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Comparison of stir bar sorptive extraction (SBSE) and liquid–liquid extraction (LLE) for the analysis of polycyclic aromatic hydrocarbons (PAH) in complex aqueous matrices

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ABSTRACT

Stir bar sorptive extraction (SBSE) is an equilibrium extraction method used amongst others for the analysis of polycyclic aromatic hydrocarbons (PAH) in aqueous samples. We compared SBSE to liquid–liquid extraction (LLE) for aqueous eluates obtained from batch and column tests of PAH contaminated soils to check whether SBSE might be considered as an alternative sample preparation method. We used soils with different particle size distribution, organic matter content, and resulting eluate turbidity to test the sample preparation methods on eluates with matrices of varying complexity. Furthermore, we studied the influence of diluted organic matter (DOM) on the PAH sorption process to the polymer coating of the stir bar during SBSE. In the majority of cases, we found higher PAH concentrations (up to 288%) with SBSE than with LLE. The turbidity correlates with the difference in PAH results, i.e. the greater the turbidity in the eluate, the more PAH we found with SBSE compared to LLE. We observed no similar trend regarding the amount of total organic carbon (TOC). The presence of DOM in the eluate seems to hamper the SBSE slightly, the PAH recovery varied between 82 and 104%.

1. Introduction

Polycyclic aromatic hydrocarbons (PAH) are severe environmental pollutants due to their harmful and partly carcinogenic properties [1]. The United States Environmental Protection Agency (US-EPA) listed 16 PAH as priority pollutants which in turn are analyzed very frequently. Aside from the classical liquid to liquid extraction (LLE) for the analysis of PAH in aqueous samples, alternative sample preparation methods, based on equilibrium extraction like solid phase extraction (SPE) [2], solid phase micro extraction (SPME) [3,4], stir bar sorptive extraction (SBSE) [5], and silicone based sorptive methods [6] have been developed. Equilibrium extraction methods have numerous potential advantages over LLE. The sample preparation is fast compared to LLE and allows for more parallel analyses. The necessary sample amount, especially for SPME and SBSE, is very low, usually only several mL compared to 200 to 500 mL necessary for LLE [7]. It requires no organic solvents except for cleaning purposes of materials and equipment and reduces possible loss of analytes through sample preparation, since for equilibrium extraction methods a sorbent applied on a carrier is immersed directly in either the sample solution or the headspace above. After the equilibrium is settled, the analyte is desorbed to be analyzed by means of a chromatographic system. LLE on the other hand requires a phase separation step and subsequent drying of the organic phase with a desiccant. Both can be hampered by a complex matrix, e.g. a high amount of particulate matter, colloids, or diluted organic matter (DOM) and thus might lead to a loss of analyte. Both sample solution and organic solvents get in contact to large container and equipment surfaces during LLE, which might lead to sorption of analytes. Evaporation and/or switching of solvents can further reduce the amount of analytes available to the analysis, especially of highly volatile compounds.

In contrast to LLE, typical equilibrium sample preparation methods like SPME usually detect only the fraction of PAH which is dissolved in the aqueous phase, but not the compounds adsorbed to dissolved organic matter (DOM) or linked to colloids [8–10]. This is due to the relatively small amount of sorbent applied on the SPME fibres, enabling equilibrium between the aqueous phase and the sorbent without disturbing the colloids/DOM – aqueous phase equilibrium. Thus, SPME and LLE derived PAH concentrations from aqueous samples are very difficult to compare, especially in the case of complex matrices. However, the colloid-linked PAH compounds might be accessible through SBSE, since the stir bars are equipped with considerably higher amounts of sorbent which can adsorb larger amounts of the analyte. This might affect the equilibrium adjustment between colloid facilitated PAH and the aqueous phase and lead to a discharge of PAH which in turn can be adsorbed additionally on the stir bar.

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Several sample preparation techniques for the analysis of PAH in aqueous samples have been compared already. Niehus et al. studied SPE and SBSE for the determination of PAH trace amounts in precipitation water [11], García-Falcon et al. compared SPE and SPME in terms of the analysis of drinking water [12], Wolska conducted an interlaboratory comparison including LLE and SPE methods [13], and Werres et al. compared SPE and LLE for PAH analysis in aqueous samples with particulate matter content [14]. Possible matrix effects have been studied for instance by Roy et al., who applied SBSE for PAH determination in spiked water as well as in natural and artificial seawater [15], by Rey-Salgueiro et al., who compared different extraction strategies for PAH in peats [16], by Haftka et al. who studied the influence of DOM and temperature on the partitioning of PAH to the SPME fibre [17,18], and Ter Laak et al., who determined the freely dissolved PAH concentrations in soil pore water [8]. The possible influence of humic substances on the determination of free and bound PAH was studied for instance by García-Falcón et al. [19] and Arias-Estévez et al. [20]. SBSE, offline coupled to HPLC for the determination of PAH in water is well described [21–23]. However, few is known so far about the differences between SBSE and LLE, especially for determination of high PAH concentrations (10–100 μg L^{-1}, sum of 15 EPA-PAH) and complex matrices like batch and column test eluates. A verification of comparability of these preparation techniques is needed in order to confirm their applicability for compliance testing (alignment of analytical data to threshold values).

Batch and column tests are laboratory-scale leaching experiments which may be used for the risk assessment of contaminated sites as well as the characterization of soil and waste materials designated for re-use in applications on soil. The leaching behaviour of contaminants is of great importance, since the soil–groundwater pathway is considered in most cases. On this account, column test [24] and batch test procedures [25,26] have been developed, standardized and validated recently in Germany [27]. The batch test method for the examination of the leaching behaviour of organic substances [25] is currently subject to validation and ruggedness testing.

In the course of these experiments, we prepared batch test and column test eluates from PAH-contaminated soils with different matrices. We applied SBSE and LLE sample preparation to the eluates to compare both methods, especially in terms of susceptibility to high PAH amounts and complex matrices. The objective was to check whether SBSE might be a possible alternative to LLE. Furthermore, we studied the influence of diluted organic matter (DOM) on the sorbed amount of PAH to the stir bar during SBSE sample preparation.

2. Materials and methods

2.1. Preparation of test materials

We used soils varying in particle size distribution, organic matter content, and resulting eluate turbidity to cover different soil matrices. We obtained reference soils characterized as loamy sand (LS), clayey loam (TL), and silty sand (US) from the Fraunhofer Institute for Molecular Biology and Applied Ecology, Schmallenberg, Germany and medium sand (MS) from a construction site at BAM Federal Institute for Materials Research and Testing, Berlin, Germany. We doped and homogenized the soils with PAH contaminated soil from a former railway sleeper preservation facility in Brandenburg, Germany. The added fraction of PAH concentrate was less than 1% in all cases. All mixtures passed the homogeneity tests, whose detailed results will be presented elsewhere. Selected properties of the contaminated test materials are given in Table 1.

Table 1
Properties of PAH contaminated test materials.

	LS	TL	US	MS
pH	5.41	6.07	6.00	8.66
C_{org} [%]	2.84	3.44	0.96	0.64
Particle size distribution				
>2 mm [%]	–	–	–	7
2–0.063 mm [%]	78	29	67	92
0.063–0.002 mm [%]	14	43	29	1
<0.002 mm [%]	8	28	4	-
Sum of 15 EPA-PAH [mg kg^{-1}]	7.68	10.65	7.66	9.41

Table 2
Numbering of 15 EPA-PAH[a] and FLD measuring conditions.

Number as listed in figures	PAH compound	FLD wavelengths [nm]	
		Excitation	Emission
1	Naphthalene	275	350
2	Acenaphthene		
3	Fluorene		
4	Phenanthrene		
5	Anthracene	260	420
6	Fluoranthene	270	440
7	Pyrene		
8	Benz[a]anthracene	260	420
9	Chrysene		
10	Benzo[b]fluoranthene	290	430
11	Benzo[k]fluoranthene		
12	Benzo[a]pyrene		
13	Dibenz[a,h]anthracene		
14	Benzo[g,h,i]perylene		
15	Indeno[1,2,3-c,d]pyrene	250	500

[a] Acenaphthylene was not measured (see experimental section).

2.2. Preparation of eluates

We performed the batch tests with a liquid to solid ratio of 2 L kg^{-1} according to E DIN 19527 [25] with representative subsamples of 250 g. Since one of the purposes of those experiments was the ruggedness testing of the leaching procedure – whose results will be presented elsewhere –, we varied agitation duration, revolution frequency of the end-over-end tumbler, and centrifuge acceleration. The respective conditions are given in Table 3. We obtained samples for measurement of pH, electric conductivity, turbidity, and PAH concentration using SBSE before and after the pressure filtration step. We took samples for total organic carbon (TOC) analysis only after the filtration, and used the remaining eluate (250–400 mL) for LLE.

We carried out the column tests as compliance tests with a liquid to solid ratio of 2 L kg^{-1} according to DIN 19528 [24] using glass columns of an internal diameter of 5.86 cm and typical weighted samples of 1.1 kg. We took samples for the analyses without prior preparation and used approximately 500 mL of each eluate for LLE. All results given in Table 3 are mean values of three replicate experiments.

We employed a PAH reference solution from a former interlaboratory comparison [28]. For preparation of this test solution, the PAH compounds were mixed with water and the solution was stabilized with surfactants. The mean PAH concentration (sum of 16 EPA-PAH) of the lab results (35 participants) was 11.0 μg L^{-1} with a relative reproducibility standard deviation of 37.9% (between-lab variability) and a relative repeatability standard deviation of 5.95% (within-lab variability).

2.3. LLE and SBSE sample preparation

We performed LLE sample preparations according to DIN EN ISO 17993 [7] which comprises double extraction with *n*-hexane,

Table 3
PAH values (SBSE, LLE) and accompanying parameters in aqueous eluates derived from different PAH contaminated soils.

Soil	Test conditions	Filtration	pH	El. cond. [μS cm^{-1}]	Turbidity [FNU]	TOC [mg L^{-1}]	PAH [μg L^{-1}][a]	
							SBSE	LLE
Reference solution		n/a	–	–	–	–	13.4	10.4
LS	24 h, 3 rpm, 20,000 × g	Before	5.94	105	66.1	–	15.8	–
		After	6.16	110	13.87	83.3	14.1	7.13
	24 h, 7 rpm, 20,000 × g	Before	6.01	107	52.0	–	18.0	–
		After	6.32	114	18.0	79.7	16.2	4.18
TL	24 h, 3 rpm, 20,000 × g	Before	6.10	327	26.8	–	19.5	–
		After	6.51	328	2.98	126	15.8	10.0
	24 h, 15 rpm, 20,000 × g	Before	6.05	330	24.6	–	19.0	–
		After	6.25	335	3.07	102	16.0	13.3
	2 h, 7 rpm, 20,000 × g	Before	5.55	266	45.6	–	18.5	–
		After	6.27	180	4.36	120	15.9	12.9
	5 h, 7 rpm, 20,000 × g	Before	5.70	283	41.5	–	18.1	–
		After	6.02	283	2.48	118	16.9	13.9
US	24 h, 7 rpm, 2000 × g	Before	6.20	83.8	36.6	–	24.1	–
		After	6.38	92.1	24.5	61.5	24.8	11.0
	24 h, 3 rpm, 20,000 × g	Before	6.03	85.6	61.7	–	37.1	–
		After	5.98	88.4	21.7	40.8	31.9	17.6
	24 h, 7 rpm, 20,000 × g	Before	6.00	85.3	49.4	–	36.7	–
		After	6.31	91.5	13.2	59.2	35.9	9.72
	24 h, 15 rpm, 20,000 × g	Before	5.95	81.4	57.4	–	41.7	–
		After	5.01	88.4	19.2	64.4	36.9	13.5
MS	24 h, 7 rpm, 2000 × g	Before	8.61	184	2.84	–	103	–
		After	8.56	186	1.04	45.0	102	117
	24 h, 3 rpm, 20,000 × g	Before	8.48	185	1.81	–	170	–
		After	8.42	186	0.87	14.9	156	125
	24 h, 7 rpm, 20,000 × g	Before	5.99	189	1.87	–	182	–
		After	6.32	191	0.96	22.1	146	120
	24 h, 15 rpm, 20,000 × g	Before	8.18	191	2.00	–	123	–
		After	7.81	197	1.04	27.0	105	120
	2 h, 7 rpm, 20,000 × g	Before	8.27	161	1.84	–	149	–
		After	7.99	162	1.26	13.2	131	129
	5 h, 7 rpm, 20,000 × g	Before	8.08	171	1.38	–	157	–
		After	7.97	175	0.86	15.3	111	114
LS	Column experiments	n/a	6.29	117	12.23	56.3	1.84	8.98
TL			5.68	307	2.24	162	6.23	6.58
US			6.17	113	2.36	39.6	0.91	1.68
MS			8.08	207	5.36	12.2	80.4	85.3
Mean relative standard deviation			1.94	1.58	18.3	9.62	18.4	20.7

[a] Sum of 15 EPA-PAH.

drying of the organic phase with Na_2SO_4 and subsequent solvent switching to acetonitrile. The SBSE sample preparations were based on the work of Popp et al. [29] and García-Falcón et al. [22]. 10 mL of the respective eluate was filled in a 15 mL glass vial, which was closed with a pre-assembled septure closure cap after adding the stir bar, and extracted for 60 min at a stirring speed of 1100 rpm. After extraction, the stir bar was collected with a magnetic stirring bar retriever, dried with a lint-free tissue, put in a 2 mL screw cap vial equipped with a 250 μL glass insert which in turn was filled with 200 μL acetonitrile and left alone for 5 min. After desorption, we injected 2.5 μL of the extract into the HPLC system. For cleaning purposes, we put the stir bars in a vial containing 5 mL of a 1:1 mixture of dichloromethane and methanol. After 5 min of ultrasonic treatment, we replaced the solvent mixture and repeated the procedure four more times. We dried the stir bars for 15 min at 90 °C in a drying cabinet. We checked the effectiveness of the cleaning procedure through desorption (as described above) of freshly cleaned stir bars. The mean value of the sum of 15 EPA-PAH in these experiments was 8 ng L^{-1} (2 experiments). We carried out control experiments through testing of deionized water with SBSE. The mean value of the sum of 15 EPA-PAH in these experiments was 19 ng L^{-1} (7 experiments).

2.4. Equipment and chemicals

We measured pH values with a Schott CG 841 pH-meter equipped with a WTW SenTix 41 pH electrode, the electric conductivity with a WTW LF 437 microprocessor conductivity meter, the turbidity with a Hach 2100 IS turbidity meter, and the TOC content with a Shimadzu TOC-VCPH analyzer. For SBSE sample preparation, we used Gerstel Twister® stir bars of 10 mm length, coated with a PDMS layer of 0.5 mm thickness, containing 24 μL of the polymer.

We determined PAH concentrations with an Agilent 1200 Series HPLC system with fluorescence detector. The excitation and emission wavelengths are given in Table 2 together with the numbering of the 15 EPA-PAH used in Figs. 3–5.

Since acenaphthylene is not available to fluorescence detection, we did not measure or discuss it in this work. We used a Zorbax Eclipse PAH column of 4.6 × 100 mm with 1.8 μm particle size for the separation. We applied a mixture of acetonitrile and water as mobile phase, starting with 40% acetonitrile, changed it within 6 min to 100% acetonitrile and held this for another 3.5 min. We purchased ultrapure acteonitrile and water from Liquid Chromatography Systems. We obtained NIST Standard Reference Material 1647e from the National Institute of Standards and Technology as PAH standard, consisting of a mixture of 16 EPA-PAH in acetonitrile. To calibrate SBSE sample preparation for PAH analysis, we prepared 8 dilutions of 1 mL of the standard solution (diluted in 10 mL acetonitrile), with 10 mL deionized water each and processed them as described in Section 2.3. The amount of acetonitrile in the PAH water solution was in all cases less than 1%, with the exception of the highest standard solution (5%). Since the PAH concentrations in the standard solution varied from 0.79 to 20.5 mg L^{-1} and due to the different water solubility of the PAH compounds, we got lin-

Table 4
DOM influence on SBSE analysis.

Soil	Test conditions		pH	El. cond. [μS cm^{-1}]	Turbidity [FNU]	PAH recovery [%]
TL	Pre-coated stir bar	Non-filtrated eluate	5.99	281	46.1	90
		Filtrated eluate	6.49	287	2.61	93
	PAH solution (eluate)	Non-filtrated eluate	5.99	281	46.1	86
		Filtrated eluate	6.49	287	2.61	82
US	Pre-coated stir bar	Non-filtrated eluate	6.67	64	126	104
		Filtrated eluate	6.11	64	35.2	98
	PAH solution (eluate)	Non-filtrated eluate	6.67	64	126	83
		Filtrated eluate	6.11	64	35.2	86

earity for from 4 up to 8 point calibrations. The correlation factors varied from 0.99853 (indeno[1,2,3-c,d]pyrene, 4 point calibration) to 0.99997 (pyrene, 8 point calibration).

2.5. *Experiments to study the influence of diluted organic matter*

To study the influence of diluted organic matter (DOM) on the sorption process of PAH to the stir bar, we prepared eluates of the non-contaminated reference soils and agitated the stir bar for 60 min to enable the DOM sorbing to the stir bar. With the so “pre-coated” stir bar we measured one of the standard solutions with a PAH concentration of 41.1 μg L^{-1} (sum of 11 EPA-PAH, since we used a highly concentrated standard solution with only 11 of the PAH compounds in linear range). In addition, we prepared the same standard solution not with deionized water but with the respective eluate (stated as “PAH solution (eluate)” in Table 4) and checked them for PAH concentrations with SBSE as described in Section 2.3. We examined the eluates of both TL and US soil, unfiltered as well as filtered.

All results given in Table 4 are mean values of three replicate experiments.

3. Results

PAH concentrations are given in Table 3 as the sum of 15 EPA-PAH, determined with SBSE as well as LLE sample preparation and subsequent HPLC analysis. In the case of batch test experiments, we distinguished the PAH values determined with SBSE before and after the filtration step.

We found higher PAH concentrations with SBSE than with LLE for the reference solution and the batch test eluates of LS, TL, and US soil materials. For the eluates of the respective column experiments we observed less PAH concentrations with SBSE (Table 3 and Fig. 1). In the case of MS soil material, two batch test eluates showed more PAH with SBSE and three less. For the column experiments we found less PAH with SBSE than with LLE (Table 3 and Fig. 2).

Fig. 3 shows that the eluates with the highest turbidity after filtration have the highest relative excess findings of PAH with SBSE.

The relative differences in PAH concentrations (SBSE compared to LLE) were the lowest for the reference solution, TL, and MS batch test eluates (−13 to 58%) and the highest for LS and US batch test eluates (81–288%). For the column experiments, the differences varied between −5 and −80%.

Table 3 shows the respective test conditions and accompanying parameters like TOC values of the eluates as well as pH, electric conductivity and turbidity before and after the filtration step. The pH value was between 5.01 and 6.53 for LS, TL, and US soil materials and usually higher after filtration. For the MS material, the pH value varied from 5.99 to 8.61 and usually decreased slightly through filtration. The electric conductivity varied from 81.4 (US) to 335 μS cm^{-1} (TL) with only minor change through filtration. The turbidity of the batch test eluates was very low for the MS soil material (<3 FNU) and was reduced even more by filtration. For TL, the filtration step reduced the turbidity about an order of magnitude, whereas for LS and UL the turbidity declined only about two-thirds. In the case of column experiments, the turbidity was low in all cases (<6 FNU) with the exception of LS (12.2 FNU). The mean values of the TOC results varied from 12.2 (MS) to 162 mg L^{-1} (TL).

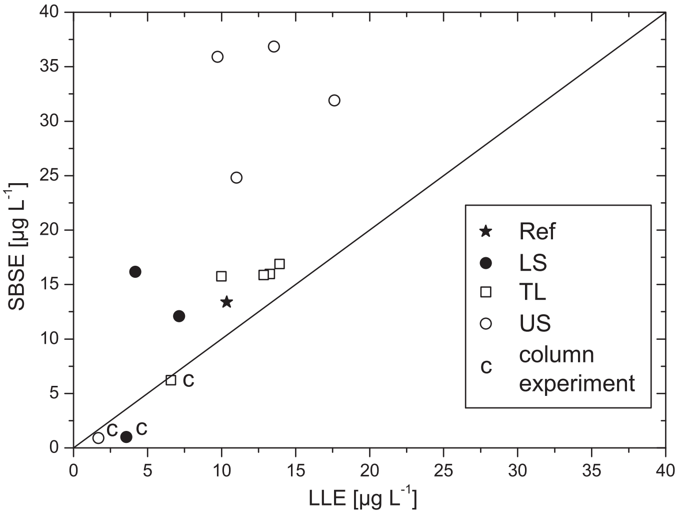

Fig. 1. Comparison of PAH concentrations in aqueous eluates (reference solution, LS, TL, US) determined with SBSE and LLE.

Fig. 4 shows that the PAH distribution in the solid matter of all tested materials is similar with only minor differences.

Fig. 5 shows the mole fractions of the 15 examined EPA-PAH in the reference solution, as determined with SBSE and

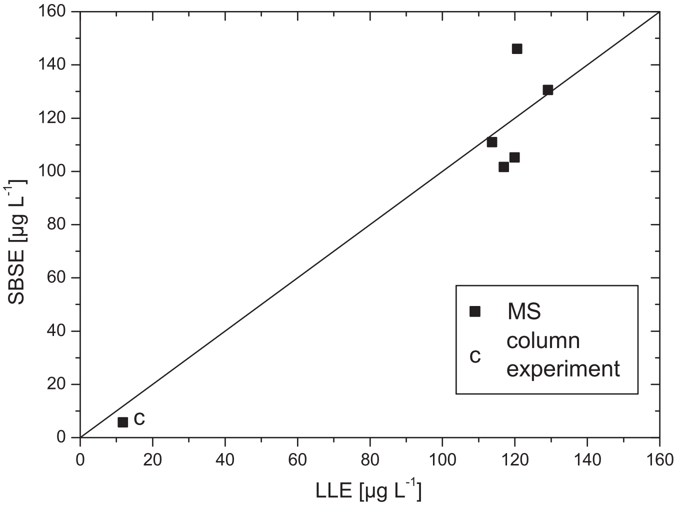

Fig. 2. Comparison of PAH concentrations in aqueous eluates (MS) determined with SBSE and LLE.

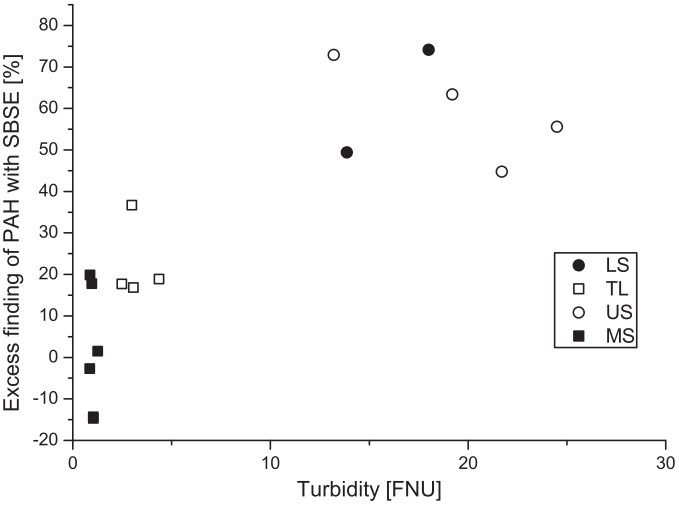

Fig. 3. Excess finding of PAH with SBSE in batch test eluates vs. turbidity after filtration.

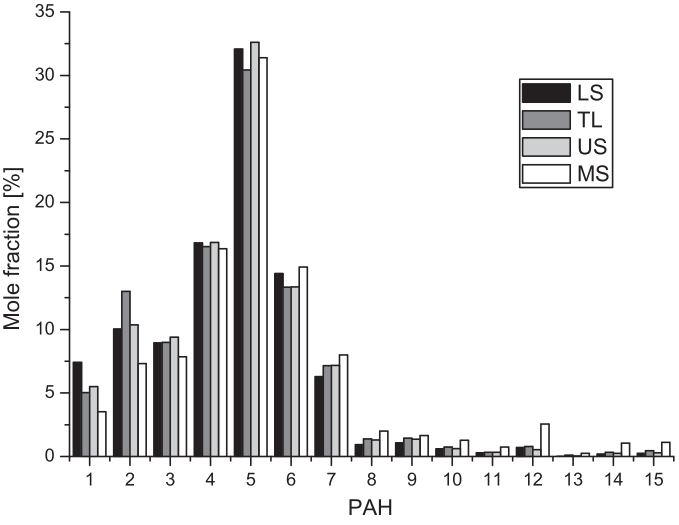

Fig. 4. PAH distribution in the solid matter of the test materials.

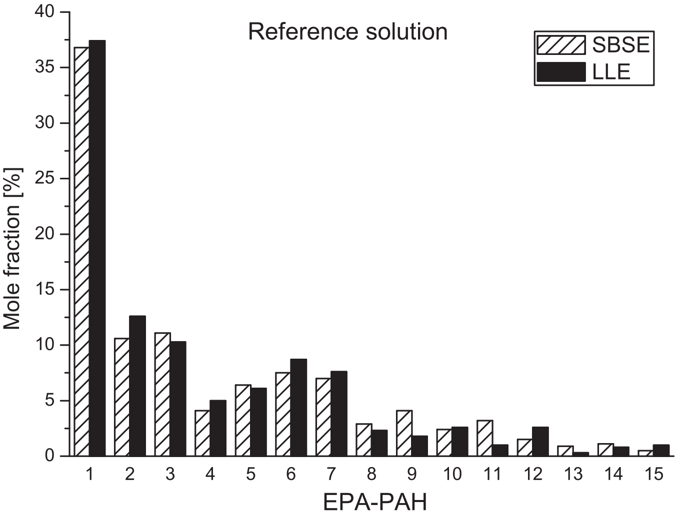

Fig. 5. Mole fractions of 15 EPA-PAH in reference solution, determined with SBSE and LLE.

LLE, respectively. The PAH distribution pattern differs only slightly and indicates the largest deviations for chrysene and benzo[k]fluoranthene. Fig. 6 illustrates the PAH distribution pattern of the batch test (left) and column test eluates (right) obtained from the US soil material. Fig. 7 shows the same for the MS material. The conditions for both batch tests were 24 h agitation at 7 rpm and centrifugation at 20,000 × *g*.

In all cases, the distribution pattern in the eluates differs significantly from those in the solid matter. In particular, naphthalene, acenaphthene and fluorene are more abundant in the eluates. SBSE and LLE show a very similar PAH distribution for batch tests. For column experiments the differences are more significant but heterogeneous. For instance, in the case of US, naphthalene was more abundant after SBSE sample preparation and acenaphthene after LLE. In the case of MS it was the other way round.

Table 4 indicates the effect of DOM on the SBSE analysis. The PAH recovery is given together with pH, electric conductivity and turbidity of the respective eluates. The determined PAH values are, with one exception, lower than that of the PAH standard solution used for the experiments. The recovery rates varied between 82 and 104%.

4. Discussion

Comparing PAH determination using two different sample preparation techniques prior to analysis (SBSE and LLE), two possible influences may explain the different results. Equilibrium extraction methods like SBSE and SPME usually measure only a fraction of the analyte in the sample. Analytes bound to suspended solid matter or sorbed to container walls might affect the analysis. Since PAH are often colloid-facilitated [8,10,30], equilibrium extraction methods might underestimate its amount. In contrast to other methods, like SPME for instance, SBSE applies a considerably high amount of extractant (24 μL polydimethylsiloxane on each stir bar). This is an excess of more than three orders of magnitude compared to the amount of PAH in each sample (9.1–17 ng in 10 mL eluate). Assuming that the Twister sorbs most of the analyte present in the free aqueous phase, the equilibrium between particle bound PAH and aqueous phase is disturbed and more PAH may be released which in progression can sorb to the stir bar. This process may reduce or even avoid the underestimation of analytes with SBSE due to the presence of colloid-facilitated PAHs.

LLE on the other hand generally extracts the total amount of available compounds in the sample but may induce loss of analytes (in particular more volatile analytes) through the sample preparation procedure. Especially a complex sample matrix can hamper the phase separation and complicate the drying of the organic phase with the need of more desiccant. The evaporation of the organic solvent can lead to loss of volatile compounds, e.g. naphthalene and the use of diverse glassware may cause sorption of analytes on container walls.

The turbidity as an indicator of suspended matter amount in the eluates, correlates with the different results obtained by SBSE and LLE. The higher the turbidity, the more PAH was determined with SBSE compared to LLE (Fig. 3). The complex matrix might have hampered the LLE leading to a loss of PAH as described above. The comparative PAH results before and after the filtration step also indicates a matrix effect. For LS and US, the filtration seemed to be less effective, resulting in a relatively high turbidity and the highest excess findings of PAH with SBSE. In the case of TL, the filtration reduced the turbidity significantly and thus the matrix probably did not hamper the LLE to the same extend. Accordingly, the results for MS, which showed a very low turbidity and presumably a simple matrix, were more comparable, indicating only a marginal effect on the LLE sample preparation.

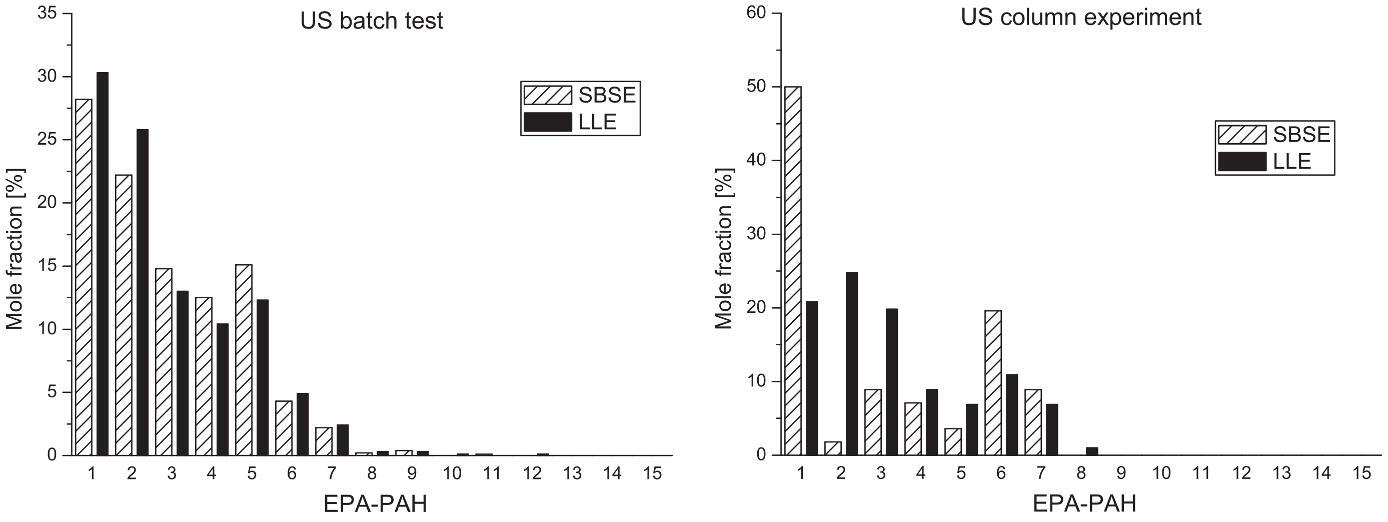

Fig. 6. Mole fractions of 15 EPA-PAH in US batch and column test eluates, determined with SBSE and LLE.

In contrast to the batch experiments, we found more PAH with LLE than SBSE in the case of column experiments. This might be due to the generally low turbidity which indicates a relatively simple matrix and less extensive sample preparation. The assembling of the sample material into the columns results in a certain self-filtration capacity [31,32], leading to a considerably lower turbidity compared to batch test eluates. The lower amount of suspended matter in the eluate, resulting in less amount of colloid-facilitated PAH, together with fewer losses in LLE is assumed as the reason for underestimation of PAH in column experiment eluates by SBSE. Considering the similar turbidity values and differences between SBSE and LLE for all studied soil materials, the column test experimental set-up seemed to level matrix effects to some extent.

The various batch test conditions (stated in Table 3) show no clear effect on the differences between SBSE and LLE sample preparation. Their influence on the general release of PAH from contaminated soils to the eluate will be discussed more in detail elsewhere. This paper is focussed on the comparison of the sample preparation prior to analysis. The accompanying parameters pH value, electric conductivity, and total organic carbon (TOC) seem to depend rather on the properties of the soil materials than on the experimental conditions. There is no correlation of these parameters to the PAH concentrations derived from SBSE and LLE, respectively.

In the case of the reference solution and the batch tests, the different sample preparation steps have only minor effects on the PAH distribution pattern. Obviously, neither different solubilities of PAH compounds nor the presumed release of colloid-facilitated PAH in the case of SBSE influences the PAH distribution. The results show no significant reduction of naphthalene concentrations through LLE (Figs. 6 and 7), indicating that it is not prone to loss through evaporation during LLE sample preparation, at least in the observed cases. However, there are some discrepancies in the PAH pattern which are not consistent and remain unclear. Further experiments are needed in order to check their significance. The deviation of the eluate's PAH distribution pattern from those of the solid matter is probably due to different water solubility and bonding conditions of PAH to the soil matrix.

The presence of DOM in a PAH standard solution as well as on a pre-coated stir bar seem to hamper the PAH sorption on the stir bar, leading to a lower amount of detected PAH. However, the effect seems to be relatively small and independent of matrix, filtration step, and accompanying parameters.

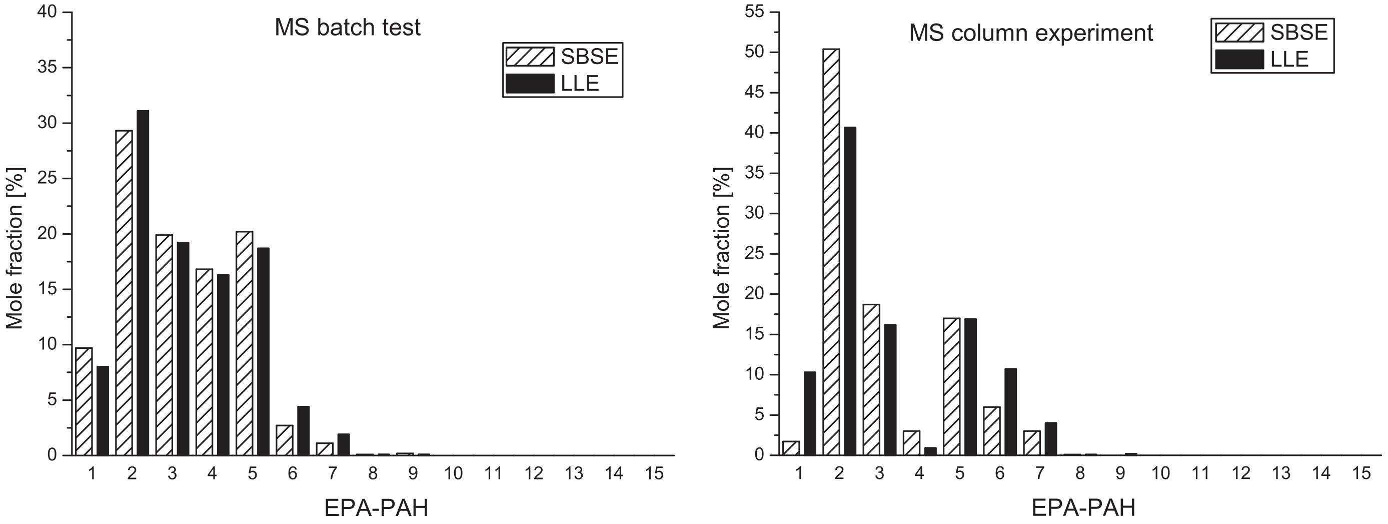

Fig. 7. Mole fractions of 15 EPA-PAH in MS batch and column test eluates, determined with SBSE and LLE.

5. Conclusions

SBSE seems to be a very promising alternative to LLE in terms of PAH analysis of soil eluates. This sample preparation is fast, simple, and in turn time saving due to the possibility of more parallel analyses. Additionally the use of organic solvents is drastically reduced. For most of the studied soil materials SBSE detects more PAH in batch test experiments than LLE. The differences depend strongly on the soil matrix: i.e. the more complex the matrix, the greater are the differences. The influence of colloid-facilitated PAH and DOM on the amount of detected PAH seems to be small. Accompanying parameters, such as pH value, electric conductivity and TOC show no significant correlation to the different sample preparation techniques.

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