Research Article

Selective Extraction of Organic Contaminants from Soil Using Pressurised Liquid Extraction

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This study focuses on the application of sorbents in pressurised liquid extraction (PLE) cell to establish a selective extraction of a variety of organic contaminants (polycyclic aromatic hydrocarbons (PAHs), chlorpyrifos, phenol, pentachlorophenol, and sterols) from soil. The selectivity and efficiency of each sorbent depend on the properties of the material, extracting solvent, capacity factor, organic compounds of interest, and PLE operating parameters (temperature, pressure, and extraction time). Several sorbents (silica, alumina, and Florisil) were evaluated and with the proper choice of solvents, polar and nonpolar compounds were successfully separated in two fractions. Nonpolar compounds (PAHs, chlorpyrifos, and pentachlorophenol) were recovered in the first fraction using a polar sorbent such as Florisil or alumina, and *n*-hexane as eluting solvent, while more polar compounds (phenol and sterols) were recovered in the second fraction using methanol. Silica (5 g) was found to be effective for selective extraction with the satisfactory recoveries for all compounds (PAHs from 87.1–96.2%, chlorpyrifos 102.9%, sterols from 93.7–100.5%, phenol 91.9%, and pentachlorophenol 106.2%). The efficiency and precision of this extraction approach and the existing EPA Method 3545 were compared.

1. Introduction

Several novel extraction techniques have been developed in an attempt to obtain more efficient extraction of the analytes from the matrix by improving the selectivity of target compounds, reducing of both extraction time and organic solvent consumption, and increasing sample throughput. Since its first introduction in 1995, pressurised liquid extraction (PLE) has been shown to be a valuable and, in some cases, superior alternative to conventional methods such as Soxhlet and ultrasonic extraction. This is an extraction technique in which liquid solvent is used as an extraction solvent under elevated temperatures and pressures. Raising the temperature increases the diffusion rates, the solubility of the analytes, and the mass transfer and decreases the viscosity and the surface tension of the solvent. These changes improve the contact of the analytes with the solvent and, thus, enhance extraction. Even though pressurised liquid extraction (PLE) has gained wide acceptance for the extraction contaminants from various environmental samples, dirty

extract was obtained due to the great extracting power of the solvents from this extraction technique [1–3]. The presence of coextracted substances requires postextraction cleanup step prior to chromatographic analysis. The method of purification commonly used is the solid-phase extraction with glass columns or commercial cartridges.

Common organic contaminants present soil/sediment including PAHs, chlorpyrifos, sterols, phenol, and pentachlorophenol were selected in this study. Analysing these compounds is a challenging task as the differences in their chemical properties (polarity, solubility, and volatility) may require several different analytical approaches. In addition, the low concentration of these compounds present in a complex matrix may require additional cleanup step prior to gas chromatographic analysis. The presence of interferences could impaired the limits of detection or even damage the chromatographic system. As a result, longer analysis time and larger amount of sample are required. The current trends in the method development for the analysis of trace organic contaminants are to simplify sample preparation steps in

order to reduce time and solvent consumption and use more selective extraction techniques [4]. The method should utilise minimum sample handling such as simultaneous extraction, derivatisation, and cleanup steps prior to chromatographic analysis. Thus, developing a simple and fast extraction step without compromising on the efficiency in the analysis of organic contaminants from soil/sediment is the main interest in this study. Therefore, in this study, PLE extraction with simultaneous cleanup approach is considered. Simultaneous cleanup is achieved by the inclusion of suitable sorbent into the PLE extraction cell. Using this approach, the selectivity in the extraction of a wide range of organic contaminants can also be achieved by extracting/eluting specific group of compounds using suitable solvent. Several studies have demonstrated the influence of the PLE operating conditions such as sample load, solvent used, solvent ratios, pressure, temperature, extraction time, and rinse volume on the efficiency of extraction of organic contaminants from the soil sample [5, 6].

2. Experimental

2.1. Samples Preparation. Uncontaminated and contaminated soils were air-dried at room temperature to a water content of less than 5% and sieved through a 600 μm pore sieve. Soil samples were stored in an air-tight container at 4°C until analysis. Spiking of samples with a mixture of seven PAHs, five sterols, chlorpyrifos, phenol, and pentachlorophenol was performed as follows. The sample (5 g) was weighed into an aluminium cup and mixed with the working standard solution of PAHs, sterols, chlorpyrifos, phenol and pentachlorophenol in the range of 5–60 μg mL^{-1}. The sample was stirred and stored for 48 hours in a screw cap glass specimen jar. Before PLE extraction, solvent was completely evaporated by stirring the soil sample for approximately 15 minutes.

2.2. Standards and Reagents. All solvents (methanol, dichloromethane (DCM), *n*-hexane, acetone, isopropanol) were of pesticide residue grade and purchased from Merck (Darmstadt, Germany). Florisil (60–100 mesh) was obtained from Fisher Scientific (Loughborough, UK). Silica gel (70–230 mesh ASTM) and alumina (70–230 mesh ASTM) were obtained from Merck (Darmstadt, Germany) and nonwashed diatomaceous earth was purchased from Sigma-Aldrich (Steinheim, Germany). Silica gel and Florisil were activated for 24 hours at 130°C before used. These were cooled in dessicator prior to use. Standard Reference Material SRM1944 (marine sediment) was obtained from the National Institute of Standards and Technology (NIST). Individual standards of PAHs: naphthalene, acenaphthene, anthracene, and pyrene were obtained from Dr. Ehrenstorfer, GmbH (Augsburg, Germany). Acenaphthylene, fluorine, benzo[a]anthracene, and benzo[a]pyrene, were obtained from Supelco (Bellefonte, USA). Individual standards of sterols, specifically 5β-cholestan-3β-ol (coprostanol), 5-cholesten-3β-ol (cholesterol), 5β-cholestan-3α-ol (stigmasterol), and stigmastanol were purchased from Sigma Aldrich (Steinheim, Germany). Internal standards, phenanthrene d$_{10}$ (Supelco, Bellefonte,
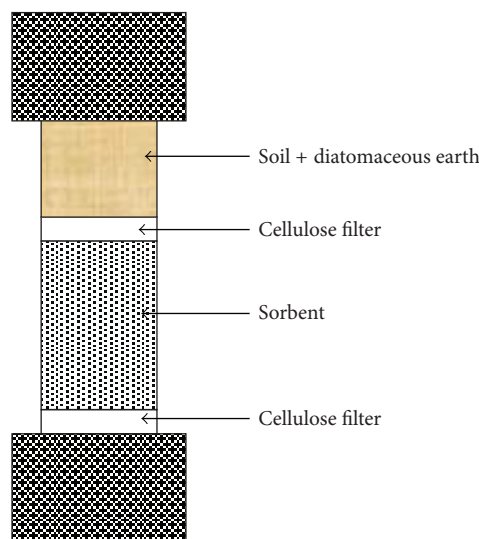

FIGURE 1: Packing of the PLE extraction cell.

USA), and 5α-cholestane (Sigma Aldrich, Steinheim, Germany) were used for quantification.

2.3. Pressurised Liquid Extraction (PLE). Extractions were done using an ASE 200 accelerated solvent extractor (Dionex, Sunnyvale, CA, USA) equipped with 33 mL and 22 mL stainless-steel cells. Cell loading was done in the following sequence: a cellulose filter was placed at the bottom of the cell, followed by 5 g of activated silica (alumina or Florisil), another cellulose filter and finally a soil sample (5 g) mixed with diatomaceous earth. The packing of the extraction cell is illustrated in Figure 1. The sample cells were then closed to finger tightness and placed into the carousel of the PLE system. Two solvents, *n*-hexane and methanol (MeOH), were utilised as extraction solvents. In the first cycle, *n*-hexane was pumped into the cell and was preheated for 2 min to reach the optimum setting temperature and pressure (125°C, 1400 psi) followed by a static extraction of 10 min. At the end of the cycle, the pressure was released and the extract was collected in 60 mL glass vials. The cell was rinsed with fresh solvent (about 80% of the extraction cell volume) and purged using pure nitrogen for 60 s. For the second extraction cycle, the sample was extracted again using MeOH under the same conditions. The extract was collected into a second collection vial. Internal standards (phenanthrene, d$_{10}$, and 5α-cholestane, 1 mL each) were added to the extracts and the volume was reduced to 1 mL prior to gas chromatograph analysis.

2.4. GC-FID Analysis. Gas chromatographic separation and identification of PAHs and sterols was performed using an HP6890 series II (Agilent Technologies Inc., Palo Alto, CA, USA) with splitless injection and flame ionisation detection. A 30 m × 0.25 mm id × 0.25 μm film thickness HP5-MS capillary column (Agilent technologies) was used to achieve separation of PAHs and sterols with the following temperature program: initial temperature, 50°C; held for

2 min; increase at $18°C$ min^{-1} to $250°C$, increase at $10°C$ min^{-1} to $310°C$; held for 11 min. The injection volume was $1 \mu L$, and the splitless period following the injection was 2 min. The detector temperature was set at $310°C$. PAH quantification was carried out using a five-point calibration plot containing 5, 10, 25, 50, and $60 \, mg \, L^{-1}$ PAH standard mixtures and $20 \, mg \, L^{-1}$ internal standard (phenanthrene, d_{10}). Sterol quantification was carried out using five-point calibration plot containing 5, 10, 25, 50, and $60 \, mg \, L^{-1}$ sterol standard mixtures and $20 \, mg \, L^{-1}$ internal standards (5α-cholestane).

2.5. GC-ECD Analysis. Separation of chlorpyrifos was achieved using HP7890A gas chromatographs equipped with 63Ni electron capture detectors, GC-ECD (Agilent Technologies Inc., Palo Alto, CA, USA). A 30 m × 0.25 mm id × 0.25 μm film thickness HP5-MS capillary column (Agilent technologies) was used for the quantitative analysis of chlorpyrifos. The injection port and detector temperatures were set at $250°C$. The injection volume was $1 \mu L$, and the splitless period following the injection was 2 min. The ECD detector utilised pure N_2 (>99.999%) as a carrier and make-up gas at a controlled constant velocity of $60 \, mL \, min^{-1}$. The temperature program of the HP5-MS column was set to $150°C$ for 1 min. then increased at $25°C \, min^{-1}$ to $260°C$ for 8 minutes. Compounds were identified based on the retention time of the standards and quantified by external standard calibration.

2.6. GC-MSD Analysis. Phenol and pentachlorophenol were analysed using an Agilent Technologies gas chromatography 6890N Network GC system equipped with an Agilent Technologies 5973 Inert Mass Selective Detector and Agilent 7683 Series Injector. Compounds were separated on a cross-linked fused silica capillary column HP5-MS (30 m × 250 m × 0.25 m). Standards and samples ($1 \mu L$) were injected in the pulsed splitless mode with a 1 min hold of injection pulse pressure at 50 kPa. The temperature programmed was setat an initial $50°C$, followed by an increase at $10°C \, min^{-1}$ to $200°C$ and a holding time of 15 min. The MS detector was operated in the full scan mode with a 70 eV electrons ionisation, by scanning a mass range of m/z 50–550 in 0.45 s.

3. Results and Discussion

Prior to this study, optimization of PLE operating parameters (extraction temperature, pressure, and static extraction time) was conducted. The parameters of the model were estimated by Multilinear regression using the Design expert 6.0.4 programme, a software for Design of Experiment and Optimisation. The effect of three independent variables at five levels, A: temperature ($50–200°C$), B: pressure (391–2409 psi), and C: static time (2–18 min), were evaluated using response surface methodology (RSM). The optimal condition was obtained using predicted equation determined by RSM. Extraction at temperature of $125°C$, pressure of 1400 psi, and static time

of 10 min were chosen as the optimised conditions with desirability of 0.899.

A number of sorbents were tested for the isolation of organic compounds from extract solutions, such as alumina, Florisil, ion exchange resins, silica, and bonded silica sorbents (octadecyl, octyl phenyl, cyanopropyl, and diol) based on SPE sorbents [7]. A preliminary study was conducted [8] using silica and Florisil packed in an ASE extraction cell to extract PAHs and sterols using two ASE elution steps: the first elution to extract nonpolar compounds (PAHs) using nonpolar solvent (*n*-hexane) and the second elution using a more polar solvent (acetone, isopropanol, DCM : MeOH (1 : 1, v/v) and DCM : Hexane (40 : 60, v/v), and methanol) to extract the more polar compounds (sterols). Methanol was found to be the most efficient solvent compared to other solvents in extracting sterols from soil [8]. These results were supported by the previous studies [2, 6, 9] wherein the nonpolar organic compounds (e.g., PAHs, OCPs) poorly retained on polar sorbents could be eluted using a nonpolar elution solvent such as hexane, heptane or a benzene-hexane mixture. According to Covaci and Voorspoels [10], activated silica can be used as a trapping layer for polar material such as cholesterol. In this study, the same approach was extended to a wide range of polarities of organic contaminants (PAHs, chlorpyrifos, pentachlorophenol sterols, and phenol). Sequential extraction using solvents with different polarities was able to selectively separate these compounds.

3.1. Effect of the Type of Sorbent on the Efficiency of Extraction. Based on previous research, in this study, silica, Florisil, and alumina were tested in the PLE extraction cell at two levels of dosages (5 g and 10 g). As shown in Table 1, in general, good recoveries and reproducibility of PAHs, chlorpyrifos phenol, sterols and pentachlorophenol (PCP) were obtained using 5 g of sorbents (silica, Florisil and alumina). The slightly low values observed for PAHs extracted using 10 g of sorbents may be due to the greater attractive forces between the carbon-hydrogen bonds in the compound and the functional groups on the sorbent surfaces at higher dosage of sorbent [11].

The recoveries of sterols and phenol were slightly higher to the recovery of PAHs when silica was used as the sorbent compared to alumina and Florisil. Silica, the most polar sorbent, has a strong capacity to retain polar compounds (phenol and sterols) and can be eluted using more polar solvent (methanol). The nonpolar PAHs and chlorpyrifos which are not retained can be easily eluted by nonpolar solvent (*n*-hexane) in the first fraction. Since pentachlorophenol has log K_{ow} quite similar to that of PAHs with four to five rings [12], it can also be eluted in the *n*-hexane fraction.

Florisil (magnesia-loaded silica gel) has been widely used in the determination of organochlorine pesticides in soils [2, 13] and sterols in marine sediment [14]. Florisil exhibited similar characteristic to those of silica and alumina, as 5 g of this sorbent was able to recover about 73.9–114.0% of PAHs, 104.7% chlorpyrifos and 68.9% of PCP in the first elution using *n*-hexane. Satisfactory recovery of phenol (98.2%) was

Table 1: Effect of various sorbent types on the multiresidual extraction of PAHs, chlorpyrifos, phenol, pentachlorophenol, and sterols from spiked soil.

	Recovery % (RSD %), ($n = 3$)											
	Silica				Alumina				Florisil			
						Fraction number						
	5 g		10 g		5 g		10 g		5 g		10 g	
Analyte	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Naphtalene	87.1 (8.8)	nd	83.2 (9.0)	nd	87.0 (4.7)	nd	87.8 (0.6)	nd	73.9 (12.9)	nd	70.4 (7.8)	nd
Acenaphtalene	91.6 (11.2)	nd	87.2 (12.4)	nd	97.4 (2.4)	nd	106.9 (4.6)	nd	89.1 (5.6)	nd	80.1 (6.2)	nd
acenaphthene	94.2 (2.1)	nd	87.8 (9.5)	nd	102.6 (1.6)	nd	104.8 (1.3)	nd	96.8 (4.1)	nd	84.7 (6.8)	nd
Fluorene	94.2 (3.4)	nd	94.8 (3.3)	nd	96.6 (1.1)	nd	90.6 (3.6)	nd	102.5 (0.7)	nd	90.0 (6.0)	nd
Pyrene	96.2 (2.8)	nd	91.3 (5.1)	nd	96.2 (1.6)	nd	86.2 (6.8)	nd	96.9 (1.9)	nd	92.7 (2.7)	nd
BaA	93.9 (10.4)	nd	67.4 (10.0)	31.2 (4.8)	65.3 (3.4)	9.6 (4.0)	44.1 (11.7)	16.5 (4.0)	98.8 (0.3)	nd	99.5 (4.0)	nd
BaP	95.8 (13.2)	nd	58.3 (2.4)	28.3 (3.4)	53.2 (5.8)	36.9 (8.5)	12.3 (4.2)	52.4 (9.2)	114.0 (4.0)	nd	106.0 (9.3)	nd
Chlorpyrifos	102.9 (1.7)	nd	22.8 (10.1)	88.0 (4.7)	106.8 (8.5)	53.3 (11.9)	27.8 (1.6)	92.8 (1.6)	104.7 (10.4)	nd	106.8 (8.5)	nd
Phenol	nd	91.9 (2.1)	n.a	n.a	nd	90.9 (2.9)	nd	101.7 (3.5)	nd	98.2 (6.3)	nd	89.6
PCP	106.2 (4.2)	nd	n.a	n.a	70.4 (9.6)	nd	24.5	nd	68.7 (10.2)	nd	36.3	nd
Coprostanol	nd	100.5 (2.1)	nd	103.3 (7.2)	nd	86.8 (1.3)	nd	88.3 (5.4)	44.2 (6.1)	32.5 (0.3)	27.7 (5.0)	50.7 (0.8)
Cholesterol	nd	100.1 (11.1)	nd	103.9 (0.6)	nd	91.7 (0.5)	nd	95.2 (8.8)	36.1 (8.0)	50.4 (4.1)	18.0 (9.2)	72.6 (0.9)
Stigmasterol	nd	97.5 (3.0)	nd	99.6 (5.8)	nd	94.5 (3.5)	nd	94.7 (4.2)	nd	98.9 (5.0)	nd	102.4 (2.3)
Stigmastanol	nd	93.7 (5.0)	nd	99.3 (3.3)	nd	94.9 (1.5)	nd	94.9 (3.9)	39.1 (3.6)	53.1 (5.2)	19.0 (4.1)	75.0 (0.5)

Fraction 1: *n*-hexane.
Fraction 2: methanol (MeOH).
n.a: not available (not tested).

obtained in the second elution using methanol. The recoveries of sterols were slightly reduced when using alumina. As shown in Table 1, sterols were eluted in both fractions (n-hexane: 36.1–44.2%; methanol: 32.5–98.9%). The results suggest that sterols were not strongly retained on Florisil and thus were partly eluted in nonpolar solvent (n-hexane) as reported by Li et al. [14]. The performance of silica and Florisil was similar for PAHs extraction (first extraction using n-hexane), whereas silica and alumina showed satisfactory recoveries for sterols and phenol (second extraction using methanol). Florisil showed good recoveries for PAHs but low recoveries of sterols and pentachlorophenol (68.7%). On the other hand, alumina gave high recoveries of sterols and slightly better results for PAHs compared to Florisil. Increasing the amount of alumina resulted in lower recovery of high molecular weight PAHs (benzo[a]anthracene, benzo[a]pyrene) and pentachlorophenol. Based on the recoveries obtained in these studies using two sorbents at two levels, silica (5 g) is a more effective sorbent for simultaneously extracting compounds with different polarity (PAHs, chlorpyrifos, phenol, pentachlorophenol, and sterols) from soil than Florisil and alumina. Therefore, further studies were conducted using silica in the PLE extraction cell.

3.2. Capacity of Silica as a Sorbent in PLE.

The capability of this sorbent to retain polar compounds was further studied using several amounts of this sorbent (1, 3, 4, 5, and 10 g). Table 2 shows the recoveries of PAHs from the first extraction using n-hexane and sterols in the second extraction using methanol. The results showed that the recoveries (%) of PAHs were in an acceptable range using 1 g to 5 g of silica. However the recoveries of benzo[a]anthracene and benzo[a]pyrene were slightly reduced (67.4% and 58.3%, resp.) when 10 g of silica were used, showing that these compounds were trapped and could not be efficiently eluted with n-hexane due to the availability of more surface area and binding sites (functional groups) at higher dosage of sorbent [11]. The recoveries of sterols were significantly reduced when less than 5 g of silica were used as some of these compounds were extracted together with the nonpolar compounds (PAHs) in the first extraction.

3.3. Method Validation.

The linearity of the method was studied using soil samples spiked with PAHs (naphthalene, acenaphtalene, acenaphthene, fluorene, pyrene, benzo[a]anthracene, and benzo[a]pyrene) and sterols (coprostanol, cholesterol, stigmasterol, stigmastanol) at levels of 5, 10, 20, 40, and $60 \, \mu g \, mL^{-1}$. Good linearity was obtained for all compounds with a correlation coefficient (r^2) in the range of 0.9910 to 0.9998 (Table 3). The method was found to be precise (RSD < 9%) and accurate, with satisfactory recoveries, between 85 to 98% for PAHs and 97 to 104% sterols in spiked soil. The instrumental limit of detection (LOD) and limit of quantification (LOQ) were calculated on the basis of 3 : 1 and 10 : 1 signal to noise ratios, respectively, using the standard solution containing the compounds at the lowest concentration levels (Table 3). In order to estimate the accuracy and precision of the method developed, a reference
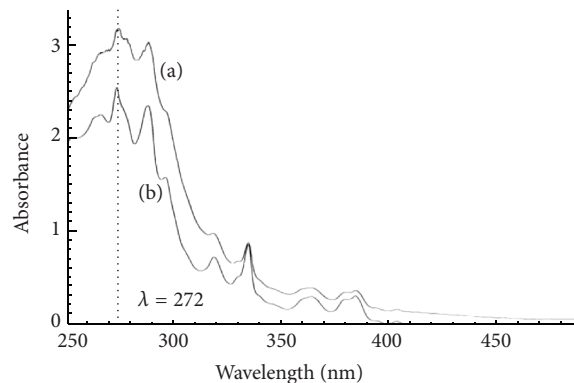

FIGURE 2: UV-vis spectra of the PLE extract (a) without silica (no cleanup) and (b) with silica [15].

soil (CRM1944) was extracted in triplicate using selective PLE at the optimum conditions. The extraction conditions and the results are presented in Table 4. It was found that no statistical differences at 95% confidence level ($P > 0.05$) for all values of PAHs (naphthalene, pyrene, benzo[a]anthracene, and benzo[a]pyrene) were obtained.

3.4. Extraction of Native Contaminated Soil.

In this study, the efficiency of the developed method was compared to the EPA Method 3545 [16] using native contaminated soil and spiked soils. The comparison results are tabulated in Table 5. It was found that the amount and recoveries of PAHs (naphthalene, acenaphtalene, acenaphthene, fluorine, pyrene, benzo[a]anthracene, benzo[a]pyrene) and sterols (coprostanol, cholesterol, stigmasterol, stigmastanol) for both extraction methods were comparable ($P > 0.05$ at 95% confidence level) with lower relative standard deviations (RSDs) compared to that of EPA Method 3545. High recoveries of benzo[a]anthracene, benzo[a]pyrene, and stigmasterol from the extraction using the standard EPA method 3545 may be associated with the coextractant present in the soil samples.

The color of the extracts may indicate the presence of coeluting interfering compounds that could damage the chromatographic system [13]. When using sorbent (silica) inside the PLE extraction cell, a pale yellow color of extract was obtained while without the presence of sorbent, a relatively dark yellow color was observed. Figure 2 shows that the absorbance of humic substances in the soil extract ($\lambda = 272$) [17] was slightly reduced due to the effect of silica cleanup. Therefore, the use of sorbent in the PLE extraction cell, followed by elution using solvent with different polarities was not only able to separate different classes of compounds, but was also able to produce a cleaner extract ready for gas chromatographic analysis.

4. Conclusion

In this study, silica (5 g) incorporated into the extraction cell was found to be an effective sorbent for performing multiresidual extraction of analytes with a broad range of

TABLE 2: Amount of silica used to perform selective extraction of PAHs and sterols from soil samples.

| Compound | Amount of silica % Recovery (RSD %); ($n = 3$) | | | | | | | | | |
| | 10 g | | 5 g | | 4 g | | 3 g | | 1 g | |
	[a]1st	[b]2nd	1st	2nd	1st	2nd	1st	2nd	1st	2nd
Naphtalene	83.2 (9.0)	nd	87.1 (8.8)	nd	94.9 (7.2)	nd	92.0 (4.1)	nd	87.5 (4.9)	nd
Acenaphtalene	87.2 (12.4)	nd	91.6 (11.2)	nd	92.9 (7.1)	nd	100.4 (7.9)	nd	95.6 (3.8)	nd
acenaphthene	87.8 (9.5)	nd	94.2 (2.1)	nd	95.4 (9.2)	nd	94.4 (4.3)	nd	95.5 (2.7)	nd
Fluorene	94.8 (3.3)	nd	94.2 (3.4)	nd	100.2 (8.8)	nd	86.3 (5.0)	nd	95.9 (4.4)	nd
Pyrene	91.3 (5.1)	nd	96.2 (2.8)	nd	99.7 (2.9)	nd	87.9 (8.8)	nd	99.6 (3.4)	nd
Benzo[a]anthracene	67.4 (10.0)	31.2 (4.8)	90.9 (10.4)	nd	97.5 (7.2)	nd	93.3 (2.8)	nd	95.3 (6.7)	nd
Benzo[a]pyrene	58.3 (2.4)	28.3 (3.4)	91.4 (13.2)	nd	94.7 (12.8)	nd	94.5 (4.0)	nd	99.1 (3.4)	nd
Coprostanol	nd	103.3 (7.2)	nd	100.5 (2.1)	12.1 (2.5)	87.0 (5.6)	23.4 (3.4)	81.0 (1.4)	52.8 (12.7)	40.2 (18.6)
Cholesterol	nd	103.9 (0.6)	nd	100.2 (11.1)	5.9 (3.9)	90.9 (5.5)	16.8 (2.7)	90.9 (4.4)	20.7 (21.3)	60.8 (3.1)
Stigmasterol	nd	99.6 (5.8)	nd	97.5 (3.0)	nd	101.0 (2.5)	nd	98.5 (0.4)	25.6 (15.6)	66.9 (5.1)
Stigmastanol	nd	99.3 (3.3)	nd	93.7 (5.0)	6.9 (1.7)	91 (4.8)	18.5 (2.1)	79.7 (3.9)	33.2 (21.4)	51.7 (7.7)

[a]1st: first extraction (*n*-hexane).
[b]2nd: second extraction (MeOH).
Note: chlorpyrifos, phenol, and pentachlorophenol were not included in this experiment.

TABLE 3: Analytical performance on the proposed method, PLE packed with silica in the extraction cell.

Compound	Linear response (r^2)	Instrumental LOD (μg/mL)	Instrumental LOQ (μg/mL)	Precision RSD (%) ($n = 7$)
Naphthalene	0.9963	0.050	0.165	2.0
Acenaphthalene	0.9990	0.050	0.165	8.8
Acenaphthene	0.9970	0.050	0.165	2.7
Fluorene	0.9965	0.100	0.333	1.0
Pyrene	0.9910	0.100	0.333	0.7
Benzo[a]anthracene	0.9944	0.100	0.333	2.5
Benzo[a]pyrene	0.9993	0.100	0.333	2.4
Chlorpyrifos	0.9975	0.054	0.018	5.1
Coprostanol	0.9997	0.100	0.333	1.8
Cholesterol	0.9992	0.100	0.333	1.9
Stigmasterol	0.9939	0.100	0.333	0.9
Stigmastanol	0.9998	0.500	1.650	1.8
β-Sitosterol	0.9972	0.200	0.667	3.8
Phenol	0.9981	0.050	0.165	3.9
Pentachlorophenol	0.9985	0.250	0.833	7.6

TABLE 4: PAH concentration found in the reference soil CRM1944 (NIST, New York/New Jersey Waterway Sediment), using selective PLE (0.5 g of soil, 5.0 g of silica packed inside the extraction cell, solvent: n-hexane, 125°C, 1400 psi, 10 min static extraction). All values are expressed in mg/kg dry mass.

Compound	Concentration found (mg/kg dry mass), $n = 3$	Certified concentration values (mg/kg dry mass)
Naphtalene	1.51 ± 0.17	1.65 ± 0.31
Pyrene	7.68 ± 0.41	9.70 ± 0.42
Benzo[a]anthracene	4.10 ± 0.29	4.72 ± 0.11
Benzo[a]pyrene	4.20 ± 0.01	4.30 ± 0.13

TABLE 5: Amount of PAHs and sterols (μg/kg) extracted from native contaminated soil and recoveries (%) of PAHs and sterols from spiked soil using optimum PLE conditions with silica (5 g) inside the extraction cell and without silica using EPA Method 3545.

Compound	Native contaminated soil ($n = 3$)		Spiked soil ($n = 3$)	
	With addition of silica in ASE extraction cell[a]	EPA method 3545[b]	With addition of silica in ASE extraction cell[a]	EPA method 3545[b]
Naphthalene	1746.2 (6.0)	1999.9 (12.0)	78.4 (7.2)	77.4 (10.2)
Acenaphthalene	770.0 (28.7)	968.4 (20.4)	90.1 (9.6)	91.4 (5.8)
Acenaphthene	1630.8 (0.8)	1399.0 (3.6)	96.7 (12.6)	95.2 (3.2)
Fluorene	1674.5 (2.9)	1666.7 (11.4)	104.1 (4.5)	105.3 (3.5)
Pyrene	851.3 (5.0)	821.8 (4.4)	99.3 (12.0)	102.8 (9.4)
Benzo[a]anthracene	1867.5 (19.7)	2136.3 (43.1)	94.2 (5.8)	122.0 (9.5)
Benzo[a]pyrene	2266.2 (13.2)	2029.6 (10.6)	92.0 (6.0)	133.6 (32.7)
Coprostanol	1888.8 (17.0)	2215.4 (15.0)	95.7 (7.9)	96.6 (2.2)
Cholesterol	4067.6 (21.3)	3135.6 (23.1)	97.0 (7.5)	104.7 (3.3)
Stigmasterol	2397.5 (20.0)	2037.0 (14.3)	123.9 (12.0)	275.4 (6.2)
Stigmastanol	1517.1 (8.1)	2074.1 (34.3)	99.1 (6.7)	96.6 (3.3)
β-Sitosterol	8169.0 (8.7)	7599.2 (19.7)	n.a	n.a

[a] 5 g silica packed in the cell; PLE parameters: 125°C, 1400 psi, 10 min (optimum conditions); solvent: (1st extraction: n-hexane, 2nd extraction: methanol).
[b] PLE parameters: 100°C, 1500 psi, 5 min (EPA Method 3545); solvent: DCM [14].
n.a: not available (not tested).
Relative standard deviation (in parentheses).
Note: chlorpyrifos, phenol, and pentachlorophenol were not included.

polarities (PAHs, chlorpyrifos, phenol, pentachlorophenol, and sterols). Using this approach, two sequential PLEs for the same sample were performed: the first with a nonpolar solvent (n-hexane) to extract the less polar compounds (PAHs, pentachlorophenol, and chlorpyrifos) and the second with a more polar solvent (methanol) to extract the more polar analytes (phenol and sterols). By using suitable sorbents and solvents, the extraction method can be manipulated and simplified for various analytes according to their polarities. In addition, the use of sorbent produces a cleaner extract for gas chromatographic analysis. Good precision (RSDs below 9%) demonstrates the promise of the developed method.

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References

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