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Simultaneous Extraction and Fractionation of Polycyclic Aromatic Hydrocarbons and Their Oxygenated Derivatives in Soil Using Selective Pressurized Liquid Extraction

Staffan Lundstedt,* Peter Haglund, and Lars Öberg

Environmental Chemistry, Department of Chemistry, Umeå University, SE-901 87 Umeå, Sweden

In this study, a selective pressurized liquid extraction (PLE) method which can extract polycyclic aromatic hydrocarbons (PAHs) and their oxygenated derivatives (oxy-PAHs) from contaminated soil and simultaneously separate them into two fractions was developed. The method uses extraction cells packed with a chromatographic adsorbent and extraction solvents of increasing polarity. Several experiments were conducted on both spiked and authentic contaminated soil samples. Different types of adsorbents, combinations of extraction solvents, and extraction temperatures were tested in order to find a method that could fulfill the purpose of the study. The final method was based on extraction cells packed with 2% deactivated silica gel. The PAHs were extracted with cyclohexane/dichloromethane (9:1) at 120 °C, after which the oxy-PAHs where extracted with cyclohexane/dichloromethane (1:3) at 150 °C. The PAHs and oxy-PAHs were efficiently separated into two fractions, and only trace amounts of some compounds were found in the inappropriate fraction. The recoveries of the PAHs were mostly above 70% and of the oxy-PAHs, above 90%. The linearity of the method was good, and the calibration curves for most compounds had a regression coefficient better than 0.99 and an intercept close to the origin of coordinates. When the selective PLE method was applied to seven authentic soil samples, the results were found to be in good agreement with those of a reference method based on Soxhlet extraction and silica gel cleanup and also in good agreement with the certified reference values available for one of the soils. The selective PLE method is faster and consumes less solvent than a traditional method based on separate extraction and fractionation steps. The selective PLE method is, therefore, suitable for the concurrent analysis of PAHs and oxy-PAHs during large-scale soil contamination studies. This will provide more information about the soil contamination and the levels of toxicity than an ordinary PAH analysis.

Polycyclic aromatic hydrocarbons (PAHs) are common pollutants in the environment, and particularly high concentrations are found at sites contaminated with coal tar and creosote.[1] PAHs are of particular concern since they are known to be toxic, mutagenic, and carcinogenic.[2] However, at contaminated sites, other toxicologically relevant compounds may also be present.[3] For example, during degradation of PAHs, a variety of transformation products may be formed, including ketones, quinones, phenols, and carboxylic acids.[4−6] Although many of these are short-lived in the environment, some are persistent and are likely to be found at significant concentrations. The PAH ketones and PAH quinones (i.e. oxygenated PAHs or oxy-PAHs) are among the most persistent of these transformation products and have thus been found, together with PAHs, in contaminated soil,[3,7] diesel exhaust,[8] fly ash,[9] urban aerosols,[10,11] sediments,[12] and sewage sludge.[13] The oxy-PAHs are formed through natural biotic and abiotic processes, but their formation may also be enhanced during processes in which the degradation of PAHs is accelerated; for instance, during soil remediation.[3,14−16] If oxy-PAHs accumulate during soil remediation, this could lead to an augmentation of soil toxicity or an increase in the persistence of toxic hazard, even if the parent PAHs are degraded. Therefore, it may be necessary to monitor not only PAHs, but also oxy-PAHs during the remediation of PAH-contaminated soil. The oxy-PAHs should also be taken into account during characterization and risk assessment

* Corresponding author. Current address: Mutagenesis Section, Safe Environments Program, Health Canada, Tunney's Pasture 0803A, Ottawa, Ontario, K1A 0K9, Canada. Phone: +1-613-957-3135. Fax: +1-613-941-8530. E-mail: staffan_lundstedt@hc-sc.gc.ca or staffan.lundstedt@chem.umu.se.

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Table 1. Description of the Soils Used during the Development of a Selective Pressurized Liquid Extraction Method for PAHs and Oxy-PAHs in Soil

soil sample	site description/activity	period of activity	soil description	LOI (%)	approximate PAH levels (mg/kg)[a]
uncontaminated Lund, Sweden	grassland		sand	1.0	<0.1
CRM 103-100	superfund site, western USA			15	7300
Husarviken, Stockholm, Sweden	gasworks	1893−1972	sandy fill material	5.5	3000
Holmsund, Umeå, Sweden	wood impregnation	1943−1983	sandy till	0.9	1600
Moråsen, Boden, Sweden	wood impregnation	1954−1998	sandy fill material	1.6	20
Luleå, Sweden	coke production	still active	sediment (from a water ditch)	9.7	400
Forsmo, Sollefteå, Sweden	wood impregnation	1933−1950	fine sand	2.2	1900
Hässleholm, Sweden	wood impregnation	1946−1965	coarse sand, fill material	1.6	1500

[a] Based on previous PAH analyses including 23 PAHs: naphthalene, 2-methylnaphthalene, 1-methylnaphthalene, acenaphthylene, acenaphthene, 2,6-dimethylnaphthalene, fluorene, 2,3,5-trimethylnaphthalene, phenanthrene, anthracene, 1-methylphenanthrene, fluoranthene, pyrene, benzo[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, dibenz[*a,h*]anthracene, indeno[*cd*-]pyrene, and benzo[*ghi*]perylene.

of contaminated sites. However, as yet, oxy-PAHs and other transformation products of PAHs have been analyzed in only a few studies, probably because the required analytical methods are costly and complex.

Analysis of PAHs and oxy-PAHs from soil generally involves exhaustive extraction techniques, such as Soxhlet[7] or ultrasonic extraction,[16] using solvent mixtures of different polarities to release all target compounds from the soil matrix. This is followed by fractionation according to polarity by open-column adsorption chromatography or solid-phase extraction (SPE) using silica or alumina as the chromatographic material.[7,11,13,16] With such a procedure, the compound classes are well-separated, and good recoveries are obtained for PAHs and oxy-PAHs present in contaminated soil; however, these methods are tedious and costly if many samples are going to be analyzed; for example, during soil remediation projects. A faster screening method is, therefore, desirable.

Recently, pressurized liquid extraction (PLE) has proven to be a fast and efficient alternative to traditional extraction methods for many types of contaminants. The technique, which is based on extraction at elevated pressure and temperature, can be used with the same solvents as those used for Soxhlet extraction.[17] The ability of PLE to extract PAHs from soil has been evaluated in several studies,[17,18] and its capability to extract oxy-PAHs from soil has also been investigated.[19] Nevertheless, the PLE extracts are still complex and need to be fractionated before analysis. The aim of this study was to develop a selective PLE method that combines exhaustive extraction with *in-cell* fractionation of PAHs and oxy-PAHs present in contaminated soil. Similar techniques have previously been used to retain fat and other interferences during extraction of polychlorinated biphenyls (PCB) from lard and fish meal;[20] polybrominated diphenyl ethers (PBDEs) from sediment;[21] PAHs from soils;[22] and dioxins from food, feed, and fly ash.[23−25] However, to the best of our knowledge, it has never been used for simultaneous extraction and class separation of organic pollutants in soil.

EXPERIMENTAL SECTION

Sample. In this study, eight different soils were used. Information about these soils is compiled in Table 1. The first soil listed was uncontaminated and was spiked with various PAHs and oxy-PAHs before use. The second soil was a certified reference material (CRM 103−100) from Resource Technology Corporation (RTC, Laramie, WY). The rest of the soils were collected at different PAH-contaminated sites in Sweden: one gasworks site, one coke-production site, and four wood-impregnation sites. The soils were sieved (2.0 mm mesh) and air-dried at room temperature before use. The organic content of the soils was determined by heating samples at 130 °C overnight, and then at 550 °C for 2 h. The loss on ignition (LOI) was determined gravimetrically. One to five grams of each soil (depending on the expected PAH concentration) was thoroughly homogenized with 20 g of anhydrous sodium sulfate prior to extraction.

Chemicals. All solvents used (acetone, cyclohexane, dichloromethane, *n*-hexane, *n*-pentane, and toluene) were of analytical or glass-distilled grade. Silica gel 60 (0.063−0.20 mm, Merck, Darmstadt, Germany), alumina (0.05−0.15 mm, pH 9.5, Fluka, Buchs Switzerland), and Florisil (60−100 mesh, Kebo Lab, Spånga, Sweden) were activated for 24 h at 130 °C prior to use. Sodium sulfate p.a. (Merck, Darmstadt, Germany) was activated for 48 h at 550 °C before use. As internal standards (IS), a mixture of perdeuterated PAHs (32−37 μg/g in toluene) and the oxy-PAH 2,3-dimethylanthracenedione (22 μg/g in toluene) was used. The mixture of perdeuterated PAHs contained [$^2H_8$]naphthalene, [$^2H_8$]-acenaphthylene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]fluorene, [$^2H_{10}$]anthracene, [$^2H_{10}$]pyrene, [$^2H_{12}$]benz[*a*]anthracene, [$^2H_{12}$]benzo[*k*]-fluoranthene, [$^2H_{12}$]benzo[*ghi*]perylene. As a recovery standard

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(RS), the perdeuterated PAH [$^2H_{10}$]fluoranthene (33 μg/g toluene) was used. All perdeuterated compounds were obtained from Cambridge Isotope Laboratories (Andover, MA). The 2,3-dimethylanthracenedione as well as all the oxy-PAHs used for quantification, that is, 1-indanone, 9-fluorenone, anthracene-9,10-dione, 2-methylanthracenedione, 7*H*-benz[*de*]anthracen-7-one, benz[*a*]anthracene-7,12-dione, naphthacene-5,12-dione, were obtained from Sigma-Aldrich (Stockholm, Sweden). The PAHs were quantified using a reference standard mixture containing 24 PAHs (SRM 2260, National Institute of Standards & Technology, Gaithersburg, MD).

Instrumentation. The selective pressurized liquid extraction was performed using an ASE 200 Accelerated Solvent Extraction system (Dionex, Sunnyvale, CA) equipped with 11-mL stainless steel extraction cells. The extracts were analyzed using a Fisons GC 8000 Top gas chromatograph (GC) with a 30 m × 0.25 mm i.d. DB-5 capillary column, film thickness 0.25 μm (J&W Scientific, Folsom, CA), coupled to an electron impact (EI) Fisons MD800 mass spectrometer. One-microliter aliquots were injected into the GC by an autoinjector. The GC was operated in splitless mode, and the MS was operated in full-scan mode for identification and single ion monitoring (SIM) mode for quantification. The target compounds were identified by mass spectra and by comparison of GC retention data with reference standards. Quantifications were performed using the internal standard technique, comparing peak areas in samples and reference standards.

PLE Extractions. Extraction cells, fitted with a cellulose filter to prevent clogging of the metal frit at the outlet of the cell, were packed with 4.0 g of silica gel or 5.0 g of either Florisil or alumina. An additional cellulose filter was placed on top of the adsorbent, and then 0.5−1 g (depending on the expected PAH concentration) of soil homogenate was added. On top of the homogenate, 50 μL of each IS mixture was added. Finally, the cells were filled with bulk material (Bulk Isolute Sorbent, International Sorbent Technology, UK), and a third cellulose filter was placed on the top. During the experiments with the uncontaminated soil, the analytes were spiked to the soil homogenate simultaneous to the IS. All extractions were performed at 14 MPa, with a flush volume of 100% and a purge time of 60 s. Two static cycles of 5 min each were used for each extraction solvent, except during the first screening experiments, in which the two first solvents (i.e. *n*-pentane and *n*-hexane) were used with one static cycle of 5 min each. During these screening experiments, the samples were extracted with four solvents in a sequence; namely, *n*-pentane, *n*-hexane, *n*-hexane/dichloromethane (3:1, v/v) and dichloromethane. However, during the following experiments, only two solvents were used, one to extract the PAHs and one to extract the oxy-PAHs. The type of adsorbent, the solvents, and the extraction temperature were varied among the experiments. All experiments were carried out in triplicate except during the initial screening, when single experiments were used. After extraction, a 10% aliquot (w/w) of each extract was transferred to a new vial, where it was evaporated down to 0.5−1 mL using a gentle stream of nitrogen. Toluene was added, and the extract was further evaporated to a final volume of 1 mL using the same technique. Before GC analysis, 50 μL of RS solution was added to each sample.

Reference Procedure. For validation of the selective PLE method, a reference procedure based on Soxhlet extraction and open-column liquid chromatography was used. About 1 g of each soil homogenate was then transferred to extraction thimbles, which were placed in a 150-mL Soxhlet apparatus. Fifty microliters of each IS mixture was added, and the soil was extracted with 150 mL of hexane/acetone (1:1, v/v) for 18 h. The extracts were evaporated to 1 mL of *n*-hexane by rotary evaporation, followed by gentle nitrogen blow down. Small portions of *n*-hexane were added a few times during this process to ensure that all acetone was evaporated from the extract. The sample extracts were fractionated using 15-mm (i.d.) columns packed with 5.0 g of silica gel (deactivated with 10% water, w/w) and 1 g of anhydrous sodium sulfate. Each column was rinsed with 20 mL of *n*-hexane before the sample was applied, and the column was eluted with 5 mL of *n*-hexane, followed by 15 mL of *n*-hexane/dichloromethane (3:1, v/v) and 30 mL of dichloromethane. The first fraction was discarded. The second fraction (containing PAHs) and the third fraction (containing oxy-PAHs) were collected in separate vials. These fractions were evaporated as described above, reconstituted in toluene, and spiked with 50 μL of RS.

RESULTS AND DISCUSSION

Method Development. Initially, the idea to selectively extract PAHs and oxy-PAHs from soil samples was tested on the soil from the gasworks site (Husarviken). Three different chromatographic adsorbents were investigated for their ability to separate the compound classes, namely, silica gel (activated and 5% deactivated), Florisil (1.2% deactivated), and alumina (1.2% deactivated). The extractions were carried out with four solvents in a sequence, that is, four fractions were collected. The results from these screening experiments are presented in Figure 1. The separation results were similar with either activated silica or deactivated Florisil packed in the extraction cells (Figure 1a and 1b). Low molecular weight PAHs were recovered mainly in the first fraction (*n*-pentane), and after the second solvent (*n*-hexane), most of the larger PAHs had also been extracted; however, significant amounts of PAHs with five or six fused rings were also found in the third fraction (*n*-hexane/dichloromethane, 3:1, v/v). These high molecular weight PAHs were retained somewhat more strongly by Florisil than by silica. Up to 25% of these PAHs were found in the third Florisil fraction, as compared to 6% in the third silica fraction. A similar pattern was also seen for the oxy-PAHs, which mainly eluted in fraction 3 when silica was used and in fraction 4 when Florisil was used. Nevertheless, the oxy-PAHs were not detected in the first two fractions in any of these experiments.

In the experiments using 5% deactivated silica, most of the PAHs were recovered in the first fraction (Figure 1c). Only PAHs with five or six fused rings were found in significant proportions in the second fraction (up to 40%). The oxy-PAHs were mainly found in fraction 3, but some started to elute already in fraction 2. In contrast, using alumina, most of the target compounds were retained until the third and fourth fractions (Figure 1d). Only PAHs with two and three fused rings were recovered to a significant extent in the first two fractions. The larger PAHs and the oxy-PAHs were eluted together in fractions 3 and 4. Surprisingly, the largest PAHs were even more strongly retained than the low molecular weight oxy-PAHs.

These screening experiments show that it might be difficult to achieve full separation of the PAHs and oxy-PAHs with alumina-packed extraction cells; however, using either silica- or Florisil-

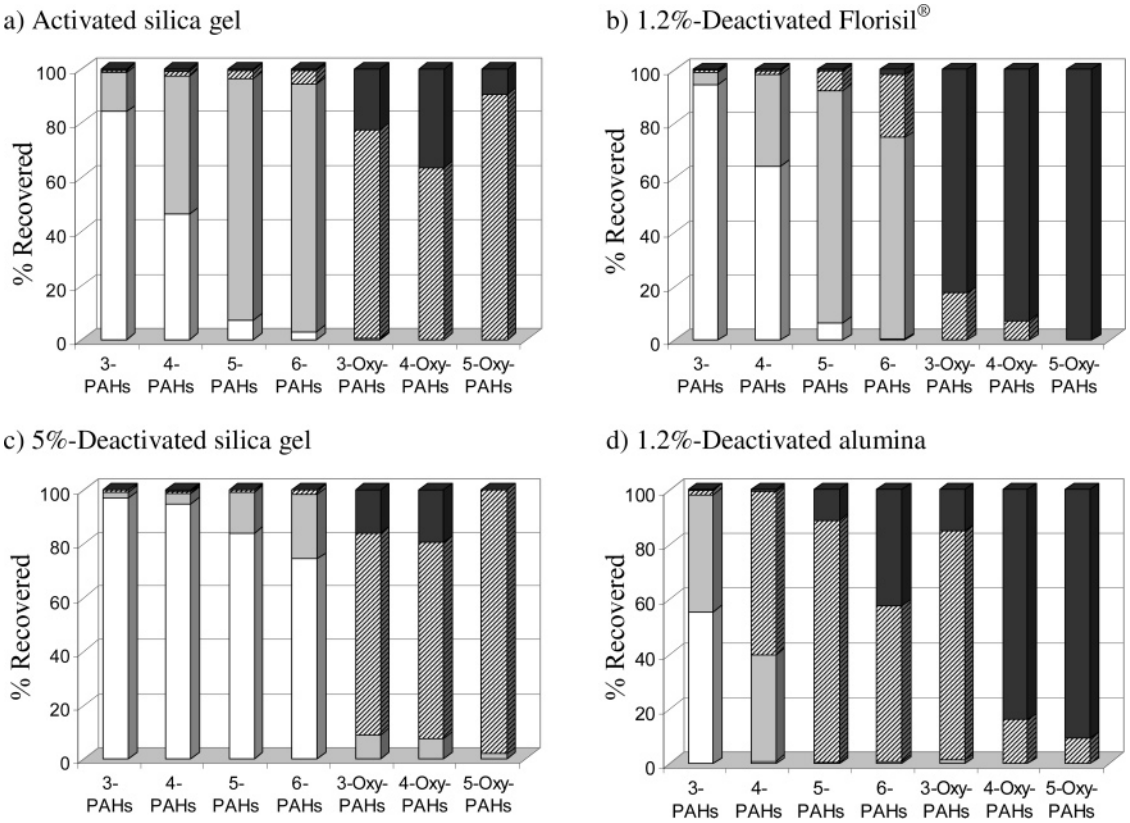

Figure 1. Results from the screening experiments performed during the development of a selective pressurized liquid extraction method for PAHs and oxy-PAHs in contaminated soil. Percentage of PAHs with three (3-PAHs), four (4-PAHs), five (5-PAHs), and six (6-PAHs) fused rings and oxy-PAHs with three (3-Oxy-PAHs), four (4-Oxy-PAHs), and five (5-Oxy-PAHs) fused rings recovered in each fraction. The samples, soil from the gasworks site at Husarviken, were extracted sequentially with *n*-pentane at 100 °C (white box), followed by *n*-hexane (gray box), *n*-hexane/dichloromethane (3:1, v/v) (striped box), and dichloromethane (black box) at 150 °C. The results are based on one experiment for each adsorbent.

filled cells, it should be possible to extract and quantitatively recover the two compound classes into separate fractions. In fact, with activated silica in the extraction cell, the separation was almost adequate, even during these first experiments. The PAHs were mainly recovered in the first two fractions, and the oxy-PAHs were exclusively recovered in the last two fractions. Silica was, therefore, chosen for the additional experiments.

Several experiments with silica-packed extraction cells were then conducted on both the gasworks soil and a soil spiked with different PAHs and oxy-PAHs. Various combinations of extraction solvents, extraction temperatures, and percentages of water in the silica gel were tested to fine-tune the separation. The choice between activated or deactivated silica was not obvious. When activated silica was used, stronger solvents were needed to elute the target compounds from the extraction cell (also seen during the screening experiments). This ensured that the target compounds were exhaustively extracted from the soil matrix. On the other hand, it also released more interfering substances from the soil and increased the risk that oxy-PAHs would be eluted in the fraction intended for PAHs. For the gasworks soil and the spiked soil, good results were obtained using a procedure with 2% deactivated silica and *n*-hexane at 150 °C to extract the PAHs, whereas many experiments with activated silica and stronger solvents at the same temperature resulted in a significant portion of the oxy-PAHs in the PAH fraction (data not shown).

However, since *n*-hexane, due to its low polarity, may have a limited capacity to desorb high molecular weight PAHs from complicated soil matrixes,[17] there is still a reason to use stronger, more polar solvents to extract the PAHs. To be able to do this without coeluting the oxy-PAHs among the PAHs, a lower extraction temperature may be used for the first fraction. Thus, the separation was optimized using cyclohexane with low percentages of dichloromethane and tuning the extraction temperature. The amount of water in the silica gel was kept at 2% during all these experiments. The optimal combination of conditions for the first fraction was found to be cyclohexane/dichloromethane (9:1, v/v) and 120 °C. In Figure 2, the results obtained using this method are compared to those obtained using 100% cyclohexane at 100 °C for the first fraction. Clearly, the latter combination was too weak to recover even the PAHs in the first fraction. The figure illustrates the importance of both extraction solvent and temperature for obtaining good separation of the compound classes. The optimal method employed 2% deactivated silica and cyclohexane/dichloromethane (9:1, v/v) at 120 °C to extract the PAHs and cyclohexane/dichloromethane (1:3, v/v) at 150 °C to extract the oxy-PAHs. This method was subjected to a subsequent validation process.

Method Validation. Initially, the method was validated through repeated extractions of a spiked soil sample. The results from these experiments are presented in Table 2. As seen, the two compound classes were well-separated and recovered from the soil. None of the oxy-PAHs were detected in the first fraction, and in the second fraction, only trace amounts of PAHs were detected (<0.5% of the amount found in the first fraction). The

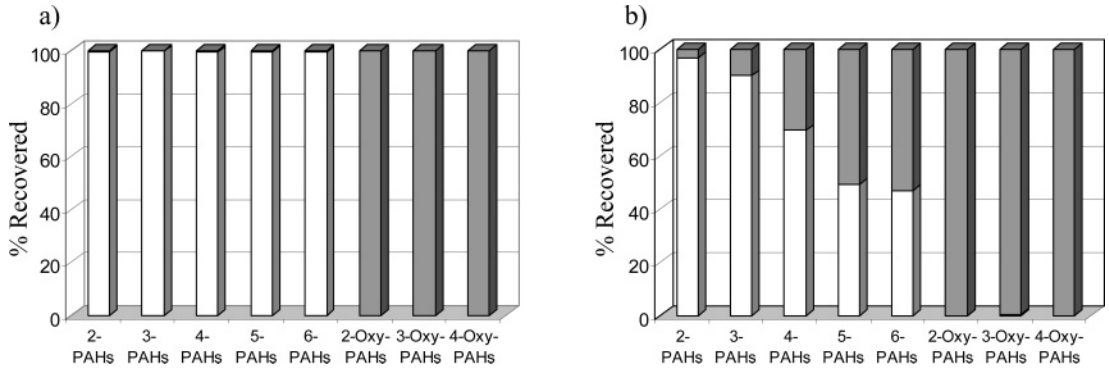

Figure 2. Results obtained during selective pressurized liquid extraction of PAHs and oxy-PAHs from a contaminated soil using (a) 2% deactivated silica gel sequentially extracted with cyclohexane/dichloromethane (9:1,v/v) at 120 °C (white box) and cyclohexane/dichloromethane (1:3, v/v) at 150 °C (gray box) and (b) 2% deactivated silica gel sequentially extracted with cyclohexane at 100 °C (white box) and dichloromethane at 150 °C (gray box). Percentage of PAHs with two (2-PAHs), three (3-PAHs), four (4-PAHs), five (5-PAHs), and six (6-PAHs) fused rings and oxy-PAHs with three (3-Oxy-PAHs), four (4-Oxy-PAHs), and five (5-Oxy-PAHs) fused rings recovered in each fraction. The results are averages based on three individual experiments.

recoveries of PAHs in the first fraction were between 55 and 91%. Lower recoveries (55−83%) were obtained for the low molecular weight PAHs, with two or three fused rings, which is not surprising considering their relatively high volatility. These compounds are frequently difficult to recover to a larger extent,[7,26] but may still be accurately quantified because the IS are lost to a similar extent. The recoveries for the oxy-PAHs were over 90% for all compounds except 1-indanone, which also is a relatively volatile compound. On the other hand, two of the oxy-PAHs showed recoveries significantly above 100%, namely, anthracene-9,10-dione (120%) and benz[*a*]anthracene-7,12-dione (129%). One possible explanation for this would be that these oxy-PAHs were formed from their parent PAHs (i.e., anthracene and benz[*a*]-anthracene) during the extraction process, and in this way increased the recovery above 100%. However, this was investigated through extractions of samples that had been spiked with PAHs only and was proven not to be the case (data not shown). Instead, the high values are probably due to coeluting interferences that increased the areas of the anthracene-9,10-dione and benz[*a*]-anthracene-7,12-dione peaks in the chromatograms. For some low-level samples, this might cause a problem. Overall, the recoveries were, however, acceptable, especially considering that the internal standards (i.e., the perdeuterated PAHs and 2,3-dimethylanthracenedione) were recovered to a similar extent as the target compounds (Table 2).

The next step in the validation process was to control the linearity of the method. Soils were spiked with PAHs and oxy-PAHs (the same as in Table 2) at four different levels (20−1500ng) and were then extracted. The linearity was good; for the naphthalenes (including the methylated naphthalenes), acenaphthylene, acenaphthene, and biphenyl, the correlation coefficient varied between 0.97 and 0.99, and for all other PAHs, it was above 0.99. For the oxy-PAHs, all correlation coefficients were above 0.99, except for benz[*a*]anthrecene-7,12-dione, for which it was 0.96. Furthermore, all intercepts were close to the origin of coordinates. In Figure 3, the calibration curves for fluoranthene and 7*H*-benz[de]anthracen-7-one are presented as examples. The spiking levels used were similar for all compounds.

Table 2. Extraction of PAHs and Oxy-PAHs from a Spiked Soil Using Selective Pressurized Liquid Extraction[a]

	fraction 1		fraction 2	
PAHs	recovered (%)	SD ($n = 3$)	recovered (%)	SD ($n = 3$)
naphthalene	55	2.0	0.47	0.17
[$^2H_8$]-naphthalene	*65*	*2.8*	*0.32*	*0.17*
2-methylnaphthalene	63	1.9	0.20	0.12
1-methylnaphthalene	63	1.9	0.21	0.11
acenaphthylene	62	2.4	0.090	0.032
biphenyl	68	2.5	0.12	0.053
acenaphthene	69	2.3	0.19	0.11
2,6-dimethylnaphthalene	68	3.2	0.10	0.023
[$^2H_8$]-acenaphthylene	*65*	*2.2*	*0.11*	*0.047*
[$^2H_{10}$]-acenaphthene	*72*	*0.73*	*0.073*	*0.063*
fluorene	73	2.1	n.d.[b]	
2,3,5-trimethylnaphthalene	72	2.0	0.077	0.012
[$^2H_{10}$]-fluorene	*76*	*0.74*	*n.d.*[b]	
phenanthrene	83	4.2	0.30	0.092
anthracene	75	1.7	0.14	0.030
[$^2H_{10}$]-anthracene	*78*	*0.76*	*0.52*	*0.13*
1-methylphenanthrene	83	0.52	0.13	0.028
fluoranthene	82	1.3	0.54	0.27
pyrene	81	1.1	0.53	0.30
[$^2H_{10}$]-pyrene	*84*	*0.69*	*0.28*	*0.24*
benzo[*a*]anthracene	88	4.3	0.39	0.072
chrysene	85	4.0	0.42	0.077
[$^2H_{12}$]-chrysene	*88*	*2.4*	*0.26*	*0.082*
benzo[*b*]fluoranthene	91	3.8	0.53	0.14
benzo[*k*]fluoranthene	83	7.1	0.40	0.050
benzo[*e*]pyrene	86	8.0	0.41	0.013
benzo[*a*]pyrene	80	8.3	0.32	0.043
perylene	74	7.5	0.24	0.10
[$^2H_{12}$]-benzo[k]fluoranthene	*86*	*5.4*	*0.31*	*0.07*
dibenz[*a,h*]anthracene	84	10	0.46	0.19
indeno[*cd*]pyrene	85	11	0.49	0.12
benzo[*ghi*]perylene	82	8.9	0.43	0.14
[$^2H_{12}$]-benzo[ghi]perylene	*85*	*7.5*	*0.43*	*0.19*
Oxy-PAHs				
1-indanone	n.d.[b]		47	18
9-fluorenone	n.d.[b]		94	5.9
anthracene-9,10-dione	n.d.[b]		120	7.2
2-methylanthracenedione	n.d.[b]		94	7.1
7*H*-benz[*de*]anthracen-7-one	n.d.[b]		129	26
benz[*a*]anthracene-7,12-dione	n.d.[b]		92	12
naphthacene-5,12-dione	n.d.[b]		114	20
2,3-dimethylanthracenedione	*n.d.*[b]		*93*	*8.7*

[a] Recoveries and standard deviations (triplicate samples) obtained by using 2% deactivated silica gel packed extraction cells, cyclohexane/dichloromethane (9:1, v/v) at 120 °C for fraction 1, and cyclohexane/dichloromethane (1:3, v/v) at 150 °C for fraction 2. Text in italics represent compounds that were added as internal standards. [b]Not detected.

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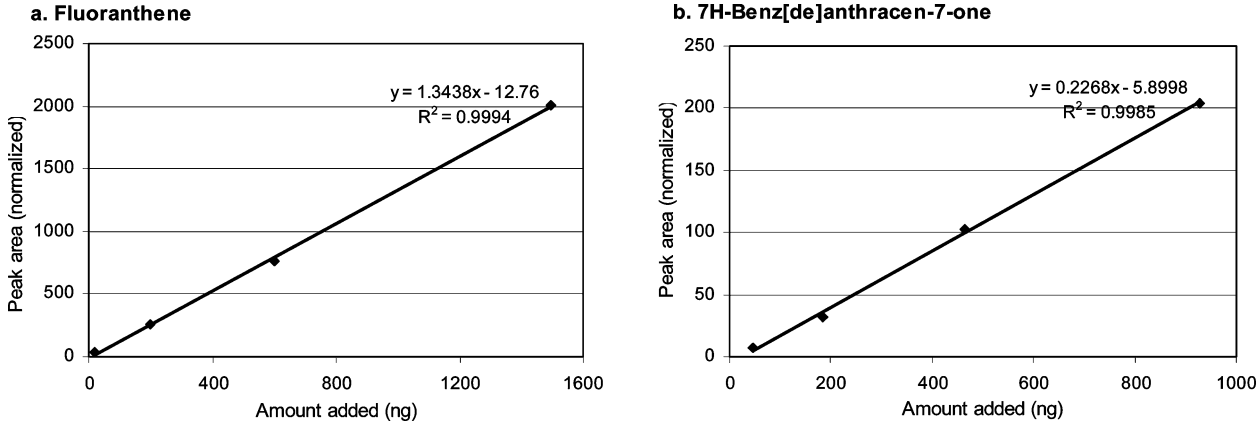

Figure 3. Selective pressurized liquid extraction of a soil spiked at four different levels. Calibration curves for (a) fluoranthene and (b) 7*H*-Benz[*de*]anthracen-7-one. Calibration curve equations and correlation coefficients are included in each panel.

Table 3. Concentrations of PAHs and Oxy-PAHs in Two Soils (Husarviken and CRM 103-100) Obtained through Selective Pressurized Liquid Extraction (PLE) and a Reference Method, Including Soxhlet Extraction and Open Column Chromatography (Sox)[a]

	Husarviken (mg/g)		CRM 103−100 (mg/g)		
PAHs	PLE	Sox	PLE	Sox	ref[a]
naphthalene	12 ± 2	13 ± 1	20 ± 1	27 ± 4	35 ± 4
2-methylnaphthalene	6.6 ± 0.7	7.9 ± 0.8	47 ± 3	43 ± 9	60 ± 7
1-methylnaphthalene	4.8 ± 0.5	6.4 ± 0.4	65 ± 5	59 ± 10	
biphenyl	3.4 ± 0.3	4.1 ± 0.3	23 ± 1	22 ± 4	
2,6-dimethylnaphthalene	6.8 ± 0.2	8.6 ± 0.2	290 ± 30	290 ± 40	
acenaphthylene	28 ± 4	19 ± 9	16 ± 2	17 ± 4	(17) ± 7
acenaphthene	2.8 ± 0.07	3.4 ± 0.3	630 ± 80	650 ± 80	627 ± 88
2,3,5-trimethylnaphthalene	2.6 ± 0.1	3.1 ± 0.2	86 ± 12	84 ± 9	
fluorene	38 ± 0.8	42 ± 0.8	370 ± 30	360 ± 50	443 ± 45
phenanthrene	410 ± 60	400 ± 70	1770 ± 130	1740 ± 360	1925 ± 209
anthracene	74 ± 10	67 ± 8	420 ± 30	420 ± 60	431 ± 42
1-methylphenanthrene	30 ± 3	27 ± 6	230 ± 30	250 ± 40	
fluoranthene	530 ± 40	510 ± 40	1270 ± 80	1200 ± 200	1426 ± 167
pyrene	370 ± 30	360 ± 30	1070 ± 70	1000 ± 180	1075 ± 141
benzo[*a*]anthracene	240 ± 20	250 ± 20	250 ± 30	250 ± 40	264 ± 24
chrysene	230 ± 30	240 ± 30	320 ± 40	320 ± 60	316 ± 30
benzo[*b*]fluoranthene	270 ± 50	250 ± 50	140 ± 10	140 ± 30	(115)
benzo[*k*]fluoranthene	110 ± 20	110 ± 20	51 ± 6	53 ± 9	(64)
benzo[*e*]pyrene	140 ± 20	140 ± 30	75 ± 6	76 ± 12	
benzo[*a*]pyrene	160 ± 30	150 ± 40	96 ± 9	96 ± 15	97 ± 12
perylene	48 ± 6	47 ± 9	24 ± 3	26 ± 2	
dibenz[*a,h*]anthracene	44 ± 10	39 ± 10	12 ± 6	11 ± 2	(14)
indeno[*cd*]pyrene	140 ± 50	130 ± 60	31 ± 4	31 ± 3	32 ± 8
benzo[*ghi*]perylene	120 ± 40	110 ± 40	30 ± 4	30 ± 2	(26)
Oxy-PAHs					
1-indanone	0.46 ± 0.2	0.69 ± 0.2	0.42 ± 0.2	0.63 ± 0.7	
1-acenaphthenone[b]	2.3 ± 0.3	1.9 ± 0.7	11 ± 1	11 ± 4	
9-fluorenone	83 ± 19	86 ± 20	340 ± 20	260 ± 50	
methyl-9-fluorenone (Σ 4 peaks)[b]	13 ± 0.2	16 ± 4	110 ± 9	91 ± 10	
anthracene-9,10-dione	51 ± 5	56 ± 11	250 ± 7	210 ± 20	
4H-cyclopenta[*def*]phenanthrene[b]	78 ± 17	110 ± 20	180 ± 4	150 ± 20	
2-methylanthracenedione	6.8 ± 0.6	8.4 ± 1	44 ± 2	38 ± 7	
4-oxapyrene-5-one[b]	3.3 ± 0.5	3.5 ± 1	3.7 ± 0.6	3.7 ± 0.9	
benzofluorenone (Σ 2 peaks)[b]	84 ± 7	81 ± 24	120 ± 8	110 ± 20	
7H−benz[*de*]anthracen-7-one	22 ± 9	21 ± 5	5.5 ± 2	5.1 ± 2	
benz[*a*]anthracene-7,12-dione	6.3 ± 1	8.8 ± 2	15 ± 4	17 ± 3	
naphthacene-5,12-dione	9.5 ± 1	7.6 ± 0.8	52 ± 4	53 ± 5	
benzo[*cd*]pyrenone[b]	67 ± 10	62 ± 34	51 ± 4	48 ± 7	

[a] Reference values (ref) for the CRM soil are also listed. Both the PLE data and the Soxhlet data are based on three individual samples of each soil. The precision of the analyses are given as the 95% confidence limits. [b] Authentic reference compounds were not available for these compounds. 1-Acenaphthenone, methyl-9-fluorenone, and 4*H*-cyclopenta[*def*]phenanthren-4-one were quantified using the response factor of 9-fluorenone. 4-Oxapyrene-5-one and benzofluorenone were quantified using the response factor of 7*H*-benz[*de*]anthracen-7-one. Benzo[*cd*]pyrenone was quantified using the response factor of benz[*a*]anthracene-7,12-dione.

Finally, the selective PLE method was tested on seven authentic contaminated soil samples, and the results were compared to those of the reference method based on Soxhlet extraction and external silica gel fractionation. The results are presented in Tables 3 and 4. The results in Table 3 are based on three individual PLE extractions and three individual Soxhlet extractions for each soil. These extractions were conducted on the gasworks soil previously used during the screening experiments and on a certified reference soil (CRM 103-100, RTC, Laramie, WY). In Table 4, the results are also based on three

Table 4. Concentrations of PAHs and Oxy-PAHs in Five Soils from Contaminated Sites in Sweden Obtained through Selective Pressurized Liquid Extraction (PLE) and a Reference Method Based on Soxhlet Extraction and Open-Column Chromatography (Sox)[a]

	Holmsund (mg/g)		Boden (mg/g)		Luleå (mg/g)		Forsmo (mg/g)		Hässleholm (mg/g)	
PAHs	PLE[a]	Sox	PLE[a]	Sox	PLE[a]	Sox	PLE[a]	Sox	PLE[a]	Sox
naphthalene	2.7 ± 2	2.9	0.075 ± 0.01	0.19	7.1 ± 0.8	13	0.54 ± 0.05	1.1	0.64 ± 0.09	1.1
2-methylnaphthalene	2.1 ± 1	1.7	0.087 ± 0.01	0.15	6.3 ± 0.7	9.8	0.79 ± 0.2	0.99	0.69 ± 0.1	0.84
1-methylnaphthalene	1.0 ± 0.4	0.86	0.055 ± 0.02	0.090	3.2 ± 0.3	4.3	0.52 ± 0.09	0.62	0.46 ± 0.07	0.52
biphenyl	0.24 ± 0.2	0.30	0.0092 ± 0.005	0.026	7.4 ± 0.8	10	0.037 ± 0.03	0.15	0.094 ± 0.02	0.16
2,6-dimethylnaphthalene	1.4 ± 0.3	1.2	0.013 ± 0.01	0.042	8.3 ± 0.9	3.7	2.9 ± 1	2.7	2.5 ± 0.2	1.6
acenaphthylene	2.2 ± 0.4	1.4	0.26 ± 0.14	0.094	2.9 ± 0.4	1.9	1.3 ± 0.5	1.0	3.8 ± 0.5	2.3
acenaphthene	28 ± 5	19	0.020 ± 0.003	0.063	10 ± 0.9	10	11 ± 5	10	38 ± 3	28
2,3,5-trimethylnaphthalene	4.3 ± 0.9	4.4	0.0066 ± 0.005	0.065	2.1 ± 0.2	5.4	11 ± 5	21	4.7 ± 0.4	6.5
fluorene	20 ± 4	19	0.079 ± 0.02	0.10	17 ± 0.9	18	26 ± 9	23	26 ± 2	25
phenanthrene	29 ± 8	31	0.17 ± 0.04	0.81	71 ± 5	120	12 ± 4	15	5.0 ± 0.2	7.0
anthracene	38 ± 9	38	0.95 ± 0.4	0.29	12 ± 1	13	53 ± 21	49	48 ± 7	44
1-methylphenanthrene	27 ± 4	33	0.026 ± 0.01	0.18	2.8 ± 0.4	5.6	53 ± 19	71	25 ± 2	33
fluoranthene	665 ± 158	667	1.6 ± 0.4	2.1	57 ± 6	65	697 ± 173	675	563 ± 66	530
pyrene	391 ± 93	395	1.2 ± 0.3	1.5	37 ± 3	42	536 ± 142	515	298 ± 30	280
benzo[*a*]anthracene	96 ± 18	106	0.54 ± 0.1	0.46	24 ± 2	27	125 ± 46	133	130 ± 9	128
chrysene	113 ± 35	109	0.76 ± 0.4	1.1	26 ± 3	30	135 ± 33	142	139 ± 32	106
benzo[*b*]fluoranthene	58 ± 12	60	3.7 ± 0.5	3.5	34 ± 5	38	73 ± 24	81	82 ± 14	86
benzo[*k*]fluoranthene	21 ± 8	19	0.89 ± 0.2	0.81	11 ± 1	13	30 ± 8	28	29 ± 5	29
benzo[*e*]pyrene	22 ± 4	23	2.6 ± 0.3	2.5	16 ± 3	18	33 ± 10	36	33 ± 2	34
benzo[*a*]pyrene	16 ± 3	17	1.0 ± 0.3	0.75	18 ± 3	13	37 ± 12	36	39 ± 4	36
perylene	4.6 ± 0.9	4.9	0.35 ± 0.2	0.33	5.2 ± 0.9	4.7	8.8 ± 2	8.8	9.9 ± 1	9.4
dibenz[*a,h*]anthracene	2.4 ± 0.6	3.0	0.35 ± 0.2	0.36	3.8 ± 0.8	4.4	4.4 ± 2	4.0	4.2 ± 0.4	3.9
indeno[*cd*]pyrene	7.9 ± 1	8.2	1.6 ± 0.3	1.5	15 ± 3	17	15 ± 3	14	15 ± 1	14
benzo[*ghi*]perylene	5.7 ± 0.9	6.4	1.3 ± 0.2	1.2	13 ± 2	15	12 ± 3	13	11 ± 1	11
Oxy-PAHs										
1-indanone	0.38 ± 0.1	0.40	0.074 ± 0.01	0.10	0.11 ± 0.01	0.24	0.65 ± 0.01	0.62	0.45 ± 0.05	0.68
1-acenaphthenoneb	1.8 ± 0.1	1.4	0.49 ± 0.05	0.22	0.30 ± 0.04	0.93	1.0 ± 0.09	0.92	1.7 ± 0.09	1.7
9-fluorenone	16 ± 0.8	11	0.70 ± 0.04	0.63	48 ± 3	37	6.5 ± 1	6.2	5.3 ± 0.1	7.0
methyl-9-fluorenone (Σ 4 peaks)[b]	6.4 ± 0.6	7.1	0.085 ± 0.02	0.19	23 ± 1	31	8.5 ± 1	12	2.2 ± 0.1	4.2
anthracene-9,10-dione	15 ± 0.5	15	2.1 ± 0.1	1.4	6.4 ± 0.2	11	15 ± 3	21	3.8 ± 0.08	6.5
4*H*-cyclopenta[*def*]-phenanthrene[b]	134 ± 12	163	1.3 ± 0.10	1.2	5.3 ± 0.5	6.6	139 ± 19	189	75 ± 2	126
2-methylanthracene-dione	4.9 ± 0.3	4.0	0.34 ± 0.002	0.20	0.75 ± 0.04	1.0	9.9 ± 3	10	1.7 ± 0.1	3.0
4-oxapyrene-5-one[b]	2.7 ± 0.1	4.7	0.30 ± 0.02	0.41	0.18 ± 0.04	0.30	3.5 ± 0.3	5.4	5.6 ± 0.1	9.8
benzofluorenone (Σ 2 peaks)[b]	21 ± 1	30	0.31 ± 0.02	0.27	10 ± 0.5	14	28 ± 8	34	18 ± 0.3	25
7*H*-benz[*de*]anthracen-7-one	4.1 ± 0.2	5.1	0.049 ± 0.03	0.054	2.8 ± 0.1	3.6	0.95 ± 0.05	0.81	1.7 ± 0.06	2.0
benz[*a*]anthracene-7,12-dione	7.6 ± 1	9.6	0.64 ± 0.08	0.51	0.71 ± 0.08	2.3	9.0 ± 2	7.9	4.7 ± 0.05	6.2
naphthacene-5,12-dione	17 ± 1	22	0.55 ± 0.08	0.52	0.41 ± 0.09	0.82	29 ± 6	38	11 ± 0.5	13
benzo[*cd*]pyrenone[b]	22 ± 2	19	2.4 ± 0.2	1.7	8.8 ± 0.7	7.7	26 ± 5	25	21 ± 1	21

[a] The PLE data are based on three individual samples of each soil; the Soxhlet data are based on one sample of each soil. The precision of the PLE is are given as the 95% confidence limits. [b] Authentic reference compounds were not available for these compounds. 1-Acenaphthenone, methyl-9-fluorenone, and 4*H*-cyclopenta[*def*]phenanthren-4-one were quantified using the response factor of 9-fluorenone. 4-Oxapyrene-5-one and benzofluorenone were quantified using the response factor of 7*H*-benz[*de*]anthracen-7-one. Benzo[*cd*]pyrenone was quantified using the response factor of benz[*a*]anthracene-7,12-dione.

individual PLE extractions, but only on one Soxhlet extraction of each soil. These extractions were conducted on soils from four different wood impregnation sites and one coke production site.

The results obtained by using the selective PLE method were in good agreement with the result obtained using the reference method and also with the certified reference values available for the CRM soil. In most cases, the 95% confidence intervals of the concentration values were overlapping. The precision of the selective PLE method, measured as standard deviation, was similar to or better than the precision of the reference method, and it was also better than the precision listed for the certified reference values. However, it should be noted that to obtain acceptable precision with the selective PLE method, a highly homogenized sample is required, especially since the amount of soil transferred to the extraction cell is so small. In the present study, 1−5 g of soil was homogenized with 20 g of sodium sulfate, of which only 0.5−1 g was transferred to the extraction cell. To obtain acceptable results, this small portion of the soil must be representative of the whole sample. Considering the heterogeneity of many contaminated soils, the need for a careful homogenization becomes even more evident. In some cases, it might be necessary to first grind the sample before a subsample is taken to extraction. However, in this study, which dealt with a wide range of contaminated soils, acceptable precision was obtained despite the fact that the samples were only sieved, air-dried, and homogenized with a spoon.

The amount of soil extracted will also affect the sensitivity of the method, since it may be difficult to detect low levels of contaminants in small samples; however, when less contaminated soils are investigated, the amount of sample in the cells can simply be increased. The PAH levels in the soils investigated in the current study were known to be high, and thus, it was not

necessary to extract larger quantities. Larger quantities of soil would have required the addition of more internal standard and would have also increased the risk of overloading of the adsorbents.

Another finding that became evident during the extractions of the authentic soil samples was that the compound 2,3-dimethylanthraquinone was not an ideal choice of internal standard for the oxy-PAHs. Extractions of samples without the addition of internal standard showed that 2,3-dimethylanthraquinone was present as a natural contaminant in some of the soils. For the present study, it did not cause any problems, since the natural levels were much lower than the spiking levels. Nevertheless, it is a reason to find another IS. The best choice would be an isotopically labeled oxy-PAH, but such compounds are not yet commercially available.

CONCLUSION

This study shows that PAHs and oxy-PAHs present in contaminated soil can be efficiently extracted and fractionated by selective PLE using extraction cells packed with 2% deactivated silica gel. The PAHs are first extracted with a mixture of cyclohexane/dichloromethane (9:1, v/v) at 120 °C, after which the oxy-PAHs are extracted from the same sample with cyclohexane/dichloromethane (1:3, v/v) at 150 °C. The resulting extracts may then be directly injected into a GC for analysis. The method is faster, less labor-intensive and uses much less solvent, as compared to a traditional method based on Soxhlet extraction and silica gel cleanup. Moreover, the resulting data is as reliable as those obtained via the traditional method.

The selective PLE method was tested on seven authentic contaminated soil samples and was proven effective. However, if the fractionation procedure for some reason, for example, due to extreme soil properties, would prove less effective for other soil matrixes, this could easily be detected by analyzing selected compounds in both fractions. Indeno[*cd*]pyrene and benzo[*ghi*]-perylene, which are among the last PAHs to elute, and 9-fluorenone and 4*H*-cyclopenta[*def*]phenanthren-4-one, which are among the first oxy-PAHs to elute, would be suitable for this purpose. These compounds are relatively common in environmental samples and it would be feasible to accurately quantify them in both fractions.

Since the selective PLE method enables rapid analysis of both PAHs and oxy-PAHs in contaminated soil, it can provide more information about contamination, hazard, and risk than ordinary PAH analyses. The relatively low labor intensity and low solvent requirements minimizes costs, and the selective PLE method is, therefore, well-suited for large screening studies, including characterizations of contaminated sites and monitoring of remedial processes.

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