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Multiresidue Analysis of Pesticides in Soil by Gas Chromatography with Electron-Capture Detection and Gas Chromatography Mass Spectrometry Detection

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In the application of pesticides in agricultural crops, a fraction of the amount used reaches the soil, even when the pesticide is applied to plant foliage.

The growing of peppers in greenhouses is one of the main cultivation activities in the Region of Murcia (Spain). It is for that reason that it is important to know the present state of contamination by pesticides in the soils of these greenhouses. In addition, the contamination of the soil by pesticides is one of the most significant problems faced by farmers when moving to Organic Farming.

An area of great social interest at present involves the availability of simple, fast and selective methods for pesticides determination in soil analysis.

A variety of multiresidue analytical methods have been developed to analyze soil for these agrochemical. Different technologies have been used for pesticides residues in soil, such a gas chromatography with electron-capture detection (ECD) (Synder et al. 1994; Castro et al. 2001; Rissato et al. 2005; You et al. 2004) for halogenated pesticides, gas chromatography with nitrogen-phosphorus detection (NPD) (Redondo et al. 1996; López-Avila et al. 1998; Pérez et al. 1998) for residues containing these atoms, gas chromatography coupled mass-selective detection (GC-MSD) (Castro et al. 2001; Pérez et al. 1998; Mogadati et al. 1999; Papadopoulou-Mourkidou et al. 1997; Sánchez-Brunete et al 2004) for to confirm the pesticide identity in soil and high-performance liquid chromatography (HPLC) (Slobodnik et al. 1996; Pacáková et al. 1996), particularly when pesticides are thermally instable.

Compared with water and food samples, the interaction between the matrix and the analytes can be very strong for soils. Therefore, liberating the bound fraction often requires some type of intensive extraction method.

Extraction of these compounds from soil is accomplished generally by agitation (Huang et al. 1990), sonication (Navarro et al. 2000; Ma et al. 2005; You et al. 2004), and soxhlet (Lartiges et al. 1995) extraction. Supercritical fluid extraction (SFE) (Synder et al. 1994; Rissato et al. 2005), microwave-assisted extraction

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(MAE) (López-Avila et al. 1998) and solid phase extraction (SPE) (Redondo et al. 1996) have also been proposed as rapid techniques for the extraction of pesticide in soil. Many conventional methods of extraction present a number of disadvantages; they are laborious, time-consuming and large quantities of solvent waste are generated as a result of determination of trace amounts of contaminants in soil.

The main objective of this study was to develop a simple method for the determination of 22 pesticides, commonly used in the growing of peppers (Vademecum 2004), in soils colleted in greenhouses of peppers from the Region of Murcia.

MATERIALS AND METHODS

Pesticide standards were obtained from Dr. Ehrenstorfer (Augsburg, Germany) with purity ranging from 93 to 100%. These compounds were selected because they were the most heavily used in the growing of peppers from the Region of Murcia.

The solvents acetone, acetonitrile, dichloromethane, ethyl acetate and cyclohexane, residue analysis grade, were purchased from Scharlau (Barcelona, Spain).

Stocks solutions (1000 μg/mL) of each pesticide standard were prepared by dissolving 0.025 g of the pesticide in 25 mL of ethyl acetate/cyclohexane (1/1, v/v).

A pesticide intermediate standard solution (10 μg/mL) was prepared by transferring 1 mL from each pesticide solution to a 100 mL volumetric flask and diluting to volume with ethyl acetate/cyclohexane (1/1, v/v) to obtain a concentration of 10 μg/mL. Several standard solutions, with concentrations of 0.05-2 μg/mL, were injected to obtain the linearity of detector response and the detection limits of the pesticides studied.
The compounds were distributed among 2 solutions (see Table 1) to avoid the interference in the determination of endosulfan alpha isomer (retention time 22.64 min) with pyrifenox II (retention time 22.62 min).

A sonic dismembrator 200 W generator equipped with standard titanium probe (Dr Hielscher GmbH. Stahnsdorf, Germany) was used in the extraction of samples.

An Eppendorf model 5810R centrifuge (Hamburg, Germany) and a Büchi model R-205 rotavapor (Flawil, Switzerland) was used in the centrifugation and evaporation to dryness of samples, respectively.

Analysis of the final extract was performed on an Agilent (Waldbronn, Germany) model HP 6890 gas chromatograph equipped with an electron-capture detector and automatic split-splitless injector model Agilent 7683. An HP-5MSI fused silica capillary column (30 m x 0.25 mm i.d.) and 0.25 μm film thickness, supplied by Agilent Technologies, was employed, with nitrogen as makeup gas at 25 mL/min. Helium was used as the carrier (constant pressure eluting, bromophos 20.08 min). A 1 μL sample was injected into the GC using split-less mode.The injector and detector were operated at 250 and 325 °C, respectively. The column temperature was maintained at 70°C for 2 min and then programmed at 25 °C/min to 150 °C, increased to 200 °C at a rate of 3 °C/min followed by a final ramp to 280 °C at a rate of 8 °C/min, and held for 10 min. The total analysis was 41.87 min and the equilibrium time 2 min.

An Agilent model HP 6890 gas chromatograph equipped with a model 5973N mass spectrometer was operated in electron impact ionization mode with an ionizing energy of 70 eV, scanning from m/z 50 to 500 at 3.21 s per scan. The ion source temperature was 230 °C and the quadrupole temperature 150 °C. The electron multiplier voltage (EM voltage) was maintained 1300 V, and a solvent delay of 4.5 min was employed. Gas chromatography was performed under the same conditions used in GC/ECD.

Analysis was performed with selected ion monitoring (SIM) mode using primary and secondary ions. The target and qualifier abundances were determined by injection of individual pesticide standards under the same chromatographic conditions using full scan with the mass/charge ratio ranging from m/z 50 to 500. Table 1 lists the pesticides along with their retention times, molecular mass, the target and qualifier ions, and their qualifier to target abundance ratios. Pesticides were confirmed by their retention times, the identification of target and qualifier ions, and the determination of qualifier-to-target ratios. Retention times had to be within ± 0.1 min of the expected time, and qualifier-to-target ratios had to be within a 10 % range for positive confirmation. The concentration of each compound was determined by comparing the peak areas in the sample with those found for mixtures of pesticide standards of known concentration.

Several standards solutions, with concentrations of 0.05-2 μg/mL, were injected in CG/ECD and CG/MSD to obtain the linearity of detector response and the detection limits of the 22 compounds studied. The ECD and MSD response for all pesticides was linear in the concentration assayed with determination coefficients >0.999 for all pesticides.

Soil (5 g) was weighed in a 100 mL beaker. Samples were extracted, according to the procedure described by Navarro et al. (2000), with some modification, with 30 mL of acetonitrile/water (2/1) by sonication (15 min at 0.5 cycles and 60 % amplitude). After sonication, were added 20 mL dichloromethane and centrifuged for 10 min at 1900 g. The extract filtered quantitatively through glass funnel containing a filter paper 1PS, 150 mm diameter (Watman Int. Ltd., Maidstone,

Table 1. Retention time (RT, min), molecular mass (MW), target (T), qualifier ions (Q_1, Q_2 and Q_3) (m/z) and abundance ratios (%) of qualifier ion /target ion (Q_1/T and Q_2/T)[a] of the studied fungicides and insecticides.

Pesticide	RT	MW	T	Q_1	Q_2	Q_3	Q_1/T	Q_2/T
Standard solution 1								
1 Chlorpyrifos methyl	16.59	322.6	286	288	125	290	68.6	48.5
2 Malathion	18.80	330.4	173	127	125	93	85.3	83.5
3 Chlorpyrifos ethyl	19.23	350.6	197	199	314	97	93.2	70.1
4 Procymidone	21.96	284.1	96	283	285	67	70.2	47.3
5 Endosulfan (alpha isomer)	22.64	406.9	241	195	239	237	98.2	90.5
6 Hexaconazole	23.52	314.2	83	214	216	82	61.9	40.9
7 Endosulfan (beta isomer)	25.16	406.9	195	237	207	241	85.0	81.6
8 Endosulfan sulfate	26.76	423.0	272	274	229	237	82.8	61.7
9 Iprodione	28.39	330.2	187	314	189	244	69.2	65.1
10 Bifenthrin	28.84	422.9	181	165	166	182	26.0	25.5
11 Phosalone	29.68	367.8	182	121	184	367	37.5	30.8
12 λ-Cyhalothrin	30.37	449.9	181	197	208	209	83.6	53.6
13 Pyridaben	31.52	364.9	147	117	148	132	13.2	12.7
14 Cypermethrin I	32.69	416.3	181	163	165	77	87.2	75.3
15 Cypermethrin II	32.84	416.3	181	163	165	209	95.0	80.3
16 Cypermethrin III	32.97	416.3	163	181	165	209	81.2	65.9
17 Cypermethrin IV	33.02	416.3	163	181	165	209	81.4	64.2
18 Deltamethrin	36.00	502.2	181	253	251	255	66.5	41.9
Standard solution 2								
19 Diazinon	14.47	304.3	179	137	152	199	96.8	67.8
20 Triadimefon	19.39	293.8	57	208	85	210	76.5	28.9
21 Pyrifenox I	21.21	295.2	171	173	262	100	67.1	20.9
22 Pyrifenox II	22.62	295.2	171	173	262	92	66.0	23.8
23 Oxyfluorfen	24.73	361.7	252	302	331	361	43.2	41.5
24 Acrinathrin	30.71	541.4	181	208	93	289	63.3	52.6
25 Cyfluthrin I	32.22	434.3	163	206	165	227	69.3	65.9
26 Cyfluthrin II	32.36	434.3	163	206	165	227	71.0	66.2
27 Cyfluthrin III	32.48	434.3	163	206	165	227	67.2	66.8
28 Cyfluthrin IV	32.54	434.3	163	206	227	199	65.7	52.4
29 Fluvalinate-tau I	34.72	502.9	250	252	209	181	33.6	29.3
30 Fluvalinate-tau II	34.85	502.9	250	252	209	181	35.0	28.6

[a] Q/T (%) ratios are the results of abundance values of the qualifier ion (Q_1, Q_2) divided by the abundance of the target ion (T) x100.

Uk). The organic phase was evaporated to dryness through rotary vacuum evaporation. The residue was redissolved to a 5 mL volumetric flask with ethyl acetate/cyclohexane (1/1, v/v) and an aliquot analyzed by GC under conditions described above.

The soil samples were taken in Campo de Cartagena, Murcia (southeastern, Spain). Soil samples were passed through 2 mm sieve, homogenized, and then extracted with their naturally occurring water content (10% moisture). The characteristics of the soils were as follows: Soil A: pH 7.80; organic matter content 2.54%, sand 15 %, silt 30 %, and clay 55%. Soil B: pH 7.70; organic matter content 1.15%, sand 25 %, silt 35 %, and clay 40%. Soil C: pH 7.91;

organic matter content 3.49%, sand 21 %, silt 33 %, and clay 46%. The developed method provides clean blank extracts without interferences during GC.

Soil samples were fortified with 0.2 and 0.5 μg/g of pesticide After evaporation of the spiking solvent, the samples were allowed to equilibrate for 2 h., before extraction and analyzed following the procedures described above. Five sample replicates, spiked at each fortification level, were extracted.

Real samples were taken in three experimental greenhouses of peppers from the Region of Murcia. Samples were colleted from the plough layer (0-20 cm). Soil samples were sieved (2 mm), homogenized and stored at -18 ºC until analysis.

RESULTS AND DISCUSSION

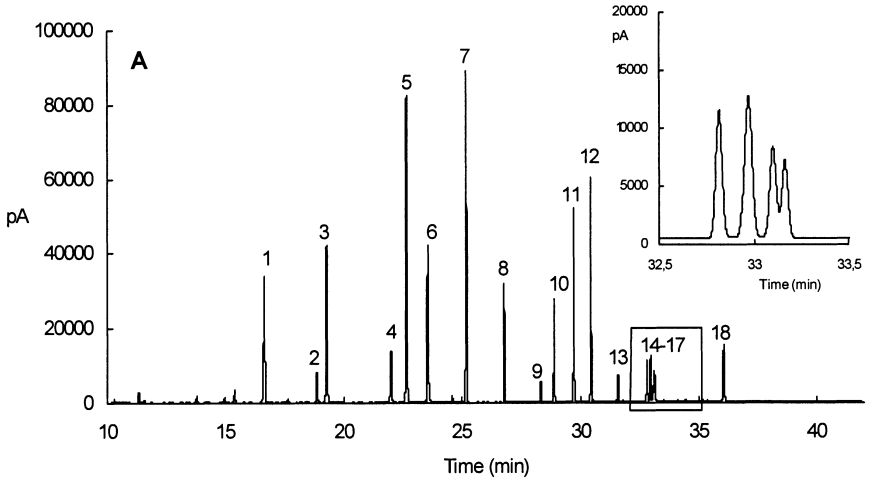
The interactions between the matrix and the analytes is stronger in soil; therefore, an extraction procedure capable of liberating the bound residues from the matrix is required. Sonication provides an efficient method for extracting tightly bound chemicals from soils, usually resulting in recoveries similar to the more time-consuming soxhlet technique.

Three solvents (acetonitrile, acetone and ethyl acetate) were tested as extractants, and the best results were obtained with acetonitrile for all compounds.

Figure 1 shows chromatograms (ECD) of a standard solution 1 and a soil sample spiked (soil A) with the compounds of the standard solution 1 (Figure 2 Idem for standard solution 2). All pesticides were satisfactorily separated with high sensitivity and selectivity (except endosulfan alpha isomer and pyrifenox II). The developed method provides clean blank extracts without interferences during GC and, therefore, cleanup of soil samples was not required.

Three control soils from different sources and with different physicochemical properties were analyzed during initial method validation. Table 2 lists the mean recoveries of spiked analytes with 0.2 and 0.5 μg/g of pesticide. The recoveries obtained for all pesticides ranged from 82.6 to 115.1 % for soil A, 85.4 to 110.6 for soil B and 82.9 to 114.6 for soil C. The relative standard deviation (RSD) was <6.9 % in the most unfavourable case. Similar recoveries have been obtained for soils with different physicochemical properties.

The repeatability of our chromatographic method was determined by performing the analysis of a sample spiked at 0.1 μg/g of pesticide. The sample was injected 10 times with an automatic injector, and the relative standard deviation (RSD) values obtained for peak areas by GC-ECD and GC-MSD ranged from 1.8 to 6.6 and 3.9 to 10.3, respectively. The relative standard deviation (RSD) values obtained for retention times by GC-ECD and GC-MSD ranged from 0.01 to 0.03 and 0.01 to 0.04, respectively.



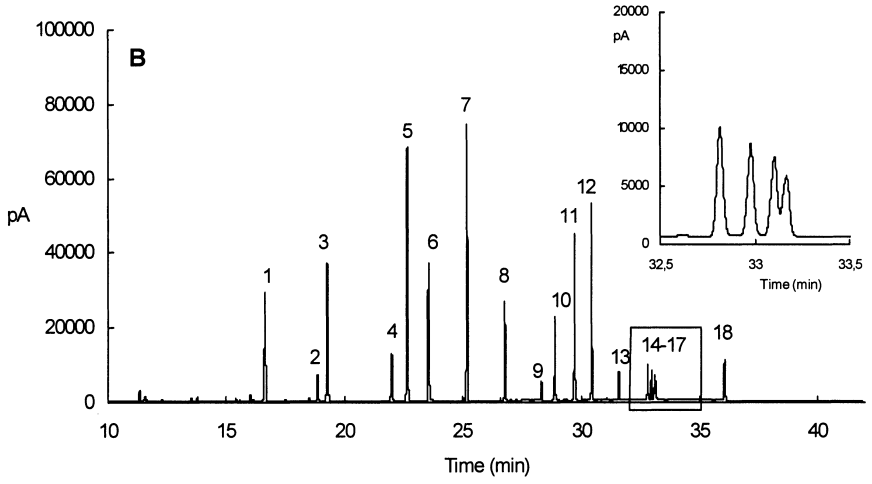


Figure 1. Chromatograms (ECD) obtained for (A) standard solution 1 (0.5 mg/Kg). (B) spiked soil sample (0.5 mg/Kg). 1=Chlorpyrifos methyl, 2=Malathion, 3=Chlorpyrifos ethyl, 4=Procymidone, 5=Endosulfan (alpha isomer), 6=Hexaconazole, 7=Endosulfan (beta isomer), 8=Endosulfan sulphate, 9=Iprodione, 10=Bifenthrin, 11=Phosalone, 12=λ-Cyhalothrin, 13=Pyridaben, 14=Cypermethrin I, 15=Cypermethrin II, 16=Cypermethrin III, 17=Cypermethrin IV, 18=Deltamethrin.

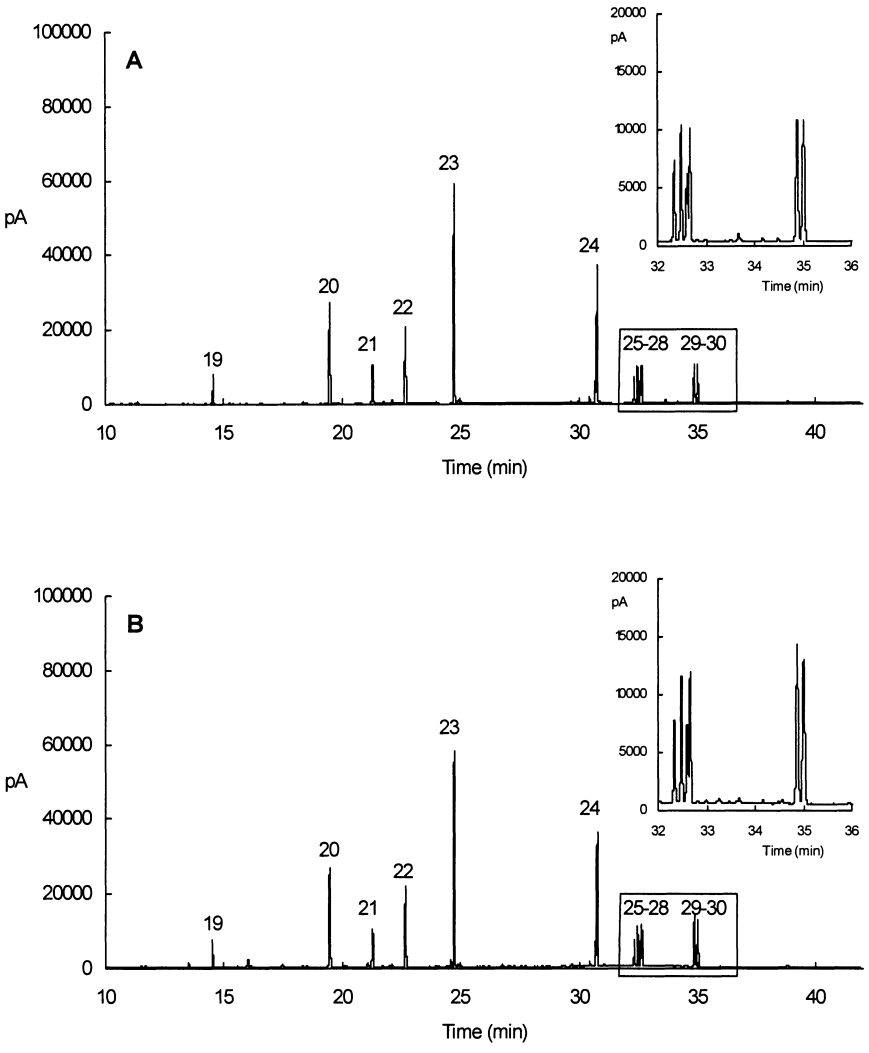


Figure 2. Chromatograms (ECD) obtained for (A) standard solution 2 (0.5 mg/Kg, except diazinon 1 mg/Kg). (B) spiked soil sample (0.5 mg/Kg, except diazinon 1 mg/Kg). 19=Diazinon, 20=Triadimefon, 21=Pyrifenox I, 22=Pyrifenox II, 23=Oxyfluorfen, 24=Acrinathrin, 25=Cyfluthrin I, 26=Cyfluthrin II, 27=Cyfluthrin III, 28=Cyfluthrin IV, 29=Fluvalinate-tau I, 30=Fluvalinate-tau II.

Table 2. Pesticide recoveries (%)[a].

Pesticide	Fortification level, μg/g	Mean recovery ± RSD[b], %[a]		
		Soil A	Soil B	Soil C
Chlorpyrifos methyl	0.2	98.3 ± 3.0	95.6 ± 3.6	96.4 ± 4.6
	0.5	100.1 ± 2.1	102.4 ± 3.5	98.2 ± 3.9
Malathion	0.2	103.2 ± 3.8	106.5 ± 4.2	104.5 ± 4.9
	0.5	101.7 ± 2.6	103.1 ± 2.4	103.7 ± 2.8
Chlorpyrifos ethyl	0.2	93.8 ± 2.7	97.3 ± 2.2	92.4 ± 4.1
	0.5	96.7 ± 2.1	99.1 ± 2.4	94.8 ± 2.9
Procymidone	0.2	82.6 ± 2.9	85.7 ± 3.3	82.9± 4.3
	0.5	89.9 ± 2.0	89.3 ± 2.9	85.4 ± 3.1
Endosulfan (alpha isomer)	0.2	89.4 ± 3.8	94.5 ± 4.6	90.0 ± 5.2
	0.5	98.3 ± 3.1	96.1 ± 3.0	97.4 ± 3.7
Hexaconazole	0.2	96.8 ± 3.4	94.9 ± 3.9	92.6 ± 3.3
	0.5	100.4 ± 3.1	97.4 ± 2.4	96.2 ± 2.7
Endosulfan (beta isomer)	0.2	90.8 ± 6.6	87.5 ± 5.5	88.8 ± 5.4
	0.5	99.5 ± 2.7	103.0 ± 2.9	97.3 ± 3.6
Endosulfan sulfate	0.2	89.6 ± 3.1	91.1 ± 3.8	92.2 ± 5.4
	0.5	96.3 ± 2.3	96.0 ± 3.5	94.6 ± 4.3
Iprodione	0.2	90.4 ± 3.3	95.3 ± 4.4	87.8 ± 4.8
	0.5	96.7 ± 2.0	98.2 ± 3.1	92.4 ± 3.4
Bifenthrin	0.2	87.3 ± 4.3	85.4 ± 3.8	89.6 ± 4.6
	0.5	90.4± 2.8	94.8± 2.9	93.2± 3.9
Phosalone	0.2	109.1 ± 4.8	106.3 ± 4.3	108.8 ± 5.7
	0.5	101.5 ± 2.6	103.6 ± 3.7	105.5 ± 2.9
λ-Cyhalothrin	0.2	92.1 ± 5.2	90.1 ± 4.3	87.2 ± 5.6
	0.5	97.8 ± 3.7	94.5 ± 3.0	93.7 ± 3.8
Pyridaben	0.2	106.8 ± 3.6	107.2 ± 3.9	105.0 ± 3.3
	0.5	102.1 ± 3.1	104.3 ± 2.6	104.2 ± 3.2
Cypermethrin	0.2	106.6 ± 3.9	104.4 ± 4.6	108.3 ± 5.7
	0.5	102.2 ± 2.8	100.7 ± 2.7	105.1 ± 4.1
Deltamethrin	0.2	108.8 ± 4.0	104.9 ± 4.7	107.6 ± 4.6
	0.5	101.6 ± 3.3	101.8 ± 3.9	102.9 ± 4.2
Diazinon	0.2	95.0 ± 2.9	93.3 ± 3.6	97.7 ± 3.8
	0.5	95.9 ± 2.7	96.2 ± 3.0	96.4 ± 3.3
Triadimefon	0.2	93.0 ± 2.4	89.6 ± 3.5	91.1 ± 4.4
	0.5	98.8 ± 1.9	95.1 ± 2.2	94.4 ± 2.6
Pyrifenox	0.2	101.2 ± 4.6	97.0 ± 5.1	101.2 ± 4.6
	0.5	98.8 ± 4.0	99.2 ± 4.5	98.8 ± 4.0
Oxyfluorfen	0.2	95.2 ± 2.7	96.3 ± 2.9	93.4 ± 4.9
	0.5	98.6 ± 2.2	97.8 ± 2.7	96.0 ± 2.8
Acrinathrin	0.2	90.1 ± 5.3	93.7 ± 4.6	91.3 ± 6.0
	0.5	95.8 ± 4.1	97.3 ± 3.2	93.6 ± 4.6
Cyfluthrin	0.2	112.5 ± 5.6	110.6 ± 6.1	113.7 ± 6.9
	0.5	107.3 ± 3.8	106.4 ± 4.0	108.1 ± 4.5
Fluvalinate-tau	0.2	115.1 ± 4.8	110.2 ± 5.6	114.6 ± 5.5
	0.5	108.4 ± 3.4	105.5 ± 3.9	109.3 ± 4.2

[a] n= 5. [b] RSD= relative standard deviation.

The LOD is an important parameter used to assess an analytical method. Table 3 summarizes the limits of detection (LOD; obtained at a signal-to signal ratio 3) obtained for the individual pesticides in three soils by GC-ECD and GC-MSD. In the case of the GC-ECD the LOD was in most cases a little lower than the

obtained by GC-MSD (in the SIM mode). The range of LOD achieved is in the lower end of that obtained by other authors (Sánchez-Brunete et al 2004; Rissato et al. 2005; Papadopoulou-Mourkidou et al. 1997). Similar LOD have been obtained for soils with different physicochemical properties.

Table 3. Limits of detection (LOD, μg/kg) of the studied pesticides by GC-ECD and GC-MSD.

	LOD (μg/kg)					
	GC-ECD			GC-MSD		
Pesticide	Soil A	Soil B	Soil C	Soil A	Soil B	Soil C
Chlorpyrifos methyl	0.6	0.4	0.7	0.5	0.7	1.0
Malathion	2.3	1.8	2.7	2.6	2.4	3.6
Chlorpyrifos ethyl	0.4	0.2	0.4	0.2	0.5	0.9
Procymidone	2.3	1.4	4.5	5.6	4.7	6.3
Endosulfan (alpha isomer)	0.2	0.3	1.5	6.3	6.5	7.0
Hexaconazole	0.3	0.5	0.8	1.3	1.9	2.5
Endosulfan (beta isomer)	0.2	0.6	0.9	6.9	5.8	8.6
Endosulfan sulfate	0.2	0.9	2.0	7.3	6.4	9.8
Iprodione	4.8	4.2	5.7	10.3	9.4	14.5
Bifenthrin	0.6	0.8	0.6	2.5	4.7	4.8
Phosalone	0.4	0.8	0.5	0.4	0.6	1.3
λ-Cyhalothrin	0.4	0.9	1.6	9.0	6.4	7.6
Pyridaben	1.9	3.5	3.8	10.3	6.2	8.7
Cypermethrin	1.6	0.6	1.8	9.8	4.6	11.4
Deltamethrin	1.8	0.7	3.4	15.6	9.4	13.9
Diazinon	4.0	2.9	3.7	3.4	4.3	4.8
Triadimefon	0.3	0.3	0.6	1.9	1.3	1.8
Pyrifenox	0.3	1.0	1.1	2.2	2.5	4.3
Oxyfluorfen	2.2	0.3	0.9	9.1	7.3	7.8
Acrinathrin	1.1	2.5	3.9	7.8	8.6	11.5
Cyfluthrin	0.7	0.8	1.3	9.7	8.3	10.6
Fluvalinate-tau	0.5	1.2	1.4	6.0	5.7	9.3

Soil from experimental greenhouses of peppers from the Region of Murcia was sampled and analyzed following the extraction methods described above. Pesticide levels encountered in the collected samples are shown in Table 4. The chromatograms (ECD) obtained for three representative soil samples are depicted in Figure 3. Analysis of real samples showed the validity of method used, which allowed the determination and identification of pesticides present in the samples.

Table 4. Pesticide residues found in real soil samples.

Soil	Procymidone[a] (μg/g)	Pyrifenox[a] (μg/g)	Endosulfan (alpha)[a] (μg/g)	Endosulfan (beta)[a] (μg/g)	Endosulfan sulphate[a] (μg/g)
A	0.45 ± 0.03				
B		0.14 ± 0.01			
C			0.09 ± 0.01	0.19 ± 0.03	0.004 ± 0.001

[a] Mean of four determinations ± RSD.

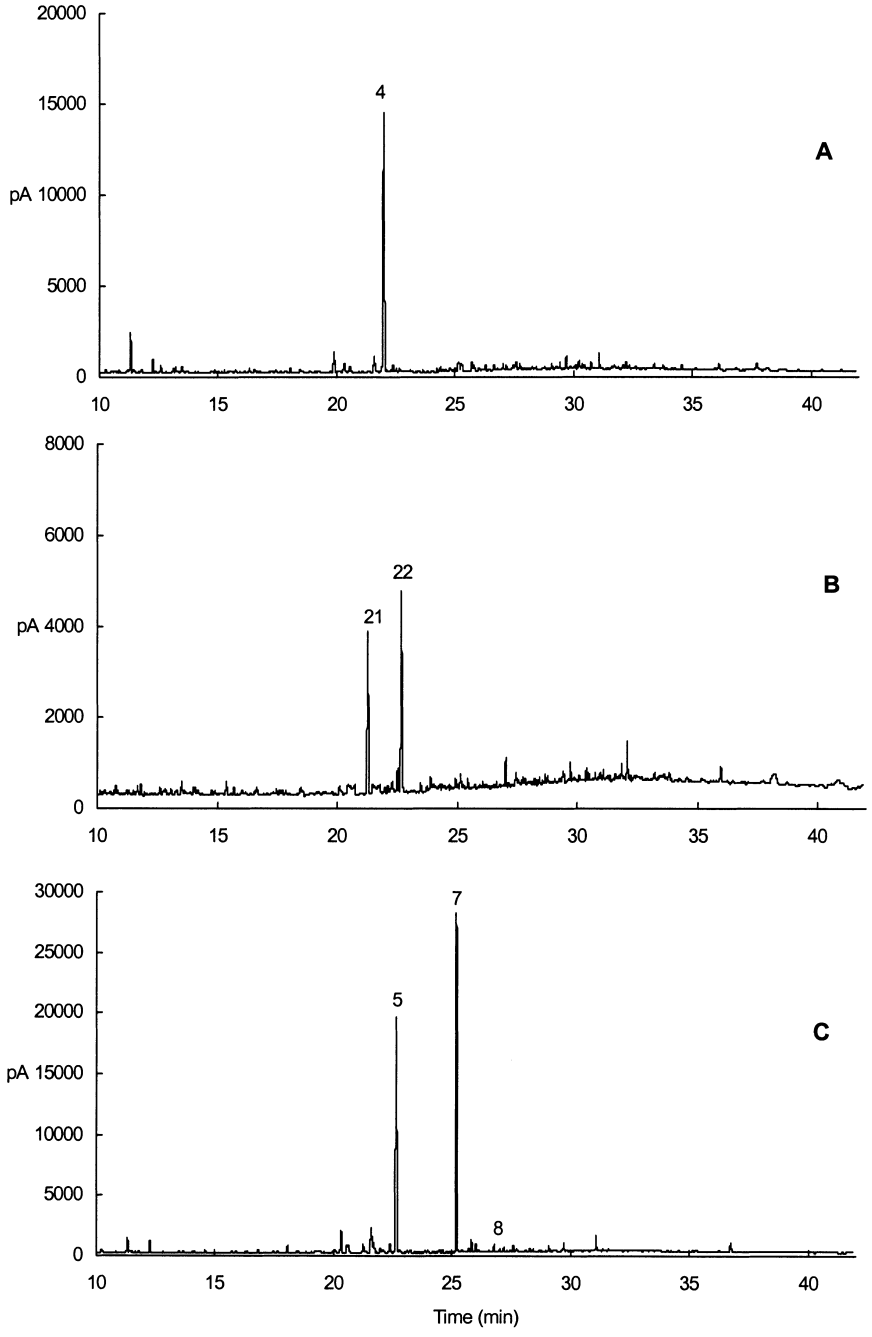


Figure 3. Chromatograms (ECD) for three soil samples (soil A, B and C) collected from experimental greenhouses of peppers from the Region of Murcia. 4=Procymidone, 5=Endosulfan (alpha isomer), 7=Endosulfan (beta isomer), 8=Endosulfan sulphate 21=Pyrifenox I, 22=Pyrifenox II.

The results of this study show that the proposed method, based on the sonication extraction of soil samples, is rapid, simple, sensitive and uses small volumes of solvents, reducing the risk for human health and the environmental. Good recovery and low detection though method was obtained for all the pesticides studied. The method presents advantages compared with other conventional methods given the use of a low volume of organic solvent in the sample extraction, short extraction time and the fact that a cleanup is not required. Another advantage of the method is the application to the analysis of pesticides in soil samples collected in experimental greenhouses of peppers from the Region of Murcia, where several pesticides were found. Finally, our method is versatile and is capable of allowing the inclusion of new pesticides used in other agricultural growing.

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