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Determination of priority phenolic compounds in soil samples by various extraction methods followed by liquid chromatography–atmospheric pressure chemical ionisation mass spectrometry

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Abstract

An analytical protocol for the determination of priority phenolic compounds: phenol, 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol, 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4-methylphenol and 2,4-dimethylphenol, in soil samples, is presented. The method uses Soxhlet extraction with methanol–water (4:1) both containing 2% triethylamine. Recoveries varied in the range from 67 to 97% with a standard deviation between 8 and 14%. Additional extraction methods of phenols from soil samples include the use of the microwave-assisted extraction procedure. Results demonstrated that most of these compounds can be recovered in good yields (>70%) from the matrix investigated, except nitrophenols that suffer degradation. Detection limits varied within a range from 20 ng/g for 2,4-dimethylphenol to 100 ng/g for pentachlorophenol, were obtained when using LC–UV. However these values were greatly improved when using LC–APCI-MS in negative ion mode. Validation of the method by analysing a reference soil sample from the BCR program containing eight polycyclic aromatic hydrocarbons and pentachlorophenol, and the analysis of a real environmental soil sample containing pentachlorophenol are also reported.

Keywords: Soil; Extraction methods; Microwave-assisted methods; Environmental analysis; Phenols; Nitrophenols; Chlorophenols

1. Introduction

Phenolic compounds of environmental interest come from a wide variety of industrial sources [1], as biodegradation products of humic substances, tannins and lignins [2] and as degradation products of many chlorinated phenoxyacids herbicides and organophosporus pesticides [3,4]. Many phenolic compounds are toxic at concentrations of a few μg/l and are also persistent. For these reasons a number of phenolic compounds are listed in the US Environmental Protection Agency (EPA) list of priority pollutants [5,6] and in the European Union (EU). Apart from the water problems certain phenols can be adsorbed onto soil. High substituted phenols such as trichlorophenols and pentachlorophenol present limited transport in water and are more likely absorbed in soil organic matter showing high persistence [7,8]. Chlorophenols were found in Swedish riverine sediments 40–50 km downstream cellulose plant discharges at low μg/g levels [9]. Pentachlorophenol and trichlorophenol levels over 1 μg/g were detected in New Zealand plants [10] and USA plants [11,12], respectively. In addition, recent studies have

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shown that phenolic compounds, in particular chlorophenols, are one of the more toxic contaminants to earthworms, which are a very good indicator for assessing the impact of organic chemicals in soils [13].

In general the isolation of phenolic compounds, e.g., pentachlorophenol and nitrophenols, from solid matrices is not straightforward due to the strong binding of some phenols with soil organic matter. Various analytical methodologies for the determination of chlorophenols in solid matrices were presented using shaking with a suitable organic solvent [8], Soxhlet [10,14], supercritical fluid [15,16] or ultrasonic extraction [17] followed by either gas chromatography (GC) or liquid chromatography (LC) with various detection systems. Soxhlet extraction, which shows high simplicity and versatility is preferred for the isolation of phenolic compounds from soil samples and also is currently used in the US EPA official methods such as 3540 B [18]. However, most of these methodologies fail when analysing both, free and bound phenols specially in the case of nitrophenols and high chlorinated phenols [8,14]. Microwave-assisted extraction (MAE) was recently introduced showing several advantages such as reduced extraction time and solvent consumption [19,20]. Use of microwave energy to extract organic compounds from a contaminated soil was first reported by Ganzler and coworkers [21,22]. Recent environmental applications of this technology are the determination of polynuclear aromatic hydrocarbons [21], organochlorine pesticides and aroclors, and organophosphorus pesticides listed in EPA Methods 8081 and 8141A, respectively [23,24]. Preliminary studies were performed with some phenols although degradation of nitrophenols can occur when analysing soils with high organic content [21,25].

The analysis of phenolic compounds from soil samples was usually performed by GC analysis (EPA 604, 625) using various detection systems such as GC–MS [26,27]. This approach has the advantage of the high sensitivity and selectivity, and the existence of mass spectra libraries for screening of unknown samples. However, there is a general trend to change to liquid chromatography (LC) methods. This should be attributed to the difficulty to derivatize phenols and nitrophenols in particular.

LC–mass spectrometry (MS) using thermospray (TSP) [28] and particle beam (PB) [29] interfaces were reported for the analysis of phenols, although problems associated with the lack of structural information and sensitivity, respectively were shown. The advent of LC–MS with atmospheric pressure ionisation (API) interfaces, mainly atmospheric pressure chemical ionisation (APCI), electrospray (ESP) and ionspray (ISP) has overcome those drawbacks [30]. A previous comparative study showed better performance of API interfaces in terms of sensitivity and structural information as respect to TSP for the entire range of phenolic compounds [31,32]. However no application of this technique was reported for the analysis of phenolic compounds in soil samples.

Regarding the different existing approaches, the aim of this work was to establish an analytical methodology for the determination of free and bound priority phenolic compounds in soil samples using Soxhlet and MAE. The optimum conditions were determined by spiking portions of uncontaminated sediment with a mixture of 11 representative phenols, included partly in the EU list and partly in the EPA list of priority pollutants. The performance of microwave extraction was also investigated and compared with those of Soxhlet extraction. Finally the application of LC–MS using an APCI interface is presented showing the advantages of this technique for the analysis of phenolic compounds in soil samples.

2. Experimental

2.1. Chemicals and materials

HPLC-grade water, methanol and acetonitrile were obtained from Merck (Darmstadt, Germany). All the solvents were passed through a 0.45-μm filter from Scharlau (Barcelona, Spain) before use. Phenol was obtained from Sigma (St. Louis, MO, USA), 2-chlorophenol, 4-chlorophenol, 2,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol (PCP), 2-nitrophenol, 4-nitrophenol, 2,4-dinitrophenol, 4-methylphenol and 2,4-dimethylphenol were purchased from Merck.

2.2. Sample preparation

Soil samples from the Ebro Delta (Tarragona, Spain) were stored at −20°C, lyophilised and sieved through a 120-μm sieve and homogenised in order to obtain a homogeneous soil material. A 10 g amount of sample at room temperature was wetted and spiked at a concentration level of 10 μg/g of each phenol. The mixtures were homogenised and stored at 4°C for 12, 24 and 48 h. Since there were no significant differences in the recovery between these storage times it was assumed that 12 h was a reasonable time to reproduce binding effects that occur in the environmental soils.

2.3. Sample extraction

2.3.1. Soxhlet extraction

Each portion was filled in a washed extraction thimble and extracted in a Soxhlet apparatus with 100 ml solvent for 12 h. Different extraction solvents were tested: methanol, acetone–methanol (1:1), acetone–methylene chloride (1:1), methanol–methylene chloride (1:2), methanol–water (4:1), methanol–water (4:1) with 2% triethylamine (TEA) and methanol–water (4:1) with 1% of acetic acid.

2.3.2. Microwave-assisted extraction

The MAE experiments reported here were carried out with a Prolabo microwave system, Model Soxwave 100, with a programming unit (Fontenay-Sous-Bois, France), this Model is characterized by having microwaves centred or focused and not pulsated. Phenolic compounds were extracted in 50-ml open vessels, made of borosilicate glass, using an open monomode focused microwave system. The emission wavelength was 2.45 GHz. The essential parameters involved include the microwave power applied and the exposure time. The available power range was from 30 W to 150 W. A 10-g portion of spiked soil was transferred to the MAE vessel, where 50 ml of a mixture consisting in methanol–water (4:1) with 2% TEA were added. Extractions were performed at 75–90 W for 30–40 min. After extraction, the vessels were allowed to cool to room temperature and the obtained extract was then filtered through a GF/F glass microfibre filter.

2.4. Clean-up

After concentration of the Soxhlet and MAE extracts under vacuum to eliminate organic solvent, the residual water was passed through a liquid–solid extraction cartridge for further clean-up. A 250 mg styrene–divinylbenzene copolymer (Isolute ENV) from International Sorbent Technology (Manchester, UK) and an automated sampler ASPEC XL (Gilson, France) were used. Conditioning of the sorbent was carried out by passing 7 ml MeOH and 3 ml of water at 1 ml/min through the cartridge. Elution was performed with 2×5 ml of acetonitrile, according with a protocol developed previously by our group [33]. The solvent was gently evaporated under a stream of nitrogen to a volume of approximately 0.5 ml and filled up exactly to 1 ml.

2.5. Chromatographic conditions

The extracts were analysed by LC–UV and LC–MS. The HPLC–UV system was purchased from Gilson and consisted of two Model 305 high-pressure pumps, a Model 811c dynamic mixing chamber, a Model 805 manometric module and a Model 117 UV detector. The LC–MS system was a VG Platform from Micromass (Manchester, UK) equipped with a standard AP) source which can be configured as APCI or ISP. A 150×4.6 mm Hypersil green ENV (C_{18}) analytical column from Shandon Scientific (UK) was used for LC separation. Eluents were water (1% acetic acid) and methanol–acetonitrile (1% acetic acid) (1:1). The LC eluent conditions varied from 75% water (10 min isocratic conditions) to 100% of organic modifier in 37 min at 1 ml/min. The UV wavelength was set at 280 nm and 310 nm. The APCI source and probe temperature were set at 150°C and 400°C, respectively. In full scan mode the range was from m/z 90 to 400 in the negative ion (NI) mode. When working in the selected-ion monitoring (SIM) mode the $[M\text{-}H]^-$ ion was monitored for all phenols. Corona discharge voltage was maintained between 2 kV and 3 kV, and cone voltage was 30 V (these parameters were optimised by our group

previously) [31]. The high-voltage lens voltage was set at 0.18 kV.

3. Results and discussion

3.1. Soxhlet extraction

Recoveries for phenols obtained when using different extraction solvents and LC–UV detection are summarised in Table 1. By increasing the polarity of the solvent (e.g., using small percentages of water) lead in general to improvements on recovery, probably because the strong solvation power of these solvent facilities the phenols release from humic matter. The use of water as a extraction solvent has been usually prevented because of its difficulty in evaporation the extract to dryness for further clean-up. Reversed-phase extract cartridges packed with styrene–divinylbenzene were used for clean-up. In this case the presence of water did not mean additional drawback. In addition it avoids the requirement to evaporate to dryness thus preventing losses of phenols by volatilisation. However, the use of water content higher than 25% was found to be disadvantageous since the amount of coextracted interferences prevented the quantification of most of the target analytes. Therefore, the methanol–water (4:1) mixture was found to be the more suitable although the problem for the extraction of some compounds such as PCP or chlorophenols still remains with recoveries ranging from 15 to 28% (Table 1). Acidification of the extraction solvent was reported by some authors for improving the extraction process [17,34]. However, the use of acetic acid resulted only in a very slight increase of recoveries. Alternatively a increase on recovery was obtained by raising the pH to a basic value using triethylamine as additive in the extraction solvent. In this case phenols present their deprotonated forms. The presence of water enhance stabilisation of the phenolate ions thus helping to displace them towards solution. However, too much basification of the extraction solvent should be avoided as some phenols, mainly nitrophenols can be degraded under these conditions [35]. Thus, using methanol–water (4:1) with 2% triethylamine, recoveries in a range from 67 to 97% could be obtained with a standard deviation (S.D.) of 8–14% improving previous results obtained applying the official US-EPA method.

3.2. Microwave extraction

MAE systems use the electromagnetic wave

Table 1
Recoveries and standard deviations ($n=6$) for phenolic compounds in spiked soil samples using Soxhlet extraction with various extraction solvents

Compound	Recovery (%)±S.D.							
	CH_3OH–acetone (1:1)	CH_3OH	Acetone–CH_2Cl_2 (1:1)	CH_2Cl_2–CH_3OH (2:1)	CH_3OH–water (4:1)	CH_3OH–water (4:1)+HAc	CH_3OH–water (4:1)+TEA	EPA method 3540
Phenol	55±14	32±12	41±13	43±10	40±10	46±13	74±11	66±14
2-Nitrophenol	76±9	55±10	54±12	48±14	50±13	50±10	88±9	n.d.
4-Nitrophenol	86±12	67±12	75±9	63±11	66±14	58±12	91±8	n.d.
2,4-Dinitrophenol	54±10	38±13	42±10	51±13	54±12	47±11	86±10	n.d.
4-Methylphenol	53±13	38±12	46±13	42±11	45±13	49±11	74±11	56±15
2,4-Dimethylphenol	32±14	22±15	25±16	23±15	15±15	30±13	67±14	n.d.
2-Chlorophenol	34±9	20±11	23±14	20±14	25±12	28±13	85±12	60±14
4-Chlorophenol	73±10	50±12	66±13	53±13	48±9	43±12	97±9	57±16
2,4-Dichlorophenol	56±8	28±10	42±12	30±13	35±10	40±10	90±9	52±13
2,4,6-Trichlorophenol	54±11	35±13	55±12	41±15	40±12	42±12	89±10	57±13
Pentachlorophenol	18±15	15±14	25±15	12±14	28±12	21±13	83±11	42±15

n.d.=Not determined.

Solvent extraction volume: 100 ml. Analysis was carried out by LC–UV at 280 nm.

Extraction time: 12 h.

Other conditions: see Section 2.5.

energy for heating a solvent which can be used for extract organic contaminants from soil samples. The system used in this work involves a non-pulsated and sample focused microwave which allows one to obtain good extraction efficiencies using an open extraction vessel. Preliminary experiments showed that the extraction performs similarly as Soxhlet extraction, being the more polar solvents the most appropriate. Hence the same solvent mixture which was found to be optimal for Soxhlet extraction (methanol–water, 4:1, 2% TEA) was used for optimise the MAE system. Recoveries obtained at various times and extraction powers are shown in Table 2. In general, the values obtained using MAE were similar than those found with Soxhlet extraction, except for 2-nitrophenol and 2,4-dinitrophenol which decreased about 50%. Since this decrease on the recovery was not observed when using Soxlhet extraction and neither in absence of the matrix in MAE experiments, this was attributed to catalytic reactions in the soil matrix induced by the microwaves irradiation, as previously suggested by other authors using non-focused devices [19,25]. On the other hand standard deviations were slightly improved when using MAE because lower volume of the extraction solvent, prevents losses during the concentration of the extract. By increasing power applied and/or exposure time, recoveries of trichlorophenol and PCP will increase, but more interferences and poor recoveries of nitrophenols are obtained.

However, in spite of the difficulty found in the nitro-derivative extraction, the use of MAE showed several advantages against Soxhlet extraction. First only 50 ml of solvent were required as compared with the 100 ml used for Soxhlet extraction. On the other hand only 30–40 min were required to achieve recoveries higher than 70% compared to 12 h for Soxhlet extraction. Moreover, since MAE can be used with the same solvent extraction mixture no additional research was done and consequently the same extraction mixture which was valid for Soxhlet could be applied for MAE.

3.3. LC–APCI-MS analysis

The peak confirmation was carried out by using LC–MS with an APCI interface in the NI mode, which provides very good sensitivity for the target phenols as well as structural information [31]. However, no response was obtained for phenol and methylphenols and it was attributed to the low acidity of these phenols which prevents their deprotonation in gas phase and require the use of an ISP interface. The detection limits obtained using either LC–UV and LC–APCI-MS are shown in Table 3. Values ranging from 20 ng/g for 2,4-dimethylphenol and 100 ng/g for PCP when using

Table 2
Recoveries and standard deviations (n=6) of phenolic compounds using MAE at various power and exposure time values

Compound	Recovery (%)±S.D.			
	75 W/30 min	90 W/30 min	75 W/40 min	90 W/40 min
Phenol	68±8	71±7	84±8	86±9
2-Nitrophenol	62±9	57±11	45±14	33±14
4-Nitrophenol	75±9	79±8	69±10	62±12
2,4-Dinitrophenol	44±10	38±17	36±19	24±21
4-Methylphenol	74±7	78±8	83±6	82±7
2,4-Dimethylphenol	77±7	81±6	86±8	92±6
4-Chlorophenol	82±5	87±8	84±7	92±8
2,4-Dichlorophenol	80±6	84±7	84±7	90±8
2,4,6-Trichlorophenol	60±8	64±7	70±8	79±7
Pentachlorophenol	53±9	68±10	64±10	77±8

Sample amount: 10 g.
Extraction solvent: 50 ml methanol–water (4:1)+2% TEA.
Concentration level: 10 μg/g. Analysis was carried out by LC–UV at 280 nm.
Other conditions: see Section 2.3.2.

Table 3
Limits of detection (LODs) of phenolic compounds in soil samples obtained with LC–UV and LC–APCI-MS in negative ion mode and MAE

Compound	LOD (ng/g)		
	LC–UV[a]	LC–APCI-MS	
		(Full scan)[b]	(SIM)[c]
Phenol	100	n.d.	n.d./93
2-Nitrophenol	50*	100	0.3/138
4-Nitrophenol	25*	30	0.05/138
2,4-Dinitrophenol	60	50	0.1/183
4-Methylphenol	40	n.d.	n.d./107
2,4-Dimethylphenol	20	n.d.	n.d./121
2-Chlorophenol	50	550	0.4/127
4-Chlorophenol	30	220	0.2/127
2,4-Dichlorophenol	40	60	0.03/161
2,4,6-Trichlorophenol	50	30	0.01/195
Pentachlorophenol	80*	20	0.007/263

n.d.=Not determined.
[a] Detection wavelength: 280 nm, except (*) 310 nm.
[b] m/z: 90–350. Cone extraction voltage was set at 30 V for calculation of LODs.
[c] Ion monitored: $[M\text{-}H]^-$ for all compounds.
Other conditions: see Section 2.5.

LC–UV were obtained. However the higher sensitivity of the LC–APCI-MS system in the SIM mode allows identification of these compounds in complex matrices at levels ranging from 0.4 to 0.007 ng/g.

A typical LC–APCI-MS (NI) full scan chromatographic profile of a spiked soil sample from the rice crops of the Ebro Delta is shown in Fig. 1. The good sensitivity obtained in full scan mode (Table 3) allows the use of this system for the determination of phenolic compounds in complex samples. However, it should be pointed out the need to remove the sample cone and skimmer assembly for cleaning every 15–20 injections similarly as reported for the analysis of high organic content water samples [32]. This represents a major drawback of these new API interfaces when applied to environmental analysis. Since the system offers high sensitivity, it should be calibrated very accurately, and therefore maximum cleanliness is essential.

4. Real soil analysis

Environment soil samples were analysed in order to check the performance of the methodology developed in this work. A dried contaminated industrial soil used as certified reference material (CRM 524) from the BCR of the European Commission containing eight polycyclic aromatic hydrocarbons and PCP was analysed. The soil sample was extracted using MAE according the protocol developed in this work and the final extract was analysed using LC–APCI-MS. The presence of other compounds in the soil sample at higher level than PCP, as well of other matrix interferences, did not represent a problem, since the structural information provided by the LC–APCI-MS allowed the unequivocal identification of the target phenol. A concentration of 52 ± 25 ng/g was monitored which is in good agreement with the certified concentration of PCP (34 ± 25 ng/g) [36]. However the higher R.S.D. obtained using LC–MS should be considered as acceptable. In previous inter-laboratory studies of water samples containing chlorinated compounds and acidic herbicides the overall R.S.D. varied from 5.5–38% and from 17–49% using either LC–UV or LC–MS (PB or TSP) [37,38]. These data were obtained using standard calibrated solutions with no sample pre-treatment. The R.S.D. obtained in the present work involve also a sample pre-treatment using MAE extraction and clean-up. The results obtained in this work enhances

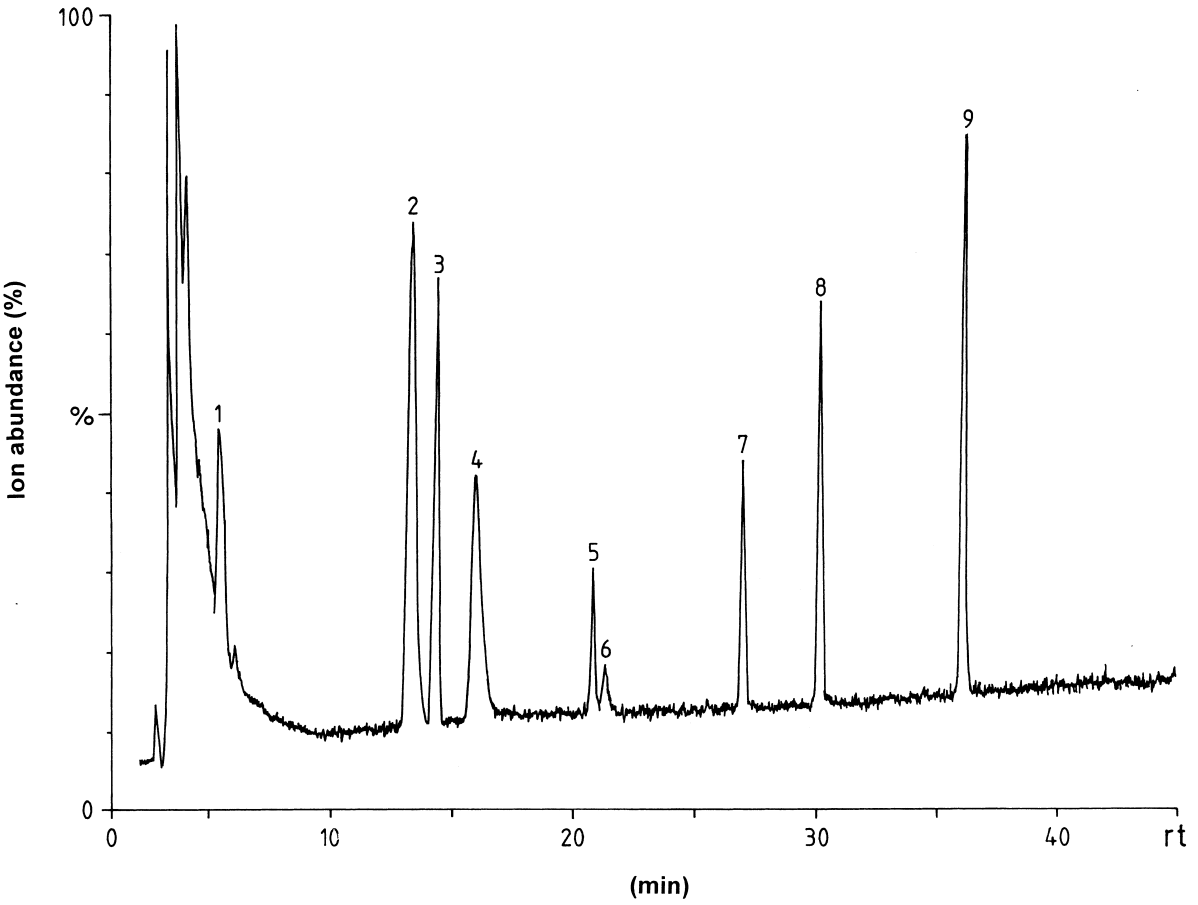

Fig. 1. LC–APCI-MS chromatographic profile, obtained in full scan mode (m/z 90 to 350) of a soil sample spiked at 0.8 μg/g with selected phenolics and analysed using the method developed in this work. (1) Catechol, (2) 4-nitrophenol, (3) 2,4-dinitrophenol, (4) 2-dinitrophenol, (5) 4-chlorophenol, (6) 2-chlorophenol, (7) 2,4-dichlorophenol, (8) 2,4,6-trichlorophenol, (9) pentachlorophenol. Other conditions: see Section 2.5.

the conclusion that LC–APCI-MS is an appropriate methodology for the environmental organic analysis of soil samples. In addition to that, it should be mentioned that the certified value was obtained with laboratories using GC techniques with prior derivatization and either electron-capture or MS detection. According to that, the results obtained in this paper represent a useful addition to the certified values of PCP in the CRM 524.

The analysis of a soil sample from Brazil suspected to contain PCP was also carried out. The soil sample was processed under the conditions optimised in this work, and the extract was analysed by using LC–APCI-MS in full scan mode. PCP was positively identified by comparison of the mass spectra at concentration of 1660 ng/g. The occurrence of such levels of PCP could be explained by a spill in a broad area of Brazil since PCP exhibits a relatively high hydrophobicity with high log K_w (5.01) as well of their low solubility which prevents their lixiviation.

5. Conclusion

An analytical protocol for the determination of phenols in soil and sediment samples was developed using either Soxhlet or MAE. A mixture consisting

of methanol–water (4:1) (2% TEA) was found to give the best recoveries since the basic pH can effectively release the bounded phenols. The use of water as extraction solvent was not a major problem since clean-up was performed using reversed-phase cartridges thus avoiding the need to remove completely the water. MAE was found as a good alternative to the conventional Soxhlet extraction since similar recoveries and improved standard deviations were obtained with important time and solvent savings. However an important fact the extraction performs similarly as Soxhlet extraction, being the more polar solvents the most appropriate. In most cases MAE could be used with the same extraction solvent than Soxhlet, thus avoiding the need to do additional experimental tests and facilitating their implementation for routine analysis.

As regards the results of a dried contaminated soil used as certified reference material from the EU, a good agreement was found when PCP residues were measured by the method developed in this work as compared to certified values. Furthermore, the method developed in this paper was applied to the analysis of real soil samples collected in Brazil, where PCP was detected at 1660 ng/g level.

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