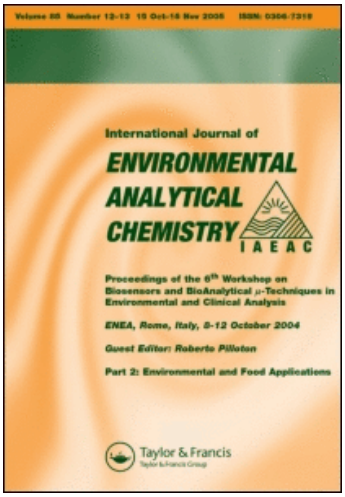

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A simple and efficient method for the determination of pollutant phenols in soils with high levels of organic matter

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A well-reproducible method to concentrate and determine Environmental Protection Agency (EPA) priority pollutant phenols from soils is developed. Alkaline extraction with 0.1 M NaOH of the phenolic compounds from soil with a high organic content is followed by their concentration in a highly cross-linked polystyrene–divinylbenzene sorbent (Bakerbond SDB-1) and HPLC-UV analysis. Detection limits ranged from 13 to 64 $\mu g\,kg^{-1}$. The effect of the amount of soil and analyte concentration is evaluated and quantitative recoveries are obtained in all the conditions tested. The proposed methodology is validated by comparing the results obtained with those achieved by applying the official EPA Method 3540C (Soxhlet extraction) and by the analysis of a certified reference soil without significant differences being observed with regards to recovery rates, although the new method proves to be faster. The method is applied to the analysis of spiked soils and to the evaluation of the stability of the analytes in these soils.

Keywords: phenols; solid-phase extraction; soil; polystyrene–divinylbenzene sorbent

1. Introduction

Phenolic compounds are major environmental pollutants which can be present in soils as natural products, derivatives from industrial use as chemical intermediates and from agricultural use as pesticides, bactericides and wood preservatives. Phenols, and particularly chlorinated ones, are toxic at concentrations in the low micrograms per litre range and also persistent in the environment [1]. As a consequence, phenolic compounds are listed in the US Environmental Protection Agency (EPA) priority list of pollutants [2] and in directive 76/464/EEC of the European Union, related to dangerous substances discharged into aquatic environments. Directive 75/440/EEC states that concentrations of phenolic compounds in surface water for drinking purposes should not exceed 1–10 $\mu g\,L^{-1}$ [3].

Several procedures have been described for the extraction of phenolic compounds from solid samples. Soxhlet extraction is the oldest and most widespread method [3–6]. However, microwave assisted extraction (MAE) [7–14] and pressurised liquid extraction (PLE, also known as accelerated solvent extraction, ASE) [15–18] are used as alternatives despite the use of high temperatures with these techniques having the potential to cause

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transformation or degradation of some of the analytes, which leads to a decrease in the recoveries and reproducibility [10]. On the other hand, other procedures such as sonication with organic solvents [8,19–21], supercritical fluid extraction (SFE) [8,22,23], purge and trap (P&T) [24] and headspace solid-phase microextraction (HS–SPME) [25] or immersion SPME [26] have been described. Although it is possible to reduce the extraction time and the amount of extraction solvent with these procedures, expensive special equipment and/or the use of hazardous organic solvents is still required.

The use of solid–liquid extraction procedures with aqueous alkaline media has been proved useful for the quantitative recovery of phenolic compounds adsorbed on soils [27,28]. It has the advantages of simplicity, the avoidance of toxic organic solvents and of not requiring the sample to be dried prior to extraction. The drawback is that a clean-up step to remove the interfering co-extracted polar compounds is needed. Solid-phase extraction (SPE) permitting a high degree of enrichment, lower the detection limits and the parallel analysis of a large number of samples, is highly recommended for this purpose [12,13,27–30].

Quantitative retentions of phenolic compounds by conventional silica sorbents [31] and polymeric matrices modified with polar groups [32] are achieved after acidification of the sample to pH 2.0–3.0, where all the analytes are protonated. The need to acidify the alkaline extract before to percolate it through the SPE sorbent results in an increased manipulation of the sample and a large error in the measurements. Highly cross-linked polystyrene–divinylbenzene (SDB) sorbents have shown themselves to be a good option for the reduction of baseline deviation due to co-extracted organic acids [28,29,33–35]. A further advantage is that SDB sorbents have a greater capacity for the retention of polar herbicides than silica sorbents [28,33–37] even in their deprotonated form at neutral or alkaline conditions due to interactions between the SDB matrix and the benzenic ring of the analytes [28,33].

In this study, we develop a method to preconcentrate and determine the 11 pollutant phenols from soils identified by the EPA has being of priority interest. This method involves the extraction of the analytes by means of a NaOH solution after which a clean-up and enrichment step using a highly cross-linked SDB sorbent is applied prior to their determination by HPLC-UV. Evaluation of the best experimental conditions and validation are undertaken by comparing the results obtained with those achieved applying the official EPA Method 3540C (Soxhlet extraction) and analysing certified reference soil CRM 112-100, which contains eight of the compounds studied at low concentrations.

2. Experimental

2.1 *Chemicals and reagents*

Phenol (Ph, 99.5%), 2-chlorophenol (2CP, 99.5%), 2-nitrophenol (2NP, 98.5%), 4-nitrophenol (4NP, 99%), 2,4-dichlorophenol (24DCP, 99.5%), 2,4-dimethylphenol (24DMP, 98%), 2,4-dinitrophenol (24DNP, 83.5%), 4-chloro-3-methylphenol (4C3MP, 99.5%) and 2-methyl-4,6-dinitrophenol (2M46DNP, 90%) were supplied by Dr Ehrenstorfer GmbH (Augsburg, Germany). 2,4,6-Trichlorophenol (246TCP, 97%) and pentachlorophenol (PCP, 98%) were obtained from Aldrich (Steinheim, Germany). Solvents used (methanol, acetonitrile, acetone and hexane) were of HPLC grade ($>99.9\%$) for pesticide residues (Carlo Erba, Milan, Italy). Ultra-pure water was obtained from a Milli-Q system (Millipore Iberica S.A., Barcelona, Spain). Hydrochloric acid

(Riedel-de-Haën, Seelze, Germany) and acetic acid (Aldrich, Steinheim, Germany) were both of analytical reagent grade.

Stock solutions (c.a. 1000 mg L^{-1}) were prepared for each of the compounds in methanol or acetonitrile. These solutions were stored in amber vials at 4°C. Working solutions were prepared daily by diluting and mixing the individual stocks in methanol, acetonitrile or Milli-Q water.

Solid-phase extraction Bakerbond SDB-1 cartridges containing 200 mg of a SDB polymeric sorbent (944 $m^2 g^{-1}$ specific surface area, 0.73 Ml g^{-1} pore volume and 30 nm pore diameter) (J.T. Baker, Deventer, Holland) were used in the clean-up and concentration steps.

2.2 *Soil samples*

Surface soil gathered from grazing land in Vilaüt (Girona, Spain) was used in this study. The physical and chemical properties of this soil (Table 1) were determined following the official methods of the Spanish Minister of Agriculture [38]. Large amounts of humic and fulvic substances are suggested by the high organic matter content (6.70%).

The CRM112–100 soil reference material (LGC Promochem, Teddington, UK) is a sandy loam soil contaminated with phenols from a wood treatment site in the Rocky Mountain Region (Table 4).

2.3 *Instruments and conditions*

Extracts were analysed by HPLC with a spectra system (Thermo Separation Products, Thermo Finnigan, San Jose, CA, USA) liquid chromatograph and a UV6000LP diode–array detector. Separations were carried out in a 20 cm × 0.46 cm i.d. column packed with a 5 μm Kromasil 100 C18 silica phase (Teknokroma, Barcelona, Spain) at 25 ± 1°C. The mobile phase consisted of an acetonitrile–water mixture containing 1% acetic acid at a flow rate of 1 mL min^{-1}. The LC gradient was 30% acetonitrile (12 min isocratic), increased to 78% acetonitrile (linearly between 12 and 24 min) and held for 11 min. Detection was conducted at 275 and 316 nm. Quantification of the analytes was performed

Table 1. Chemical and physical properties of the soil evaluated.

Parameter	Value found
Organic matter (%)	6.70
Clay (%)	52.35
Mud (%)	39.85
Sand (%)	7.80
pH	6.95
Conductivity (dS m^{-1})	2.40
Carbonate (%)	6.75
CEC (meq g^{-1})	0.637
Ca^{2+} (meq g^{-1})	0.499
Mg^{2+} (meq g^{-1})	0.106
K^{+} (meq g^{-1})	0.033
Na^{+} (meq g^{-1})	0.025

by multivariate regression at the two wavelengths indicated. Samples were injected by means of a Rheodyne 7725i injector (Rohnert Park, CA, USA) with a 20 μL sample loop.

3. Experimental procedures

3.1 *Soil spiking*

Soils were air-dried and sieved to a particle size ≤2 mm. Predetermined weights (1–10 g) of soil samples were spiked with a spiking solution (1–10 mL) containing the 11 phenols under investigation in methanol. The mixture was agitated to ensure adequate contact between the analytes and the soil. Then, the solvent was allowed to evaporate over several days at room temperature before to proceed to the alkaline extraction (slurry spiking).

A different soil spiking methodology was used for the evaluation of the performance of the SPE sorbent used. A total of 1 mL of the spiking solution (a methanol solution containing the 11 phenols) was added to a weighted mass of non-contaminated soil (5–10 g) and alkaline extraction was immediately undertaken (spot spiking). This procedure does not reproduce the same real status of pollutants in soil samples but does allow the evaluation of the effect of the soil matrix components on the recovery performance of the sorbent used, and helps to determine the most appropriate conditions for the analysis of the compounds of interest. In both methods, the concentration of phenols in the spiked soils was calculated as being between 0.2 and 20 $\mu g\,g^{-1}$.

3.2 *Phenol extraction and clean-up*

The spiked soil samples (1–10 g) were placed into glass tubes and phenols were extracted with 10 or 20 mL of 0.1 M NaOH in a rotatory mixer (Dinko Instruments, Barcelona, Spain) at 30 rpm for 30 min at 25 ± 1°C. Alkaline extracts were centrifuged at 2000 rpm for 20 min to separate the soil supernadants, filtered through 0.45 μm cellulose acetate membrane filters (Whatman, Maidstone, UK), and their pH were adjusted to 6 with hydrochloric acid. Then, acidified soil extracts were cleaned-up and preconcentrated by SPE using Bakerbond SDB-1 cartridges. The SPE process was performed as follows: (1) cartridges were conditioned by adding 2 mL of acetonitrile, 2 mL of methanol and 2 mL of slightly acidified water (pH = 6.0); (2) acidified soil extracts (pH = 6.0) were passed through the SPE cartridges at 5 $mL\,min^{-1}$ by means of a Minipuls3 peristaltic pump (Gilson, Villiers–Le–Bel, France) fitted with silicone pumping tubes; (3) cartridges were then washed with 2 mL of water at pH = 6.0 and the remaining water was eliminated allowing the passage of an air flow through the cartridge for 5 min; and (4) the retained phenols were eluted with 3 mL of acetonitrile.

3.3 *Soxhlet extraction*

Soxhlet experiments were performed in accordance with the official EPA Method 3540C [6]. A total of 10 g of a 20 $\mu g\,g^{-1}$ spiked soil was used.

4. Results and discussion

4.1 *Evaluation of the alkaline extraction*

Phenols were extracted from soil samples with aqueous NaOH solutions as described in the experimental section. Previous studies report the use of high concentrations of alkaline solutions for the extraction of phenolic compounds from soils [39–41]. In this study, a single extraction with 0.1 M NaOH proved to be sufficient to obtain quantitative recoveries for all the compounds evaluated. It has been found that NaOH concentrations higher than 0.1 M did not significantly improve the recovery of phenolic compounds but rather resulted in the co-extraction of larger amounts of humic and fulvic substances [28]. Kinetic studies showed that a mixing time of 30 min was sufficient to obtain quantitative recoveries of phenols from soils.

4.2 *SPE clean-up and concentration*

The high organic content (6.70%) of the soil evaluated yields a large amount of co-extracted humic and fulvic compounds during the alkaline extraction. It can be seen in Figure 1 that after recording the signal of an acidified extract of a non-contamined soil for more than 10 min the baseline has still not been recovered. A clean-up of soil extracts is necessary to allow the adequate quantification of the compounds which are less retained by the chromatographic column (e.g. phenol, $t_R = 7.5$ min). The use of the Bakerbond SDB-1 sorbent for this purpose results in the elimination of an important amount of the fulvic and humic substances. The baseline is recovered in about 5.5 min (Figure 1), which allows the appropriate quantification of all analytes.

The results obtained in the evaluation of the recoveries of the 11 phenols of interest by the SDB-1 sorbent at different pH values are given in Table 2. As indicated in the experimental section, the spot spiking method has been used to characterise the clean-up/preconcentration step. This does not reproduce the same real status of pollutants in soil samples, but it yields a solution with similar matrix interferences due to humic and fulvic substances as may be obtained in the analysis of a contaminated soil. The pH of the extract

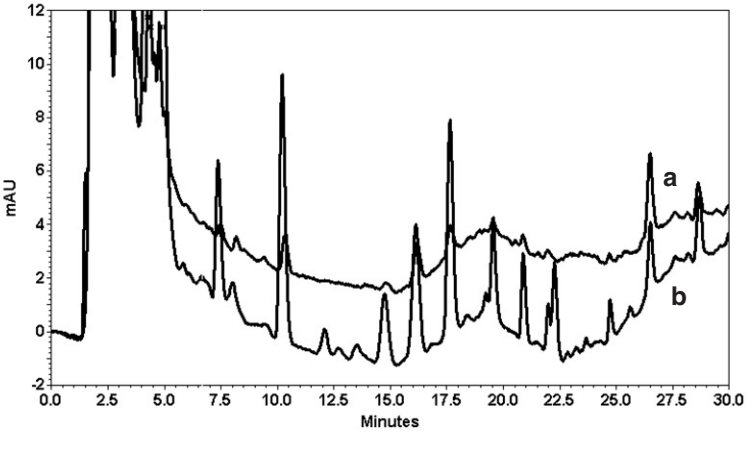

Figure 1. Chromatograms obtained for an alkaline extract from a non-contaminated soil before (solid line) and after (dashed line) SPE clean-up with the SDB-1 sorbent.

Table 2. Mean recoveries ($n=3$) and their uncertainties ($\pm ts/\sqrt{n}$, $\alpha=0.05$) at different pH in the solution extract, obtained by analysing 10 mg of soil spiked at 1 μg g^{-1} (spot spiking).

	Soil extract pH					
	2	4	6	8	10	12
4C3MP	103 ± 6	101 ± 2	99.0 ± 0.7	99 ± 2	100 ± 5	89 ± 8
24DCP	104 ± 3	97 ± 8	96 ± 1	90 ± 13	n.d.	93 ± 5
2CP	78 ± 2	n.d.	79 ± 4	76 ± 7	58 ± 16	5 ± 2
24DMP	103 ± 4	101.8 ± 0.7	102 ± 1	102 ± 2	102 ± 2	100.2 ± 0.4
24DNP	94 ± 3	n.d.	89.3 ± 0.9	92 ± 4	91 ± 3	99 ± 2
2M46DNP	105 ± 3	n.d.	101.5 ± 0.4	102.6 ± 0.3	103 ± 3	102 ± 3
2NP	106 ± 4	104.2 ± 0.6	101 ± 1	70 ± 6	78 ± 7	19 ± 4
4NP	108 ± 4	100 ± 5	96 ± 7	86 ± 5	83 ± 6	56 ± 6
PCP	101 ± 5	n.d.	n.d.	107 ± 9	96 ± 17	96 ± 4
Ph	108 ± 9	102 ± 1	104 ± 2	104 ± 2	104 ± 1	10 ± 2
246TCP	103 ± 4	98 ± 3	96.4 ± 0.9	n.d.	91 ± 2	88 ± 4

n.d.: not determined.
Experimental: Extraction with 10 mL of 0.1M NaOH. The pH of the extract was adjusted with hydrochloric acid before percolating the solution through the Bakerbond SDB-1 cartridge. Elution with 3 mL acetonitrile. Each replicate corresponds to the single analysis of a new sample of spiked soil.

was adjusted to predetermined values with hydrochloric acid before percolating the solution through the SPE cartridge.

Statistical analysis of the results (ANOVA test) showed that all the compounds were quantitatively recovered without significant differences at acidic pH values (pH ≤ 6.0) with the SDB-1 sorbent ($p > 0.05$ for each individual analyte). However, recoveries at alkaline pH were not quantitative for all the analytes although some phenolic compounds gave better results than others. 24DCP, 24DMP, 24DNP and 2M46DNP did not show significant differences when the solution pH increased up to 12 ($p = 0.29$, 0.86, 0.87, 0.63, respectively). 4C3MP and Ph only showed statistically equivalent recoveries at pH ≤ 10.0 ($p = 0.59$ and 0.05, respectively). 2CP showed equivalent recoveries at pH ≤ 8.0 ($p = 0.70$). Finally, 2NP, 4NP and 246TCP were only quantitatively recovered at pH ≤ 6.0 ($p = 0.11$, 0.09 and 0.08, respectively). PCP is not included in the statistical analysis of the data as the detection limit for this compound with the HPLC method is 0.7 mg L^{-1} [32], which is too high to give reliable results at the spiked concentration used.

Using conventional C18 sorbents, it is necessary to acidify the extracts until pH 2.0–3.0 in order to have the analytes in their non-ionised form for quantitative recovery. At these low pH values a precipitate of the humic and fulvic substances can be formed if the organic matter content of the soil is high as was the case here (6.70%). This precipitate may adsorb some of the analytes reducing their recoveries and increasing the determination error. The results obtained in this study indicate that soil extracts only need to be slightly acidified to pH ≤ 6.0 before percolation through the SDB-1 sorbent if the 11 analytes have to be determined. This is due to the fact that the primary sorption mechanism for SDB polymeric sorbents is via π–π interactions with aromatic analytes [33,42], and it is not necessary for the protonated form of the analyte to be present to allow adsorption of the analyte (e.g. 24DNP has $pK_a = 4.04$ but can be quantitatively recovered at pH up to 12 where it is 100% ionised in the solution). The fact that it is only necessary to acidify the

Table 3. The effect of the amount of the soil sample (spiked at $1\,\mu g\,g^{-1}$ using the spot spiking procedure) on phenolic compound recoveries ($n = 3$) after analyte extraction with 0.1 M NaOH and adjusting the pH of the extract to 6.

	Weight of soil					
	1 g		5 g		10 g	
	R (%)	RSD (%)	*R* (%)	RSD (%)	*R* (%)	RSD (%)
4C3MP	86	3	83	2	75	5
24DCP	92	2	94	3	89	5
2CP	116	5	99	1	82	10
24DMP	79	1	86	3	83	7
24DNP	94	2	73	3	71	3
2M46DNP	100	2	90	2	90	4
2NP	99	3	94	2	98	2
4NP	100	3	98	4	102	4
Ph	112	3	121	2	128	2
246TCP	97	1	96	3	94	2

RSD: Relative Standard deviation

extracts to pH = 6.0 with the SDB-1 sorbent helps to prevent losses of the analytes due to the precipitation of the humic and fulvic substances.

Table 3 shows the effect that the amount of soil employed has on the recovery efficiency of the SDB-1 cartridge. Portions of 1, 5 and 10 g of soil were spiked at $1\,\mu g\,g^{-1}$ for each analyte using the spot spiking procedure. Statistical analysis shows that the recoveries obtained are not equivalent ($p < 0.05$). The larger the amounts of sample the lower the recovery, particularly for the most polar compounds. This result is explained by the increase in the amount of humic and fulvic substances co-extracted with the analytes that can partially saturate the cartridge.

4.3 *Method validation*

To validate the proposed method, the slurry spiking procedure was used to fortify the soil samples. Accuracy, precision at three concentration levels and detection limits were evaluated to validate the method.

Two procedures were used to evaluate the accuracy. First, we compared the results obtained with those achieved by applying the official EPA Method 3540C (Soxhlet extraction). Recoveries with the Soxhlet method were not significantly different from those obtained with alkaline extraction and SDB-1 sorbent clean-up for nine of the phenolic compounds evaluated (Figure 2). However, 2CP and 2M46DNP showed significant differences ($p < 0.05$) as greater recoveries were obtained with the method proposed in this study. The accuracy was also validated by analysing a certified reference material (CRM112-100) containing eight of the phenols studied with concentrations ranging from 2 to $6\,\mu g\,g^{-1}$ (Table 4). Except for the cases of 2M46DNP and 2NP, the concentrations determined with the proposed method fell within the certified intervals of the reference material where applicable.

To determine the precision of the proposed method, 1-g aliquots of soil were spiked at levels equivalents to 1, 10 and $20\,\mu g\,g^{-1}$ of each phenol (Figure 3). Statistical analysis

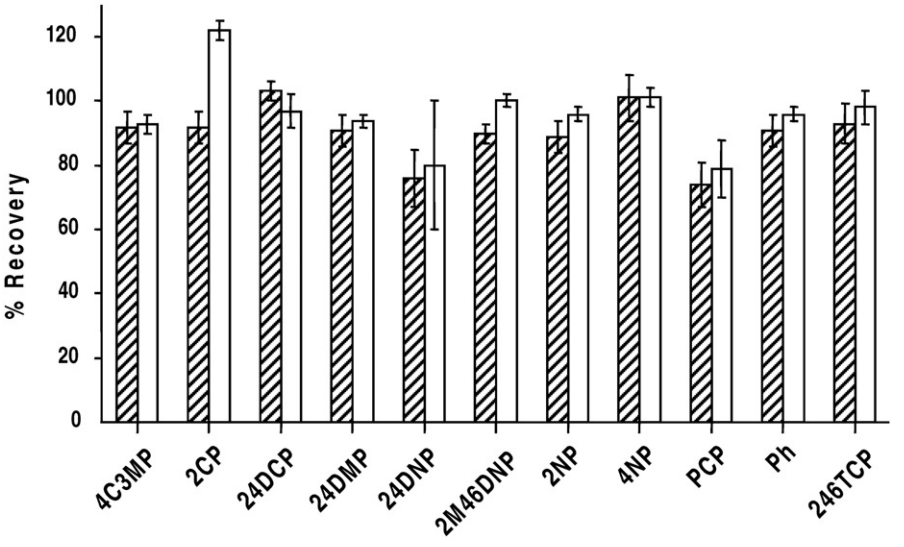

Figure 2. Recoveries ($n = 3$) obtained using the proposed method (white bars) and EPA Method 3540C (soxhlet extraction) (striped bars). Lines at the top of the bars indicate the standard deviation from the indicated value.

Table 4. Recoveries (%) obtained in the analysis of CRM112-100 certified soil sample using the proposed method.

	Certified value ($\mu g\,g^{-1}$)	Interval ($\mu g\,g^{-1}$)	Proposed method ($n = 6$) ($\mu g\,g^{-1}$)
4C3MP	4.94	3.04–6.84	5.4 ± 0.4
2CP	2.38	1.35–3.41	2.9 ± 0.2
24DNP	0.65*	n.c.v.	1.3 ± 0.4
2M46DNP	4.75	2.35–7.15	8.8 ± 0.4
2NP	4.33	2.40–6.27	6.9 ± 0.2
4NP	5.66	2.56–8.76	5.8 ± 0.4
PCP	5.05	2.12–7.98	6 ± 1
Ph	2.45	1.35–3.55	2.42 ± 0.04

Note: *Proposed concentration; n.c.v.: no certified value.

showed no significant differences in the recoveries obtained at the three concentration levels evaluated ($p = 0.14$).

The limits of detection (LOD) for the proposed method were experimentally determined using the spot spiking procedure. Values were determined by spiking 5 g portions of non-contaminated soil at different levels and then analysing the extracts. The detection limits indicated in Table 5 were those obtained with a signal/noise ratio ≥ 3 in the resulting chromatograms. LOD were in the 13–65 $ng\,g^{-1}$ range except for PCP. As indicated previously, the detection limit for PCP ($0.7\,mg\,L^{-1}$) obtained using the HPLC method is too high to permit the determination of all the phenols in the range of $ng\,g^{-1}$ for soil samples [32].

The results obtained in validating the method show that it is suitable for trace level determination of 10 of the 11 priority pollutant phenolic compounds in soil samples.

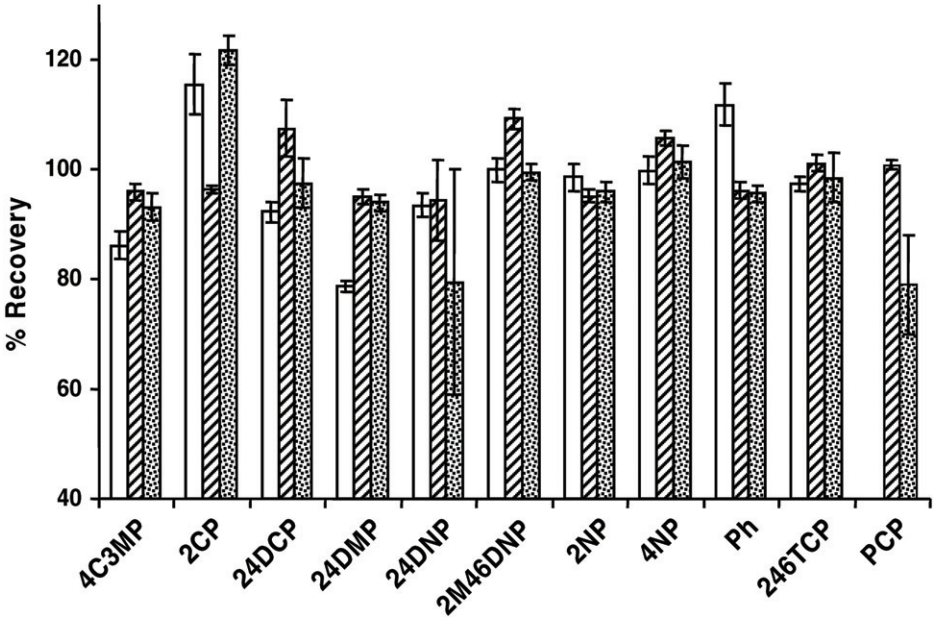

Figure 3. Recoveries ($n = 3$) obtained in the extraction of 1 g of soil spiked at 1 $\mu g\,g^{-1}$ (white bars), 10 $\mu g\,g^{-1}$ (striped bars) and 20 $\mu g\,g^{-1}$ (dotted bars). Soils were extracted with 10 mL of 0.1M NaOH and cleaned-up with the Bakerbond SDB-1 cartridges after acidification of the extract to pH = 6.0. Lines at the top of the bars indicate the standard deviation of the value.

Table 5. Experimental detection limits ($\mu g\,g^{-1}$) determined for the analysis of the phenolic compounds in soils using the proposed method.

	Detection limit (ng^{-1})
4C3MP	64
2CP	22
24DCP	18
24DMP	30
24DNP	20
2NP	20
4NP	20
Ph	22
246TCP	65
2M46DNP	13

Analyses of 5 g soil samples spiked using the spot spiking procedure.

The proposed method has the advantage of being faster and less environmentally aggressive than other standard methodologies.

4.4 *Evaluation of the analyte stability in soils*

The action of enzymes and metal oxides catalyse the binding and the incorporation of phenolic compounds into humic macromolecules [43]. This can result in the

Table 6. Recovery percentages obtained ($n = 3$) in the study of the degradation of the phenolic compounds in spiked soil (slurry spiking).

		Soil B	
	Soil A	B1 (soil at −21°C)	B2 (soil at 4°C)
4C3MP	75 ± 3	74 ± 3	57 ± 4
24DCP	84 ± 10	84 ± 6	66 ± 8
2CP	55 ± 3	31 ± 5	2 ± 1
24DMP	30 ± 1	19 ± 5	2 ± 1
24DNP	72 ± 3	74 ± 4	69 ± 7
2M46DNP	82 ± 2	87 ± 2	80 ± 9
2NP	56 ± 3	46 ± 2	21 ± 2
4NP	85 ± 4	89 ± 2	89 ± 9
Ph	53 ± 2	48 ± 4	36 ± 2
246TCP	87 ± 3	85 ± 3	85 ± 4

Experimental: A total of 25 g soil sample spiked at 1 μg g^{-1} of each phenol. Preliminary sample was subdivided in three 8 g portions. Three 2 g aliquots were analysed for each portion. Soil A: portion of soil analysed immediately after solvent evaporation (5 days); Soil B: portion of soil stored for 1 month (B1: stored at 4°C; B2: stored at −21°C).

biodegradation and/or chemical decomposition of the analytes in soils, which affects the recovery levels of these substances during soil analysis. The use of conventional spiking methods such as slurry spiking, where the solvent present in the spiking solution is allowed to evaporate for several days before analyte determination, can result in the modification of the sample. Both the time required for solvent evaporation and the storage temperature made contribute to the degradation of the analytes and, as a result, a reduction in the recovery levels obtained in spiked soils. In our case, after slurry spiking the solvent was left to evaporate at a controlled temperature of 25 ± 1°C for 5 days. The recoveries obtained were in the range 30–87% (Table 6), which is significantly less than recoveries obtained using the spot spiking method. Storage conditions for the conservation of the soil between field sampling and laboratory analysis is also an important factor as the use of the wrong conditions may lead to the formation of artifacts and resulting concentrations being lower than those present in the soil at the sampling time. Table 6 shows the results obtained in the evaluation of the analytes over time at different conservation conditions. The slurry spiking procedure (5 days for the solvent evaporation at 25 ± 1°C) was used to spike a 25 g soil sample with 25 mL of a phenolic solution at 1 μg g^{-1} of each phenol. The sample was then divided into three portions. The first was analysed immediately after the solvent evaporation period and the other two where stored for 1 month, one at 4°C and the other at −21°C, before being analysed. Only 2CP, 24DMP and 2NP showed significantly smaller recoveries when the soil was stored at −21°C, indicating that some degradation took place for these three phenols in these conditions. When the soil was stored at 4°C, the same three compounds showed larger degradation and their recoveries where very small. Moreover, three more compounds (4C3MP, 24DCP and Ph) also showed significantly smaller recoveries when the soil was stored in these conditions. From these results we can conclude that sample preservation at 4°C is insufficient to prevent the degradation processes of the analytes.

5. Conclusions

The proposed method consists of alkaline extraction of the phenolic compounds from soils with 0.1 M NaOH and clean-up and preconcentration of the extract using the highly cross-linked SDB sorbent Bakerbond SDB-1, allowing the quantitative recovery of all the analytes at pH = 6. The detection limits obtained for the determination of 10 phenolic compounds of the EPA priority list in soils are in the 1.3–6.4 ng g^{-1} range. This method has been validated by comparison with the official 3540C EPA method and by analysing the CRM112-100 certified reference material.

A soil with a high content of organic matter (6.70%) was used to evaluate the method. The use of 0.1 M NaOH for the extraction of the analytes resulted in a large amount of co-extracted humic and fulvic substances, which are known to interfere in the detection of the analytes of interest with HPLC. The adequate clean-up of these substances by the polystyrene sorbent proved that the method can be adequately used for another soils with lower organic matter contents.

The analysis of the degradation of the phenolic compounds during storage has demonstrated that soil preservation at 4°C is not sufficient to prevent further degradation of these compounds. Soil samples need to be frozen at very low temperatures (below −21°C) in order to prevent degradation of phenolic compounds in soils containing a high content of organic matter.

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