May 95)				
15 May 95	15	3825	15	315
	30	359	30	207
	60	270	60	66

In relation with metribuzin mobility, it can be seen that when applied to soil this herbicide can easily migrate through the unsaturated zone (similarly to atrazine) reaching in this case a maximum depth of 60 cm (limited by the characteristics of the unsaturated zone of Gran Canaria). Concentrations measured one week after application were high in both soil and soil-solution samples with values that can be easily detected using the methods proposed in this paper, clearly over the detection limits of the method (Table V). Again, the use of the GC-MSD allowed the identification of some metribuzin transformation products (metribuzin desamino diketo and metribuzin desamino) in soil and soil-solution samples. Figure 3 shows the GC-MSD chromatogram corresponding to a soil sample extract (0–20 cm depth) as well as the spectra of metribuzin and its transformation products.

Concentration of atrazine and metribuzin in groundwater samples from the two experimental sites were found to be lower than 0.1 $\mu g.l^{-1}$ during the sampling period.

So, according to the results presented in Table IV and V the behaviour of the two herbicides tested is consistent with what should be expected from the K_d values obtained from batch adsorption experiments which grouped these two herbicides as probable leachers according to the GUS index.

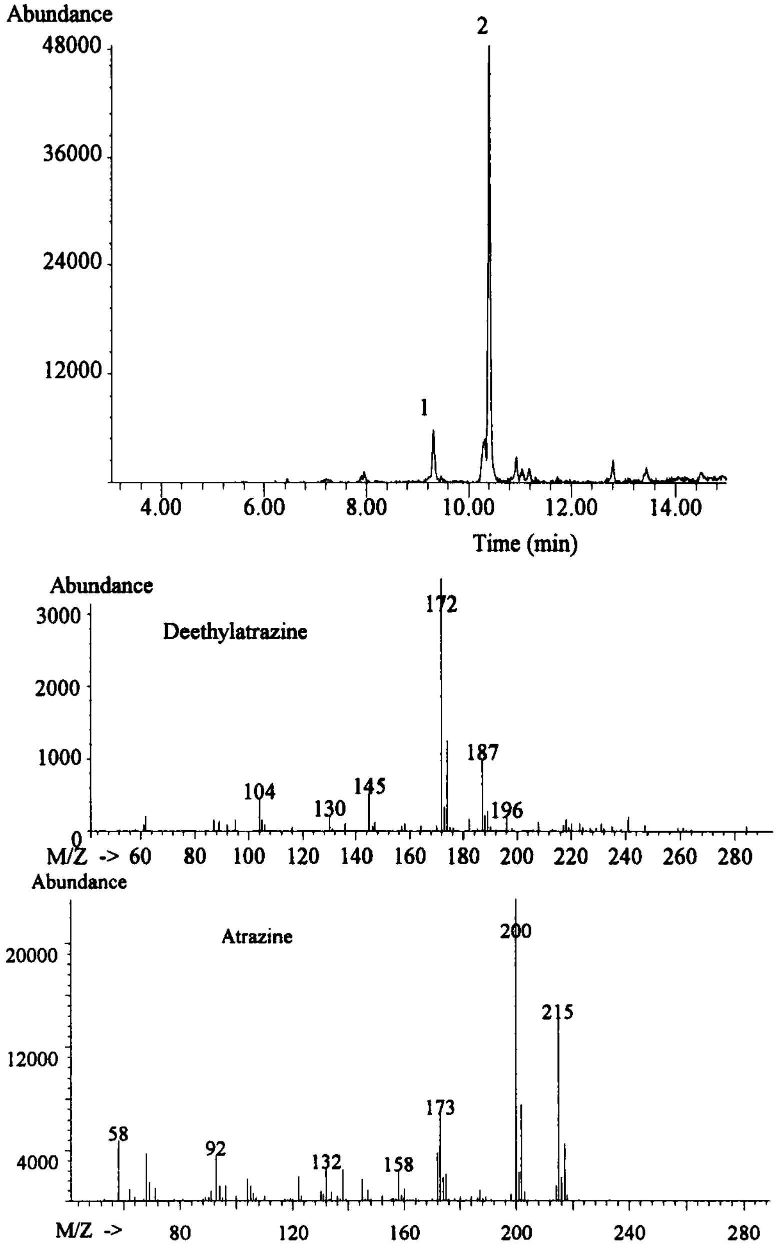

FIGURE 2 Extracted ion chromatogram (m/z 172+200 and full spectra obtained by GC-MS (full scan mode) from a soil sample (0–20 cm) after extraction with acetone and C_{18}-SPE. (1) Deethylatrazine; (2) Atrazine

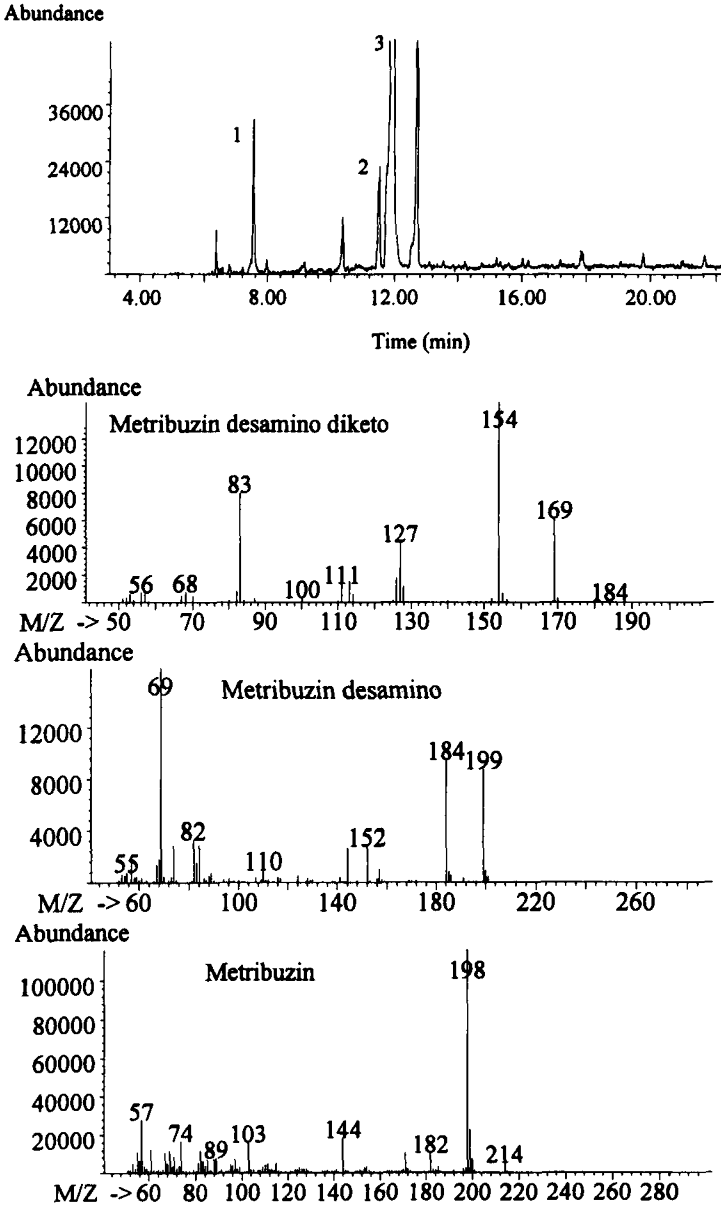

FIGURE 3 Extracted ion chromatogram (m/z 154+184+198 and full spectra obtained by GC-MS (full scan mode) from a soil sample (0–20 cm) after extraction with acetone and C_{18}-SPE. (1) Metribuzin desamino diketo; (2) Metribuzin desamino; (3) Metribuzin

Finally, it is interesting to compare the results obtained for metribuzin in both types of samples, soil and water, collected at the same depth. Contents in soil samples are higher than those in the water collected (soil-solution) by means of ceramic cups. The later provide information on mass pesticide being leached through the unsaturated zone while the former includes the pesticide sorbed on the soil and removed during the extraction of soil.

In this way, it is important to remark that monitoring in the unsaturated zone provides early prediction of pesticide migration, but representativity of each type of sample must also be taken into account. In fact, dual-flow conditions can be expected in most of soils depending of distribution of macropores and micropores; in these cases, leached pesticides could bypass the finer pores in such a way that water flowing through the macropores has different pesticide content than that of micropores. In addition, water in micropores is more strongly retained than that transported by free drainage and consequently is not available for vacuum samplers used to collect the soil-solution. Nevertheless, when soil core samples are taken, extraction procedures do not distinguish between both types of water which can be joint removed. As a consequence, the pesticide content in soil core samples is considerably higher than that of soil-solution samples obtained from vacuum samplers at the same depth.

Acknowledgements

This study is a part of the EU project entitled "Development of analytical and sampling methods for priority pesticides and relevant transformation products in aquifers" (contract EV5V-CT93–0322) in the framework of a research agreement between Dirección General de Aguas del Gobierno de Canarias, Universitat Politècnica de Catalunya and Universitat Jaume I.

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