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# Multiresidue analysis of fungicides in soil by sonication-assisted extraction in small columns and gas chromatography

C. Sánchez-Brunete, E. Miguel, J.L. Tadeo\*

*Departamento de Medio Ambiente (INIA), Carretera de La Coruña, Km 7, 28040 Madrid, Spain*

## Abstract

A rapid multiresidue method for the simultaneous determination of 14 fungicides in soil was developed. Fungicides were extracted from soil, placed in small columns, by sonication-assisted extraction with ethyl acetate. The effect of residue residence time and soil moisture content on the fungicide recovery was studied. Residue levels in soil were determined by gas chromatography with electron-capture and nitrogen–phosphorus detection. Residue identities were confirmed by gas chromatography coupled with mass spectrometry, in the selected ion monitoring mode. Recovery studies were carried out at 0.5, 0.1 and 0.05  $\mu\text{g/g}$  fortification levels for each fungicide, and average recoveries obtained for these compounds ranged from 80 to 104% with relative standard deviations between 1 and 8%. The method is linear over the range assayed, 0.5–0.05  $\mu\text{g/g}$ , and the detection limit for the fungicides studied varied from 2 to 10  $\mu\text{g/kg}$ .

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## 1. Introduction

Fungicides used in agriculture to control plant diseases belong to various chemical classes, such as azol, benzimidazole, carbamate, dicarboximide, pyrimidine or acetamide. These compounds can be applied pre- or post-harvest, and a certain proportion of the amount applied may reach the soil where it is transformed or distributed in the environment.

Analytical methods for the determination of fungicides in soil are scarce in the available scientific literature. In the conventional methods, pesticides are extracted from soil samples using liquid extraction, with subsequent clean-up of extracts, in some cases, before GC determination. Conventional methods

employ large amounts of toxic solvents and are time consuming. These drawbacks may be overcome by using supercritical fluid extraction (SFE) [1–3] or solid-phase extraction (SPE) [4,5]. In addition, a method based on the sonication of soil samples placed in small columns (sonication-assisted extraction in small columns, SAESC) has recently been developed in our laboratory for the rapid and sensitive analysis of herbicides and insecticides in soil [6,7].

Several chromatographic methods have been published for the determination of different classes of fungicides in various matrices, mainly food products. Fungicide residues have often been analysed by gas liquid chromatography with nitrogen–phosphorus (NPD) or electron-capture (ECD) detection [8–10]. Moreover, gas chromatography with mass spectrometry (GC–MS) has been used in multiresidue methods for pesticide analysis in soil [11,4].

\*Corresponding author. Tel.: +34-91-347-6856; fax: +34-91-357-2293.

E-mail address: [tadeo@inia.es](mailto:tadeo@inia.es) (J.L. Tadeo).

The aim of this work was to develop a rapid method for the determination of fungicides in soil, based on the sonication extraction of soil samples with low volumes of organic solvents. The compounds included in this study were widely used fungicides belonging to several chemical classes: azole (triadimefon, myclobutanil, cyproconazole), dicarboximide (procymidone), organophosphate ester (tolclofos-methyl, pyrazophos), pyrimidinyl carbinol (nuarimol, fenarimol), acylalanine (benalaxyl), acetamide (ofurace, oxadixyl), *N*-trihalomethylthio (dichlofluanid), quintozene and chlorothalonil. In addition, the effect on the fungicide recovery of the residence time of residues and the soil moisture content was also studied.

## 2. Experimental

### 2.1. Chemicals

Tolclofos-methyl, triadimefon, procymidone, myclobutanil, cyproconazole, oxadixyl, ofurace, benalaxyl, nuarimol, fenarimol, pyrazophos, dichlofluanid, quintozene and chlorothalonil standards (99% purity) were obtained from Reidel–de Haën (Seelze, Germany).

Acetone, ethyl acetate and methanol, all residue analysis grade were purchased from Scharlau (Barcelona, Spain). Anhydrous sodium sulfate, reagent grade, was obtained from Merck (Darmstadt, Germany).

### 2.2. Standards

Stock solutions of each fungicide (500 µg/ml) were prepared in ethyl acetate. A set of standard mixtures for fortification of soil samples was prepared containing 0.5, 1 and 5 µg/ml of each fungicide in ethyl acetate. Another set of calibration standard solutions of 0.05, 0.1 and 0.5 µg/ml, was also prepared.

### 2.3. Equipment

#### 2.3.1. GC–NPD

A Hewlett-Packard 6890 (Waldbronn, Germany) gas chromatograph equipped with an automatic

split–splitless injector Model HP 7683 and an NPD system was used for the analysis of fungicides. A fused-silica capillary column (HP-1), crosslinked dimethylpolysiloxane, as nonpolar stationary phase (30 m×0.25 mm I.D.) and 0.25-µm film thickness, supplied by Agilent (Madrid, Spain), was employed. The injection port and detector temperatures were 270 and 300 °C, respectively, with helium as carrier gas at a flow-rate of 1 ml/min. The oven temperature was kept at 120 °C for 1 min and then programmed at 15 °C/min to 230 °C, held for 3 min and programmed at 20 °C/min to 280 °C, held 6 min, total time 19.6 min. A 2-µl volume was injected in the pulse splitless mode, with the valve closed for 1 min, in a double-taper glass liner with a nominal volume of 870 µl. The constant flow-rates of the hydrogen and air were 3.0 and 60.0 ml/min, respectively, with nitrogen as make-up gas.

#### 2.3.2. GC–ECD

A Hewlett-Packard 5890 Series II (Waldbronn, Germany) gas chromatograph equipped with an <sup>63</sup>Ni ECD system and an automatic split–splitless injector Model HP 7673, was used for the analysis of fungicides. A non-polar fused-silica capillary column, HP-1 (30 m×0.25 mm I.D. and 0.25 µm film thickness) supplied by Agilent (Madrid, Spain) was employed, with helium as carrier gas at 1 ml/min. The column temperature was maintained at 140 °C for 1 min, then programmed at 8 °C/min to 230 °C, held 0.5 min and programmed at 30 °C/min to 280 °C, held 6 min, total time 20.4 min. The injector port was maintained at 270 °C and the detector temperature was 300 °C. A 2-µl volume was injected in the splitless mode.

#### 2.3.3. GC–MS

GC–MS analysis was performed with a Hewlett-Packard 6890 (Waldbronn, Germany) gas chromatograph equipped with an automatic split–splitless injector Model HP 7683, and a MS detection system Model HP 5973. A fused-silica capillary column (HP-5MS), diphenyl dimethylpolysiloxane as non-polar stationary phase (30 m×0.25 mm I.D.) and 0.25 µm film thickness, supplied by Agilent (Madrid, Spain), was employed, with helium as carrier gas at a flow-rate of 1 ml/min. The injection port and interface temperatures were 250 and 280 °C, respec-

tively. The oven temperature was held at 110 °C for 1 min, programmed at 20 °C/min to 230 °C and then programmed at 15 °C/min to 280 °C, held for 5 min, total time 15.9 min. A 1- $\mu$ l volume was injected splitless, with the split valve closed for 1 min.

Mass spectrometric parameters: electron impact ionisation with 70 eV energy; ion source temperature 230 °C; quadrupole temperature 150 °C; mass range  $m/z$  50–450; scan rate 3.62 s per scan; EM voltage 1200; solvent delay 5 min.

#### 2.3.4. Extraction equipment

Polypropylene and glass columns (20 ml) with Whatman No.1 filter paper circles of 2 cm diameter (Whatman, Maidstone, UK) and polyethylene frits of 20  $\mu$ m pore size (Varian, USA) were used in the extraction step.

An ultrasonic water bath, (Raypa, Barcelona, Spain) was employed. The generator of this ultrasonic bath has an output of 150 W and a frequency of 35 kHz.

A vacuum manifold Visiprep (Supelco, Madrid, Spain) was used to filtrate the extraction solvent.

#### 2.4. Soil samples

Soil samples were collected from the plough layer (0–10 cm) of two experimental plots located in the regions of Guadalajara (soil A) and Madrid (soil B) (Spain). These samples were sieved (2 mm) and stored at room temperature until fortified. The physico-chemical characteristics of these soils are the following: soil A: sandy loam, organic matter 0.71, pH 7.4, field capacity 15.96% and soil B: sandy loam, organic matter 1.75, pH 6.7, field capacity 13.30%.

#### 2.5. Procedure

A polyethylene frit and two filter paper circles were placed at the end of the plastic or glass columns, closed with screw-type valves; then 5 g of the sieved soil were placed in the columns. Soil samples were fortified with 0.5 ml of a mixture of the different fungicides to reach final concentrations of 0.05, 0.1, and 0.5  $\mu$ g/g and the moisture content was adjusted by adding water to the soils in the columns. Some samples were extracted after 20 min,

to allow solvent evaporation, and the remainder of the samples were capped and stored at 4 °C prior to analysis at different times (1, 15 and 30 days).

Soil samples were extracted with 4 ml of ethyl acetate for 15 min in an ultrasonic water bath at room temperature. The water level in the bath was adjusted to equal the extraction solvent level inside the columns, which were supported upright in a tube rack. After extraction, the columns were placed on the multiport vacuum manifold where the solvent was filtered and collected in graduate tubes. Soil samples were extracted again with another 4 ml of ethyl acetate (15 min). The extracting solvent was filtered and soil samples washed with 1 ml of additional solvent. The total extract collected was concentrated with a gentle stream of air to an appropriate volume (2–5 ml) and stored at 4 °C until analysed by GC. A small amount of anhydrous sodium sulfate was added to dry the concentrated extract.

#### 2.6. Quantitation

Sample extracts were analysed by GC with NPD and ECD. The concentration of each compound was determined by comparing the peak areas in the sample with those found for mixtures of fungicide standards of known concentration.

### 3. Results and discussion

#### 3.1. Solvent extraction

Fungicide residues were extracted from soil using methanol or ethyl acetate. Table 1 shows the results obtained at the 0.5  $\mu$ g/g fortification level. In general, recoveries obtained with methanol were lower than the ones achieved with ethyl acetate, being those recoveries lower than 50% in some cases. Extraction with acetone was also assayed, but recoveries were as low as the methanol ones (data not shown). Therefore, ethyl acetate was selected as extraction solvent for the fungicides studied.

#### 3.2. Soil water content

Soil water content may affect the efficiency of

Table 1  
Influence of the extraction solvent on fungicide recovery<sup>a</sup> from soil

Fungicide	ECD				NPD			
	Ethyl acetate		Methanol		Ethyl acetate		Methanol	
	A	B	A	B	A	B	A	B
Quintozene	92.0 (4.6)	90.3 (5.5)	59.8 (5.3)	60.0 (2.3)				
Chlorothalonil	97.3 (5.7)	98.8 (6.9)	50.3 (4.6)	56.3 (7.5)				
Tolclofos-methyl	100.1 (1.5)	101.6 (3.8)	59.4 (4.9)	59.9 (4.5)	99.0 (1.1)	99.9 (1.4)	54.0 (1.4)	53.8 (5.8)
Dichlofluanid	93.3 (2.9)	90.5 (4.1)	40.5 (4.1)	50.3 (7.0)	94.1 (3.7)	100.9 (2.7)	49.6 (1.0)	42.5 (1.3)
Triadimefon	99.8 (2.6)	100.2 (2.7)	71.1 (4.4)	75.8 (2.1)	99.8 (2.1)	99.3 (2.5)	74.5 (3.9)	71.3 (3.2)
Procymidone	93.5 (2.6)	93.6 (3.5)	67.8 (4.2)	70.0 (2.6)	97.4 (4.0)	103.0 (2.8)	71.2 (2.6)	75.0 (1.8)
Myclobutanil	100.3 (1.2)	101.0 (2.6)	73.2 (3.9)	75.9 (3.3)	103.7 (3.9)	102.5 (0.6)	80.5 (3.8)	79.3 (2.5)
Cyproconazol					105.0 (2.4)	103.6 (2.1)	85.8 (5.6)	81.5 (2.4)
Oxadisyl					100.1 (3.1)	91.3 (3.1)	63.0 (4.2)	58.8 (5.0)
Ofurace	97.2 (3.6)	99.3 (1.9)	80.2 (4.0)	88.0 (2.2)	101.0 (5.2)	96.8 (3.0)	70.5 (5.1)	83.1 (4.3)
Benalaxyl					98.5 (1.3)	98.8 (1.0)	75.8 (2.9)	78.5 (2.9)
Nuarimol	96.8 (3.4)	90.0 (4.0)	72.0 (5.5)	73.7 (3.1)	100.2 (2.1)	103.0 (3.2)	79.5 (4.1)	80.8 (1.9)
Fenarimol	92.8 (3.2)	94.5 (3.3)	72.5 (5.4)	73.9 (5.0)	102.6 (1.1)	102.2 (2.5)	86.5 (4.2)	84.3 (4.0)
Pyrazophos					99.5 (4.2)	94.5 (8.1)	67.0 (9.1)	59.8 (5.3)

<sup>a</sup> Results are the mean of five replicates (RSD) at the 0.5 µg/g level.

pesticide extraction [12]. With the aim of assessing the effect of soil water content on fungicide recovery, soil samples were fortified at 0.05 µg/g, soil moisture content was adjusted to 10 or 1% and fungicides extracted with ethyl acetate following the procedure described above. Table 2 shows the recoveries obtained for the fungicides studied.

Good recoveries, higher than 90%, were obtained

under both water content conditions for all fungicides except oxadisyl and myclobutanil in soil A at 1% water content. Under these conditions, oxadisyl was not detected at the low fortification level used and recoveries of myclobutanil were somewhat lower than average. Therefore, recovery of these compounds from some soils may be affected when soil samples with low water content are analysed.

Table 2  
Influence of water content (1 or 10%) on fungicide recovery<sup>a</sup> from soil A

Fungicide	ECD		NPD	
	1%	10%	1%	10%
Quintozene	102.3 (4.1)	104.0 (2.8)		
Chlorothalonil	100.6 (5.0)	98.0 (2.8)		
Tolclofos-methyl	103.3 (3.8)	101.4 (3.2)	105.5 (2.5)	103.0 (3.3)
Dichlofluanid	99.2 (3.5)	104.1 (2.3)	100.5 (1.0)	98.0 (2.8)
Triadimefon	102.8 (2.9)	105.5 (2.7)	103.5 (4.2)	92.3 (1.6)
Procymidone	102.0 (1.6)	103.6 (3.2)	102.4 (0.5)	105.2 (2.0)
Myclobutanil	78.3 (2.0)	101.0 (1.4)	79.0 (2.0)	105.5 (2.7)
Cyproconazol			105.0 (1.8)	103.6 (3.2)
Oxadisyl			N.D.	101.0 (1.4)
Ofurace	100.0 (1.9)	100.3 (2.8)	102.0 (7.5)	100.3 (2.8)
Benalaxyl			101.3 (2.2)	102.1 (3.1)
Nuarimol	102.0 (3.4)	100.4 (3.4)	98.5 (4.7)	100.5 (3.4)
Fenarimol	101.9 (1.7)	103.4 (2.9)	104.3 (4.3)	103.4 (2.9)
Pyrazophos			105.0 (2.8)	102.5 (2.5)

<sup>a</sup> Results are the mean of five replicates (RSD) at the 0.05 µg/g level.

### 3.3. Recovery

Untreated soil samples were spiked with 0.05, 0.1 or 0.5 µg/g of the studied fungicides dissolved in ethyl acetate, the water content adjusted to 10%, and fungicide residues analysed by GC–ECD and GC–NPD following the procedure described above. Average recoveries varied from 87 to 111% for GC–ECD, with relative standard deviations between 0.7 and 5.9%, and from 89 to 106% for GC–NPD, with relative standard deviations ranging from 0.8 to 7.9% (Table 3) with agreement between both GC methods.

Figs. 1 and 2 depict representative chromatograms of blank samples and fortified soils at 0.05 µg/g analysed by GC with ECD and NPD, respectively. The chromatographic program used allowed a good resolution of this fungicide mixture. The SAESC method proposed for the analysis of fungicides in soil provided clean blank extracts and, therefore no clean-up step was necessary.

### 3.4. Residence time

To study the influence of the residue residence time on fungicide recoveries, soil samples were fortified at 0.1 µg/g, kept at 4 °C and analysed at 1, 15 and 30 days after application of fungicides. Glass

columns were used in this assay, instead of plastic columns, to avoid possible effects of column material on fungicide recoveries, after a long contact time. Table 4 summarises the results obtained with the two soils studied.

Fungicide recoveries higher than 80% were obtained for all compounds after 1 day of storage and, in general, good recoveries were obtained along the whole storage period of 30 days. Nevertheless, recoveries of chlorothalonil and dichlofluanid decreased with time, giving values around 50% or lower after 15 or 30 storage days, respectively.

### 3.5. Detection limit and linearity

The limit of detection of the proposed method for the fungicides studied was calculated using the equation reported by Seiber [13]:  $MDL = t_{0.99}s$ , where MDL is the method detection limit,  $s$  is the standard deviation of readings from the identically spiked matrix portions and  $t_{0.99}$  is the confidence interval about the mean, as determined by Student's  $t$  from statistics tables. The MDL obtained for fungicides, determined by GC with NPD and ECD, ranged from 2 to 10 µg/kg. The limit of quantitation (LOQ), supported by the recovery data presented,

Table 3  
Fungicide recoveries<sup>a</sup> from soil samples (10% water content)

Fungicide	ECD						NPD					
	0.5 µg/g		0.1 µg/g		0.05 µg/g		0.5 µg/g		0.1 µg/g		0.05 µg/g	
	A	B	A	B	A	B	A	B	A	B	A	B
Quintozene	98.6 (4.5)	94.8 (3.8)	100.3 (1.7)	105.5 (2.8)	100.6 (0.9)	107.6 (3.5)						
Chlorothalonil	100.1 (0.9)	96.0 (1.5)	100.9 (1.5)	101.0 (3.6)	101.0 (1.4)	101.7 (1.7)						
Tolclofos-methyl	97.3 (3.6)	96.5 (1.7)	102.8 (5.9)	101.7 (1.5)	101.7 (5.2)	105.6 (5.0)	100.1 (1.4)	97.8 (0.6)	97.5 (5.5)	94.0 (9.6)	93.5 (3.4)	93.5 (4.5)
Dichlofluanid	100.2 (2.3)	101.2 (2.1)	97.1 (2.8)	99.7 (3.2)	103.4 (1.4)	101.0 (2.7)	102.0 (1.7)	96.0 (1.9)	95.0 (6.1)	97.5 (3.4)	93.3 (3.2)	97.2 (4.9)
Triadimefon	100.3 (1.6)	97.4 (2.8)	100.4 (3.1)	101.5 (2.1)	103.5 (2.3)	102.8 (4.0)	101.9 (2.0)	99.4 (0.8)	98.8 (3.6)	94.9 (1.6)	99.7 (5.0)	96.2 (4.2)
Procymidone	87.2 (4.6)	92.3 (2.6)	103.4 (3.4)	101.7 (1.1)	106.1 (3.4)	104.2 (2.6)	98.1 (1.4)	106.1 (3.0)	103.0 (1.8)	100.0 (7.9)	101.7 (2.4)	104.5 (1.3)
Myclobutanil	94.8 (2.7)	88.3 (1.9)	105.0 (3.0)	99.7 (2.2)	111.0 (1.1)	95.8 (4.4)	100.6 (3.5)	105.0 (2.4)	102.5 (1.6)	103.7 (1.7)	102.8 (2.9)	101.5 (1.7)
Cyproconazole							103.7 (1.0)	103.0 (2.7)	102.4 (2.3)	102.0 (6.2)	102.4 (2.4)	100.6 (1.0)
Oxadixyl							94.7 (3.9)	104.6 (2.3)	95.0 (4.1)	99.7 (2.1)	95.0 (7.1)	97.4 (1.9)
Ofurace	98.4 (5.8)	96.4 (2.3)	104.2 (2.7)	101.5 (2.5)	101.7 (0.7)	103.8 (1.7)	103.0 (4.2)	97.0 (1.7)	97.3 (1.7)	105.5 (4.0)	99.3 (6.7)	103.2 (1.7)
Benalaxyl							100.2 (0.8)	99.3 (5.9)	100.6 (4.6)	101.0 (4.1)	104.2 (5.7)	98.8 (3.0)
Nuarimol	101.1 (1.1)	96.2 (2.9)	100.4 (0.7)	104.3 (4.1)	100.1 (1.0)	105.3 (2.4)	96.6 (4.0)	99.6 (3.1)	92.5 (1.9)	99.7 (4.3)	92.8 (2.7)	96.0 (4.0)
Fenarimol	97.6 (5.0)	96.9 (3.2)	103.8 (4.7)	102.7 (0.9)	103.3 (2.6)	105.2 (3.0)	103.1 (4.6)	101.5 (1.6)	94.1 (3.9)	99.3 (3.5)	98.9 (4.6)	103.5 (2.1)
Pyrazophos							98.8 (4.7)	95.8 (6.7)	100.0 (6.4)	89.0 (3.7)	103.0 (2.7)	100.0 (4.9)

<sup>a</sup> Results are the mean of five replicates (RSD).

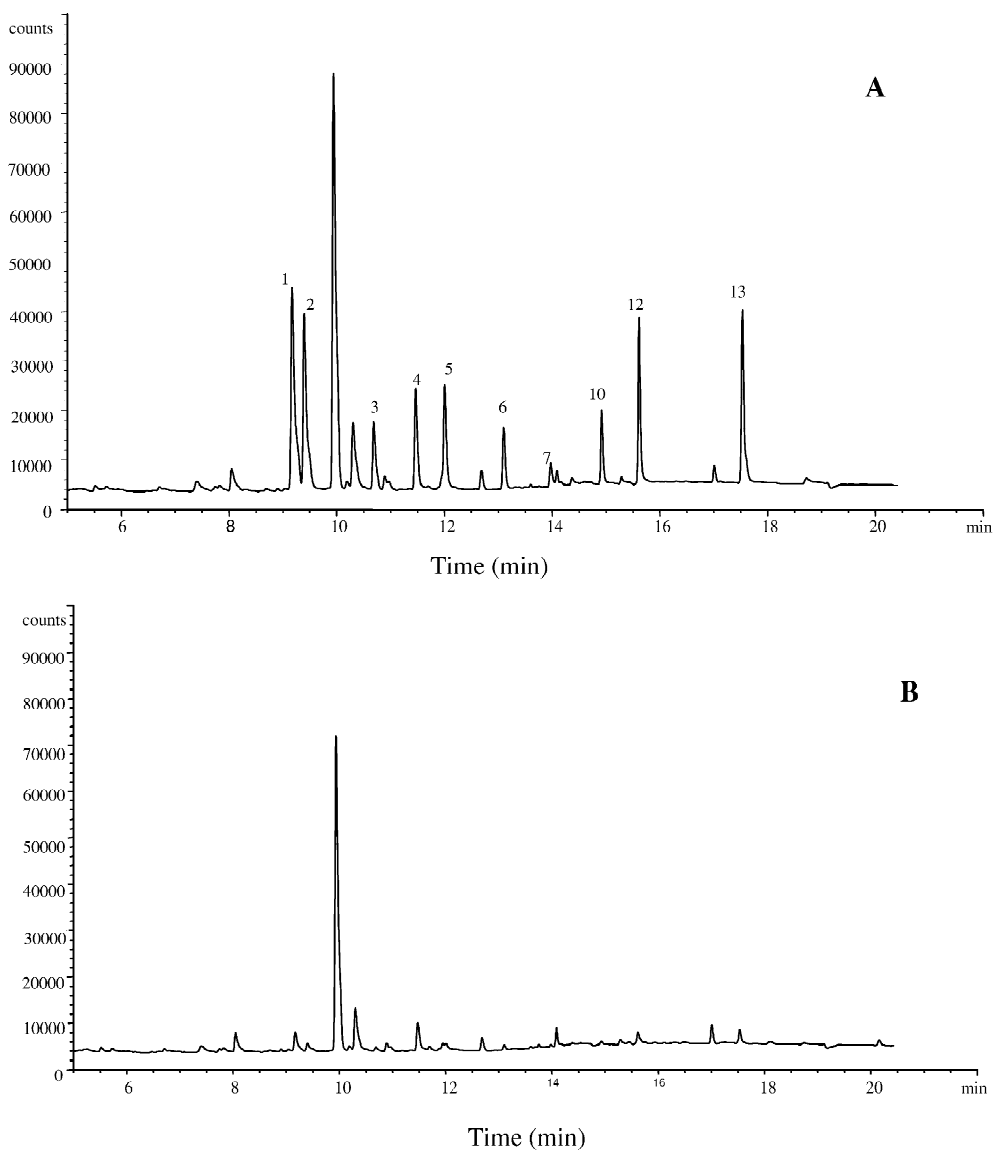


Fig. 1. GC–ECD chromatogram of a fortified soil sample at 0.05 µg/g (A) and of an unfortified soil sample (B). For peak numbers see Table 4.

was 50 µg/kg. Nevertheless, a lower LOQ could be obtained for some of the fungicides studied, according with their MDL. These values appear to be adequate for monitoring fungicide residues in soil.

The detector response was linear in the range of concentrations studied (0.05–0.5 µg/ml). Good correlation coefficients for these compounds were ob-

tained, ranging from 0.999 to 1.000 for NPD and from 0.993 to 0.999 for ECD.

### 3.6. GC–MS confirmation

Residue identities of fungicides were confirmed by GC–MS in the selected ion monitoring (SIM) mode.

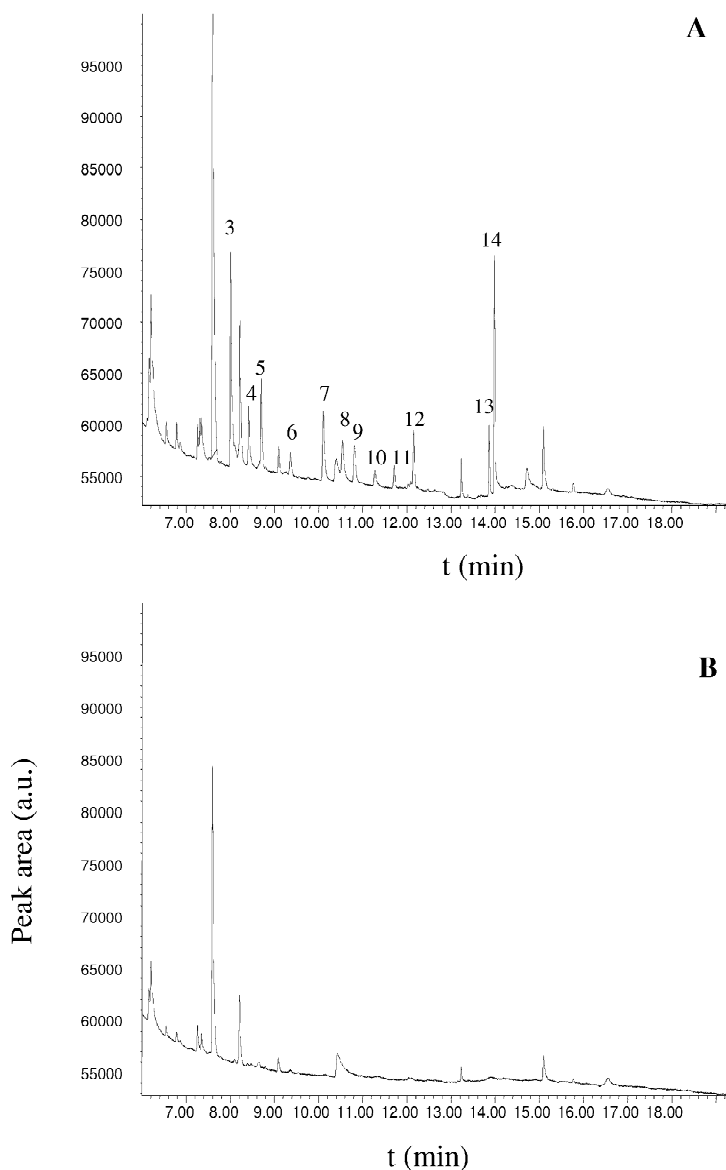


Fig. 2. GC–NPD chromatogram of a fortified soil sample at 0.05 µg/g (A) and of an unfortified soil sample (B). For peak numbers see Table 4.

Table 5 summarises fungicide retention times, the main ions of the mass spectrum obtained for each compound and their relative abundances. The mass spectra obtained are in agreement with those previously reported by others authors [11,14–17]. The absence of co-extracted interferences was confirmed by blank extracts analysis. All the compounds

studied can be identified by their mass spectra, in the PEST library, at levels near 10 ppb per compound.

#### 4. Conclusions

The results of this study show that the proposed

Table 4  
Influence of the residence time on fungicide recoveries from soil<sup>a</sup>

Compound	Fungicides	1 day		15 days		30 days	
		A	B	A	B	A	B
1	Quintozene	95.8 (2.5)	94.9 (3.7)	85.0 (2.7)	85.0 (4.2)	72.0 (4.5)	79.3 (1.1)
2	Chlorothalonil	92.0 (4.2)	83.1 (4.6)	54.8 (3.0)	29.7 (4.0)	37.5 (3.7)	17.0 (1.0)
3	Tolclofos-methyl	97.3 (3.0)	93.2 (2.0)	99.8 (1.2)	100.8 (1.0)	73.0 (3.3)	80.3 (1.5)
4	Dichlofluanid	101.5 (1.7)	100.6 (2.9)	50.9 (2.3)	71.8 (2.5)	31.7 (3.3)	57.4 (2.3)
5	Triadimefon	99.0 (1.1)	100.2 (3.4)	99.9 (1.1)	103.7 (7.3)	100.7 (2.0)	96.3 (5.5)
6	Procymidone	102.3 (6.8)	102.0 (0.9)	92.0 (0.8)	94.5 (4.5)	102.2 (1.1)	103.3 (0.9)
7	Myclobutanil	99.8 (4.3)	95.5 (1.7)	99.3 (1.2)	102.2 (0.9)	101.2 (2.2)	102.3 (1.4)
8	Cyproconazole	102.0 (1.2)	97.5 (2.8)	102.0 (5.5)	99.9 (4.7)	93.5 (2.1)	98.7 (1.2)
9	Oxadixyl	92.8 (4.7)	98.6 (4.2)	81.0 (6.3)	97.4 (2.9)	99.0 (1.4)	99.7 (1.8)
10	Ofurace	101.3 (1.0)	100.3 (3.9)	101.5 (1.3)	102.3 (1.7)	99.7 (1.1)	98.8 (1.7)
11	Benalaxyl	98.5 (1.7)	98.8 (1.5)	77.5 (9.0)	92.0 (2.8)	100.5 (2.9)	100.1 (2.2)
12	Nuarimol	100.3 (0.9)	99.0 (4.1)	101.4 (0.9)	101.0 (2.2)	97.8 (3.3)	95.0 (2.6)
13	Fenarimol	100.0 (1.4)	95.7 (2.4)	99.3 (1.2)	103.0 (2.4)	93.3 (1.0)	88.7 (2.3)
14	Pyrazophos	101.8 (2.1)	90.2 (4.6)	100.3 (5.3)	93.3 (3.1)	100.2 (1.3)	91.5 (1.5)

<sup>a</sup> Fungicides have been analyzed by GC–ECD, except cyproconazole, oxadixyl, benalaxyl and pyrazophos that were determined by GC–NPD. Results are the mean of five replicates (RSD) with soil fortified at 0.1 µg/g.

method, based on the sonication assisted extraction of soil samples placed in small columns, is a rapid a sensitive procedure for the simultaneous determination of fungicides in soil. The method is simple and uses low volumes of ethyl acetate as extracting solvent, reducing the human exposure to toxic solvents and the environmental impact of the analytical procedure.

Good recoveries though the method were obtained for all the fungicides studied. In general, soil water

content or residence time in soil did not affect fungicide recoveries. Nevertheless, low recoveries of oxadisyl and myclobutanil were obtained in one soil at low soil moisture content, and recoveries of chlorothalonil and dichlofluanid decreased with the residence time of residues in soil.

The detection limit of the proposed method varies from 2 to 10 µg/kg for the fungicides studied and residue identities can be confirmed at levels near 10 µg/kg.

Table 5  
Main ions and their relative abundance in the mass spectra of fungicides

Fungicide	$t_R$ (min)	Masses, $m/z$
Tolclofos-methyl	6.91	125 (20) 250 (10) 265 (100)
Dichlofluanid	7.24	123 (100) 167 (40) 224 (30) 332 <sup>a</sup> (5)
Triadimefon	7.39	57 (100) 208 (20) 293 <sup>a</sup> (5)
Procymidone	7.93	96 (90) 255 (15) 283 <sup>a</sup> (100)
Myclobutanil	8.52	150 (50) 179 (100) 288 <sup>a</sup> (10)
Cyproconazole	8.72	125 (30) 139 (50) 222 (100)
Oxadixyl	9.01	132 (60) 163 (70) 233 (20) 278 <sup>a</sup> (10)
Ofurace	9.24	132 (90) 160 (100) 232 (80) 281 <sup>a</sup> (70)
Benalaxyl	9.28	91 (60) 148 (100) 206 (30) 325 <sup>a</sup> (10)
Nuarimol	9.57	203 (60) 235 (100) 314 <sup>a</sup> (50)
Fenarimol	10.77	107 (80) 139 (100) 219 (20) 330 <sup>a</sup> (5)
Pyrazophos	10.79	221 (100) 232 (30) 373 <sup>a</sup> (20)
Quintozene	6.25	142 (50) 214 (60) 237 (100) 249 (70) 295 <sup>a</sup> (80)
Chlorothalonil	6.50	109 (20) 229 (15) 266 <sup>a</sup> (100)

<sup>a</sup> Molecular ion.



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