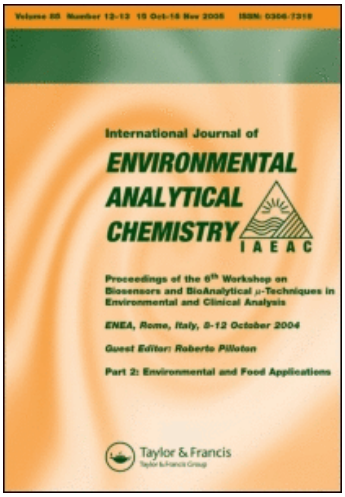

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ANALYSIS OF PHENOLIC COMPOUNDS IN SOIL AND SEDIMENT BY USING SPE-DISKS AND GAS CHROMATOGRAPHY TECHNIQUES

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Styrene-Divinylbenzene (SDB) extraction disks were used for the isolation and trace analysis phenol, cresols, xylenols and chlorophenols from soil and sediment samples. The extracts were devided into two fractions for free and acetylated compounds. Extract fractions were then analysed in a GC-FID with DB-1 capillary column and in a GC-ECD with DB-5 capillary column. Confirmation of phenols identity was carried out by GC-MSD in the selected ion monitoring (SIM) mode. Recoveries of all selected phenolic compounds from a SCL soil and a CL sediment were increased after acetylation. Recoveries of cresols from soil and sediment were lower at 49.4–60.5 % and increased after acetylation up to 48.3–77.4 %. Recoveries of xylenols were also increasead from a level of 62.1–95.4 % for free compounds to 71.2–98.3 % for their acetates. Finally, recoveries of tri- tetra – and pentachlorophenols were strongly increased after the acetylation from 84.5–99.2 % to 95.3–112.8 %.

Keywords: Phenolic compounds; SPE-disks; capillary GC; soil; sediments

INTRODUCTION

Phenolic compounds represent a major class of contaminants released into the environment through many industrial processes and also as a result of the degradation of pesticides such as chlorophenoxy compounds and hexachlorobenzene[1–3]. Higher chlorophenols, pentachlorophenol, 2,3,4,6-tetrachlorophenol and 2,4,6-trichlorophenol, are used as pesticides, mainly as fungicides for wood preservation. The interest for chlorophenols as envrironmental contaminants is due to their high toxicity[4] since they are accumulated through the food chain [5,6] Even small amounts of these substances (at μg/L levels) have an adverse effect on the taste and odour of drinking water and food products [7].

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Phenolic compounds are relatively polar compounds and soluble in water with low vapour pressures and their lipophilic character is increased with the number of substituents. The result of their chemical and physical properties is a variety of phenolic behaviour in the environment, depending on the nature and number of substituents. Consequently, phenol and monosubstituted derivatives are transfered easily in environmental waters. In contrast the multisubstituted derivatives and especially pentachlorophenol present limited transport in water and they are strongly adsorbed in soil organic matter, where they show high persistence[8–10].

TABLE I Retention times (Rt-min) and relative response factor (RRF- relative to 2,4-diclorophenol) and limits of detection (LODs in ng/g) of free phenols and their acetylated derivatives in GC-FID with capillary column DB-1. 30 m long

Peak No/ Phenols	*Free phenols*			*Acetylated phenols*		
	Rt	*RRF*	*LOD*	*Rt*	*RRF*	*LOD*
1. Phenol	4.63	0.45	2.5	6.40	0.66	1.5
2. o-cresol	6.20	0.48	1.0	8.27	0.69	0.5
3. m-cresol	6.67	0.60	1.0	8.91	0.62	0.5
4. p-cresol	6.65	0.51	1.0	9.04	0.65	0.5
5. 2,6-xylenol	7.56	0.55	0.5	10.13	1.50	0.3
6. 2,4-xylenol	8.52	0.46	0.5	11.04	0.73	0.3
7. 2,5-xylenol	8.56	0.50	0.5	10.88	0.55	0.3
8. 3,5-xylenol	9.00	0.49	0.5	11.54	0.60	0.3
9. 2,3-xylenol	9.28	0.48	0.5	11.70	0.60	0.3
10. 3,4-xylenol	9.62	0.50	0.5	12.38	0.60	0.3
11. 2,4-dichlorophenol	9.26	1.00	0.4	12.32	1.00	0.3
12. 2,4,6-trichlorophenol	14.25	1.08	0.2	16.60	1.25	0.1
13. 2,3,4,6-tetraclorophenol	19.33	1.52	0.2	21.41	2.69	0.1
14. Pentachlorophenol	24.55	4.04	0.1	26.23	2.78	0.05

Many analytical methods for the determination of phenols in soils and sediments have been published [11–13]. The main extraction method in soils was Soxhlet [14] but the required time was too long [15]. In addition a clean-up step was necessary because of the large amount of co-extracted compounds. Further-

more, the conversion of phenolic compounds and especially the chlorinated ones into less polar derivatives prior to GC is usually employed. The introduction of capillary GC has permitted the analysis of phenols also as free compounds.

The chromatographic step of a method for organic micropollutants determination at low levels in environmental soil and sediments requires previous efficient solvent extraction and concentration procedures [16, 17] which can make pesticide determination a time-consuming and laborious analytical process involving consumption of large volumes of organic solvents. To overcome these problems, solid-phase extraction has been applied to the extraction of pesticides present in soil samples. The adsorbed compounds are then eluted from the solid phase by an organic solvent. In the last 5 years the solid phase extraction disks have been employed as an alternative method for the trace enrichment of organic compounds in water and soil. The solid phase extraction disks are available in a diameter of 47 and 90 mm similar to LC solvent filters. At present such disks have been tested for different groups of compounds, including pesticides, organotins and phthalates[18].

The purpose of this work is to develop a method for routine analysis for a wide range of phenolic compounds in soil and sediment samples as well as to carry out an extraction method by the use of solid phase extraction with Empore SDB disks. After the isolation, phenolic compounds in half of the extracts are converted into their acetyl derivatives. Both parts, free and acetylated derivatives of phenols, are analysed by GC-FID and GC-ECD. Confirmation of compound identity is carried out by using GC-MS in the selected ion monitoring (SIM) mode. The method has been applied for determination of phenolic pollutants in agricultural soils and estuarine sediments of Loudias river and Thermaikos Gulf (Greece).

METHODS AND MATERIALS

Chemicals

Phenolic compounds: phenol; o-, m- and p- cresol; 2,6-, 2,4-, 2,5-, 3,5- 2,3- and 3,4-xylenol were commercial products (analytical standards kits obtained from PSC-Poly Science Corporation (Niles, Illinois, USA). The tested chlorophenols, 2,4-dichlorophenol, 2,4,6-trichlorophenol, 2,3,4,6-tetrachlorophenol and pentachlorophenol were available from Chem Service Inc. (West Chester, U.K.). All these standards were used without further purification. Standard mixtures were

prepared in acetone at 100 μg/mL for spiking purposes. All solutions were kept in the dark at 4°C.

Empore extraction disks were manufactured by 3M and distributed by Varian (Harbor City, CA). The disks used were 47 mm in diameter and 0.5 mm thick. Each disk contained about 500 mg of styrene-divinylbenzene (SDB) (90±2%) and 10±2% PTFE.

HPLC-grade water, acetone, n-hexane and dichloromethane were residue analysis grade from Pestiscan (Labscan Ltd, Dublin, Ireland). Acetic anhydride and hydrochloric acid were analytical-reagent grade from Mallinckrodt Chemical Works (St. Louis, USA).

Fortification and extraction of soil samples

Soil samples for fortification tests were collected from the region of Preveza, that does not have previous history of pesticide uses or other industrial pollution sources. The type of soils was sandy-clay loam (SCL) with 0.67% organic matter and the type of selected sediment was sandy-clay (SC) with 2.45% organic matter. Ten g of soil or sediment were spiked with 100 μL phenol mixture in acetone at appropriate concentrations of 0.25, 0.10 and 0.05 μg/g. They were mixed well with a spatula and equilibrated for 30 min before extration.

Spiked soil or sediment samples of 10 g were placed into a 100 mL Erlenmeyer bottle and 15 mL of distilled water and shaken by sonication in a Fritish ultrasonic bath for 10 min. The mixture was subsequently extracted with 5 ml of acetone by sonication for 15 min and by shaking in an automatic instrument for 5 min. Then the mixture was centrifuged at 6,000 g for 5 min. The supernatant phase was collected and the above extraction procedure was repeated once more. The combined water-acetone extractions were decanted into a reservoir and diluted to a volume of 500 ml with distilled water. Sodium chloride 10% was added in the solution prior to extraction through sorbent disk.

The sample pH was adjusted to 2 with sulfuric acid 1:1 (v/v). The disk was placed in the conventional Millipore apparatus, and both were washed with 10 mL of of acetone with the vacuum on and with 10 mL of methanol for 3 min with the vacuum off. The disk was not allowed to become dry and 10 mL of reagent grade water was added. The vacuum was applied and the sample was mixed well and allowed to percolate through the disks with a flow rate of 50 mL/min under vacuum. After sample extraction is completed, the residual water was removed as possible from the disk by applying vacuum for 5–10 minutes. The compounds trapped in the disk were collected by using 2 × 10 mL of dichloromethane as eluting solvent. The fractions were evaporated to 4 mL in a gentle stream of nitrogen. The concentrated extract was devided in two equal parts (2 mL each) and they were transfered into glass test tubes with screw cup lined with teflon.

TABLE II Retention times (Rt-min) and mean recoveries of chlorophenols and their acetylation derivatives in GC-ECD with capillary column DB-5, 25 m long. Fortified levels 0.10, 0.01 and 0.001 ng/g (n=3)

Peak No/ Phenol	*Rt*		*% Recovery*			
			SCL soil		*CL sediment*	
	Free	*Acetylated*	*Free*	*Acetylated*	*Free*	*Acetylated*
1. 2,4-dichlorophenol	4.80	7.02	97	104	95	99
2. 2,4,6-trichlorophenol	9.65	11.73	99	114	98	105
3. 2,3,5,6-tetrachlorophenol	14.32	16.20	105	116	97	108
4. Pentachlorophenol	19.41	20.51	104	121	103	115

Sample preparation

The first part was used for the acetylation procedure after concentration to ca 0.5 mL under a gentle stream of nitrogen and 2 ml of acetone addition. Then, 3 mL of 0.1 M K_2CO_3 followed by 2 mL n-hexane containing 50 µL acetic anhydride were added to the extract. The contents in the test tubes were immediately mixed in a vortex for one minute. After separation (standing for 30 min) and dehydration with sodium sulphate crystals, the n-hexane extract was concentrated to ca. 0.1 mL and used for GC analysis[19].

The second part of dichloromethane extract was used for the analysis of free phenols (without acetylation step). Three mL of n-hexane were added in the concentrated extract and evaporated by nitrogen stream to ca 1 mL. The dehydration procedure was the same as described above. The dried n-hexane solution was concentrated to ca 0.1 mL and used in GC analysis. Retention times, limits of detection and recoveries obtained for the phenolic compounds are indicated in Tables I and II.

Chromatographic conditions

GC-FID

Single phenol standards and 1.5 µL of extracts from the analytical procedure were injected in the splitless mode in a Shimadzu 14A capillary gas chromatograph equipped with flame ionization detector (FID) at 250°C. The DB-1 column, 30m × 0.32mm i.d., contained 5% phenyl methyl silicone (J & W Scientific, Folsom, CA). The column was programmed from 100° C (2 min) to 210° C (20 min) at 5° C/min. The injection temperature was 220° C.

TABLE III Characteristic ions (m/z) used for selected ion monitoring of phenolic compounds by GC-MSD and their relative intensity (%)

Phenolic compounds	*Characteristic ions (m/z)*			
	$[M]^+$	$[M\text{-}CH_3]^+$	$[M\text{-}2Cl]^+$	*Other*
1. Phenol	94 (100), 95 (6.4)			66 (24.4)
2. o-cresol	108 (100), 107 (91.6)	79 (44)		90 (25.6)
3. m-cresol	108 (100), 107 (80)	79 (30)		90 (8.8)
4. p-cresols	108 (90.8),107 (100)	79 (20.8)		90 (8.8)
5. 2,6-xylenol	122 (97.2), 121 (36.4)	107 (100)		77 (34.4)
6. 2,4-xylenol	122 (74.8), 121 (46)	107 (100)		77 (34.4)
7. 2,5-xylenol	122 (92.8), 121 (37.2)	107 (100)		77 (36.8)
8. 3,5-xylenol	122 (100), 121 (38)	107 (79.6)		77 (18)
9. 2,3-xylenol	122 (83.2), 121 (27.2	107 (100)		77 (28)
10. 3,4-xylenol	122 (80), 121 (44.8)	107 (100)		77 (24)
11. 2,4-dichlorophenol	162 (100), 164 (62.8)		98 (38.4)	126 (12.8)
12. 2,4,6-trichlorophenol	196 (100), 198 (88.4)		132 (37.2)	97 (67.2)
13. 2,3,4,6-tetraclorophenol	230 (80.8), 232 (100)		168 (20.8)	131(38)
14. Pentachlorophenol	264 (65.6), 266 (100)		202 (30.8)	165 (58.5)

Helium was used as the carrier and nitrogen was used as make-up gas. The detector gases were hydrogen and air, and their flow rates were regulated according to results given through the simplex optimization of the analytical variables, in this instance air and hydrogen flow-rates in the detector. The splitless mode was used for injection of 1.5 μL volume

GC-ECD

Single phenol standards and 1.0 μL of extracts from the analytical procedure were injected in the split mode in a Shimadzu 14A capillary gas chromatograph equipped with ^{63}Ni electron capture detector at 300°C. A DB-5 fused silica capillary column was used, coated with 5% phenyl-95% methyl polysiloxane 25 m × 0.25 mm i.d. (J & W Scientific, Folsom, CA). The column was programmed from 100° C (2 min) to 210°C (20 min) at 5°C/min. The injection temperature was 220° C.

Helium was used as the carrier and nitrogen as make-up gas and their flow rates were regulated according to the results given through the simplex optimiza-

tion of the analytical variables. The splitless mode was used for injection of 1.0 μL volume

GC-MS

A Shimadzu QP5000 equipped with column DB-5 30 m × 0.32 mm i.d. (J & W Scientific, Folsom, CA) was used. Helium was used as carrier gas at 25 cm/sec and nitrogen as make up gas at 25 mL/min. The injection temperature was 240°C. The column was programmed from 55°C (2 min) to 210°C at 5°C/min and to 270°C at 20°C/min (4 min). The ion source was maintained at 200°C and El mass spectra were obtained at 70 eV. The splitless mode was used for injection of 1.0 μL volume.

Three or four ions for each phenolic compound were chosen for screening analysis in selected ion monitoring (SIM). The ion traces were devided into seven groups that were recorded sequentially during the injection, on the basis of the retention times of the single substances; the first group was from 4.2 to 6.0 min, the second from 6.0 to 7.4 min, the third from 7.4 to 9.2 min, the fourth from 9.2 to 11.0 min, the fifth from 11.0 to 16.0 min, the sixth from 16.0 to 20.0 min and the seventh from 20.0 to 26.0 min. These groups and the m/z values of characteristic masses for 14 selected phenols are shown in Table III.

Quantitation

Quantitation was performed by "internal" calibration using authentic standards. Sample analyses were run in triplicate and relative standard deviations of less than 12% were generally achieved. Reagent blanks were also investigated. Tables I and II give the retention times and relative responce factor (RRF) for internal standard 2,4 -dichlorophenol for 14 selected phenols in GC-FID with DB-1 column and in GC-ECD with a HP-5 column. The concentration (C) of phenolic compounds in terms of μg/mL in the final solution was calculated by using the relative response factor of as follows:

$$C = RRF \cdot C_{is} \cdot (A / A_{is})$$

where: RRF is the relative responce factor (correction factor) determined relative to 2,4-dichlophenols (internal standard), C_{is} is the concentration of internal standard in the final solution in μg/mL, and A and A_{is} are the corresponding peak areas of analytes and internal standard respectively.

The calculated LOD were determined using the standard deviation from the validated recovery results.

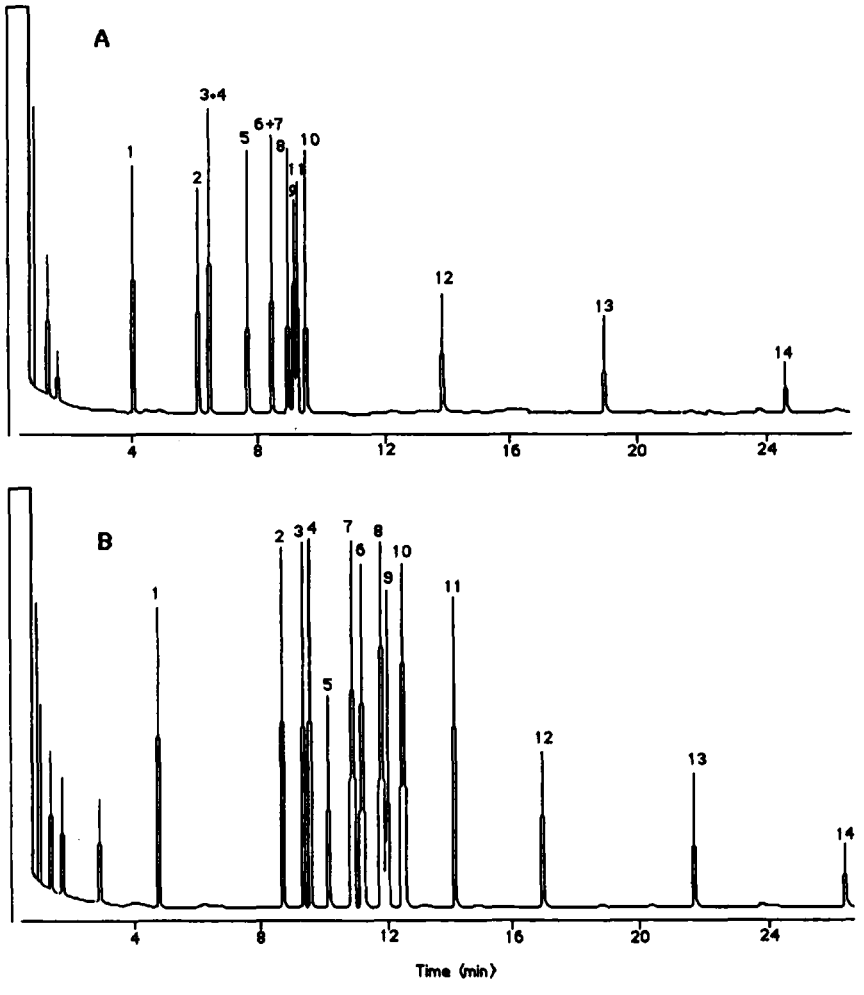

FIGURE 1 GC-FID chromatograms obtained of (A) free and (B) acetylated extract from soil sample fortified to 100 ng/g for each phenol. A DB-1 column 30 m long containing 5% phenyl methyl silicone was programmed 100° C (2 min) to 210° C (20 min) at 5° C/min. For peak numbers see Table I

RESULTS AND DISCUSSION

Gas chromatographic techniques

Tables I and II give the retention times and relative responce factor (RRF) for internal standard 2,4 -dichlorophenol for 14 selected phenols in GC-FID with DB-1 column and in GC-ECD with a HP-5 column. Figures 1 and 2 show the

simultaneous determination of the typical chromatograms obtained for free and acetylated derivatives of phenols in fortified soil samples at 0.1–0.01 μg/g levels. The specific analysis of the above selected phenols seems feasible when using the combination of free and acetylated derivatives of a high resolution capillary column such as DB-1 with the flame ionization detector. Furthermore, the quantitive recoveries were obtained from soil containing as low as 0.01μg/g of phenol and alkyl-phenols (cresols and xylenols). The acetylated derivatives show a significant increase of FID and ECD responses as compared with non-acetylated compounds.

TABLE IV Mean recoveries of free phenols and their acetylated derivatives in GC-FID with capillary column DB-1, 30 m long. Fortified levels 0.25 – 0.05 μg/g (n=3)

Peak No/ Phenols	*Recovery % (±SD)*			
	Free phenols		*Acetylated phenols*	
	SCL soil	*SC sediment*	*SCL soil*	*SC sediment*
1. Phenol	73.5 (3.5)	59.3 (2.3)	78.4 (4.7)	64.3 (3.6)
2. o-cresol	49.4 (5.3)	54.1 (4.3)	56.3 (4.9)	61.4 (4.7)
3. m-cresol	44.3 (3.4)	61.2 (3.6)	48.3 (3.6)	71.2 (2.6)
4. p-cresol	53.2 (2.5)	60.5 (3.1)	63.6 (2.6)	76.6 (4.6)
5. 2,6-xylenol	76.4 (4.3)	65.1 (4.7)	87.4 (4.3)	75.8 (3.8)
6. 2,4-xylenol	78.4 (3.4)	62.1 (3.8)	85.2 (7.3)	71.2 (4.3)
7. 2,5-xylenol	72.3 (4.7)	69.0 (3.6)	86.3 (4.3)	69.5 (5.1)
8. 3,5-xylenol	88.3 (3.8)	87.3 (4.1)	89.6 (5.1)	86.5 (6.2)
9. 2,3-xylenol	86.5 (3.8)	79.8 (4.6)	90.4 (5.5)	86.3 (3.7)
10. 3,4-xylenol	95.4 (6.7)	89.2 (5.1)	98.3 (5.4)	90.2 (4.9)
11. 2,4-dichlorophenol	93.2 (8.2)	87.4 (6.0)	94.6 (6.2)	89.5 (4.8)
12. 2,4,6-trichlorophenol	95.4 (4.1)	87.2 (7.3)	97.4 (6.2)	92.3 (65.3)
13. 2,3,4,6-tetraclorophenol	99.2 (5.2)	85.2 (6.3)	112.8 (4.4)	104.2 (5.6)
14. Pentachlorophenol	96.3 (4.6)	84.5 (5.9)	98.5 (5.0)	95.3 (4.8)

(SD) = standard deviation

The elution order of free and acetylated derivatives of 14 selected phenols matches very well in DB-1 column and the resolution is much better for acetylated forms. Free compounds of m- and p- cresols as well as 2,5- and 2,4 xylenols are overlapped (Figure 1) while their acetylated derivatives are separated clearly. However, because the flame ionization sensitivities for these chorophenol acetates are lower than phenol and cresols and xylenols (Tables I and II), these free chlorophenols are normally undetectable by a FID at levels usually found in environmental samples. An electron capture detector is preferable to be used for the free and derivatised forms of chlorophenols (Figure 2 and

Table II). Although mass selective detector does not have a discriminating sensitivity effect against the cresols, xylenols and monochlorophenols[16], the use of selected ion monitoring programmes allow their identification and quantative determination at levels similar to polychlorinated phenols (Figure 3).

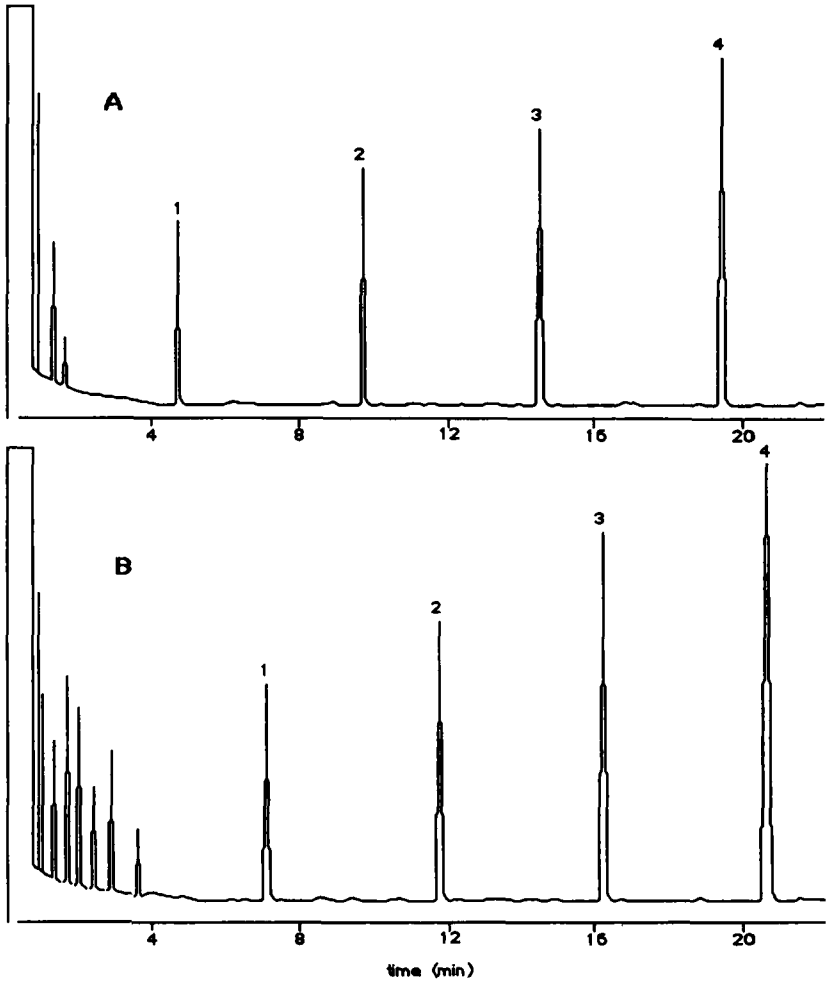

FIGURE 2 GC-ECD chromatograms obtained of (A) free and (B) acetylated extract from soil sample fortified to 10 ng/g for each chlorophenol. A DB-5 column 25 m long containing 5% phenyl 95% methyl polysiloxane, was programmed 100° C (2 min) to 210° C (20 min) at 5° C/min. For peak numbers see Table II

Recovery studies

Mean percent recoveries of selected phenols from the test soil are summarized in Table IV for the system GC-FID with DB-1 column. Recoveries of phenol from SCL soil were 63.5 % and increased after acetylation up to 79.4% while its recoveries from CL sediment were almost at the same level, 59.3 and 64.3 % for free and acetylated derivertives, respectively. Recoveries of cresols from SCL soil and CL sediment were lower, at 49.4–60.5 %, and were increased after acetylation up to 48.3–77.4 %. Recoveries of 2,3-, 2,4-, 2,5-, and 2,6- xylenols from soil and sediment samples also increasead from a level of 62.1–86.5 % for free compounds to 71.2–90.4 % for their acetates. On the contary, recoveries of 3,4- and 3,5-xylenols from soil and sediment samples seem to be increased slightly after acetylation from 87.3 and 95.4 % to 88.5 and 98.3 %. Finally, recoveries of tri- tetra – and pentachlorophenols were strongly increased after the acetylation from 84.5–99.2 % to 95.3–112.8 %. The same increase of recoveries for acetylated derivatives of chlorophenols was also observed in the system of GC-ECD although the electron capture detector show better sensitivity for acetylated forms of chlorophenols (Table II and Figure 2).

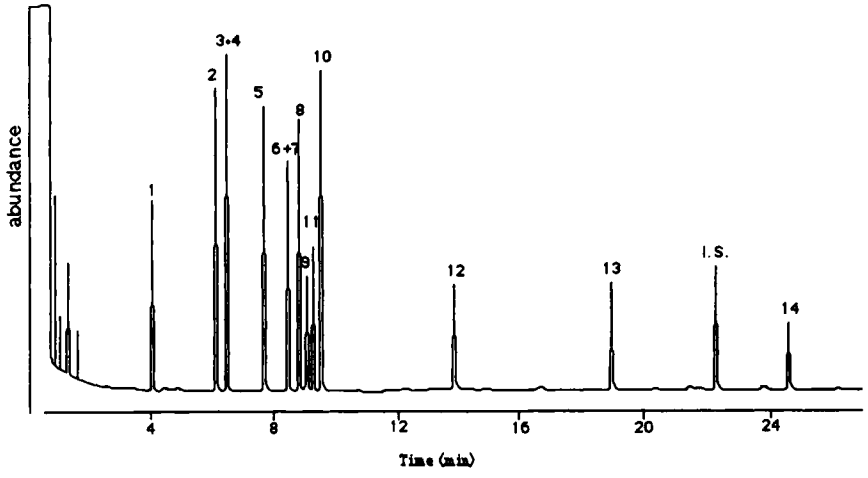

FIGURE 3 GC-MSD chromatograms obtained of (A) free phenols extracted from soil sample fortified to 10 ng/g for each chlorophenol. A DB-1 column 30 m long containing 5% phenyl methyl silicone was programmed 100° C (2 min) to 210° C (20 min) at 5° C/min. For peak numbers see Table I

TABLE V Concentrations (ng/g) of detected phenols in SCL soil samples of Thessaloniki plain and sediments of Loudias river estuary and Thermaikos Gulf, collected in September 8, 1997 (n=5)

Phenolic Compounds	*SCL soil Thessaloniki plain*	*SL sediment Loudias estuary*	*SC sediment Thermaikos gulf*
Phenol	1.24	2.35	4.21
o-cresol	bdl[a]	0.56	0.75
m-cresol	bdl	0.32	0.85
p-cresol	bdl	bdl	bdl
2,6-xylenol	bdl	bdl	bdl
2,4-xylenol	bdl	bdl	bdl
3,5-xylenol	bdl	1.31	0.14
2,3-xylenol	bdl	bdl	bdl
3,4-xylenol	bdl	0.32	0.17
2,4-DCP	0.12	0.21	0.24
2,4,6-TCP	bdl	bdl	bdl
2,3,4,6-TeCP	bdl	bdl	bdl
PCP	0.24	2.34	0.09

[a] bdl =below detection limit.

Environmental levels

The soil and sediment samples analysed were collected from an agricultural area of Thessaloniki plain, Loudias river estuary and Thermaikos gulf (North-Greece). The sampling was done in september 1997. The screening analysis by GC with FID and ECD showed the presence of phenol, o- and m-cresols, 3,4-, and 3,5-,xylenols, 2,4-DCP and PCP compounds at ng/g levels. Confirmatory analyses were made with GC-EI-MS. Contamination of the soil by phenols around an industry with wood preserving facilities is shown in Table V.

CONCLUSIONS

In conclusion, the development of multiresidue methodology provides a rapid, efficient and reproducible method for the simultaneous determination of various phenols in soil and sediment samples. The present GC-FID, GC-ECD and GC-MSD data are useful for analysis of 14 studied phenols and related compounds. The best separation of compounds studied was observed for acetylated derivatives on both used capillary columns, DB-1 and DB-5. GC-FID is the best

choice for the confirmation of phenol, cresols and xylenols showing better response for acetylated derivatives of these compounds. GC-ECD is recommended for chlorophenols, showing higher responce for acetylated molecules. The combination of free and acetylated derivatives of phenols permits the application of the method in GC systems with different detectors and the same column. This method is valid for chlorintaed phenols and several cresol and xylenols.

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References

[1] O.M. Aly and M.A. El-Dib, in : Fate of Organic Pesticides in the Aquatic Environment (F. F.Gould, ed. Advances in Chemistry Series III, ACS, Washington DC, 1972) pp. 210–243.

[2] G.D.Crosby, in: Fate of Organic Pesticides in the Aquatic Environment, (F. F. Gould, ed. Advances in Chemistry Series III, ACS, Washington DC, 1972) pp, 173–188.

[3] J. Hajslova, V. Kocourek, I. Zemanova, F. Pudil and J. Davidek, *J. Chromatogr.*, **439** 307–316 (1988).

[4] A.L. Buikema, M.J. McGinnis and J. Cairns, Jr., *Mar. Environ. Res.*, **2**, 87–92 (1979).

[5] J. Paasvirta, J. Särkka, T. Leskjärvi and A. Roos, *Chemosphere*, **9**, 441–447 (1980).

[6] B. Holmberg, S. Jensen, A. Larson, K. Lewander and M. Olsson, *Comp. Biochem. Physiol. B*, **43**, 171–175 (1972).

[7] J.M.H. Bemelmans and M.C. Ten Noever de Brauw, *J. Agric. Food Chem.* **22**, 1137–1141 (1974).

[8] S.A. Boyd, *Soil Science*, **134**, 337–343 (1982).

[9] K. Schellenberg, C. Levenberger and R.P. Schwarzenbach, *Environ. Sci. Technol.* ,**18**, 652–657 (1984)

[10] S.K. Banerji, S.M. Wei and R.K. Bajpai, *Water, Air and Soil Pollution*, **69**, 149–157 (1993).

[11] M.C. Goldber and E. R. Weiner, *Anal. Chim. Acta*, **115**, 373–378 (1980).

[12] R. Valo, V. Kitunen, M. Salkinoja-Salonen and S. Räisänen, *Chemosphere*, **13**, 835–844 (1984).

[13] T. Humppi, *Chemosphere*, **14**, 523–528 (1985).

[14] H.B. Lee, Y. D. Stokker and A.Y. Chau, *J. Assoc. Off Anal. Chem.*, **70**, 1003–1008 (1987).

[15] A.J. Wall, and G.W. Stratton, *Chemosphere*, **22**, 99–106 (1991).

[16] J. Manes, Y. Pico, C.J. Molto and G. Font, *J. High Resolution Chromatogr.*, **13**, 843–845 (1990).

[17] A. Ambrus, J. Lantos, E. Visi, I. Csaltos and L. Sarvari, J. *Assoc. Off Anal. Chem.*, **64**, 733–742 (1981).

[18] D. Barcelo, G. Durand, V. Bounvot and M. Nielen, *Environ. Sci. Technol.*, **27**, 271–277 (1993).

[19] T.G. Danis and T.A. Albanis, *Toxicol. Environ. Chem.*, **53**, 9–18 (1996).