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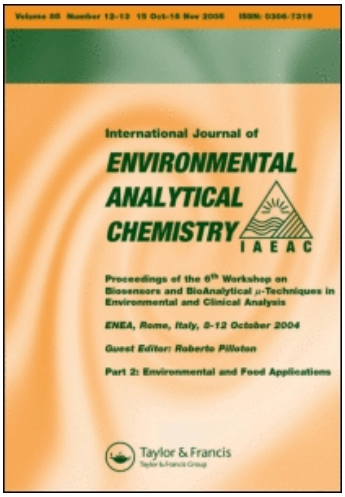

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AUTOMATED SOXHLET EXTRACTION AND SINGLE STEP CLEAN-UP FOR THE DETERMINATION OF ORGANOCHLORINE PESTICIDES IN SOIL BY GC-MS OR GC-ECD

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Automated Soxhlet extraction has been evaluated for the determination of 21 organochlorine pesticides (DDT analogues, HCH isomers, hexachlorobenzene, aldrin, endrin, dieldrin, alachlor, heptachlor, heptachlorepoxide, α- and β-endosulphan, endosulphan sulphate, methoxychlor and mirex) from soil. The Soxhlet extraction method was compared with ultrasonic extraction. Recoveries obtained by hot Soxhlet were higher than for ultrasonic extraction and ranged from 70 to 102% for the lowest fortification level (5 ng/g dry soil). A single clean-up step on Florisil and silica was used to remove interfering material. Because of complementary, GC-ECD and GC-MS were used for the analysis. The detection limits were between 0.1 and 0.2 ng/g dry soil for GC-ECD and 0.2 and 0.4 ng/g dry for GC-MS, respectively.

Keywords: Organochlorine pesticides; Soil; Automated Soxhlet; Gas chromatography

INTRODUCTION

Due to their persistence, accumulation in the food chain and possible health effects on wildlife and humans, organochlorine pollutants are still of great concern [1]. Decades after being banned, they can be found in the

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environment, even in remote regions [2]. Different procedures are reported for the extraction of persistent organochlorine pollutants (POPs) from soil. While ultrasonic [3] and Soxhlet [4–8] extraction represent the classical methodology for the extraction of lipophilic compounds from solid samples, new methodologies based on supercritical fluid extraction [9,10], steam distillation [3], microwave assisted extraction [3,11] or accelerated solvent extraction [12–15] have been described. Lower solvent volumes and shorter extraction times are required. However, most of these methods require costly equipment and the efficiency may be lower than for Soxhlet procedure. Because extractions are done at elevated temperature and pressure, thermal degradation of DDT and endrin is of potential concern in accelerated solvent extraction [12].

In a previous work [16], we have shown that the use of automated Soxhlet in hot extraction mode may reduce the extraction time for 8–16 h to 2 h, with acceptable efficiency for the extraction of POPs from soil samples. However, due to the use of destructive clean-up with concentrated sulphuric acid impregnated silica, the method was restricted to the determination of pesticides stable in acid medium (DDTs and HCHs) and could not be used for the determination of more labile pesticides (dieldrin, endrin or endosulfan).

In this study, automated hot Soxhlet has been evaluated for the extraction of organochlorine pesticides from soil and compared to ultrasonic extraction. Furthermore, a non-destructive single step clean-up on mixed Florisil–silica cartridge was used to overcome the problem of labile analytes. Two capillary columns with different polarity were used to solve possible coelutions.

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EXPERIMENTAL

Chemicals

Anhydrous sodium sulphate (p.a), silica gel and Florisil for column chromatography were obtained from Merck (Darmstadt, Germany). All adsorbents were washed with hexane and heated at 160° for 4 h before use. Dichloromethane (DCM) for organic trace analysis (BDH Laboratory Supplies, Poole, England) and acetone, *n*-hexane for organic trace analysis (Merck) did not yield any interfering GC peak when concentrated from 10 ml to 100 µl. All analytical standards of pesticides (o,p′-DDE, p,p′-DDE, o,p′-DDD, p,p′-DDD, o,p′-DDT, p,p′-DDT, HCH isomers

(α, β and γ), hexachlorobenzene, aldrin, endrin, dieldrin, alachlor, heptachlor, heptachlorepoxide, α- and β-endosulphan, endosulphan sulphate, methoxychlor and mirex) were obtained from Dr. Ehrenstorfer Laboratories (Augsburg, Germany). Pentachloronitrobenzene (IS1) and PCB 190 (IS2) were used as internal standards. Solutions were individually prepared in hexane to give a concentration of 1 μg/μl. Dilution to 10 ng/μl for each pesticide. A stock mixture solution with concentration of 1 ng/μl for each pesticide and two dilutions of the stock solution (0.1 and 0.01 ng/μl, respectively) were prepared. All dilutions were stored at −20°C. Seven levels of calibration were obtained by obtained by addition of 50 μl of internals standards (0.5 ng/μl) to different volumes of the three dilutions to have final concentrations between 0.001 and 0.5 ng/μl for each pesticide. If necessary, hexane was added to a final volume of 200 μl.

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Apparatus and Materials

A rotary vacuum evaporator (Heidolph VV 2000), SPE vacuum manifold (JT Baker, Deventer, The Netherlands), ultrasonic bath (Vel, Leuven, Belgium), automated Soxhlet extractor B-811 (Buchi, Switzerland) and glass fibre extraction thimbles (Schleicher & Schuell, Dassel, Germany) were used.

A Hewlett Packard 6890 (Palo Alto, CA, USA) gas chromatograph was connected via direct interface with a HP 5973 mass spectrometer. A DB-1 (J&W Scientific, Folsom, USA) fused silica capillary column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used with helium as carrier gas at constant flow of 1 ml/min. A Gerstel PTV injector with a multi baffled empty liner of 1.5 mm i.d. was kept at 265°C. One μl was injected in pulsed splitless mode (pulse pressure = 20 psi, pulse time = 1 min and splitless time = 1 min). The temperature program of the oven started from 90°C stay for 1 min, then with a rate of 15°C/min to 150°C, stay 1 min, by 6°C/ min to 230°C, stay for 1 min and further by 10°C/min to 275°C, stay for 5 min.

The MS acquisition parameters were: ion source 180°C, electron ionisation 70 eV, solvent delay 10 min, electron multiplier voltage 1900 V. Two specific ions (the most abundant as quantification ion, and another ion for confirmation) were monitored for each pesticide (Table I). Retention time and relative abundance of the qualifier ion to the quantification ion were used as identification criteria. A deviation of ion ratio of less than ±20% from the theoretical value was considered acceptable.

TABLE I GC-MS and GC-ECD acquisition parameters

Compounds	*GC-MS (column DB 1)*				*GC-ECD (column HT 8)*	
	RT interval (min)	*Correlation*	*Qualifier ion*	*Quantification ion*	*RT* (min)	*Correlation*
PCNB (IS1)	11.75–11.95	ns	293	295	15.85	ns
α-HCH	10.37–10.77	0.998	219	181	14.3	0.999
γ-HCH	10.78–11.18	0.998	219	181	15.59	0.999
HCB	10.94–11.34	0.999	286	284	14.54	0.999
β-HCH	11.28–11.68	0.999	219	181	15.78	0.999
Alachlor	13.75–14.15	0.999	188	160	16.75	0.999
Heptachlor	13.87–14.27	0.999	272	274	17.25	0.999
Aldrin	14.96–15.36	0.999	261	263	18.54	0.999
Heptachlorepoxide	16.09–16.49	0.997	353	253	20.11	0.999
PCB 190 (IS2)	23.21–23.41	ns	396	394	27.08	ns
o,p′-DDE	16.90–17.30	0.999	248	246	20.92	0.995
α-endosulphan	17.10–17.50	0.993	339	241	21.28	0.994
p,p′-DDE	17.85–18.25	0.999	248	246	22.09	0.996
Dieldrin	17.85–18.25	0.996	277	263	22.24	0.996
o,p′-DDD	17.98–18.38	0.999	237	235	22.51	0.995
Endrin	18.39–18.79	0.995	279	263	23.07	0.998
β-endosulphan	18.48–18.88	0.997	339	241	23.6	0.995
o,p′-DDT	18.89–19.29	0.999	237	235	23.35	0.995
p,p′-DDD	19.18–19.58	0.999	237	235	23.76	0.995
Endosulphan sulphate	19.75–20.15	0.996	387	272	25.03	0.997
p,p′-DDT	20.26–20.66	0.997	237	235	24.56	0.999
Methoxychlor	21.85–22.25	0.999	228	227	25.64	0.998
Mirex	23.09–23.49	0.999	274	272	26.34	0.995

A HP 6890 gas chromatograph with a micro electron capture detector (μ-ECD) was equipped with a HT-8 (SGE, Zulte, Belgium) capillary column (25 m × 220 μm i.d. × 0.25 μm film thickness). Helium was used as carrier gas at constant flow of 1 ml/min. One μl was injected in pulsed splitless mode (pulse pressure = 20 psi, pulse time = 1.5 min and splitless time = 1.5 min). The detector was kept at 320°C and Ar/CH4 was used as make-up gas at a flow of 40 ml/min. The GC temperature program started at 90°C, stay 1 min, then at 15°C/min to 150°C, followed by 6°C/min to 230°C, stay 1 min and further with 10°C/min to 290°C, stay 5 min.

Good linearity was achieved for all compounds with correlation coefficients higher than 0.993 for GC-MS and 0.994 for GC-ECD, respectively (Table I).

Sampling and sample preparation

Multiple soil samples (25 mm diameter and 100 mm depth) were taken from four locations: three agricultural lands (Wilrijk and Hasselt, Belgium) and

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one public park (Wilrijk). The last location has undergone minimal disturbance of the top layer in contrast with agricultural sites with significantly disturbed top layers. After collection, each soil sample was immediately placed in a cleaned polypropylene vessel. All samples were dried at room temperature, homogenized, sieved and stored at room temperature until analysis. Two grams of soil were used for each analysis.

Extraction and Clean-up Procedure

Hot Soxhlet Extraction

Two grams of soil were weighted in an extraction thimble and 25 µl of internal standards (concentration 0.5 ng/µl) were added. Hot Soxhlet extraction was performed for 2 h with 60 ml of hexane : acetone = 3 : 1. The method included an automated evaporation step, after which approximately 1.5 ml of concentrated extract were obtained and further subjected to clean-up.

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Ultrasonic Extraction

Two grams of soil were spiked with internal standards as described previously and extracted with 60 ml hexane : acetone = 3 : 1 by ultrasonication for 2 × 1 h. The mixture was filtered, concentrated to about 1.5 ml with the rotavapor and further cleaned-up.

Clean-up Step Procedure

Into a 25 ml empty catridge, 2 g of activated silica, 1 g activated Florisil and 0.5 g of anhydrous sodium sulphate were added successively. The cartridge was washed with 6 ml hexane and the concentrated extract was applied. Elution was done with 2 × 5 ml hexane : dichloromethane = 3 : 1. The eluates were concentrated to about 200 µl and transferred to vials for automated GC injection.

Evaluation of Recoveries

Two grams soil were spiked with 25 µl of each internal standard (concentration 0.5 ng/µl) and subjected to whole procedure. Before GC analysis, the concentrated extract was adjusted to a final volume of 200 µl. In parallel, 25 µl of each internal standard were transferred to a vial and 150 µl

hexane added in order to have the same dilution factor as for the extract. The internal standard recoveries were evaluated by comparison of the peak areas obtained with or without the procedure.

In order to evaluate the recoveries for investigated compounds, 25 g soil were extracted with 50 ml of methanol (hot Soxhlet extraction mode for 2 hours) and the residue dried at 100°C. The dried residue was conserved in a polypropylene bowl and used for further experiments. Four levels of fortification (5, 10, 25 and 50 ng/g dry weight) were performed and the spiked soils were subjected to the same extraction and clean-up procedures as described before except that the internal standards were added prior to GC analysis.

RESULTS AND DISCUSSION

Hot Soxhlet versus Sonication

The Soxhlet system offers four modes of extraction (hot extraction, warm extraction, standard Soxhlet and continuous mode). Each of them consists mainly of three steps: extraction, rinsing, and concentration, which can be performed in stages for gradual solvent evaporation until near dryness. During hot extraction mode, the solvent is distilled into the extraction chamber, while the upper heating element is turned on. The solvent is always kept above a fixed level by means of an optical sensor. This insures equilibrium between the rate of fresh solvent entering the extraction chamber and solvent leaving the chamber. Thus, the sample is permanently in contact with hot, but not boiling solvent.

In a previous work [16], we have found that the extraction mixture (hexane : acetone = 3 : 1) extracts less interfering material and presents an easy evaporation step through azeotropic distillation. The use of a mixture containing DCM lead to more interfering material and a higher noise background. For the same extraction time, hot Soxhlet lead to higher recoveries than sonication (Table II) with lower relative standard deviation for targeted organochlorine pesticides. This is in agreement with our previous findings for PCB extraction from soil [16] and might be explained by the high number of manipulations for ultrasonic extraction.

It was suggested [13] that hot solvents were able to penetrate more effectively solid matrices, while it is difficult to achieve complete extraction because of irreversible binding of certain fractions to the matrix [10].

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TABLE II Recoveries of organochlorine pesticides from spiked soil samples at four levels of fortifications using Soxhlet and ultrasonic extractions ($n = 3$). Ultrasonic extraction efficiency is given as percentage of Soxhlet extraction efficiency

Compounds	*Fortification levels*											
	5 ng/g *dry soil*			*10* ng/g *dry soil*			*25* ng/g *dry soil*			*50* ng/g *dry soil*		
	Soxhlet	*Sonication*	*%*	*Soxhlet*	*Sonication*	*%*	*Soxhlet*	*Sonication*	*%*	*Soxhlet*	*Sonication*	*%*
α-HCH	82 (3)	60 (4)	73	85 (3)	63 (6)	86	89 (2)	67 (4)	75	88 (3)	68 (4)	77
HCB	93 (3)	90 (4)	96	95 (3)	93 (5)	97	91 (3)	94 (4)	103	93 (2)	90 (2)	97
γ-HCH	90 (2)	70 (7)	78	91 (2)	77 (4)	99	89 (2)	76 (3)	77	87 (2)	74 (3)	85
β-HCH	88 (3)	64 (4)	80	91 (2)	69 (4)	85	85 (3)	67 (3)	79	87 (3)	75 (3)	86
Alachlor	75 (2)	59 (2)	79	81 (3)	60 (3)	74	83 (3)	65 (3)	78	83 (2)	62 (3)	75
Heptachlor	93 (3)	72 (2)	77	94 (3)	85 (3)	90	97 (2)	80 (3)	82	98 (1)	84 (2)	86
Aldrin	77 (3)	72 (5)	93	83 (3)	82 (3)	99	89 (3)	83 (4)	93	87 (2)	84 (2)	96
Heptachlorepoxide	91 (3)	81 (2)	89	93 (3)	85 (4)	91	94 (3)	87 (3)	92	93 (2)	86 (2)	92
o,p′-DDE	101 (3)	97 (4)	96	102 (2)	93 (4)	91	104 (3)	90 (3)	86	101 (2)	92 (3)	91
α-endosulphan	94 (3)	83 (3)	88	93 (3)	84 (3)	90	98 (3)	83 (3)	85	97 (2)	84 (3)	87
p,p'DDE	101 (2)	89 (4)	88	98 (2)	87 (3)	89	99 (2)	89 (2)	90	98 (3)	90 (3)	92
Dieldrin	69 (2)	62 (3)	90	91 (2)	80 (2)	88	94 (2)	87 (4)	93	92 (3)	91 (3)	99
o,p′-DDD	101 (2)	84 (3)	83	95 (3)	86 (5)	90	94 (3)	84 (3)	89	94 (3)	90 (3)	96
Endrin	86 (2)	67 (4)	78	93 (5)	69 (4)	74	95 (3)	67 (2)	70	95 (3)	68 (3)	72
o,p′-DDT	101 (3)	84 (3)	83	96 (4)	85 (3)	88	93 (2)	83 (4)	89	98 (2)	84 (3)	86
β-endosulphan	92 (3)	67 (4)	73	89 (3)	70 (4)	79	91 (3)	75 (2)	82	96 (3)	74 (3)	77
p,p′-DDD	93 (2)	87 (4)	93	93 (3)	87 (3)	93	98 (3)	87 (3)	93	99 (2)	83 (2)	84
p,p′-DDT	99 (3)	88 (4)	88	98 (3)	85 (5)	91	91 (3)	63 (3)	69	93 (2)	65 (3)	70
Endosulphan sulphate	83 (2)	67 (6)	81	89 (4)	69 (4)	77	89 (3)	63 (2)	71	95 (2)	66 (2)	69
Methoxychlor	97 (3)	90 (5)	93	101 (3)	89 (3)	88	96 (2)	93 (3)	97	102 (2)	91 (2)	89
Mirex	87 (2)	70 (4)	80	94 (3)	78 (3)	97	95 (2)	87 (2)	92	98 (2)	87 (3)	89

Clean-up

The single step clean-up allowed relative clean chromatograms (Figs. 1–4). The order of absorbents was important since the coloured material was retained by florisil on the top of the cartridge while the use of silica enabled the separation of organochlorine pesticides from humic substances found in soil extract [17]. Combination of these two absorbents in one cartridge will increase the clean-up efficiency and lead to a shorter manipulation time. 25% DCM in hexane was used to improve the elution of more polar compounds such as endosulfans. The increase of DCM percentage will lead to more interference and will not significantly improve the recoveries.

GC Analysis

Retention time for targeted compounds on the HT 8 and DB 1 columns are shown in Table II. All the target analytes including the two internal standards were baseline separated on HT8 column (Fig. 1). Several coeluting pairs were found on the DB1 column (o,p'-DDE/dieldrin and mirex/PCB 190). However, due to different acquisition ions, unambiguous identification and quantification were possible (Table II). Due to different polarity of the columns used, the elution order was changed for the pairs: γ-HCH/HCB, o,p'-DDT/β-endosulfan, endosulphan sulphate/p,p'-DDT (Figs. 1 and 3). No degradation of endrin and DDT during GC analysis was observed due the use of deactivated empty glass liners and of pulsed splitless injection, which enables a short residence time in the injector.

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Analytes Recoveries

Average recoveries and relative standard deviations for the pentachloronitrobenzene (IS1) were $89 \pm 8\%$ and $91 \pm 6\%$ for sonication and hot Soxhlet extraction respectively. For PCB 190 (IS2), they were $89 \pm 7\%$ and $94 \pm 6\%$, respectively. GC analysis of spiked samples did not yield any interfering peak at the retention time of internal standards. Recoveries of target compounds were calculated as described previously (see Experimental) and are presented in Table II. It can be seen that recoveries increase with increasing levels of fortification with our method. A good repeatability of the method was demonstrated by low relative standard deviations ($< 10\%$). However, results should be interpreted carefully, since it was suggested that the pesticide residential time in soil increases, the extractability of pesticides decreases and thus, recovery of pesticides from fresh spiked

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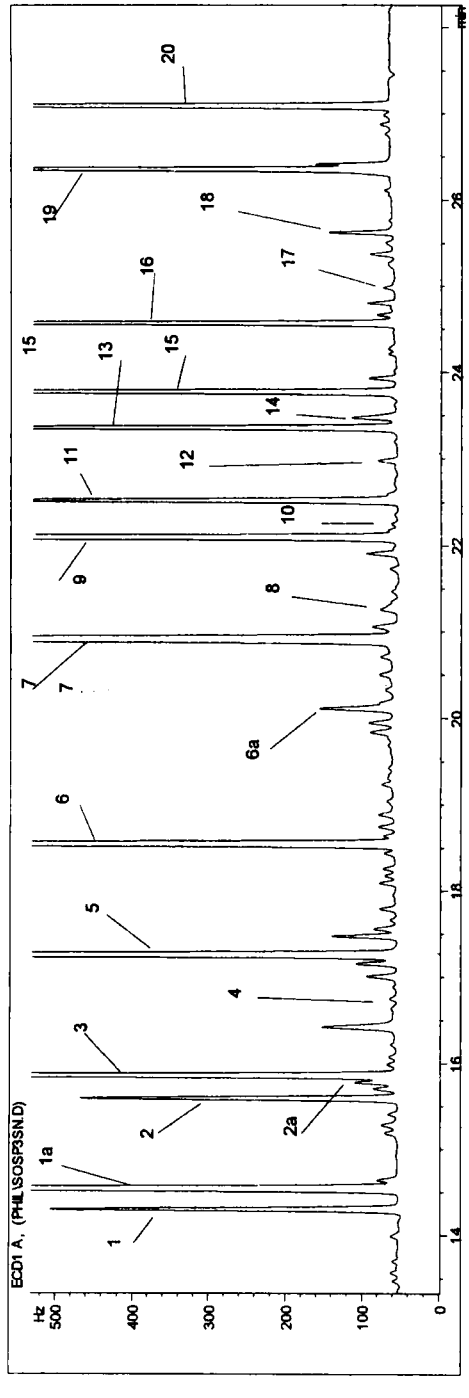

FIGURE 1 GC-ECD chromatogram on HT-8 column of fortified soil at level of 25 ng organochlorine pesticide per g dry weight. Peak identification: 1. α-HCH, 1a. HCB, 2. γ-HCH, 2a. β-HCH, 3. PCNB (IS1), 4. alachlor, 5. heptachlor, 6. aldrin, 6a. heptachlorepoxide, 7. o,p′-DDE, 8. α-endosulphan, 9. p,p′-DDE, 10. dieldrin, 11. o,p′-DDD, 12. endrin, 13. o,p′-DDT, 14. β-endosulphan, 15. p.p′-DDD, 16. p,p′-DDT, 17. endosulphan sulphate, 18. methoxychlor, 19. mirex, 20. PCB 190 (IS2).

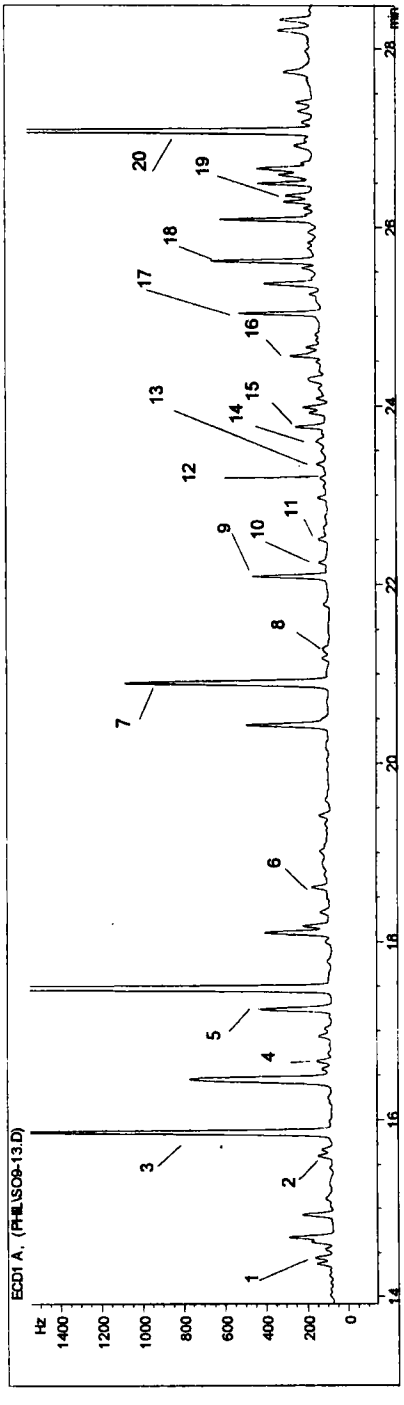

FIGURE 2 GC-ECD chromatogram on HT-8 of a real soil sample. Peak identification as described for Fig. 1.

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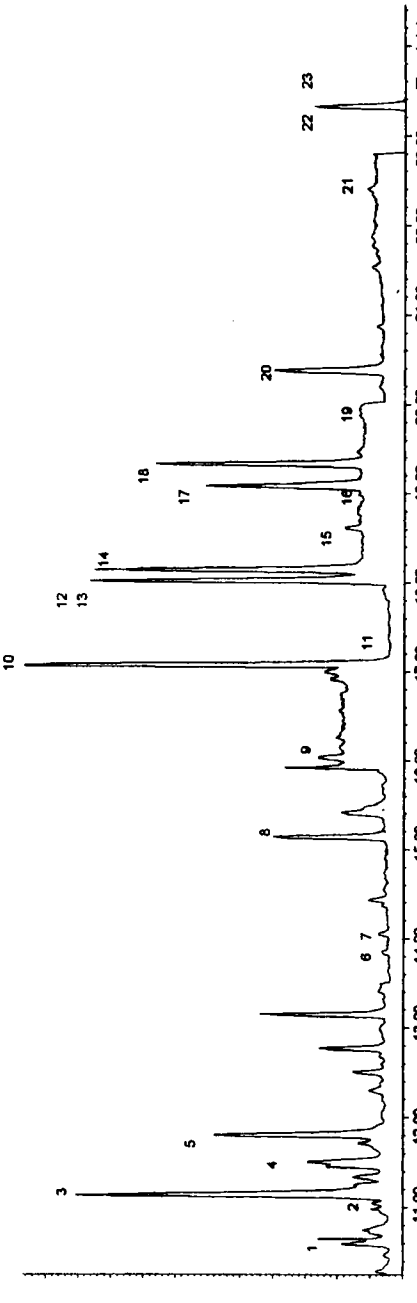

FIGURE 3 GS-MS chromatogram on DB-1 column of fortified soil at a level of 5 ng/g dry soil. Peak identification: 1. α-HCH, 2. γ-HCH, 3. HCB, 4. β-HCH, 5. PCNB (IS1), 6. alachlor, 7. heptachlor, 8. aldrin, 9. heptachlorepoxide, 10. o,p′-DDE, 11. α-endosulphan, 12. p,p′-DDE, 13. dieldrin, 14. o,p′-DDD, 15. endrin, 16. β-endosulphan, 17. o,p′-DDT, 18. p,p′-DDD, 19. endosulphan sulphate, 20. p,p′-DDT, 21. methoxychlor, 22. mirex, 23. PCB 190 (IS2).

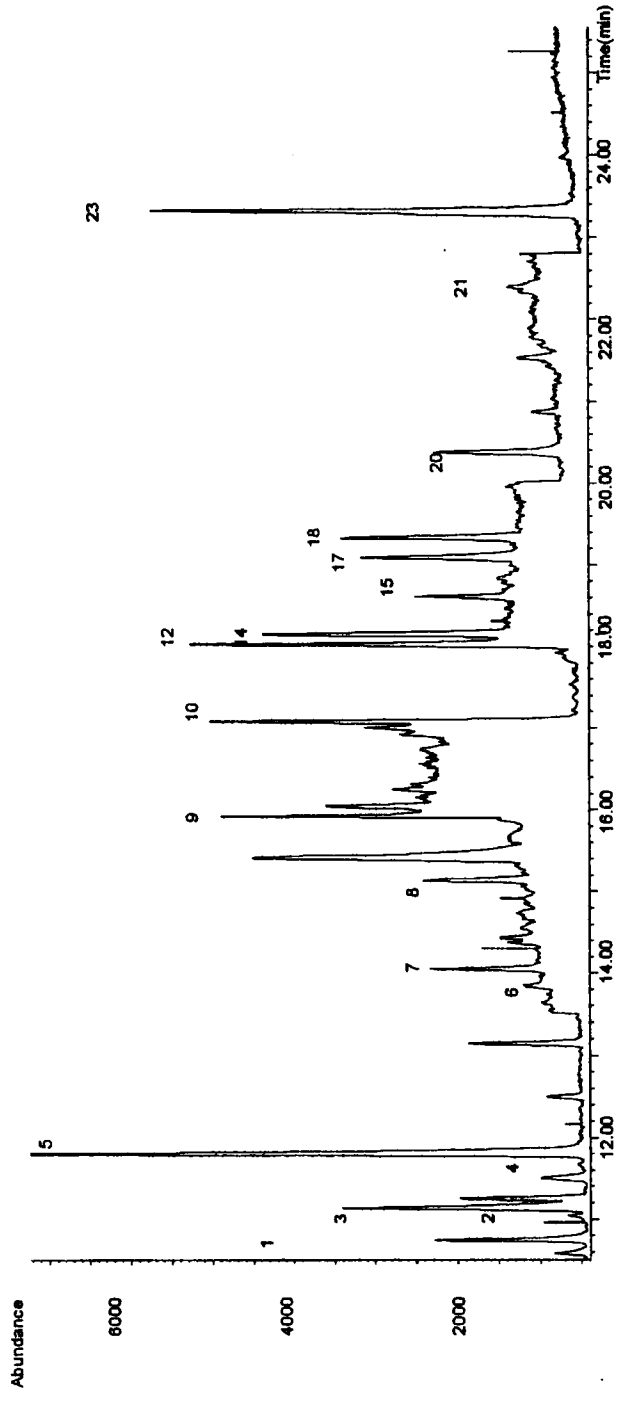

FIGURE 4 GC-MS chromatogram on DB-1 of a real soil sample. Peak identification as described in Fig. 3.

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samples is not necessary indicative of the ruggedness of an extraction method [13].

Limit of Detection

If no peak appears at retention time of the analyte, the limit of detection was calculated by multiplying by three the area of this section of the baseline. When a peak was present at the retention time for the targeted analyte, but failed to fulfil all identification criteria, the concentration corresponding to the recorded area was taken as the detection limit.

As expected, the limit of detection of all compounds were lower for ECD (0.1–0.2 ng/g) than MS (0.2–0.4 ng/g). Due to different response factors, higher detection limits were obtained for endrin (1 ng/g soil) and endosulphans (1.5 ng/g soil). These values were calculated only for hot Soxhlet extraction, since this method was chosen for further analysis.

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Analysis of Real Soil Samples

Mean concentrations of organochlorine pesticides in soil are in general low (Table III). Soil samples collected in the park showed lower concentrations of pesticide residues than soils from cultivated areas. Concentrations of HCH isomers were less than 3 ng/g dry soil, except for maize field with a concentration of 22.9 ng/g soil. Similar γ-HCH/sum HCHs ratios were found in all locations. HCB was detected in all samples with concentrations between 1 and 20 ng/g soil. Low concentrations of DDTs were measured in the park (less than 3 ng/g soil), while concentrations were higher in cultivated areas (up to 100 ng/g soil). In all samples, DDE was the main contributor to the sum of DDTs, confirming that the transformation of DDT to DDE is favoured in aerobic systems [18]. Concentrations of aldrin, dieldrin, endrin, heptachlor and its metabolite (heptachlorepoxide) were under the detection limit for most of the samples. Proportions of α- and β-endosulphan in the soil (β-isomer in higher concentration) differ from those in technical endosulphan (64–76% for α- and 29–32% for β-endosulphan, respectively) [19], due to the more rapid degradation of the α-isomer. Indeed, measured half-lives for α- and β-endosulphan were 60 and 800 days, respectively [20]. Concentrations of endosulphan sulphate were higher than the 2 isomers as it is the major degradation product of endosulfan by soil bacteria [19]. Mirex was found in all samples in low concentrations (up to 3 ng/g soil), while methoxychlor was ranging between 8 and 29 ng/g soil.

TABLE III Concentrations of organochlorines pesticides (ng/g dry soil) in 4 locations from Belgium

Compounds	*mean (SD)*			
	Apple field (Hasselt) n=6	*Maize field (Wilrijk) n=9*	*Potato field (Wilrijk) n=7*	*Public park (Wilrijk) n=3*
α-HCH	0.9 (0.4)	9.7 (11.8)	0.9 (0.5)	0.8 (0.6)
β-HCH	nd	8.4 (14.2)	0.4 (1.0)	nd
γ-HCH	0.9 (0.8)	4.9 (4.1)	1.1 (0.4)	0.9 (0.9)
Sum HCH	**1.8**	**22.9**	**2.4**	**1.7**
γ-HCH/sum HCH	0.49	0.21	0.45	0.53
HCB	1.9 (1.5)	19.9 (23.2)	1.2 (1.1)	0.9 (1.3)
Alachlor	21.1 (41.4)	2.9 (2.5)	1.9 (0.6)	0.9 (1.3)
Heptachlor	0.9 (0.4)	7.4 (6.5)	4.8 (3.2)	1.1 (0.4)
Heptachlorepoxide	nd	1.0 (2.6)	nd	nd
o,p′-DDE	3.2 (3.8)	26.9 (31.9)	27.9 (32.1)	0.8 (0.2)
p,p′-DDE	15.6 (10.2)	12.7 (34.6)	5.4 (5.5)	0.2 (0.1)
o,p′-DDD	9.0 (19.5)	3.9 (7.0)	0.5 (0.4)	nd
p,p′-DDD	2.3 (2.5)	8.8 (25.1)	1.5 (1.2)	0.2 (0.2)
o,p′-DDT	2.5 (1.8)	34.0 (98.2)	0.2 (0.5)	0.2 (0.5)
p,p′-DDT	10.9 (8.3)	6.4 (12.1)	1.1 (0.6)	0.6 (1.0)
Sum DDT	**43.4**	**92.6**	**36.5**	**2**
p,p′-DDT/sum DDT	0.25	0.06	0.02	0.30
Aldrin	nd	0.4 (0.7)	0.8 (0.5)	nd
Dieldrin	nd	0.3 (0.7)	nd	nd
Endrin	10.6 (19.5)	nd	nd	nd
Methoxychlor	8.4 (10.1)	27.8 (43.4)	3.8 (7.0)	5.3 (8.3)
Mirex	1.5 (1.7)	2.8 (3.3)	1.1 (1.9)	2.3 (3.0)
α-endosuphan	3.1 (7.4)	nd	nd	nd
β-endosulphan	14.6 (24.9)	nd	nd	nd
Endosulphan sulphate	47.0 (83.4)	nd	3.1 (2.4)	nd
Sum endosulphans	**17.8**	**nd**	**3.1**	**nd**

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CONCLUSION

The developed automated hot Soxhlet extraction and the single step clean-up based on mixed Florisil–silica cartridges can be a simple alternative method for monitoring of organochlorine pesticide residues. The possibility of automation in the extraction step, and the clean-up procedure reduced to one step lead to a simple method with good repeatability and high recoveries of the target analytes.

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