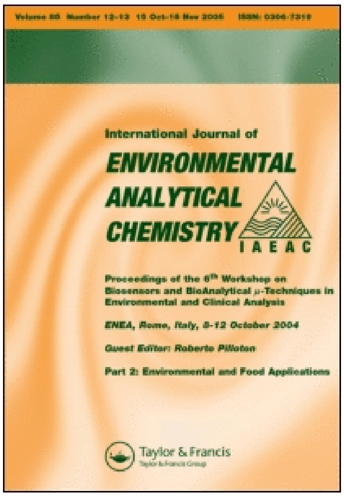

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EFFICIENCY OF DIFFERENT METHODS AND SOLVENTS FOR THE EXTRACTION OF POLYCYCLIC AROMATIC HYDROCARBONS FROM SOILS

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The efficiencies of supercritical fluid extraction (SFE), accelerated solvent extraction (ASE), Soxhlet, and ultrasonic extraction in the analysis of polycyclic aromatic hydrocarbons (PAHs) in soils were evaluated. Solvents with different polarity were used to extract the PAHs from two soils, one with high and one with low contamination level. ASE showed good results with all solvents almost independent of the solvent polarity and the best results with acetone–toluene (1 : 1). Ultrasonic extraction with acetone–toluene for the uncontaminated soil and acetone–ethanolamine for the highly contaminated also showed good recoveries. The time-consuming Soxhlet extraction with pentane or dichloromethane was less effective. The PAH recovery from SFE was related to the soil matrix or the contamination level. The best extraction conditions (CO_2/10% pentane) are successful for the soil with a low contamination level and a high humic acid content whereas the extractions of the highly contaminated soil gave poor results irrespective of the solvent used.

Keywords: SFE; ASE; Ultrasonic extraction; Soxhlet extraction; Soil; PAH

INTRODUCTION

The extraction is the main bottle neck in the determination of polycyclic aromatic hydrocarbons (PAHs) in soils and other matrices since these hydrophobic compounds are often strongly sorbed. The extraction yield depends on the method used and especially on the type of solvent. In recent years supercritical fluid extraction (SFE) [1], accelerated solvent extraction (ASE) [2,3] and microwave extraction [4–7] have become important new methods for soil extraction. These methods are less time consuming and need smaller amounts of solvent than classical methods like Soxhlet extraction, ultrasonic extraction and shaking [8,9]. For SFE and ASE the acceptance as standard methods by the US Environmental Protection Agency (EPA) enable their use in analytical laboratories [10,11]. However, disadvantages are the

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high investment and maintenance costs for the instruments that are needed for SFE, ASE and microwave extraction.

The results of the different extraction methods depend strongly on the physical and chemical characteristics of the compounds that have to be extracted. Extraction of the hydrophobic PAHs from soil, sludge or sediment samples is difficult and often incomplete due to strong PAH matrix interactions [1,12,13]. The international standardization organization (ISO) standard for extraction of PAHs from soils [14] recommends different extraction techniques for different contamination levels. For soils with low contamination level solvent extraction with acetone is adviced and for highly contaminated soils Soxhlet extraction with toluene is recommended. However, the disadvantage of toluene is its incompatibility with the subsequent HPLC analysis so that the solvent has to be changed prior to quantitation.

Comparing Soxhlet and ultrasonic extraction Brilis and Marsden [15] showed for 10 soil samples from a wood preserving site that Soxhlet with hexane : acetone (1 : 1) gave slightly higher recoveries than sonication with dichloromethane : acetone (1 : 1). In some other studies the difference between these two methods were within experimental error [16–18]. For extraction from sludge and sediment Noordkamp *et al.* [5] observed significantly better recoveries by shaking than with ultrasonic treatment but microwave extraction with acetone : water (4 : 1) or *N*-methyl-2-pyrrolidinone provided the highest yields. In the infancy of SFE, the results from spiked samples indicated that SFE was significantly more efficient than the other extraction techniques. However, when SFE was performed with authentic samples it became clear that SFE conditions developed on spiked samples often yielded poor recoveries [15,16]. Lee *et al.* [19] only obtained sufficient recoveries from sediments being comparable to Soxhlet values when extraction conditions were optimized with e.g. high temperature (120°C), modifier addition (methanol, dichloromethane) and long extraction time. Similar results were found for PAH extraction from sediment and urban dust using CO_2 with modifiers [20] or additionally high temperature [18,21]. However, in some investigations higher recoveries from real soil samples were obtained with SFE and high temperature or modifier than with Soxhlet extraction [22,23]. Especially, the SFE recoveries of the volatile PAHs such as naphthalene were sometimes higher than the Soxhlet results due to higher evaporative losses during Soxhlet procedure [19]. Good extraction recoveries were achieved by SFE as well as by shaking using supplemental bases or acids which were attributed to the effective disruption of the PAH matrix interactions [24,25]. ASE, the most recently developed method, showed especially for the PAHs very good extraction efficiency compared to Soxhlet extraction [26,27]. It was found that for ASE increasing temperature led to an increasing recovery of PAHs [26,28]. In contrast, Heemken *et al.* [29] reported that recoveries and precision of ASE and SFE are comparable to the classical extraction methods.

The aim of this study was to compare the extraction yields obtained by Soxhlet, ultrasonic, supercritical fluid, and accelerated solvent extraction to get a better understanding of the suitability of SFE and ASE for standard extractions of PAHs from soils. Therefore two authentic soil samples with different levels of PAH contamination were selected. Since not only the method but also especially the solvent influences the extraction results for each method several solvents differing in there physical and chemical properties were tested. In addition to polar and non-polar organic solvents mixtures consisting of two organic solvents or of acetone and a base (ethanolamine) or an acid (acetic acid) were used.

EXPERIMENTAL

Soil Samples and Solvents

Two authentic soil samples with a high (HC soil) and a low (LC soil) PAH concentration were chosen for the experiments (Table I). The samples were air-dried and ground in a mill reaching particle diameter smaller than 1 mm. For the study of SFE, ASE and ultrasonic extraction three replicates were performed for each condition and the data received were averaged out. Soxhlet extractions were only performed two times so that the values are to a less degree valid.

Acetone, dichloromethane, *n*-pentane and toluene were purchased from Merck (Darmstadt, Germany) in SupraSolv® quality. Acetonitrile (Mallinckrodt Baker, Deventer, The Netherlands) and methanol (Merck, Darmstadt, Germany) were used in HPLC grade quality. Ethanolamine (99%) was delivered from Aldrich (Steinheim, Germany) and acetic acid (100%, p.a.) from Merck (Darmstadt, Germany).

Soxhlet Extraction and Ultrasonic Extraction

Soxhlet extractions were performed extracting 30 g of soil for 8 h with 300 mL *n*-pentane or with dichloromethane at the boiling point of the solvents. For ultrasonic extraction 10 g soil sample were extracted with 100 mL solvent for 40 min at room temperature (approximately 25°C) in a ultrasonic bath (20 kHz, Branson, Danbury, USA) and the extract was filtered through filter paper (mesh 4–7 µm, Schleicher & Schuell, Dassel, Germany) in a büchner funnel. The extracts received by Soxhlet and ultrasonic extraction with non-water-miscible solvents were concentrated in a rotary evaporator, 10 mL acetonitrile were added as keeper, and the extracts were subsequently concentrated to 10 mL. The toluene extracts were evaporated to dryness and 5 mL acetonitrile were added. Water-miscible extracts were also concentrated in a rotary evaporator to 5 mL.

Supercritical Fluid Extraction

The SFE experiments were performed using a Dionex SFE Model 723 consisting of an extractor and a co-solvent addition module (Dionex Corp., Sunnyvale, USA). The fluids used were pure SFE grade carbon dioxide (Linde, Höllriegelskreuth, Germany) or carbon dioxide with co-solvents. The modifiers were mixed dynamically during the extraction to a concentration in the fluid of 4 or 10 mol%. The 10 mL-cells were filled consecutively with clean sand (Aldrich, Steinheim, Germany), 5 g soil sample

TABLE I Characterization of the soil samples

		Soil HC	*Soil LC*
Water content (%)		3.9	2.3
Organic carbon ($g\,kg^{-1}$)		55	50
Aliphatic hydrocarbons ($g\,kg^{-1}$)		35	n.d.
Humic acids ($g\,kg^{-1}$)		< 0.1	63
PAHs ($mg\,kg^{-1}$) ± *SD*	Soxhlet extraction with dichloromethane	888 ± 11	6.0 ± 0.2
PAHs ($mg\,kg^{-1}$) ± *SD*	Soxhlet extraction with *n*-pentane	1039 ± 25	8.7 ± 0.4

n.d.: not determined.

mixed with 0.5 g hydromatrix (ICT-ASS-Chem Handels GmbH, Bad Homburg, Germany), approximately 1 g copper granulate and finally clean sand.

The extractions were started with a pressure of 10 MPa, which in the following was raised performing 5 MPa-steps each in 3 min intervals up to 40 MPa. The final pressure was kept for further 22 min. The extraction cell temperature was kept at 90°C and the restrictor temperature was regulated at 180°C. The restrictors had a flow rate of 500 mL/min CO_2 at 34 MPa. All extracts were collected in 12 mL acetone in 30 mL vials which were cooled down to 5°C and the volume was adjusted to 10 mL.

Accelerated Solvent Extraction

The ASE experiments were performed using a Dionex ASE 200 instrument (Dionex Corp., Sunnyvale, USA). Soil samples (5 g) were extracted at 90°C and 14 MPa in an 11 mL-cell. The cell was filled up with clean sand. After a static extraction for 5 min the sample was extracted dynamically for 100 sec. Water-miscible extracts were filled up to a volume of 10 mL. Acetonitrile (10 mL) was added as keeper to the pentane extracts and the extracts were subsequently concentrated to 10 mL. The extracts with toluene were evaporated to dryness and 10 mL acetonitrile were added.

HPLC Analysis

PAH analysis was performed using a Hewlett-Packard 1050 HPLC-system with Beckmann pumps (model 126, Beckmann, München, Germany). Separation was achieved on a 250 mm × 3 mm I.D. RP-C18 column (particle size 5 µm) with a 12.5 mm × 3 mm I. D. pre-column (both MZ-Analytical, Mainz, Germany). The column was held at 35°C in a peltier thermostated column oven (BFO-04, Optilab, Berlin, Germany). An acetonitrilel–water gradient from 60 to 100% acetonitrile in 35 min was used as mobile phase with a total flow rate set to 0.6 mL/min. For detection, fluorescence and diode array detectors were used in series. A time program was utilized to detect the different PAHs at optimal excitation and emission wavelengths (Fig. 1). Quantitative analysis of the 16 EPA-PAHs except acenaphthylene was performed using external standard calibration with a reference standard solution (Promochem, Wesel, Germany) diluted appropriately. Prior to HPLC-analysis all extracts were filtered through regenerated cellulose (mesh 0.2 µm, Schleicher & Schuell, Dassel, Germany). As examples a chromatogram of one extract of each soil sample obtained by ultrasonic extraction is shown in Fig. 1. The peaks were identified by the retention time and by their UV–spectra. The limit of detection ranged without enrichment from 1.2 $\mu g\,L^{-1}$ for benzo[k]fluoranthene to 12.5 $\mu g\,L^{-1}$ for pyrene and the limit of quantitation from 4.2 $\mu g\,L^{-1}$ for benzo[k]fluoranthene to 42.8 $\mu g\,L^{-1}$ for pyrene.

RESULTS AND DISCUSSION

Soxhlet Extraction

The Soxhlet extractions were performed with dichloromethane as polar and *n*-pentane as non-polar solvent. High boiling solvents like toluene were not used to avoid the loss of the more volatile PAHs, such as naphthalene and acenaphthene. The recovery during the sample preparation was determined by addition of 1,1-binaphthyl as internal

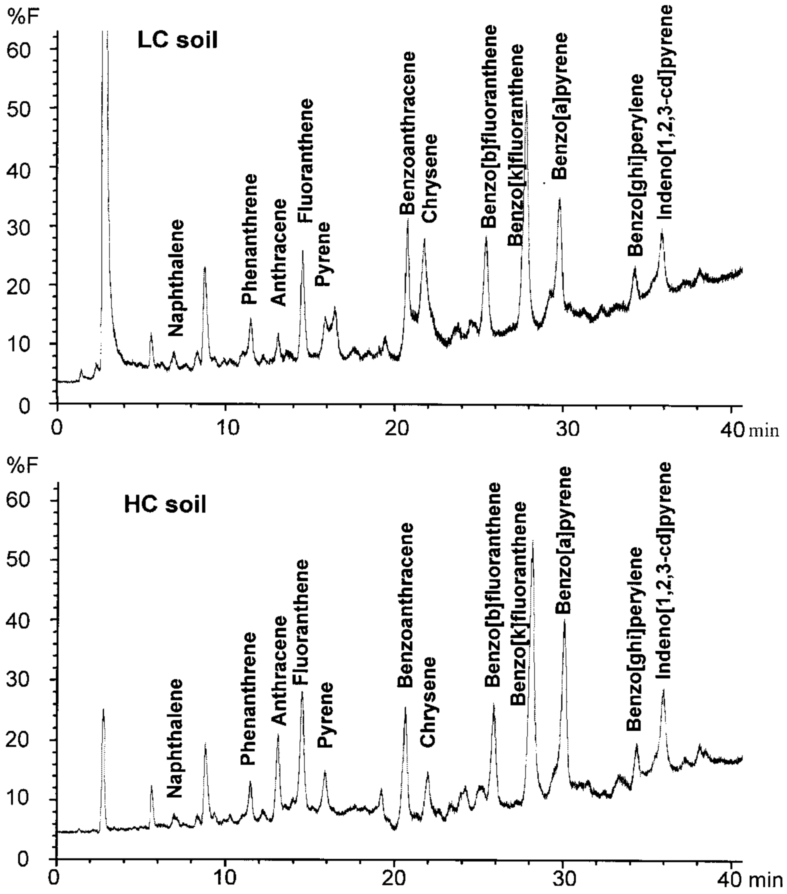

FIGURE 1 HPLC chromatograms from the LC soil (top) and the HC soil (bottom, diluted 1 : 100) obtained with fluorescence detection after ultrasonic extraction with acetone–ethanolamine (0–12.5 min: λ_{ex} 275 nm, λ_{em} 350 nm; 12.5–13.6 min: λ_{ex} 260 nm, λ_{em} 420 nm; 13.6–19.0 min: λ_{ex} 270 nm, λ_{em} 440 nm; 19.0–22.3 min: λ_{ex} 260 nm, λ_{em} 420 nm; 22.3–34.9 min: λ_{ex} 290 nm, λ_{em} 430 nm; 34.9–55 min: λ_{ex} 250 nm, λ_{em} 500 nm).

standard (10 mg kg^{-1}) to the extracts prior to the sample preparation. The recovery of 1,1-binaphthyl was with a mean value of 98% sufficient. The extraction with pentane gave higher yields than dichloromethane for both soils with low and high contamination level (Table I). The increase amounted to 146% for the LC soil and 117% for the HC soil sample. Especially for the HC soil the yield of the higher molecular weight PAHs increased more than of the lower molecular weight PAHs. Perhaps the non-polar solvent *n*-pentane can extract this non-polar PAHs better than dichloromethane.

Ultrasonic Extraction

The results of the ultrasonic extractions reveals that the extraction with the polar solvents methanol and acetonitrile are not effective for either soils (Fig. 2). The less polar solvents dichloromethane and acetone were the best extraction solvents for the LC soil. This may be due to the higher solubility of PAHs in acetone as observed

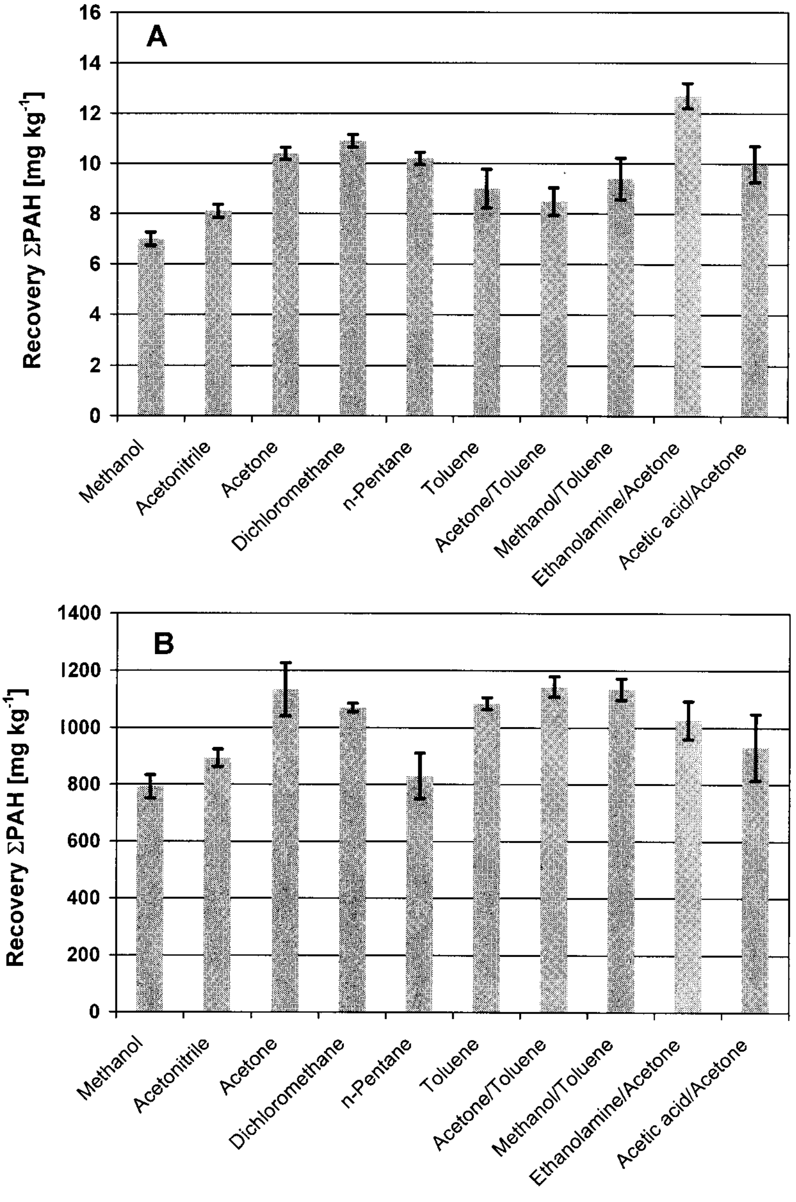

FIGURE 2 PAH yields of the ultrasonic extractions from the LC soil (A) and HC soil (B) with various solvents (error bars represent standard deviation in all figures).

for an industrial soil [5]. For example, the solubility of anthracene in methanol is approximately 17 times lower than that in acetone [30]. Nevertheless acetonitrile was proposed in the instructions of the Environmental Agency of Northrhine Westphalia (Germany) as possible extraction solvent prior to the analysis by HPLC [31]. Also in case of the HC soil, the non-polar solvents except *n*-pentane yielded good extraction efficiency. It seemed to be possible that the use of two solvents with different properties lead to higher extraction recoveries. Therefore two solvent mixtures consisting of a polar and a non-polar organic solvent (50 : 50 v/v) were tested. However, these mixtures (acetone : toluene and methanol : toluene) did not give better yields than the single solvents. The addition of acetic acid (2% v/v) and ethanolamine (2% v/v) to acetone lead to a significant higher recovery only for the PAH extraction from the LC soil with a high humic acid content. This may be caused by the modification of the humic substances by the base or acid which led to the release of PAHs out of the matrix. The saponification with KOH–methanol was described as an effective extraction method elsewhere [5,32].

Supercritical Fluid Extraction

In the study of SFE the same solvents and solvent mixtures used for the ultrasonic extraction were added to the carbon dioxide as modifiers (Fig. 3). The PAH recovery during SFE and the following sample preparation was determined by extraction of a spiked sea sand sample (10.94 mg PAHs). The recovery ranged from 81% for anthracene to 109% for benzoanthracene with a mean value of 96%.

In general, for the LC soil the addition of modifiers led to increasing PAH yields compared to pure carbon dioxide (Fig. 3). This shows that the solvents are more useful to break PAH matrix interactions than pure carbon dioxide as described often in literature [23–25]. With 10% pentane the best PAH recovery was obtained, indicating that the hydrophobic interactions between the PAHs and the matrix are most relevant. As opposed to the ultrasonic extraction methanol as modifier improved the extraction efficiency of the fluid more than the less polar solvents acetone and dichloromethane. This indicates that methanol, which shows some Brønsted acidity and is highly capable of building hydrogen bonds, broke PAH matrix interactions and substituted PAHs on the active site of the matrix. This is in accordance with several literature data and our previous investigations with other soils [25,33,34]. The extraction efficiency was not further improved by the use of modifiers consisting of two organic solvents. The addition of ethanolamine or acetic acid to acetone did also not led to increasing PAH recoveries.

For the highly polluted soil neither the addition of polar or non-polar solvents nor pure carbon dioxide gave rise to similar extraction results which are significant lower than reached by the other extraction methods. The SFE method is obviously not powerful enough for quantitative extraction of the PAHs. This may be due to the extraction time of 40 min (about 40 mL fluid) which is insufficient for a complete PAH extraction. In comparison Lee *et al.* [19] extracted sediments 70 min to achieve SFE results comparable to Soxhlet values.

Accelerated Solvent Extraction

For ASE similar solvents as for SFE and ultrasonic extraction as well as the solvent mixture dichloromethane–acetone recommended from Dionex (Dionex Corp., Sunnyvale, USA) were used (Fig. 4). The best results for both soils were reached with ASE using acetone–toluene (1 : 1). Toluene has $\pi \leftrightarrow \pi$ interactions with the PAHs and was also effective in other investigations [26,35]. However, the solvent properties are less relevant for the recoveries than for the other extraction methods as described elsewhere [28]. Especially the results from the HC soil using different solvents are very similar taking into account the standard deviations.

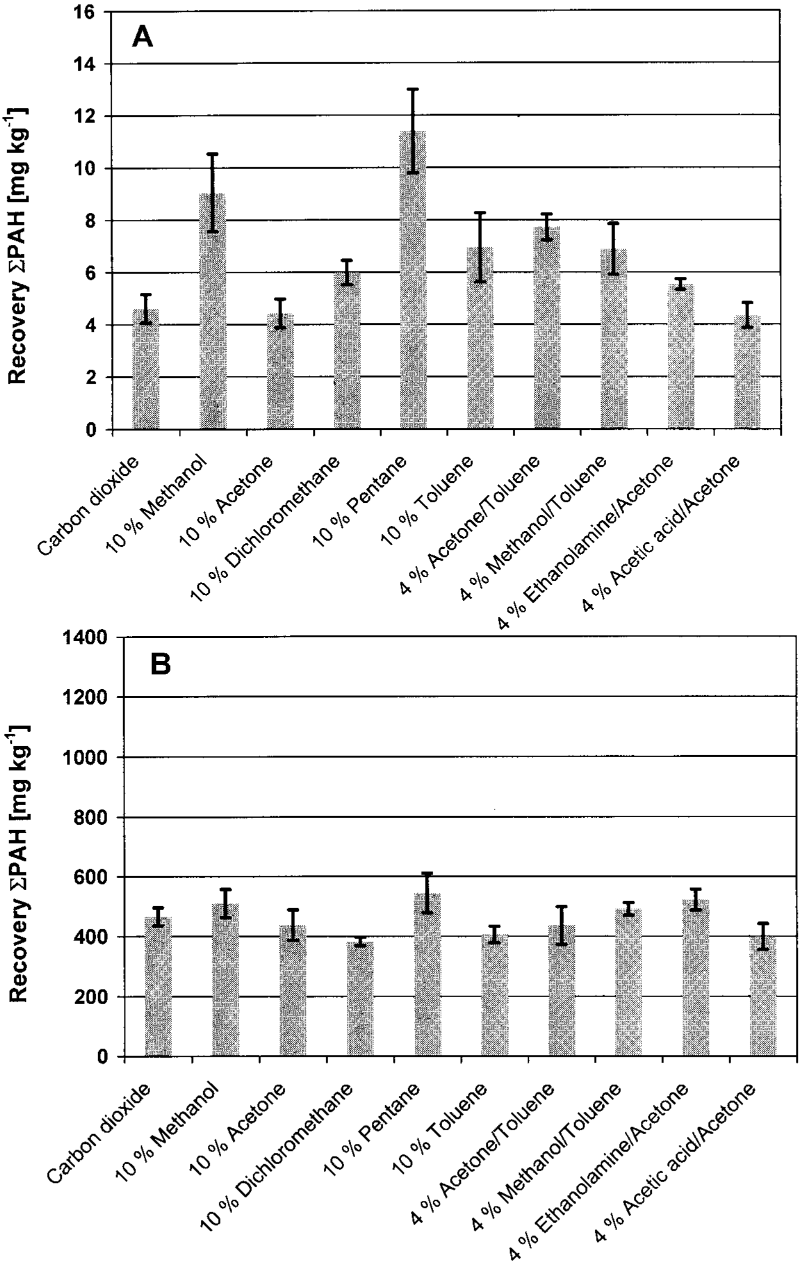

FIGURE 3 PAH yields of the SFE from the LC soil (A) and HC soil (B) with various modifiers.

Comparison of the Different Extraction Methods

In Tables II and III the best results of the different extraction methods are compared for both soils. Ultrasonic extraction, SFE and ASE yielded significantly better recoveries for the LC soil than Soxhlet extraction. The best result was reached with ASE using the solvent mixture acetone–toluene. In contrast, the best solvent for ultrasonic

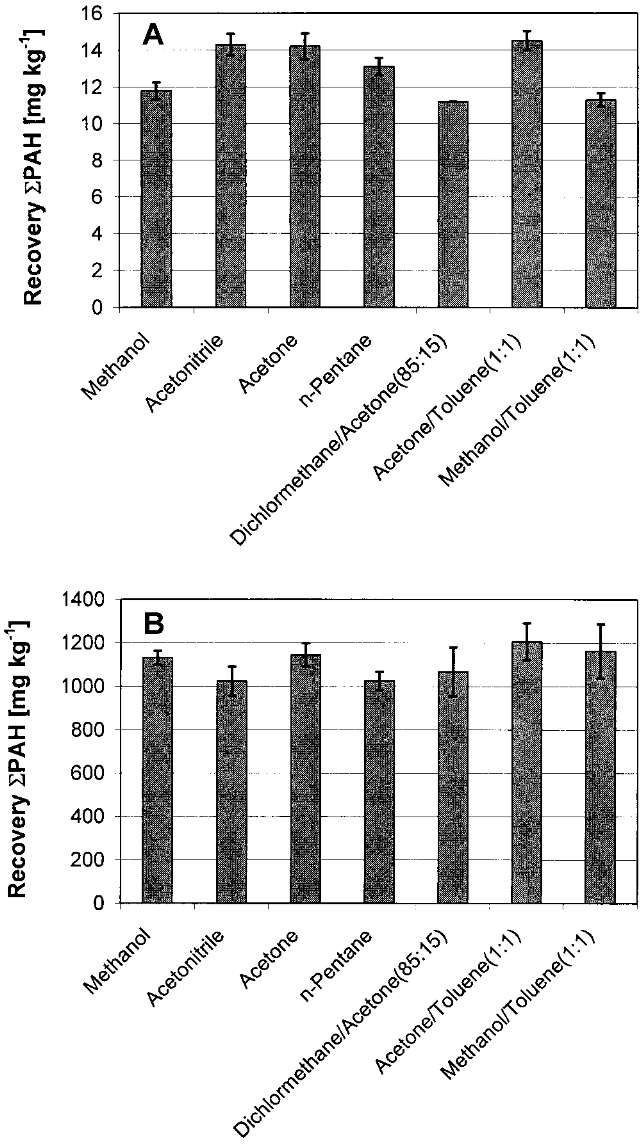

FIGURE 4 PAH yields of the ASE from the LC soil (A) and HC soil (B) with various solvents.

extraction is the polar acetone–ethanolamine mixture. The modification of the organic soil matrix by the polar solvent is obviously important for the ultrasonic extraction.

The extraction yield achieved by Soxhlet extraction from the HC soil is slightly lower than application of ultrasonic extraction and ASE. SFE is unsatisfactory with 50% lower recovery. Perhaps an optimized SFE method could improve the recovery but it is not useful if an extraction method has to be optimized extensively for each soil sample. Non-polar solvents or mixtures with non-polar solvents are obviously most suitable to disrupt the PAH matrix interactions in all extraction methods as also found by others [22,26,35].

TABLE II Comparison of the PAH recoveries of SFE, ASE, ultrasonic and Soxhlet extraction from the LC soil using the best extraction solvent, respectively

PAH	*Recovery with different extraction methods and solvents* [mg kg^{-1} ± *SD*]*			
	Soxhlet pentane	*Ultrasonic extraction acetone–ethanolamine*	*SFE CO$_2$/10% pentane*	*ASE acetone–toluene*
Naphthalene	3.23 ± 0.08	< 0.05	3.73 ± 0.58	< 0.05
Acenaphthene	0.08 ± 0.04	< 0.05	0.07 ± 0.01	0.19 ± 0.05
Fluorene	0.04 ± 0.02	< 0.05	0.08 ± 0.02	0.19 ± 0.01
Phenanthrene	0.40 ± 0.21	0.67 ± 0.03	0.18 ± 0.02	1.26 ± 0.10
Anthracene	0.12 ± 0.04	0.08 ± 0.02	0.15 ± 0.01	0.23 ± 0.01
Fluoranthene	0.93 ± 0.04	1.51 ± 0.52	1.41 ± 0.22	2.33 ± 0.16
Pyrene	1.40 ± 0.08	2.86 ± 0.12	1.74 ± 0.09	4.23 ± 0.46
Benzoanthracene	0.31 ± 0.06	0.54 ± 0.02	0.68 ± 0.05	0.89 ± 0.02
Chrysene	0.41 ± 0.02	0.54 ± 0.03	0.94 ± 0.14	1.01 ± 0.04
Benzo[*b*]fluoranthene	0.48 ± 0.06	0.64 ± 0.02	0.80 ± 0.08	1.09 ± 0.03
Benzo[*k*]fluoranthene	0.23 ± 0.04	0.28 ± 0.01	0.18 ± 0.02	0.48 ± 0.01
Benzo[*a*]pyrene	0.36 ± 0.06	0.44 ± 0.04	0.48 ± 0.04	0.81 ± 0.04
Dibenz[*a*,*h*]anthracene	0.07 ± 0.04	0.09 ± 0.01	0.10 ± 0.02	0.16 ± 0.02
Benzo[*g*,*h*,*i*]perylene	0.35 ± 0.06	0.41 ± 0.02	0.47 ± 0.08	0.86 ± 0.06
Indeno[1,2,3-*cd*]pyrene	0.33 ± 0.04	0.46 ± 0.03	0.35 ± 0.05	0.78 ± 0.04
Total	8.7	12.7	11.4	14.5

*The standard deviation given for SFE, ASE and ultrasonic extraction was based on three replicate extractions. For Soxhlet extraction only two replicate extractions were used, so that the values are to a less degree valid.

TABLE III Comparison of the PAH recoveries of SFE, ASE, ultrasonic, and Soxhlet extraction from the HC soil using the best extraction solvent, respectively

PAH	*Recovery with different extraction methods and solvents* [mg kg^{-1} ± *SD*]			
	Soxhlet pentane	*Ultrasonic extraction acetone–toluene*	*SFE CO$_2$/10% pentane*	*ASE acetone–toluene*
Naphthalene	0.6 ± 0.2	< 0.05	< 0.05	6.9 ± 4.9
Acenaphthene	1.1 ± 0.1	< 0.05	< 0.05	5.2 ± 0.7
Fluorene	16.1 ± 0.2	< 0.05	5.2 ± 0.1	15.3 ± 1.0
Phenanthrene	59.5 ± 0.4	75.4 ± 15.2	38.8 ± 1.9	71.0 ± 3.9
Anthracene	64.1 ± 0.2	51.8 ± 3.0	27.4 ± 2.5	43.5 ± 20.8
Fluoranthene	82.0 ± 1.8	125.4 ± 71.0	107.3 ± 8.1	198.8 ± 21.1
Pyrene	233.2 ± 0.2	374.1 ± 44.7	141.4 ± 9.2	361.5 ± 15.3
Benzoanthracene	106.7 ± 0.2	85.2 ± 1.6	55.4 ± 3.0	88.0 ± 8.6
Chrysene	85.7 ± 0.2	64.5 ± 1.5	43.8 ± 3.7	64.9 ± 6.6
Benzo[*b*]fluoranthene	84.3 ± 0.2	81.3 ± 6.8	37.9 ± 4.9	85.4 ± 6.5
Benzo[*k*]fluoranthene	39.8 ± 0.2	44.2 ± 2.7	13.3 ± 0.8	38.4 ± 2.6
Benzo[*a*]pyrene	113.4 ± 0.2	81.3 ± 5.9	37.4 ± 3.3	87.8 ± 6.1
Dibenz[*a*,*h*]anthracene	8.4 ± 0.2	< 0.05	6.5 ± 0.7	16.9 ± 3.2
Benzo[*g*,*h*,*i*]perylene	77.2 ± 0.2	64.2 ± 3.6	15.6 ± 2.9	62.6 ± 5.2
Indeno[1,2,3-*cd*]pyrene	66.6 ± 0.2	96.7 ± 5.8	14.7 ± 2.4	76.5 ± 7.5
Total	1038	1144	544	1222

Comparing the standard deviations of the PAH yields for the different extraction methods, SFE showed the highest deviations (Figs 2–4). Probably, this is caused by the sensitivity of the SFE against partly plugging of the restrictor resulting in slightly lower solvent flow rates and thereby slightly lower extraction volumes. However, SFE lead to the lowest levels of impurities in blanks. Probably, due to the highest solvent consumption followed by extensive evaporation of the solvent, soxhlet extraction showed the highest levels of impurities in the first part of the chromatogram until 10 min. Therefore the purity of the PAH peaks especially the naphthalene peak was checked by the UV spectra in the peak.

The extraction yields for the single PAHs are partly different between the methods resulting in different relative distributions and ratios of the single PAHs (Tables II and III). For investigations such as source assessment studies for which the relative distribution of the PAHs is important this can be a serious problem. However, no important trend towards improved extraction of lower or higher molecular weight PAHs was observed as reported elsewhere [19].

In conclusion, the preferable method is ASE if taking also into account criteria like solvent consumption, extraction time and handling. Prior to the HPLC analysis the water-miscible single solvent acetone and not the slightly more effective solvent mixture acetone–toluene is recommended as extraction solvent. However, if a ASE instrument is not available ultrasonic extraction with acetone is a simple and also sufficient extraction method.

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