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# Extraction of polycyclic aromatic hydrocarbons from polluted soils with binary and ternary supercritical phases<sup>1</sup>

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## Abstract

Supercritical fluid extractions (SFE) using carbon dioxide and modifiers (*n*-hexane, cyclohexane, toluene, methyl *tert*-butyl ether, methoxybenzene, dichloromethane, propanone, pyridine, methanol) as well as modifier mixtures (methanol-containing diethylamine, 2-aminoethan-1-ol, acetic acid) were performed to extract polycyclic aromatic hydrocarbons (PAHs) from real environmental samples polluted to a minor extent by mineral oil products and highly contaminated by brown coal tar. Comparing the results with those from Soxhlet extraction utilizing dichloromethane and SFE using pure carbon dioxide show that acidic or basic co-solvents give the highest PAH yields in all cases. Extraction efficiency decreases with reduced polarity of the modifier used and increases at higher concentrations of co-solvent. To explain the SFE results we discuss several mechanisms of disruption of matrix–PAH interactions: first the competition between the modifier molecules and the active sites of soil's organic and inorganic matter to interact with non-covalent bondings to the analytes; and second the splitting of electron donor–acceptor complexes between humic substances and PAHs induced by Lewis acids or Lewis bases. © 1997 Elsevier Science B.V.

**Keywords:** Soil; Extraction methods; Environmental analysis; Polynuclear aromatic hydrocarbons

## 1. Introduction

In recent years supercritical fluid extraction (SFE) has become an important method for the analytical-scale extraction of environmental samples [1–5]. In any case, its acceptance as a standard method by the US Environmental Protection Agency (EPA) [6] established its enhanced use in analytical laboratories. Investigations of real contaminated soils using supercritical carbon dioxide show that the interactions between the analytes and the matrix are very

strong, so that pure carbon dioxide is not able to extract all analytes [1,7–11]. The latter are not only sorbed on the surface of the soil as in spiked samples, but the analytes are chemically sorbed to active sites and physically trapped inside the matrix pore system [12,13].

Variation of SFE parameters like temperature or fluid composition can vastly improve analyte yields from real world samples. Extracting polluted soils or sediments at higher temperatures release much more analytes from the active sites of environmental samples [14–17]. The addition of small concentrations of organic solvents to the supercritical carbon dioxide leads to an increase in extraction efficiency. These modifiers having different physical

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and chemical properties can break the analyte–matrix interactions like van-der-Waals forces, electron donor–electron acceptor (EDA) interactions and hydrogen bonding. Further their dipole moment or their Brønsted acidity, or basicity, are useful properties for disrupting the analyte–matrix interactions [13,17,18]. Additionally, modifiers can alter the matrix by swelling, facilitating the transport of analytes from interstitial pores to the surface of the matrix [19–22]. The modifier most employed in SFE has been methanol, which has minor Brønsted acidity and dispersed interactions, and is highly capable of building hydrogen bonds. In some investigations, methanol soluted in carbon dioxide has given very good extraction results in comparison with pure carbon dioxide [11,19,23]. Toluene used as co-solvent has shown good results, too [18]. For the extraction of polycyclic aromatic hydrocarbons (PAHs), modifiers showing acidic or basic characteristics and having a permanent dipole moment appear to be the most suitable co-solvents [13,17,18].

Besides the type of modifier, its mode of addition to the sample has an effect on the extraction efficiency [4,5,12,17]. The static addition of modifier to the sample allows only a short contact time with the sample because the co-solvent elutes from the extraction cell in a short period of time. The dynamic addition extends the contact time, but a higher volume of solvent will be used and two pumps are required; one for the carbon dioxide and another one

for the modifier. Standard instructions for the extraction of different types of analytes cannot be given here because the difference between matrices influences to a major part the extract yields of PAHs.

This study describes the supercritical fluid extraction of three real environmental samples having different matrix types and different levels of PAH contaminants with carbon dioxide containing one or two modifiers. To investigate the influence of several modifiers on analyte recoveries, all other important SFE parameters like pressure, temperature, flow-rate, etc., were kept constant. Twelve co-solvents differing in their physical and chemical properties (Table 1) were used. In addition to often used modifiers (*n*-hexane [11], toluene [17,18], dichloromethane [11,14,17,18,23,25], propanone [11,18], methanol [11,14,15,17–19,23]) some unusual solvents (cyclohexane, methyl *tert.*-butyl ether, methoxybenzene, pyridine, diethylamine [17,18], 2-aminoethan-1-ol, acetic acid [18]) were also utilized. Each of the latter three co-solvents was soluted in carbon dioxide containing 10% methanol yielding the ternary mixtures used in the SFE experiments. These mixtures were used to enhance the extract yield improving the modifier–matrix interactions and reducing the analyte–matrix interactions. Different amounts of modifier were used to determine the concentration effect on the extraction efficiency. For comparison, Soxhlet extraction and SFE using pure CO<sub>2</sub> were carried out on the soil samples.

Table 1  
Selected physical and chemical parameters of modifiers

Modifier	Solubility parameter at 25°C [24]				Capability for electron donor acceptor bonding	
	$\delta_d$ (MPa <sup>0.5</sup> )	$\delta_p$ (MPa <sup>0.5</sup> )	$\delta_h$ (MPa <sup>0.5</sup> )	$\delta_l$ (MPa <sup>0.5</sup> )	$n \leftrightarrow \pi^*$	$\pi \leftrightarrow \pi^*$
<i>n</i> -Hexane	4.9	0.0	0.0	14.9		
Cyclohexane	16.8	0.0	0.2	16.8		
Methyl <i>tert.</i> -butyl ether <sup>a</sup>	14.5	2.9	5.1	15.8	weak	
Toluene	18.0	1.4	2.0	18.2		moderate
Methoxybenzene	17.8	4.1	6.8	19.5	weak	strong
Dichloromethane	18.2	6.3	6.1	20.3	moderate	
Propanone	15.5	10.4	7.0	20.0	moderate	weak
Pyridine	19.0	8.8	5.9	21.8	strong	strong
Methanol	15.1	12.3	22.3	29.6	moderate	
Diethylamine	14.9	2.3	6.1	16.3	strong	
2-Aminoethan-1-ol	17.2	15.6	21.3	31.5	strong	
Acetic acid	14.5	8.0	13.5	21.4	moderate	weak

<sup>a</sup> Solubility parameter values of diethyl ether.

## 2. Experimental

### 2.1. Characterization of the samples

Three real contaminated soil samples were used in this study. Sample Nos. 45 and 46 were obtained from different sites of a municipal waste disposal site, sample No. 185 was a coal tar-contaminated soil. Sample Nos. 45 and 46 were ground, sieved through a 1-mm sieve and homogenized for uniformity. Sample No. 185 was only homogenized in a mortar, because of the high content of coal tar. Water content was determined according to DIN 51718 (1978). Due to the high water content the samples were dried by freeze-drying about 24 h ( $< -50^{\circ}\text{C}$ ,  $< 1\text{ Pa}$ ) and the water content was determined again. TOC analysis on the samples were performed using a LECO CR-12 carbon determinator. The pore size distribution and the specific surface area of samples Nos. 45 and 46 were determined by the BET method [26] using nitrogen porosimetry on an Omnisorp 100. The contents of humic substances were determined by gravimetric analyses after extraction with alkaline solution, and reprecipitation of the soluted humic acids with hydrochloric acid and filtration, these procedures were repeated three times. Quantitative mineral analysis on the samples Nos. 45 and 46 by X-ray diffractometry were performed using a Philips PW1050 X-ray diffractometer (Philips, Almelo, The Netherlands). The resulting data were computed after the Rietveld method using the program system WYRIET (Schneider EDV-Vertrieb, Germany).

### 2.2. Soxhlet extraction

Fifty g of soil was Soxhlet-extracted for 24 h with dichloromethane. The extracts were concentrated to 5 ml by rotary evaporation and subsequently concentrated to dryness using a gentle stream of clean nitrogen. After gravimetric analysis, the extracts were resolved in dichloromethane and added to the top of a silica gel column ( $160 \times 12\text{ mm I.D.}$ ,  $63\text{--}200\text{ }\mu\text{m}$ ; Merck, Darmstadt, Germany). The column was successively eluted with each 40 ml of *n*-hexane, dichloromethane and methanol (all solvents from Merck) to separate aliphatic, aromatic and polar

hydrocarbons. The dichloromethane fraction containing the PAHs was analyzed by HPLC.

### 2.3. 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, Sunnyvale, CA, USA). The fluids used were SFE grade carbon dioxide (Air Products, Hattingen, Germany) or mixtures of it and co-solvents, which were mixed dynamically during the extraction. Pro-analysis-grade solvents (Merck, and Fluka, Neu-Ulm, Germany), 10-ml extraction cells, and restrictors having a flow-rate of 500 ml/min  $\text{CO}_2$  at 34 MPa were used in all experiments. The cells were filled consecutively with clean sand (Aldrich, Steinheim, Germany); the soil sample mixed with 0.5 g hydromatrix (ICT-ASS-Chem. Handels GmbH, Germany) to remove traces of water; approximately 1 g copper granulate to remove elemental sulphur [27,28]; and at least clean sand again. Sample sizes of 5.00 g were used from sediment Nos. 45 and 46 and 0.50 g from the highly contaminated soil sample No. 185; void volumes were filled with clean sand.

The extractions were started with a pressure of 20 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 a further 27 min. The flow of the gaseous  $\text{CO}_2$  was measured in the outlet stream after passing through the collection vial and consecutively through a solid-phase filter trap (RP-18, Dionex). The solid-phase filter trap was used to retain volatile compounds (Dionex, private communication). With the chosen extraction time of 39 min, a volume of at least 50 ml supercritical fluid was used by applying the law of ideal gases. Fifty ml fluid corresponds to five times the volume of the extraction cell, which was found to be enough for quantitative extraction [29]. The extraction cell temperature was kept at  $90^{\circ}\text{C}$  due to the elevated critical temperatures of the binary and ternary fluid mixtures. The critical parameters of these mixtures (Table 2) were calculated by applying the equations of Benedikt–Webb–Rubin [30]. The restrictor temperature was regulated at  $180^{\circ}\text{C}$ . All extracts were collected in 12 ml propanone in 30-ml vials which were cooled to  $5^{\circ}\text{C}$ . The solid-phase filter trap was

Table 2

Critical pressure and critical temperature of binary mixtures of CO<sub>2</sub> and selected modifiers calculated by applying the equation of state after Benedikt–Webb–Rubin [30]

Modifier	Critical pressure (MPa)				Critical temperature (K)			
	1 mol.%	3 mol.%	5 mol.%	10 mol.%	1 mol.%	3 mol.%	5 mol.%	10 mol.%
<i>n</i> -Hexane	7.3	7.1	7.0	6.6	307.9	315.3	322.3	338.6
Cyclohexane	7.3	7.3	7.2	7.0	308.2	316.1	323.8	42.1
Methyl <i>tert.</i> -butyl ether	7.3	7.2	7.1	6.7	307.5	314.0	20.3	335.0
Toluene	7.3	7.3	7.2	7.0	308.8	318.0	326.9	348.0
Methoxybenzene	7.4	7.3	7.3	7.1	309.7	320.5	331.0	55.9
Dichloromethane	7.4	7.4	7.4	7.4	306.7	311.8	316.8	329.2
Propanone	7.4	7.3	7.2	7.1	307.0	312.8	318.5	322.2
Pyridine	7.4	7.4	7.4	7.4	308.5	317.2	325.7	346.3
Methanol	7.4	7.4	7.5	7.5	306.2	310.5	314.8	325.5
Diethylamine	7.3	7.2	7.1	6.8	307.3	313.4	319.4	33.6
Acetic acid	7.4	7.4	7.4	7.4	307.9	315.3	322.7	40.6

eluted with 5 ml propanone and the eluate was combined with the collection solvent. 1,1-Binaphthyl (10 mg/ml) was added as internal standard after SFE prior to HPLC analysis. Extracts were then concentrated under a gentle stream of clean nitrogen to a volume of approximately 1000 µl.

Duplicate extractions were performed at each condition and the data received were averaged. The extraction of sample No. 45 with pure CO<sub>2</sub> was done five times for statistical calculation. The percent relative standard deviation extended from 4.6% (benz[*b*]fluoranthene) to 20.1% (chrysene) for individual PAHs with a medium standard deviation for all PAHs of 12% [31,32].

#### 2.4. HPLC analysis

Finally PAH analysis was performed using a Hewlett-Packard 1050 HPLC system with Beckmann pumps (Model 126, Beckmann, München, Germany). Separation was achieved on a 250×3 mm I.D. Zorbax C<sub>18</sub> column (SB-C<sub>18</sub>, 5 µm) with a 12.5×4 mm I.D. pre-column (AS-RT-1219, Zorbax, Germany). The column was temperature stabilized at 23°C with the Peltier thermostat BFO-04 (Optilab, Berlin, Germany). An acetonitrile–water gradient (0–5 min, 60% acetonitrile; 5–32 min, 85% acetonitrile; 32–33 min, 100% acetonitrile (held 2 min); 35–37 min, 60% acetonitrile (held 12 min)) was used as mobile phase with a total flow-rate set to 0.7 ml/min. For detection, fluorescence and UV detectors were used in series. A time program was used to

detect the different PAHs at optimal absorption and emission wavelengths. Quantitative analysis of the 16 EPA-PAHs was performed using external standard calibration with a reference standard solution (Promochem, Wesel, Germany) diluted appropriately.

#### 2.5. Gas chromatography

For the characterization of the soluble organic matter, aliphatic and aromatic hydrocarbon fractions were studied by gas chromatography using a Carlo Erba 5160 HRGC (Fisons, Mainz, Germany) equipped with a capillary column (25 m×0.25 mm I.D.) coated with chemical-bonded SE-54 (*d<sub>F</sub>*=0.25 µm; CS-Service, Langerwehe, Germany). Hydrogen (1.2 ml/min) was utilized as carrier gas. The analyses were performed using the following temperature program: 80°C held 2 min isothermal; heating rate, 4°C/min up to 300°C; final temperature held for 20 min. Injector and detector temperatures were 305 and 310°C, respectively; detection was by FID; and data acquisition and processing were performed using a Minichrom data system (Fisons).

### 3. Results and discussion

#### 3.1. Sample characterization

The mineral matter of sample Nos. 45 and 46 (differing data in parentheses) consisted of 77.6%

(w/w) (79.2%, w/w) quartz, 3.5% (w/w) calcite, 3.1% (w/w) (1.4%, w/w) muscovite, 11.4% (w/w) (4.6%, w/w) microcline, 2.4% (w/w) (2.1%, w/w) clinochlor and 2.0% (w/w) (1.4%, w/w) epistilbite, additionally sample No. 46 contained 7.8% (w/w) of an unknown substance non-identifiable by X-ray diffractometry.

The samples contained 22.7% (w/w) (No. 45), 16.9% (w/w) (No. 46) and 33.6% (w/w) (No. 185) water according to DIN 51718 (1978). Due to the high water content the samples were freeze-dried, yielding 1.3% (w/w) (No. 45), 0.9% (w/w) (No. 46) and 16.2% (w/w) (No. 185) water content. The last sample, especially, contained a lot of highly-volatile hydrocarbons, so these data have been kept with caution. Nevertheless, it was necessary to add hydro-matrix to the sample, removing the water.

Sample Nos. 45 (1.1%, w/w) and 46 (1.8%, w/w) have a low TOC content, meanwhile soil No. 185 contains 21.0% (w/w) TOC because of its high pollution with brown coal tar. The contents of humic substances, which are extractable with alkaline solution, are 0.02% (w/w) (No. 45) and 0.2% (w/w) (No. 46).

Soil No. 45 has a specific surface area of 6.2 m<sup>2</sup>/g and contains mainly large pores having a diameter greater than 50 µm, meanwhile sample No. 46 has vastly smaller pores (diameter, 5–7 µm) and also a higher specific surface area (15.4 m<sup>2</sup>/g). Determinations of the pore size distribution and specific surface area of soil No. 185 failed because of its high contamination.

### 3.2. Soxhlet extraction and SFE with pure carbon dioxide

All samples contain mainly alicyclic and aliphatic, as well as aromatic and polar hydrocarbons. Two soils, Nos. 45 and 46, studied here using the Soxhlet method are contaminated with EPA-PAHs to a minor extent (6 mg/kg), meanwhile the third soil, No. 185, is heavily polluted by EPA-PAHs (>2500 mg/kg) and aliphatic hydrocarbons (23 800 mg/kg) [31,32]. The main EPA-PAHs, determined by Soxhlet extraction with dichloromethane and by supercritical fluid extraction using pure carbon dioxide in soil Nos. 45 and 46, are chrysene, pyrene, and fluoranthene (No. 45), and benzo[*a*]anthracene (No. 46) (see Table 3). No acenaphthylene was found in any samples; naphthalene and acenaphthene (data not shown here) are minor components in soil Nos. 45 and 46. Further, some alkylated biphenyls, naphthalenes and phenanthrenes were identified in the aromatic fractions of the samples. The distribution pattern of the gas chromatograms (not shown here) of the aliphatic and aromatic fractions show that soil Nos. 45 and 46 are polluted by mineral oil, and that these contaminations have been aged and altered by microorganisms, too. Further, sample No. 185 is a sand highly polluted by brown coal-derived tar [31].

Comparing Soxhlet extraction with dichloromethane versus supercritical fluid extraction with pure carbon dioxide (see Table 4 and Table 5), Soxhlet extraction seems to be the better method for the

Table 3  
PAH yields of Soxhlet extracts

PAH	Soil sample (mg/kg)		
	No. 45	No. 46	No. 185
Phenanthrene	0.50	0.27	245.2
Anthracene	0.04	0.01	67.2
Fluoranthene	1.41	0.28	55.1
Pyrene	0.76	0.76	210.9
Benzo[ <i>a</i> ]anthracene	0.48	0.56	48.8
Chrysene	0.68	3.29	132.4
Benzo[ <i>b</i> ]fluoranthene	0.59	0.33	26.4
Benzo[ <i>k</i> ]fluoranthene	0.24	0.11	6.7
Benzo[ <i>a</i> ]pyrene	0.34	0.08	14.5
Dibenzo[ <i>a,h</i> ]anthracene	0.14	0.12	23.8
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	0.57	0.24	31.7

Table 4  
PAH recoveries<sup>a</sup> from soil No. 45 using modifier-assisted SFE

PAH	None	<i>n</i> -Hexane			Cyclohexane			Methyl <i>tert</i> -butyl ether			Toluene
		1%	5%	10%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	90	83	116	71	75	112	90	89	98	85	80
Anthracene	128	125	163	113	113	200	150	175	188	163	138
Fluoranthene	68	63	79	43	50	77	71	65	78	68	60
Pyrene	118	77	116	61	69	107	94	90	102	93	87
Benzo[ <i>a</i> ]anthracene	88	61	92	49	55	96	81	81	97	90	75
Chrysene	109	79	113	60	75	124	87	91	99	90	86
Benzo[ <i>b</i> ]fluoranthene	81	33	72	36	47	103	70	84	102	98	71
Benzo[ <i>k</i> ]fluoranthene	68	46	65	31	42	94	67	71	83	83	56
Benzo[ <i>a</i> ]pyrene	59	43	60	28	31	82	65	66	79	84	50
Dibenzo[ <i>a,h</i> ]anthracene	62	46	57	29	29	43	93	79	89	93	46
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	70	60	74	44	12	33	68	79	96	118	65

  

PAH	Toluene		Methoxybenzene		Dichloromethane			Propanone			Methanol
	5%	10%	1%	3%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	88	128	111	96	83	97	86	99	105	109	115
Anthracene	100	163	200	138	138	175	150	150	163	175	63
Fluoranthene	66	93	71	68	71	73	74	70	72	85	67
Pyrene	119	185	101	144	87	97	102	90	90	102	93
Benzo[ <i>a</i> ]anthracene	88	111	92	115	83	91	89	81	83	92	80
Chrysene	79	113	104	125	100	99	104	101	103	110	104
Benzo[ <i>b</i> ]fluoranthene	82	108	75	98	79	97	97	75	81	94	75
Benzo[ <i>k</i> ]fluoranthene	71	98	73	98	73	83	92	73	77	92	60
Benzo[ <i>a</i> ]pyrene	60	96	66	84	68	82	88	72	74	88	53
Dibenzo[ <i>a,h</i> ]anthracene	68	100	68	96	64	82	93	82	71	93	46
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	90	154	91	105	39	85	65	45	41	58	60

  

PAH	Methanol		Acetic acid		Pyridine			Diethylamine		2-Aminoethan-1-ol	
	5%	10%	0.5%	1.67%	1%	3%	5%	1%	2%	0.5%	2%
Phenanthrene	124	99	151	132	103	81	111	97	81	81	98
Anthracene	200	175	238	175	175	125	263	175	150	150	200
Fluoranthene	99	79	100	102	63	67	91	89	108	66	88
Pyrene	119	89	125	116	87	94	123	94	113	89	105
Benzo[ <i>a</i> ]anthracene	115	88	119	110	76	73	86	92	90	91	96
Chrysene	122	134	126	103	89	82	100	100	96	92	100
Benzo[ <i>b</i> ]fluoranthene	97	85	119	104	56	68	95	87	86	94	97
Benzo[ <i>k</i> ]fluoranthene	92	75	110	98	52	60	79	88	83	81	85
Benzo[ <i>a</i> ]pyrene	85	74	112	94	46	54	84	84	74	76	84
Dibenzo[ <i>a,h</i> ]anthracene	86	71	118	96	46	64	93	79	100	93	96
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	114	135	166	142	30	41	102	129	100	101	100

<sup>a</sup> Recoveries normalized on Soxhlet PAH yield in percent.

extraction of lightly polluted soils, because soil sample Nos. 45 and 46 yielded only 70–80% of total PAHs using pure CO<sub>2</sub> than performing Soxhlet extraction. Meanwhile, releasing aromatic com-

pounds from the highly polluted soil No. 185 using these methods shows an opposite trend. Here the supercritical fluid shows more extraction power, yielding 16% more EPA-PAHs than Soxhlet extrac-

Table 5  
PAH recoveries<sup>a</sup> from soil No. 46 using modifier-assisted SFE

PAH	None	<i>n</i> -Hexane			Cyclohexane			Methyl <i>tert</i> -butyl ether			Toluene
		1%	5%	10%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	123	83	113	102	100	98	145	100	75	55	102
Anthracene	139	200	250	300	100	150	300	100	100	50	250
Fluoranthene	68	134	107	98	82	77	102	66	63	71	96
Pyrene	73	89	103	82	74	145	199	61	67	104	100
Benzo[ <i>a</i> ]anthracene	90	96	113	108	108	103	138	102	101	93	104
Chrysene	78	93	101	95	97	88	124	93	88	81	87
Benzo[ <i>b</i> ]fluoranthene	56	73	88	91	26	86	109	52	27	24	91
Benzo[ <i>k</i> ]fluoranthene	65	45	86	91	91	82	105	82	100	91	73
Benzo[ <i>a</i> ]pyrene	72	50	113	119	119	94	131	81	100	63	100
Dibenzo[ <i>a,h</i> ]anthracene	48	54	92	88	21	63	92	71	50	33	79
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	42	19	50	79	21	52	58	33	52	46	40

  

PAH	Toluene		Methoxybenzene		Dichloromethane			Propanone			Methanol
	5%	10%	1%	3%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	7	111	111	117	109	172	111	126	119	102	98
Anthracene	150	0	250	200	100	200	100	100	350	50	200
Fluoranthene	71	89	88	116	95	111	80	93	93	77	89
Pyrene	69	61	97	123	79	193	125	113	131	84	116
Benzo[ <i>a</i> ]anthracene	71	113	114	129	119	137	116	108	109	96	136
Chrysene	71	98	96	118	105	123	97	96	94	81	121
Benzo[ <i>b</i> ]fluoranthene	100	106	83	98	80	112	111	147	86	67	115
Benzo[ <i>k</i> ]fluoranthene	77	91	86	118	82	100	105	100	82	68	86
Benzo[ <i>a</i> ]pyrene	813	113	81	119	88	113	125	113	106	94	100
Dibenzo[ <i>a,h</i> ]anthracene	67	104	92	96	67	96	83	75	75	63	88
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	52	83	48	65	40	40	79	29	42	65	40

  

PAH	Methanol		Acetic acid		Pyridine			Diethylamine		2-Aminoethan-1-ol	
	5%	10%	0.5%	1.67%	1%	3%	5%	1%	2%	0.5%	2%
Phenanthrene	130	108	160	185	100	134	126	128	143	100	115
Anthracene	400	350	200	400	200	50	50	300	400	0	50
Fluoranthene	116	100	138	145	80	102	111	159	171	68	104
Pyrene	109	78	173	113	170	74	60	101	122	60	62
Benzo[ <i>a</i> ]anthracene	121	96	143	131	115	120	113	117	145	108	106
Chrysene	107	77	118	111	109	104	95	96	132	93	89
Benzo[ <i>b</i> ]fluoranthene	109	88	121	129	79	79	115	94	130	30	29
Benzo[ <i>k</i> ]fluoranthene	114	91	114	109	68	773	91	100	109	118	114
Benzo[ <i>a</i> ]pyrene	125	119	125	125	81	106	131	119	125	113	119
Dibenzo[ <i>a,h</i> ]anthracene	117	108	167	117	54	67	79	133	183	63	75
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	102	96	88	117	13	50	65	90	125	88	73

<sup>a</sup> Recoveries normalized on Soxhlet PAH yield in percent.

tion with dichloromethane has done (see Table 6). We suggest that the longer contact time used in Soxhlet extraction enables the solvent to break analyte–matrix interactions in minor polluted soils,

because there are only thin layers of analytes on the surface of the matrix, as determined by microscopical analyses [31]. The higher extract yield from the highly contaminated soil using SFE is caused by

Table 6  
PAH recoveries<sup>a</sup> from soil No. 185 using modifier-assisted SFE

PAH	None	<i>n</i> -Hexane			Cyclohexane			Methyl <i>tert.</i> -butyl ether			Toluene
		1%	5%	10%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	109	105	104	98	125	108	101	112	94	108	89
Anthracene	122	106	124	105	144	125	102	125	93	109	96
Fluoranthene	90	90	110	86	92	102	73	83	72	86	78
Pyrene	109	99	113	92	105	102	82	94	84	102	85
Benzo[ <i>a</i> ]anthracene	85	89	109	96	82	94	67	78	67	70	82
Chrysene	100	98	114	93	112	105	91	108	81	93	87
Benzo[ <i>b</i> ]fluoranthene	97	94	114	89	101	93	79	92	76	85	79
Benzo[ <i>k</i> ]fluoranthene	118	107	127	101	104	107	95	104	96	105	89
Benzo[ <i>a</i> ]pyrene	112	103	123	101	155	116	130	144	115	124	83
Dibenzo[ <i>a,h</i> ]anthracene	99	133	151	131	98	114	79	87	71	80	104
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	94	90	119	101	133	96	100	90	60	101	82

  

PAH	Toluene		Methoxybenzene		Dichloromethane			Propanone			Methanol
	5%	10%	1%	3%	1%	5%	10%	1%	5%	10%	1%
Phenanthrene	103	104	95	111	101	93	102	99	101	94	131
Anthracene	63	60	99	67	112	96	126	114	117	105	143
Fluoranthene	34	41	85	44	88	93	100	99	98	90	124
Pyrene	96	116	91	107	89	87	100	100	98	90	131
Benzo[ <i>a</i> ]anthracene	73	72	92	83	92	90	92	100	93	86	131
Chrysene	92	82	90	90	100	95	103	105	98	91	131
Benzo[ <i>b</i> ]fluoranthene	94	83	75	90	83	80	92	90	90	78	130
Benzo[ <i>k</i> ]fluoranthene	109	147	87	107	100	95	109	108	106	94	151
Benzo[ <i>a</i> ]pyrene	111	98	70	104	100	103	116	113	114	98	136
Dibenzo[ <i>a,h</i> ]anthracene	132	136	128	127	93	90	111	110	108	97	173
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	118	104	67	108	83	89	97	101	98	86	122

  

PAH	Methanol		Acetic acid		Pyridine			Diethylamine		2-Aminoethan-1-ol	
	5%	10%	0.5%	1.67%	1%	3%	5%	1%	2%	0.5%	2%
Phenanthrene	60	100	106	116	102	109	121	110	101	117	102
Anthracene	58	101	116	117	105	102	105	116	113	132	115
Fluoranthene	55	94	101	111	72	77	86	111	96	94	77
Pyrene	58	97	107	115	83	89	93	113	101	115	90
Benzo[ <i>a</i> ]anthracene	52	85	112	113	67	76	80	126	135	81	64
Chrysene	55	88	105	110	89	99	103	118	116	106	89
Benzo[ <i>b</i> ]fluoranthene	61	92	100	112	81	90	91	102	87	96	76
Benzo[ <i>k</i> ]fluoranthene	72	101	118	130	100	108	105	109	97	141	97
Benzo[ <i>a</i> ]pyrene	67	99	108	114	128	131	146	104	93	134	100
Dibenzo[ <i>a,h</i> ]anthracene	82	116	140	164	76	82	74	135	133	91	74
Indeno[1,2,3- <i>cd</i> ]pyrene + benzo[ <i>ghi</i> ]perylene	76	105	107	117	86	94	107	103	87	118	72

<sup>a</sup> Recoveries normalized on Soxhlet PAH yield in percent.

the enhanced flow-rate of the supercritical carbon dioxide, which removes the solvated analytes faster than a solvent under Soxhlet conditions. It is known that the flow-rate of the supercritical fluid influences

the extraction efficiency. High recoveries were obtained using high flow-rates during SFE [33]. In samples with high analyte concentrations, especially, the solvation capacity of the fluid can be restored



immediately by a high flow-rate of the solvent. In sample No. 185 there are much bigger layers of solubles on the particle surfaces, of which the outer layers first must be released and solvated before the inner layers can be attacked by the solvent.

Comparing the results of SFE experiments involving minor polluted soils (Nos. 45 and 46) on the one hand, and a highly contaminated soil (No. 185) on the other, it is obvious that the supercritical fluid's capacity to solute the analytes is a limiting factor for an efficient soil extraction. For most PAHs extracted from the heavily polluted soil, pure carbon dioxide or its mixtures with non-polar modifiers gave similar PAH yields. Extract yields increased only to a minor extent using polar modifiers. To remove the analytes located in the outer layers, where only weak interactions between analyte molecules exist, modifier support is not needed.

Therefore, a method using a fluid having a higher diffusivity and a lower viscosity than a liquid should be capable of removing the analytes faster from the pore system of the sample, and should yield more extract. Similar observations were made by Götz and co-workers [20–22] studying SFE of bituminous coals which contain different amounts of soluble hydrocarbons trapped in their pore system.

### 3.3. SFE using binary mixtures

The addition of non-polar co-solvents, like *n*-hexane, cyclohexane, and toluene, or minor polar modifiers like methoxybenzene or dichloromethane, at moderate to high concentrations (5–10%) to carbon dioxide have improved the solvent power of supercritical CO<sub>2</sub>. In most cases, all of the PAHs extracted from sample Nos. 45 and 46 were found in higher yields using these binary fluid phases compared to pure supercritical carbon dioxide or the studied Soxhlet method (see Table 4 and Table 5). For sample No. 185, only high concentrations of *n*-hexane, cyclohexane, toluene or dichloromethane give results comparable to pure carbon dioxide (see Table 6). Methoxybenzene and methyl *tert.*-butyl ether used as additives reduce the efficiency of carbon dioxide for the extraction of tri- and tetracyclic aromatic hydrocarbons from the highly polluted soil. Modifying the supercritical carbon dioxide with methyl *tert.*-butyl ether give higher PAH yields

from soil No. 45, but the extraction behaviour of PAHs from soil No. 46 was uneven.

The addition of polar modifiers, like propanone, pyridine and methanol, yields more PAHs from both lightly polluted soils. The best extraction solvent for most PAHs is the 5% methanol solution. The addition of a basic co-solvent, like pyridine, during the SFE of lightly contaminated soils also enhances the yield of PAHs.

Extracting soil No. 185 with binary mixtures containing a polar co-solvent, a significant effect compared to non-polar modifiers is observable. Already the addition of small modifier quantities improves the PAH yields, indicating the breakdown of analyte–matrix interactions and the substitution of analytes by the modifier on the active sites of the matrix.

### 3.4. SFE using ternary mixtures

To study the influence of Lewis bases or acids diethylamine, 2-aminoethan-1-ol and acetic acid were added in minor quantities to methanol. These solutions were utilized as modifier (10%) in the SFE experiments.

Strong organic acids or bases, like diethylamine or acetic acid, gave the best results of all experiments performed in this study, meanwhile small amounts of a weak base like 2-aminoethanol improved the PAH yield only to a minor extent. For some PAHs their extract yields are considerably improved by a factor of 1.5–2.0 using basic or acidic modifiers, compared to pure carbon dioxide, and they are also often enhanced compared to Soxhlet extraction [17,18].

### 3.5. Modifier concentration effects

Increasing modifier concentrations up to 10% in the supercritical fluid gave higher extraction yields of PAHs in most cases if non-polar or polar co-solvents were used. The organic solvent molecules compete with the active sites of the soil matter to interact with the analytes. Then, substitution of the analytes takes place if a sufficient amount of modifier molecules have occupied all accessible active sites of the soil components. Van der Waals interactions, hydrogen bondings and electron donor–acceptor complexes disrupt depending on the physical and chemical

parameters of the co-solvent. Therefore, Soxhlet extraction also gave good extraction results, because the longer contact time allows the solvent molecules to substitute the analytes from the active sites of soil components.

Strong organic bases and acids enhance the amounts of released analytes already at small concentrations, in contrast to the other co-solvents utilized here (see Section 3.6). The increase of acid and base concentration in the fluid leads to higher analyte yields, as also seen using other polar modifiers.

### 3.6. Matrix effects

Soil components like minerals, especially clays and their weathering products, as well as humic substances, are able to interact with analytes resulting in a physi- or chemisorption of these compounds on the active sites of the inorganic or macromolecular substances. We suppose that analyte–soil interactions, like Van der Waals forces and electron donor–acceptor complexation are the major non-covalent bonding types for PAHs, whereas hydrogen bonding plays a minor role for the adsorption of PAHs on soil components. But, nevertheless, addition of Lewis acids or Lewis bases improves the extract yield for most PAHs studied here.

Therefore, we favor a hypothetical reaction mechanism in which humic substances adsorbing the PAHs will be attacked by electrophilic or nucleophilic fluid species resulting in a breakdown of the electron donor–acceptor complexes and charge transfer complexes, between PAH and humic substance. After disruption of this  $\pi$ – $\pi^*$  interaction the analyte should be solvated rapidly by the fluid components and should be transported away from its former bonding site to make the process irreversible. For extraction efficiency it is unimportant where the attack of the Lewis acid or Lewis base takes place: whether at the aromatic part of a given humic substance or at hydroxyl or carboxyl groups attached to an aromatic carbo- or heterocycle. In all cases, resonance effects weaken the charge-transfer bonding resulting, in some cases, in the splitting of the electron donor–acceptor complex. An attack of Lewis base or acid on a PAH should also lead to the

splitting of the electron donor–acceptor bonding of a humic substance–PAH complex.

Further the geometry and topology of the pore system built up by the aggregated humic substances and minerals can play an important role for the access of the supercritical fluid to analytes trapped in the soil, and the transport of solvent loaded with analytes out of the sample.

## 4. Conclusions

Utilizing modifiers in supercritical fluid extraction of polycyclic aromatic hydrocarbons from polluted soils at constant physical parameters PAH yield depends on: (1) the concentration of analytes in the soil; (2) the concentration and nature of solvent used as modifier; (3) the physi- and chemisorption of analytes on the active sites of humic substances and minerals; (4) the geometry and topology of the pore system in which analytes are trapped.

In order of the extraction power of the methods used, the highest extraction efficiency for the highly polluted soil was: with SFE with basic or acidic co-solvents; followed by the other SFE experiments favoring polar modifiers in higher concentrations (5–10%); and then the non-polar co-solvents and Soxhlet extraction with  $\text{CH}_2\text{Cl}_2$ .

Lightly contaminated soils yielded the highest amounts of PAH in the following order: extraction with Lewis acids or bases added to supercritical carbon dioxide; followed by Soxhlet extraction and SFE using polar modifiers in higher concentrations (>5%). Pure  $\text{CO}_2$  and its mixtures with non-polar solvents is not effective enough to release all PAHs from lightly polluted soil.

The most important processes on a molecular level for the extraction of PAHs or similar compounds from soils, and the release of organic analytes from solid surfaces, are: (1) the competition between solvent molecules and analytes of different polarity in order for the active sites of the matrix to interact by non-covalent bondings like Van der Waals forces, hydrogen bonding and electron donor–acceptor complexes, and (2) specific reactions of Lewis bases and acids splitting electron donor–acceptor complexes consisting of an analyte, in this case a PAH, and a humic substance.

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