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Comparison of supercritical fluid extraction and Soxhlet extraction for the analysis of native polycyclic aromatic hydrocarbons in soils

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Abstract

Two supercritical fluid extraction (SFE) methods were compared to Soxhlet extraction for the analysis of native polycyclic aromatic hydrocarbons (PAHs) in soil. Dichloromethane cosolvent was added directly to the soil sample in the "Manual" method, whereas isooctane–dichloromethane (1:3, v/v) was introduced to the CO_2 during dynamic extraction in the "Pump" method. Recoveries of native PAHs from reference marine sediment HS-4 using the Manual and Pump SFE methods were generally equivalent to or better than those using Soxhlet extraction. The recoveries of five deuterated surrogate PAHs spiked onto ten different soils were generally greater than 70% with intra-assay precisions of ±7 and ±4% for the Pump and Manual SFE methods, respectively. For the analysis of native PAHs present in these soils, the average intra-assay precision of the SFE methods was ±16%, which was similar to that for Soxhlet extraction of ±13%. The accuracies of the observed native PAH concentrations in these ten soils using SFE (relative to Soxhlet extraction) were generally low and variable: both the Pump and Manual methods showed average accuracies of 0.6 ± 0.4. Analysis of variance showed that ca. 85% of this accuracy variability was due to an apparent matrix effect (relative to Soxhlet extraction), and that ca. 15% was due to error in the SFE analytical methods. Due to this high apparent matrix effect observed for these ten soils analyzed, the two SFE methods tested were not validated for the analysis of client samples. Additional sample processing, such as cryogenic grinding, may be required for SFE.

1. Introduction

Supercritical fluid extraction (SFE) of polycyclic aromatic hydrocarbons (PAHs) from soil has several advantages compared to Soxhlet extraction. These include: (1) the essential elimination of the use of (often chlorinated) organic solvent, and (2) extracts may be analyzed directly by GC–MS, without cleanup.

SFE performs equivalent to or better than Soxhlet extraction for the analysis of PAHs in standard reference materials (SRMs) [1–5]. However, at the time of this work, no studies were found which compared SFE and Soxhlet extraction for the analysis of native PAHs in ten or more different soils, such as those typically received by a commercial testing laboratory.

The objective of this work was to conduct a validation study of two SFE methods, one employing manual cosolvent addition (Manual method), and the other employing a HPLC pump for cosolvent addition (Pump method). The validation study examined the precision and accuracy of the SFE methods relative to Soxhlet

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extraction for the analysis of native PAHs in different soils. Based on the results of this study, a decision was made regarding the replacement of the Soxhlet extraction method by a SFE method for the routine testing of PAHs in soil.

2. Experimental

2.1. Samples and standards

Set 1

Ten soil samples were collected in the Vancouver BC area which contained native PAHs. They were stored in glass jars at 4°C prior to extraction. One of these samples was analyzed in duplicate ($n = 2$) using Soxhlet extraction, and the other nine were not Soxhlet-extracted in replicate ($n = 1$), due to our quality assurance/quality control policy of analyzing 10% of client samples in duplicate. All ten samples were analyzed in duplicate using the SFE methods.

Set 2

Set 2 consisted of a group of twelve soil samples also collected in the Vancouver area which contained native PAHs. These samples were collected and analyzed in duplicate over a period of 4 months using Soxhlet extraction. These results were used to calculate the intra-assay precision of observed PAH concentration for the Soxhlet method.

HS-4 Marine Sediment Reference Material was purchased from the National Research Council of Canada, Marine Analytical Chemistry Standards Program, Halifax, Canada. A 200 μg/ml spiking standard solution was prepared by diluting 1.00 ml of 2000 μg/ml PAH mixture (US-106, ULTRA Scientific, Kingstown, RI, USA) to 10.00 ml with dichloromethane. A 10 μg/ml surrogate standard ([$^2H_8$]naphthalene, [$^2H_{10}$]acenaphthene, [$^2H_{10}$]phenanthrene, [$^2H_{12}$]chrysene and [$^2H_{12}$]perylene) was prepared by diluting 1.25 ml of 400 μg/ml Semivolatile Internal Standard Mixture (US-108, ULTRA Scientific) to 50.00 ml with dichloromethane. An internal standard was prepared by diluting 500 μl of 988 μg/ml [$^2H_{10}$]fluorene (MSD Isotopes, Pointe Claire-Dorval, Canada) and 500 μl of 974 μg/ml [$^2H_{10}$]anthracene (Aldrich, Milwaukee, WI, USA) to 50.00 ml with isooctane, for 9.88 and 9.74 μg/ml, respectively. A calibration standard was prepared by combining 5 μl of spiking standard, 100 μl of surrogate standard, 100 μl of internal standard and 800 μl of hexane in a GC vial.

2.2. GC and MS analysis

Extracts and standards were analyzed using a Hewlett-Packard 5890 series II chromatograph equipped with a 5970 mass-selective detector, a 7673 autosampler–injector with controller, a 59940A MS ChemStation (HP-UX Series) equipped with Target Compound Analysis Software, and a DB-5 column (30 m × 0.25 mm I.D., 0.25 μm film; J & W Scientific, Rancho Cordova, CA, USA). The GC oven was temperature-programmed from 80°C (hold 1 min) to 215°C at 10°C/min, then to 230°C at 1.5°C/min, and finally to 285°C at 6°C/min (hold 15 min). The total run-time was 49 min. The injector temperature was 250°C and the transfer line temperature was 290°C. Two μl of extracts were injected in the splitless mode.

2.3. SFE methods

Manual cosolvent addition ("Manual" method)

The bulk soil sample was thoroughly mixed by hand. A clean 7-ml extraction thimble (steel tube), capped at one end, was plugged with silanized glass wool. A 0.5-g amount of dried (160°C, overnight) $MgSO_4$ was added, followed by 1 g of sample. On the soil were placed 100 μl of surrogate standard plus 300 μl of dichloromethane [6] for a total of 400 μl of dichloromethane cosolvent. The thimble was plugged with another 0.5 g of $MgSO_4$ and silanized glass wool, and capped. The sample was immediately extracted to avoid evaporation of cosolvent, using a Hewlett-Packard (Richmond, BC, Canada) 7680T instrument. The thimble was pressurized to 370 atm (120°C) with SFC/SFE grade CO_2 (Air

Products and Chemicals, Allentown, PA, USA) and held for 10 min (static extraction) (1 atm = 101 325 Pa). CO_2 was then pumped through the sample (370 atm, 120°C) at 1 ml/min for 40 min (dynamic extraction) and depressurized, through a variable restrictor (50°C), into a trap (10°C) containing C_{18}-silica (30 μm). The system was depressurized and the restrictor and trap (25°C) were washed with 1 ml of hexane (1 ml/min) which was collected in a glass vial (the extract). The restrictor and trap were then rinsed with 1 ml of dichloromethane and hexane which were discarded. Internal standard (100 μl) was added to the extract followed by GC–MS analysis based on US Environmental Protection Agency (EPA) Method 8270 [7].

HPLC pump cosolvent addition ("Pump" method)

This method was similar to that reported by Lee et al. [1]. The bottom of the extraction thimble was plugged with two Whatman #41 filter paper discs (cut to fit) followed by silanized glass wool. One gram of soil sample was added to the thimble followed by the addition of surrogate standard (100 μl) and 500 μl of distilled water on top of the soil. The sample was covered with filter paper discs and glass wool as above, and the thimble was capped. In the first extraction the sample was pressurized with pure CO_2 (static extraction) for 2 min (333 atm, 120°C, restrictor 55°C, trap 15°C) followed by a dynamic extraction for 10 min (2 ml/min). The trap and restrictor (45°C) were then washed with 1.5 ml of isooctane–dichloromethane (1:3, v/v) which was collected in a glass vial. A second extraction was performed as described above, except: (1) 1% MeOH and 4% dichloromethane were introduced to the supercritical CO_2 by a HPLC pump and the total (dynamic extraction) flow-rate was 4 ml/min, (2) the static and dynamic times were 1 and 30 min, respectively, (3) the restrictor was at 45°C and (4) the trap was not washed with solvent. A third short extraction was then performed as described for the first extraction except: (1) the CO_2 flow-rate was 4 ml/min, (2) the static and dynamic times were 0 and 2.5 min, respectively and (3) the restrictor was at 45°C. The isooctane–dichloromethane extract was collected in a glass vial. (The SFE instrument was programmed to run this multistep extraction automatically.) The extracts were combined and the solvent exchanged to isooctane (0.9 ml). This extract was analyzed by GC–MS after addition of internal standard (100 μl).

2.4. Soxhlet extraction

The Soxhlet extraction method was based on EPA Method 3540 [8]. In summary, 30 g of soil were mixed with sufficient anhydrous Na_2SO_4 (dried 160°C, 12 h; Canlab, Burnaby, BC, Canada) to adsorb moisture, and Soxhlet-extracted with 300 ml dichloromethane for 16 h. One third of the extract was concentrated to ca. 10 ml on a rotary evaporator or Kuderna–Danish apparatus. The solvent was exchanged to 1 ml of hexane followed by alumina column ("LC-alumina-N", 3-ml tube; Supelco, Bellefonte, PA, USA) cleanup using 15 ml dichloromethane. The extract was concentrated, exchanged to 0.9 ml of isooctane, and analyzed by GC–MS after adding 100 μl of internal standard solution.

2.5. Calculations

As mentioned above, the ten (set 1) soil samples were analyzed using SFE and Soxhlet extraction methods. All observed PAH concentrations less than 0.1 μg/g were eliminated from the data set as being too close to the detection limit and having unacceptably high relative error. The accuracy (Acc) of each remaining observed PAH concentration was calculated using Eq. 1;

$$\text{Acc} = \frac{[\text{SFE}]}{[\text{SOX}]} \qquad (1)$$

where [SFE] and [SOX] were the observed PAH concentrations in the soil sample using SFE and Soxhlet extraction respectively. Multiplying Acc by 100 gives SFE recovery relative to Soxhlet extraction. For each soil sample (analyzed in duplicate by SFE) average accuracies (Acc_{av}) were calculated (one for each duplicate sample).

Table 1
Recoveries of PAHs from reference marine sediment HS-4, relative to certified values

Analyte	SFE, Manual		SFE, Pump Recovery (%)($n = 1$)	Soxhlet	
	Average recovery (%) ($n = 7$)	R.S.D. (%)[a]		Average recovery (%) ($n = 14$)	R.S.D. (%)[b]
Phenanthrene	101	6	85	82	13
Anthracene	110	8	136	91	13
Fluoranthene	83	6	86	72	10
Pyrene	93	6	97	85	10
Benzo[*a*]anthracene	103	9	84	87	11
Chrysene	93	8	90	86	14
Benzo[*b* and *k*]fluoranthene	106	8	96	96	19
Benzo[*a*]pyrene	71	9	59	77	19
Indeno[1,2,3-*cd*]pyrene	64	14	59	76	24
Dibenzo[*a,h*]anthracene	97	19	71	70	27
Benzo[*ghi*]perylene	44	9	36	64	33
Average	88	9	82	81	17

[a] Intra-assay.
[b] Inter-assay.

A "two-level nested design" analysis of the variance of Acc_{av} was conducted as described by Taylor [9]. In this analysis the variance (V_{Acc}) was split into two components: that due to the analytical method (V_{Meth}), and that due to the matrix (V_{Mtx}) as shown in Eq. 2.

$$V_{Acc} = V_{Meth} + V_{Mtx} \tag{2}$$

V_{Acc} and V_{Meth} were determined from the accuracy results, and V_{Mtx} was calculated from Eq. 2.

A matrix effect relates to the dependence of the recovery efficiency of a native analyte on

Table 2
Properties of the ten (set 1) soil samples

Sample	Moisture (%)	TOC (%)[a]	Colour	Texture
1	5	2.28	Grey brown	Fine, pebbles
2	5	2.74	Grey brown	Fine, pebbles
3	11	3.85	Brown	Sandy, pebbles
4	15	6.59	Brown	Sandy, pebbles
5	9	5.48	Brown	Silty, pebbles
6	11	2.41	Brown	Silty, pebbles
7	19	1.84	Grey	Sandy clay
8	19	1.24	Grey	Sandy, fine pebbles
9	21	2.94	Grey	Sandy clay
10	18	3.21	Grey	Sandy clay

[a] Total organic carbon.

Table 3
Average ($n = 2$) observed native PAH concentrations and their relative deviations for the ten (set 1) soils using Pump and Manual SFE methods

Analyte	Soil sample																			
	1		2		3		4		5		6		7		8		9		10	
	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)	Average concentration (µg/g)	RD (%)
Pump cosolvent addition																				
Naphthalene	0.90	21	1.12	7	4.96	2	9.94	43	0.70	34	0.38	4	0.56	9	0.40	12	0.48	4	0.41	1
Acenaphthylene	0.24	19	0.30	14			1.17	24					0.11	3						
Acenaphthene	0.48	2	0.83	19	1.44	0	2.90	22					0.29	11	0.11	10	0.14	6		
Fluorene	0.28	3	0.41	15	1.17	11	4.52	11					0.29	16	0.14	2	0.18	4	0.13	12
Phenanthrene	2.21	12	2.44	16	5.15	12	13.69	13	0.64	19	0.40	11	1.23	27	0.70	0	0.88	6	0.67	15
Anthracene	0.81	15	1.12	32	6.46	18	47.86	8	0.18	17	0.16	25	0.50	39	0.24	4	0.25	1	0.21	17
Fluoranthene	1.94	13	2.30	18	4.74	5	11.28	10	0.93	10	0.35	20	1.67	13	1.06	5	1.01	5	0.90	6
Pyrene	2.51	16	2.93	16	5.64	9	12.95	7	0.72	10	0.29	23	1.72	17	1.08	6	1.00	4	0.91	6
Benzo[*a*]anthracene	0.77	15	0.94	27	2.31	3	4.13	12	0.41	9			0.62	16	0.37	5	0.33	15	0.33	7
Chrysene	0.99	9	1.63	50	2.11	3	7.50	10	0.94	6	0.55	52	0.70	14	0.43	5	0.38	13	0.39	6
Benzo[*b* and *k*]fluoranthene	1.23	12	1.31	25	2.30	4	5.79	9	0.65	8	0.25	48	1.12	32	0.53	8	0.40	15	0.44	3
Benzo[*a*]pyrene	0.83	16	0.87	25	1.42	2	3.47	7	0.16	6			0.44	1	0.30	10	0.20	16	0.22	5
Indeno[1,2,3-*cd*]pyrene	0.55	13	0.55	39	0.57	3	1.35	7	0.11	8			0.19	28	0.17	11			0.10	0
Dibenzo[*a,h*]anthracene					0.22	3	0.51	15												
Benzo[*ghi*]perylene	0.52	17	0.57	25	0.71	0	1.71	5					0.18	18	0.14	16				
Overall average relative deviation 13%																				
Manual cosolvent addition																				
Naphthalene	0.89	6	1.30	35	5.11	9	23.66	45	[a]	[a]	0.58	5	0.63	1	0.49	14	0.60	7	0.59	11
Acenaphthylene	0.26	6	0.39	35	0.83	8	2.14	41					0.13	3						
Acenaphthene	0.57	9	1.07	19	2.02	7	5.34	44					0.31	22	0.14	19	0.15	11		
Fluorene	0.38	6	0.63	24	1.56	13	7.45	39					0.34	15	0.18	17	0.16	0		
Phenanthrene	2.43	7	3.69	31	5.43	17	21.20	26			0.73	2	1.48	22	0.82	13	0.69	1	0.57	13
Anthracene	0.78	9	1.47	41	7.92	42	49.04	40			0.36	8	0.84	54	0.30	8	0.21	5	0.19	16
Fluoranthene	1.82	9	2.78	39	4.23	17	13.74	14			0.63	11	1.79	16	1.17	11	0.83	3	0.71	16
Pyrene	2.35	10	3.44	37	5.16	14	14.50	22			0.52	8	1.81	20	1.19	12	0.82	5	0.70	16
Benzo[*a*]anthracene	0.61	11	1.11	41	1.75	20	3.73	8			0.29	20	0.72	22	0.43	14	0.27	3	0.24	21
Chrysene	0.75	9	1.34	38	2.30	21	7.12	1			0.77	18	0.84	26	0.50	15	0.32	6	0.29	21
Benzo[*b* and *k*]fluoranthene	0.86	2	1.55	41	2.42	15	6.07	8			0.41	45	1.00	21	0.67	12	0.35	5	0.33	21
Benzo[*a*]pyrene	0.54	3	1.03	42	1.61	14	3.60	1			0.19	29	0.57	27	0.36	12	0.18	0	0.16	23
Indeno[1,2,3-*cd*]pyrene	0.26	19	0.54	40	0.96	12	1.96	11					0.28	32	0.18	13				
Dibenzo[*a,h*]anthracene					0.22	16	0.73	5												
Benzo[*ghi*]perylene	0.24	21	0.53	38	0.92	10	2.58	19					0.25	35	0.16	15				
Overall average relative deviation 18%																				

[a] Sample not analyzed in duplicate.

some variable matrix parameter such as soil organic matter content, clay mineral structure, etc. If V_{Acc} is unacceptably large, and V_{Mtx} is the major component of this variability, then this is consistent with a matrix effect.

The relative deviation (RD) of duplicate results (X_a and X_b) about their average (Avg) was calculated using Eq. 3.

$$\%RD = \frac{|X_a - X_b|}{2Avg} \cdot 100 \qquad (3)$$

3. Results and discussion

Recoveries of native PAHs from reference marine sediment HS-4 using the Manual and Pump SFE methods were generally equivalent to or better than those using Soxhlet extraction (Table 1). The average intra-assay precision of recoveries using the Manual SFE method was ±9% R.S.D. These results indicated satisfactory performance of the Manual SFE method relative to Soxhlet extraction for the analysis of this SRM.

Ten soil samples (set 1) containing native PAHs were analyzed in duplicate by SFE (Manual and Pump methods) and by Soxhlet extraction ($n = 1$). The soils were obtained from different sites and represented a range of textures as listed in Table 2. The observed PAH concentrations in these soils ranged from ca. 0.05 to 70 μg/g (SFE: Table 3; Soxhlet: Table 4). As noted above, concentrations less than 0.1 μg/g were excluded from the data set.

The recoveries of deuterated surrogate PAHs from these samples using SFE were generally greater than 70% (Table 5). Their relative intra-assay precisions were ±7 and ±4% for the Pump and Manual SFE methods, respectively. The relative intra-assay precisions of the concentrations of native PAHs observed in the same soils were poorer at ±13 and ±18% for the Pump and Manual SFE methods, respectively (Table 3). This additional error may have been due to subsampling error in obtaining 1-g duplicate soil samples for SFE.

From a different set (set 2) of twelve soil samples analyzed in duplicate using Soxhlet extraction, the relative intra-assay precision of the observed concentrations of native PAHs was ±13% (Table 6). Comparing this value to the

Table 4
Concentrations of native PAHs observed in the ten (set 1) soils using Soxhlet extraction

Analyte	Concentration (μg/g)									
	Soil sample									
	1	2	3	4	5	6	7	8	9	10
Naphthalene	1.31	1.73	6.38	12.26	0.35	0.37	0.40	0.59	0.28	0.51
Acenaphthylene	0.40	0.63	0.93	2.12			0.13	0.17		
Acenaphthene	0.88	1.77	2.75	6.06			0.18	0.22	0.12	0.31
Fluorene	0.57	1.11	2.51	7.52			0.25	0.30	0.20	0.37
Phenanthrene	4.24	6.72	9.11	25.42	0.69	3.63	1.25	1.50	0.83	2.25
Anthracene	1.23	2.35	12.19	57.92	0.17	1.30	0.39	0.47	0.21	0.64
Fluoranthene	3.56	6.10	6.78	20.08	0.85	4.80	1.66	2.13	0.91	2.22
Pyrene	4.75	9.58	8.36	25.03	0.76	3.97	1.60	2.15	0.80	2.02
Benzo[*a*]anthracene	1.60	2.56	2.67	12.30	0.45	2.40	0.80	1.04	0.36	1.06
Chrysene	1.93	3.05	3.95	14.32	0.68	3.56	0.87	1.08	0.40	1.09
Benzo[*b* and *k*]fluoranthene	2.73	3.94	4.28	13.66	0.81	2.35	1.15	1.60	0.73	1.44
Benzo[*a*]pyrene	1.98	3.17	3.06	10.26	0.40	1.78	0.74	1.04	0.32	0.86
Indeno[1,2,3-*cd*]pyrene	1.29	1.99	1.80	6.24	0.26	1.08	0.44	0.71	0.18	0.44
Dibenzo[*a*,*h*]anthracene	0.19	0.28	0.30	0.97			0.11	0.14		
Benzo[*ghi*]perylene	1.38	2.15	1.94	6.84	0.24	0.92	0.38	0.58	0.16	0.36

Table 5
Average ($n = 2$) recoveries of deuterated surrogate PAHs and their relative deviations for the ten (set 1) soils using Pump and Manual SFE methods

Analyte	Soil sample																			
	1		2		3		4		5		6		7		8		9		10	
	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)	Average recovery (%)	RD (%)
Pump method																				
[$^2H_8$]Naphthalene	80	3	61	27	43	22	71	1	65	14	73	1	79	2	76	0	67	10	79	2
[$^2H_{10}$]Acenaphthene	89	4	73	24	65	26	96	4	72	17	76	1	82	1	81	0	78	5	82	0
[$^2H_{10}$]Phenanthrene	95	5	78	23	74	21	101	3	78	15	81	1	92	0	92	2	92	2	91	0
[$^2H_{12}$]Chrysene	102	5	88	24	81	16	105	3	82	14	76	5	98	2	99	4	98	4	99	2
[$^2H_{12}$]Perylene	102	6	86	26	71	11	100	6	81	7	63	6	91	2	86	4	85	4	88	5
Overall average relative deviation 7%																				
Manual method																				
[$^2H_8$]Naphthalene	87	1	87	0	78	0	111	26	89	0	88	7	91	1	90	1	114	0	114	2
[$^2H_{10}$]Acenaphthene	92	1	95	2	91	1	125	24	88	0	89	2	93	1	94	2	115	1	112	1
[$^2H_{10}$]Phenanthrene	94	1	97	2	96	1	117	15	88	0	86	3	96	1	95	2	117	1	119	2
[$^2H_{12}$]Chrysene	67	0	84	2	91	1	90	1	83	0	66	1	88	4	93	4	116	8	112	1
[$^2H_{12}$]Perylene	42	7	60	0	71	1	69	11	69	0	47	2	76	6	85	7	101	12	91	2
Overall average relative deviation 4%																				

Table 6
Relative deviations of average ($n = 2$) native PAH concentrations observed in the twelve (set 2) soils using Soxhlet extraction

Analyte	RD (%)											
	Soil sample											
	1	2	3	4	5	6	7	8	9	10	11	12
Naphthalene		33	3	18	4	12	5	15		24	5	11
Acenaphthylene		35	3	25	1		0			23	9	15
Acenaphthene		11		2	2	26	2		10	25	7	4
Fluorene		5		0	2	31	2	30	8	23	9	8
Phenanthrene	15	7	1	3	1	33	3	25	15	23	2	14
Anthracene	9	18		5	6	14	0		13	19	8	1
Fluoranthene	9	26	1	10	0	20	2	48	15	21	6	14
Pyrene	2	24	7	12	4	23	0	68	15	21	10	11
Benzo[*a*]anthracene	2	27		10	1	18	2		18	33	4	14
Chrysene	1	24	14	14	4	19	4	44	43	34	8	8
Benzo[*b* and *k*]fluoranthene	6	26		10	6	18	2	29	17	24	7	14
Benzo[*a*]pyrene	8	25		5	3	14	6		18	15	0	10
Dibenzo[*a*,*h*]anthracene	6	27		5	10	12	5		16	14	6	11
Benzo[*ghi*]perylene		27		2						15		14
Indeno[1,2,3-*cd*]pyrene	4	26		7	12		10	10	17	14		9
Overall average relative deviation 13%												

For the twelve soils, the average PAH concentrations ranged from 0.5 to 360 μg/g with an overall averge of 37 μg/g.

average precision of the SFE methods of ±16%, the above-mentioned apparent subsampling error was thought to be acceptably low.

The accuracies of the SFE methods relative to Soxhlet extraction are shown in Table 7. For each of the (set 1) soil samples analyzed in duplicate, the average accuracy ($\mathrm{Acc}_{\mathrm{av}}$) was calculated and plotted in Fig. 1 for the Pump and Manual SFE methods. The results are summarized below:

(1) The average accuracies ranged from 0.2 to 1.4. The overall average accuracy for both the Pump and Manual methods was 0.6 ± 0.4 (67% R.S.D.) (Table 7), indicating that, on average, the extraction efficiencies of these SFE methods were considerably lower than that of Soxhlet extraction for the native PAHs in these ten soils.

(2) The accuracies were not correlated to soil moisture or total organic carbon contents of the ten soils (data not shown).

(3) Both the Pump and Manual SFE methods showed similar accuracy patterns, e.g., sample 10 showed low accuracies and sample 7 showed high accuracies for both methods (Fig. 1).

(4) As indicated above, the average accuracies ($\mathrm{Acc}_{\mathrm{Av}}$) were quite variable. Analysis of this variance (described under *Calculations*) indicated that soil-to-soil variability (V_{Mtx}) of average accuracies accounted for most of the accuracy variability (V_{Acc}) and that method (intra-assay) variability (V_{Meth}) was a small component. Specifically, V_{Mtx} for the Pump and Manual methods were 93 and 78% of the total accuracy variance (V_{Acc}), respectively (Table 8).

(5) The Pump and Manual methods performed similarly with respect to precision and accuracy, despite their differences which were mainly in the cosolvents employed and the extraction steps.

Due to the high variability (V_{Acc}) observed for the average accuracies, the SFE methods tested in this study were not considered valid for use in our commercial testing laboratory. The relatively high V_{Mtx} component was consistent with a

Table 7
Accuracies (relative to Soxhlet extraction) of observed native PAH concentrations in set 1 soils using SFE

Analyte	Soil sample																			
	1		2		3		4		5		6		7		8		9		10	
	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B	A	B
Pump cosolvent addition																				
Naphthalene	0.83	0.54	0.70	0.60	0.79	0.76	0.47	1.16	2.50	1.52	0.99	0.91	1.31	1.55	0.59	0.76	1.79	1.65	0.82	0.81
Acenaphthylene	0.72	0.50	0.53	0.40			0.42	0.68					0.81	0.87						
Acenaphthene	0.56	0.54	0.56	0.38	0.52	0.53	0.37	0.59					1.80	1.43	0.46	0.56	1.21	1.08		
Fluorene	0.51	0.48	0.43	0.31	0.52	0.42	0.53	0.67					1.32	0.96	0.47	0.49	0.85	0.91	0.38	0.30
Phenanthrene	0.58	0.46	0.42	0.31	0.63	0.50	0.47	0.61	1.11	0.75	0.12	0.10	1.26	0.72	0.47	0.46	0.99	1.12	0.35	0.25
Anthracene	0.76	0.56	0.63	0.32	0.62	0.44	0.76	0.89	1.26	0.90	0.16	0.09	1.79	0.79	0.53	0.49	1.16	1.19	0.38	0.27
Fluoranthene	0.62	0.47	0.45	0.31	0.73	0.67	0.50	0.62	1.20	0.99	0.09	0.06	1.14	0.88	0.47	0.52	1.17	1.05	0.43	0.38
Pyrene	0.61	0.44	0.35	0.26	0.74	0.61	0.48	0.55	1.04	0.85	0.09	0.06	1.25	0.90	0.47	0.53	1.31	1.19	0.48	0.43
Benzo[*a*]anthracene	0.56	0.41	0.47	0.27	0.89	0.84	0.30	0.38	0.98	0.82			0.91	0.66	0.34	0.37	1.04	0.77	0.33	0.29
Chrysene	0.56	0.46	0.80	0.27	0.55	0.52	0.47	0.58	1.47	1.29	0.23	0.07	0.92	0.69	0.37	0.42	1.07	0.82	0.38	0.33
Benzo[*b* and *k*]fluoranthene	0.50	0.40	0.42	0.25	0.51	0.56	0.39	0.46	0.87	0.74	0.16	0.05	1.29	0.67	0.31	0.36	0.64	0.47	0.31	0.30
Benzo[*a*]pyrene	0.49	0.35	0.35	0.21	0.46	0.47	0.32	0.36	0.43	0.39			0.59	0.60	0.26	0.32	0.74	0.53	0.27	0.25
Indeno[1,2,3-*cd*]pyrene	0.48	0.37	0.38	0.17	0.31	0.33	0.20	0.23	0.47	0.40			0.31	0.56	0.21	0.26			0.24	0.23
Dibenzo[*a*,*h*]anthracene					0.75	0.70	0.45	0.60												
Benzo[*ghi*]perylene	0.44	0.31	0.33	0.20	0.36	0.36	0.24	0.26					0.38	0.55	0.21	0.29				
Average (Acc$_{av}$)	0.59	0.45	0.49	0.30	0.60	0.55	0.42	0.58	1.13	0.86	0.26	0.19	1.08	0.84	0.40	0.45	1.09	0.98	0.40	0.35
Overall average accuracy 0.60 ± 0.36 (60% R.S.D.)																				
Manual cosolvent addition																				
Naphthalene	0.72	0.64	0.49	1.02	0.87	0.73	1.05	2.81	[a]	[a]	1.65	1.50	1.59	1.62	0.71	0.93	2.27	1.98	1.30	1.03
Acenaphthylene	0.69	0.60	0.41	0.85	0.96	0.82	0.60	1.42					1.03	0.97						
Acenaphthene	0.71	0.59	0.49	0.72	0.79	0.69	0.50	1.27					2.09	1.33	0.52	0.77	1.12	1.39		
Fluorene	0.71	0.63	0.43	0.71	0.70	0.54	0.60	1.38					1.56	1.15	0.50	0.70	0.81	0.80		
Phenanthrene	0.61	0.53	0.38	0.72	0.70	0.50	0.62	1.05			0.20	0.20	1.45	0.93	0.47	0.62	0.84	0.82	0.22	0.29
Anthracene	0.69	0.58	0.37	0.88	0.92	0.37	0.50	1.19			0.30	0.26	3.36	1.00	0.60	0.70	1.05	0.94	0.24	0.34
Fluoranthene	0.56	0.46	0.28	0.63	0.73	0.52	0.59	0.78			0.12	0.15	1.26	0.91	0.49	0.61	0.94	0.88	0.27	0.37
Pyrene	0.55	0.44	0.23	0.49	0.70	0.53	0.45	0.71			0.12	0.14	1.36	0.90	0.48	0.62	1.07	0.98	0.29	0.40
Benzo[*a*]anthracene	0.42	0.34	0.25	0.61	0.79	0.53	0.33	0.28			0.10	0.14	1.10	0.70	0.35	0.47	0.77	0.72	0.18	0.28
Chrysene	0.43	0.36	0.27	0.61	0.71	0.46	0.50	0.49			0.18	0.26	1.23	0.72	0.39	0.53	0.85	0.75	0.21	0.32
Benzo[*b* and *k*]fluoranthene	0.32	0.31	0.23	0.56	0.65	0.48	0.48	0.41			0.10	0.25	1.06	0.69	0.37	0.47	0.51	0.46	0.18	0.28
Benzo[*a*]pyrene	0.28	0.26	0.19	0.46	0.60	0.45	0.35	0.35			0.08	0.14	0.98	0.57	0.31	0.39	0.57	0.56	0.15	0.24
Indeno[1,2,3-*cd*]pyrene	0.16	0.24	0.16	0.38	0.59	0.47	0.35	0.28					0.84	0.43	0.22	0.29				
Dibenzo[*a*,*h*]anthracene					0.83	0.60	0.72	0.79												
Benzo[*ghi*]perylene	0.14	0.21	0.15	0.34	0.52	0.43	0.31	0.45					0.91	0.43	0.23	0.32				
Average (Acc$_{av}$)	0.50	0.44	0.31	0.64	0.74	0.54	0.53	0.91			0.32	0.34	1.42	0.88	0.43	0.57	0.98	0.93	0.34	0.39
Overall average accuracy 0.64 ± 0.44 (69% R.S.D.)																				

A and B are duplicates.
[a] Sample not analyzed in duplicate.

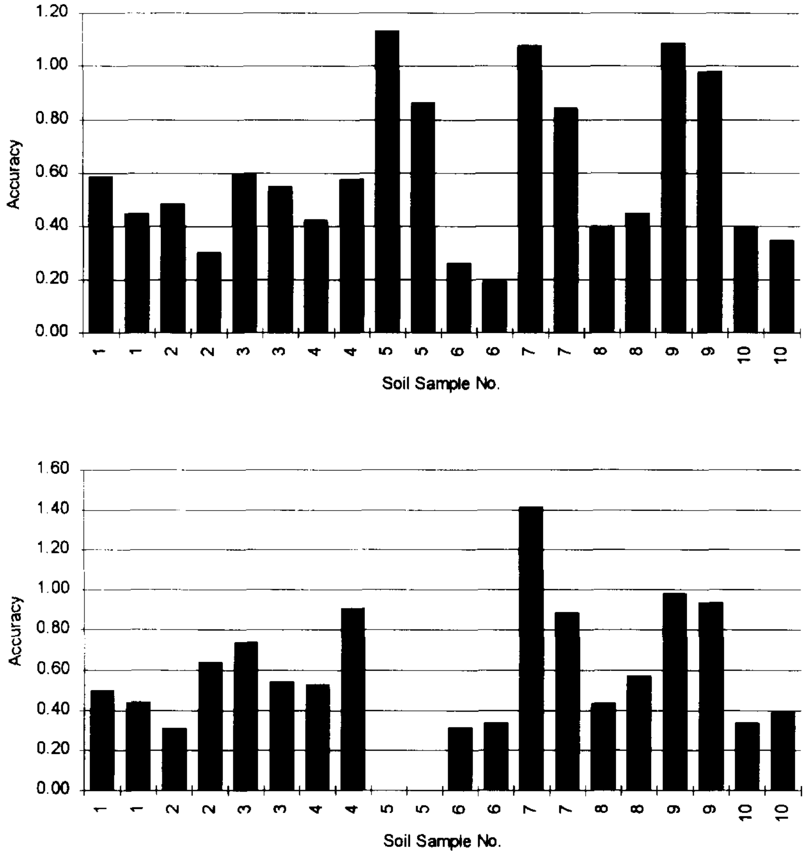

Fig. 1. Average accuracies (Acc_{av}) of the Pump (top) and Manual (bottom) SFE methods plotted for the duplicate set 1 soil samples.

Table 8
Analysis of variance

SFE Method	Variance		
	V_{Acc}	V_{Meth}	V_{Mtx}
Pump	0.084 100%	0.006 7%	0.079 93%
Manual	0.077 100%	0.017 22%	0.060 78%

The variability of average accuracies (V_{Acc}) was the sum of method variability (V_{Meth}), due to method error, and matrix variability (V_{Mtx}), which was an indicator of a matrix effect (see *Calculations*).

matrix effect (relative to Soxhlet extraction) for the analysis of native PAHs in these ten (set 1) soils using SFE. A possible cause of this apparent relative matrix effect may have been related to sample preparation. These SFE methods performed similar to the Soxhlet method for the extraction of the SRM marine sediment (HS-4), which was a fine homogeneous powder. Such favourable performance has also been reported for other standard reference materials [1–5]. Typically these materials are finely divided powders. On the contrary, the ten (set 1) soils in this study were extracted "as received" from the "field" after thorough manual mixing as is typically done for Soxhlet extraction. No effort was made to grind the samples to reduce their particle size. SFE methods were reported in which the soil samples were cryogenically ground (in the presence of liquid nitrogen), which performed well compared to solvent extraction [10,11]. Therefore, additional sample processing to homogenize the bulk sample and reduce its soil particle size, such as cryogenic grinding, may have improved the performance of the Manual and Pump SFE methods.

In the course of developing the Manual SFE method, dichloromethane was found to be the best cosolvent of several tested including acetonitrile, methanol, benzene, toluene and isooctane (data not shown). The use of other cosolvents has also been reported including aniline and a toluene–methanol mixture, which improved the recovery of PAHs from air particulates [12], as did increasing the extraction temperature from 50 to 200°C [3]. It was also subsequently reported that native (field-contaminated) PAHs had relatively low extraction rates compared to fortified analytes [13] (mathematically modelled in [14]), and that SFE for 60 min extracted significantly more PAHs than a 40-min extraction (as was used here).

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