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1 Applying no-depletion equilibrium sampling and full-depletion
2 bioaccessibility extraction to 35 historically polycyclic aromatic
3 hydrocarbon contaminated soils

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19 Abstract

20 Assessing the bioaccessibility of organic pollutants in contaminated soils is
21 considered a complement to measurements of total concentrations in risk assessment
22 and legislation. Consequently, methods for its quantification require validation with
23 historically contaminated soils. In this study, 35 such soils were obtained from various
24 locations in Switzerland and Cuba. They were exposed to different pollution sources
25 (e.g., pyrogenic and petrogenic) at various distance (i.e., urban to rural) and were
26 subject to different land use (e.g., urban gardening and forest). Passive equilibrium
27 sampling with polyoxymethylene was used to determine freely dissolved
28 concentrations (C_{free}) of polycyclic aromatic hydrocarbons (PAHs), while sorptive
29 bioaccessibility extraction (SBE) with silicone rods was used to determine the
30 bioaccessible PAH concentrations (C_{bioacc}) of these soils.

31 The organic carbon partitioning coefficients of the soils were highest for skeet soils,
32 followed by traffic, urban garden and rural soils. Lowest values were obtained from
33 soil exposed to petrogenic sources. Applicability of SBE to quantify C_{bioacc} was
34 restricted by silicone rod sorption capacity, as expressed quantitatively by the
35 Sorption Capacity Ratio (SCR); particularly for soils with very high K_D . The source
36 of contamination determined bioaccessible fractions (f_{bioacc}). The smallest f_{bioacc} were
37 obtained with skeet soils (15%), followed by the pyrogenically influenced soils, rural
38 soils, and finally, the petrogenically contaminated soil (71%). In conclusion, we
39 present the potential and limitations of the SBE method to quantify bioaccessibility in
40 real soils. These results can be used for additional development of this and similar
41 bioaccessibility methods to guarantee sufficient sorption capacity to obtain reliable
42 results.

43 Keywords

44 Bioavailability, SBE, passive sampling, sink capacity, PAH, soil

45 **Capsule**

46 Freely dissolved concentrations and bioaccessible fractions of PAHs in soils depended
47 on pollutant source and site characteristics, while the sink capacity was limiting
48 during bioaccessibility extractions of soils with low PAH content and high K_D values.

49

50

51 Introduction

52 Regulatory guidelines for the assessment and treatment of soil contamination by
53 polycyclic aromatic hydrocarbons (PAHs) are still based on their total concentration
54 in dry bulk soil as indicators of the potential exposure of soil-dwelling organisms,
55 plants and humans (Regulation (EC) No 1907/2006 of the European Parliament and of
56 the Council, 2006 ; Swiss Confederation, 2016). However, this criterion is
57 increasingly disputed because it does not describe the pollutant fraction that is best
58 linked to PAH exposure toxicity and mobility in soils (Reid et al., 2000a).

59 Recently, Ortega-Calvo et al. (2015) discussed the concept of “bioavailability” to
60 organic soil contaminants and identified essential points that need to be accepted by
61 environmental regulators before it can be incorporated into risk assessment
62 frameworks. This requires the consistent use of the concept of “bioavailability”, the
63 establishment of corresponding operational standards and robust methods to quantify
64 it. The concept of bioavailability comprises two parameters, both of which are
65 valuable, valid and complementary to each other (Reichenberg and Mayer, 2006). The
66 first is the chemical activity of a contaminant, that is closely linked to freely dissolved
67 concentrations (C_{free}), e.g., in pore water and characterises the potential for
68 partitioning and diffusion processes. It represents the readily available pollutant
69 concentration, and is often called bioavailability. The second includes those molecules
70 that are or can become available for interaction with biotic receptors. It includes the
71 fraction of a contaminant that is freely dissolved plus the fraction that can become
72 rapidly available through desorption from solid surfaces; this is called bioaccessible
73 portion (Reichenberg and Mayer, 2006).

74 Numerous polymer-based sampling techniques have been developed to determine the
75 chemical activity and bioaccessibility of organic contaminants (Bao and Zeng, 2011;

Cui et al., 2013; Cachada et al., 2014). The conventional way to assess the chemical activity of an organic contaminant (i.e., C_{free}) is to use non-depletive equilibrium passive sampling (Reichenberg and Mayer, 2006). The depletion of the PAHs by the polymer needs to be negligible, e.g., 5% of the total amount, to avoid an artefactual reduction of C_{free} before it is measured. To fulfil this condition, previous investigations have proposed the following relationship between the polymer and the sample (Eq. 1) (Mayer et al., 2003; Witt et al., 2013; Lang et al., 2015):

$$\frac{K_{PS} m_{PS}}{K_{OC} m_{OC}} < 5\% \quad (\text{Eq. 1})$$

where m_{oc} is the mass of the organic carbon (OC) in the sediment or soil subjected to the experiment, K_{oc} is the compound-specific OC to water partitioning coefficient of the sediment or soil, K_{PS} is the partitioning coefficient between the passive sampler (PS) and the water and m_{PS} is the mass of the PS used for the experiment.

For sorptive bioaccessibility extractions, the sorbent is intended to deplete the sample (Smedes et al., 2012); this can be expressed as (Eq. 2):

$$K_{PS} m_{PS} > K_{OC} m_{OC} \quad (\text{Eq. 2})$$

For non-depletion equilibrium sampling and for full-depletion bioaccessibility extraction, the sorption capacity ratio (SCR) of the polymer sorbent has recently been introduced (Hilber et al., 2017) and can be estimated as:

$$SCR = \frac{K_{PS} m_{PS}}{K_{OC} m_{OC}} \quad (\text{Eq. 3})$$

Until now, the SCR has only partially been taken into account. It has not yet been fully implemented in the validation of bioaccessibility quantification method,

particularly with polymeric passive sampling techniques in historically contaminated soils.

According to this concept, chemical activity is quantified by placing a non-depletive PS such as polyoxymethylene (POM), low-density polyethylene (LDPE), or polydimethylsiloxane (PDMS) in soils or sediment slurries. Among these, POM possesses the following advantages: it has a smooth surface and is physical robust, it is commercially available and it is inexpensive. In addition, POM results showed a strong correlation to PAH accumulation in earthworms and plants roots (Gomez-Eyles et al., 2011) and has been successfully applied to historically contaminated soils (Arp et al., 2014).

Conversely, bioaccessibility is measured by mild extractions (Reid et al., 2000b; Cuypers et al., 2002; Liste and Alexander, 2002) and depletive sampling methods (e.g., Tenax®) (Cornelissen et al., 1997; Cornelissen et al., 1998; ten Hulscher et al., 2003). Recently, a sorptive bioaccessibility extraction (SBE) method using silicone rods was proposed to quantify bioaccessible PAH concentrations (Gouliarmou and Mayer, 2012; Collins et al., 2013; Zhang et al., 2015). Silicone rods are used here as a sorptive sink (i.e., full depletion) in order to measure bioaccessibility. The silicone rod is ideal for this purpose since it provides a desirable combination of a high partitioning coefficient and a high diffusivity for hydrophobic compounds. This results in a small internal diffusive resistance within the polymer and facilitates continuous absorption of the mobilised PAHs. In addition, silicone rods can be separated quite easily from the suspended matrix at the end of the experiment, in contrast to the well-established Tenax® method. Finally, the SBE method includes the silicone rods as an additional sorptive sink in the solution, which increases the extraction capacity in comparison to other methods (Gouliarmou and Mayer, 2012;

Gouliarmou et al., 2013). Although the SBE method has effectively been used in some studies (Gouliarmou and Mayer, 2012; Collins et al., 2013; Gouliarmou et al., 2013; Mayer et al., 2016), it has not been systematically evaluated whether SBE provides a sufficient sorption capacity for a wide variety of soil and sediment samples, taking account of the essential pre-requisite given by Equation 2.

The aim of the present study is to test the suitability of the SBE method as a practical tool to characterise PAH bioaccessibility in soil. We selected 35 different sites with historical PAH contamination encompassing 28 soil samples from Switzerland (Bucheli et al., 2004; Desaulles et al., 2008; Agarwal and Bucheli, 2011; Gubler et al., 2015; FaBo, 2017), which can be considered representative of soils from Central Europe, and seven soil samples from Cuba, to include soils from tropical and Caribbean regions. We investigated how the extractability of PAH by means of SBE in this variety of soils related to total and POM-measured freely dissolved concentrations of the PAH, in dependence of sources of contamination and soil properties. Our intention was first to test the feasibility of the SBE method and the possibility of including it in future risk assessment. The results will help evaluate the potential applicability of the SBE method, including its difficulties and limitations. All results are gathered from historically contaminated soils which are known to have sorption characteristics that are different from “laboratory-spiked” soil, essentially due to “aging” (Alexander, 2000; Cornelissen et al., 2005).

2. Materials and Methods

2.1. Chemicals

The PAHs we analysed included the following 16 compounds (PAH₁₆), as prioritised by the US Environmental Protection Agency (EPA) (NTP, 2005; Andersson and

Achten, 2015): naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benzo[*a*]anthracene (BaA), chrysene (CHR), benzo[*b*]fluoranthene (BbF), benzo[*k*]fluoranthene (BkF), benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IPY), dibenzo[*a,h*]anthracene (DBA) and benzo[*ghi*]perylene (BPE). The sum of these is abbreviated as ΣPAH_{16} . The logarithms of their octanol-water (K_{OW}) (Smedes et al., 2009), POM-water ($K_{\text{D,POM}}$) (Hawthorne et al., 2011) and silicone rod-water partitioning coefficients ($K_{\text{D,silirod}}$) (Smedes et al., 2009) are summarised in the supplementary information file (SI), Table S1.

2.2. Selection and description of soil samples

The soil samples (N=35) included 21 samples (KABO1- KABO21) from the monitoring network (KABO) of the Canton of Zurich, Switzerland (FaBo, 2017), seven samples (NABO1- NABO7) from the Swiss National Monitoring Network (NABO) (Bucheli et al., 2004; Desaulles et al., 2008; Agarwal and Bucheli, 2011; Gubler et al., 2015), and seven samples (CUBA1- CUBA7) from Cuba. The latter were collected in collaboration with the Centro Nacional de Sanidad Agropecuaria (CENSA) in San José de las Lajas, Cuba.

The main prerequisites for the selection of the soil samples included representing different petrogenic and pyrogenic sources of contamination (SI, Table S2 and Table S3), soil properties such as total organic carbon (TOC) and black carbon (BC) (SI, Table S4) and a large range of total soil PAH concentrations (C_{tot}) (SI, Table S5) (Bucheli et al., 2004; Desaulles et al., 2008; Agarwal and Bucheli, 2011; Gubler et al., 2015; FaBo, 2017). Total organic carbon and BC were quantified using the method

developed by Agarwal and Bucheli (2011). The C_{tot} of the ΣPAH_{16} varied over four orders of magnitude, from 0.4 to 2137 mg kg⁻¹ (FaBo, 2017).

2.3. Quantification of freely dissolved PAH concentrations (C_{free}) in soil suspensions
Polyoxymethylene (POM; 75 μm thick. CSHYDE Company, Lake Villa, USA) was used for equilibrium passive sampling to quantify the C_{free} of the native PAHs in the soil suspensions. Polyoxymethylene strips were cut into rectangles of 2 cm $\times$ 4 cm (ca. 100 mg) (Hale et al., 2012). Before the experiment, POM strips were cleaned by sequential solvent extraction, twice in heptane, twice in methanol and finally twice in Milli-Q water (Millipore, Billerica, MS, USA) with the aid of sonication, and stored in Milli-Q water until use.

For each analysis, a POM strip and a soil aliquot (around one gram) were suspended in 40 mL of Milli-Q water, to which 0.2 g L⁻¹ NaN₃ had been given to prevent microbial PAH degradation, in a 100 mL glass bottle (Schott Duran, Mainz, Germany) and closed with a Teflon (PTFE)-lined screw cap. The bottles were shaken for 30 days at 150 rpm on a horizontal orbital shaker (SM 25, Haska AG, Bern, Switzerland) at constant room temperature in the dark. Then the POM strips were removed from the soil suspension, washed carefully with Milli-Q water, cleaned and dried with a lint-free tissue to remove any soil particles and placed in a conical flask (with glass stoppers) with 20 mL of an acetone/heptane solution (20:80, vol/vol). The extraction solution was spiked with a d-PAH internal standard containing the 16 corresponding perdeuterated PAHs. After two days, the extracts were concentrated in a Syncore Analyst (Büchi Labortechnik AG, Flawil, Switzerland) to 1 mL and spiked with recovery standard (Indeno[1,2,3-*cd*]fluoranthene) for gas chromatograph-mass spectrometry (GC-MS) analysis. The PAHs within the extracts were quantified using

the internal standard method and calibration standards with different amounts of analytes ($10 - 2500 \mu\text{g L}^{-1}$).

The values of the POM-water partitioning coefficient ($K_{D,POM}$) (SI, Table S1) for the individual PAH compounds were taken from Hawthorne et al. (Hawthorne et al., 2011). The soil- water partitioning coefficients (K_D) were calculated as the ratio between the C_{tot} as previous reported studies (FaBo, 2017) and the C_{free} quantified here, which refers to the chemical's concentration in the solution (Schwarzenbach et al., 2005).

2.4. Sorptive Bioaccessibility Extraction (SBE)

The bioaccessible PAH concentrations of the soil samples were determined as described by Gouliarmou and Mayer (2012) from the PAH mass quantified in the silicone rods (C_{bioacc} , $\mu\text{g kg}^{-1}$ soil dry weight (dw)). Translucent silicone rods were used as absorptive sinks. These rods were custom made and supplied by Altec (Cornwall, UK), and their partitioning properties for PAHs were recently referenced against a wide range of other silicon materials and one LDPE material (Gilbert et al., 2016) ($\log_{10}K_{D,silirod}$ values are listed in the SI, Table S1). They had a diameter of $3 \text{ mm} \pm 0.15 \text{ mm}$ and a nominal hardness of 60°Shore A. To clean them before use, they were first washed with detergent by hand and then by machine to remove talc particles. Thereafter, they were Soxhlet extracted with ethyl acetate for 100 h. The cleaned rods were stored in a sealed bottle with acetone until use. Before starting an experiment, the rods were soaked three times for at least one hour in Milli-Q water to remove any absorbed acetone.

Three meters of cleaned rod (mass of the silicone rod, $m_{silirod} = 24 \text{ g}$) were placed in a 100 mL glass bottle type Schott Duran (Mainz, Germany) with Teflon (PTFE)-lined

screw caps. Depending on C_{tot} , one to 10 g of soil was added, and the bottle was filled with 50 mL of a hydroxylpropyl-cyclodextrin (HPCD) solution ($75 \text{ g}_{\text{HPCD}} \text{ L}^{-1} \text{ Milli-Q-water}$) and $200 \text{ mg L}^{-1} \text{ NaN}_3$. The HPCD solution was added to enhance PAH transfer from the soil into the silicone rod (Gouliarmou and Mayer, 2012). The bottles were shaken for seven days at 40 rpm in an overhead shaker at room temperature in the dark. As PAH uptake into silicone rods is fast, these conditions allow for a complete mass transfer of desorbed PAHs into the silicone rod (Gouliarmou and Mayer, 2012). Thereafter, the silicone rods were removed, rinsed with Milli-Q- water, cleaned and dried with a lint-free tissue to remove any remaining soil particles from the surface. PAH extraction from the rods was carried out overnight, by immersing the rods into 100 mL acetone, spiked with a d-PAH internal standard solution containing the 16 corresponding perdeuterated PAHs. This procedure was repeated with another 100 mL acetone over a second night. The two acetone extracts were combined and concentrated to 1 mL in a Syncore Analyst. The extracts were cleaned by means of 9:1 (vol/vol) N,N-dimethylformamide-Milli-Q water liquid-liquid partitioning, followed by a column of water-deactivated silica gel to remove any silicone residues. Finally, the PAH_{16} were analysed by GC-MS. The PAHs within the extracts were quantified using the internal standard method and calibration standards with different amounts of analytes ($10\text{--}2500 \mu\text{g L}^{-1}$).

2.5. Quality control and assurance

Method detection (MDL) and quantification (MQL) limits were determined for each individual PAH by three and ten times the signal over the noise of soil extract chromatograms, respectively, and corresponding quantified concentrations. They were obtained as median values from six soils of different types or with different sources of

contamination. The MDL and MQL of C_{free} ranged from 0.002 to 6.12 ng L⁻¹_{PW} and from 0.006 to 20.4 ng L⁻¹_{PW}, respectively (SI, Table S7). The MDL and MQL of C_{bioacc} ranged from 0.084 to 0.492 µg kg⁻¹_{soil}, and from 0.279 to 1.64 µg kg⁻¹_{soil}, respectively (SI, Table S13).

For both chemical methods, analyses were carried out in triplicate with sample replicates processed and analysed in different batches. The C_{free} and C_{bioacc} of all PAH compounds were well above the corresponding MDLs (Figures S2 and S4, respectively, solid lines). Generally, concentrations were also above the MQL (dashed line) and blank levels (yellow dashed lines). For the interpretation of the results, MDLs were taken as lower limits. Average extraction standard recoveries for the C_{free} and C_{bioacc} of the 16 deuterated PAHs ranged from 32 to 73% and from 12 to 77%, respectively (SI, Table S10 and S17). While low absolute recoveries of low molecular weight PAHs (LMW PAHs) were reported earlier, it is possible to compensate successfully for these losses by the use of deuterated analogues (Bucheli et al., 2004).

Blanks and control samples were included in duplicate in each batch. The control soil was a well characterised soil sample of the NABO (KB6) and was selected because its C_{tot} was high enough to be quantified by these chemical methods ($C_{\text{tot}, \Sigma\text{PAH}_{16}} = 4326$ µg kg⁻¹). Analytical repeatability (from the same batch) and reproducibility (among batches) from control results were calculated for each PAH compound individually, and ranged from 0.071 to 135.00 ng L⁻¹_{PW} and 0.085 to 111.00 ng L⁻¹_{PW}, respectively, for C_{free} (SI, Table S9) and from 0.58 to 342.23 µg kg⁻¹_{soil} and from 0.64 to 291.90 µg kg⁻¹_{soil}, respectively, for C_{bioacc} (SI, Table S15). The relative standard deviations (RSDs, standard deviation over mean concentration) of the analytes ranged from 0.21 to 24% for C_{free} and from 0.9 to 49% for C_{bioacc} .

While PAHs can adsorb to glassware during POM passive sampling and SBE (Hsieh et al., 2011), this issue was negligible in our experiments due to the drastically higher sorption capacity of the silicone rod and the POM strips in comparison with the glass surface (roughly three and five orders of magnitude, respectively) (SI, Figure S7).

2.6. Data evaluation

The hypothesis leading to an Analysis of Variance (ANOVA) were (1) soil parameters such as TOC, pollutant properties such as K_{OW} , and the source of contamination influence the K_D of the PAH compounds, and (2) the same properties influence f_{bioacc} . Thus, the data were processed with R (software version 0.99.896) for an ANOVA. One was run with K_D as dependent variable and pollutant sources (SI, Table S2), K_{OW} (SI, Table S1), and TOC (SI, Table S4) as independent variables and one with f_{bioacc} as dependent and the same independent variables. If p-values were ≤ 0.05 the influence of the parameters on K_D or f_{bioacc} was significant.

3. Results and Discussion

3.1. Soil specific K_{OC} values for the range of PAH contaminated soils

The C_{free} for the ΣPAH_{16} ranged from 0.05 to $5.8 \mu g L^{-1}_{PW}$. It was dominated by NAP, PHE and FLT, which contributed more than 60% to the total (data for individual compounds are presented as SI in Table S6).

The compound specific organic carbon to soil-water partitioning coefficients were calculated according to Eq. 4. The K_{OC} values of individual PAHs were plotted against the respective values of the octanol-water partitioning coefficient (K_{OW}) in Figure 1.

$$K_{OC} = \frac{C_{tot}/C_{PW}}{f_{TOC}} = \frac{K_D}{f_{TOC}} \quad (\text{Eq. 4})$$

Figure 1: Measurements of the compound specific organic carbon to soil-water partitioning coefficients (K_{OC}) vs. octanol-water partitioning coefficient (K_{OW}) for the 16 US EPA PAHs analysed in the 35 experimental soils of this study. The grey band represents the range of K_{OC} values predicted by various TOC based partitioning models (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach and Westall, 1981). Results are arranged by source of contamination and land use. A: skeet soils (N=9), B: traffic soils (N=12), C: urban garden soils (N=6), D: rural soils (N=6), E: forest soil (N=1) and F: petrogenically contaminated soil (N=1).

Figure 1 shows that the log₁₀K_{OC} values ranged from 2.5 for NAP to 10.3 for BPE. The measured K_{OC} values were, in all cases, considerably higher than the predictions obtained using empirical models (Karickhoff et al., 1979; Means et al., 1980; Schwarzenbach and Westall, 1981). The deviation between measurements and model prediction may be due to the fact that current models are based on data from

artificially contaminated soils, where the aging time is mostly too short to establish phase distribution equilibrium (Alexander, 2000; Brand et al., 2013) and that the amount of sorbents, either amorphous or condensed, was limited (Cornelissen et al., 2005). Furthermore, these models are based on experiments in which high concentrations of PAH were applied as spikes. In contrast, all measurements in the present study were based on native PAHs in historically contaminated soils. This implies an aging effect and also means that the concentrations were generally in a lower range than those used in the models. Finally, for calculating the experimental K_{OC} values presented here, we used the $K_{D,POM}$ values published by Hawthorne et al. (Hawthorne et al., 2011), which were recommended by Arp et al. (Arp et al., 2015). These values, however, are in the upper range of the published values and translated into relatively high K_{OC} values.

The first hypothesis of the chapter 2.6 was tested and ANOVA results showed a significant influence of source and K_{OW} on the K_D ($p < 2E-16$) of the PAH compounds but not so the TOC. This is in the line with previous studies where, in case of severe pollution, the nature of the pollutant source plays a more important role for PAH partitioning and bioavailability than native soil parameters (Baumard et al., 1998; Kołtowski et al., 2016; Xia et al., 2016). This was probably the case for most of the (contaminated) soils investigated here, since no clear influence of soil TOC and BC content (SI, Table S4) on C_{free} and K_{OC} was discernible. In our experiment, the skeet soils that were contaminated by coal-tar pitch exhibited the highest $\log_{10}K_{OC}$ values, ranging from 5.2 for NAP to 9.4 for BaP (Figure 1A). These are in concordance with the values found by Xia et al. (Xia et al., 2016). This is plausible because weathered coal-tar components of pitch contain BC, in the form of soot, coke and cenospheres. In the production process, these BC materials are incorporated in firing the clay-tar

composite. An increase in sorption capacity of soil and sediments contaminated by weathered coal-tar pitch has already been reported (Khalil et al., 2006; Smith et al., 2011; Xia et al., 2016). The soils with pyrogenic contamination (traffic road and urban garden) showed intermediate K_{OC} values (Figures 1B and 1C). The soils that had been exposed to traffic emissions (Figure 1B), and thus mainly to soot-like material, showed higher K_{OC} values than those of urban garden soils (Figure 1C), where the contaminants presumably originated from the combustion of charcoal or coal material. Such source-dependent differences, with the highest K_{OC} values for traffic soot, and lower ones for charcoal are in agreement with earlier findings (Jonker and Koelmans, 2002). The lowest K_{OC} values were observed in the soil contaminated from a petrogenic source (Figure 1F). This is because of the rubbery-like carbon material. PAHs entering soils with petrogenic materials are known to be more available than PAHs from pyrogenic inputs (Koelmans et al., 2006). The rural soils showed a particularly high variability in K_{OC} values. These soils were exposed to various diffuse sources, including emissions from industry, traffic and households. The only soil sample taken in a forest had a rather low K_{OC} value (Figure 1E).

In summary, these results are in line with earlier findings of lower K_{OC} values and corresponding higher C_{free} values of PAHs in soils the PAH contamination of which is associated with amorphous organic matter, rather than with condensed carbonaceous material (i.e., pyrogenic PAHs) (Thorsen et al., 2004; Xia et al., 2016). In addition, the high K_{OC} values of pyrogenic PAHs are attributed to their co-emission with corresponding geosorbents, such as soot. Our K_{OC} values were, on average, slightly higher than those obtained by the POM method in other historically contaminated soils or sediments (Jonker and Smedes, 2000; Arp et al., 2014) (SI, Figure S3). This is

mainly due to the large contribution in the data set (N=9) of the high K_{OC} results obtained from the skeet soils.

3.2. Sorptive bioaccessibility extraction (SBE) of PAHs from soils

3.2.1. Influence of sorption capacities ratio (SCR) on bioaccessibility

Irrespective of the SCR, the C_{bioacc} obtained by SBE ranged for individual PAHs from 0.005 for IPY to 17280 $\mu\text{g kg}^{-1}_{dw}$ for FLT (median= 57.1 $\mu\text{g kg}^{-1}_{dw}$ SI, Figure S4 and Table S12). Their corresponding fractions (f_{bioacc}) ranged from 0.012% to 100%, or numerically even higher in a few individual cases (see below), which were calculated by C_{bioacc} over C_{tot} . While f_{bioacc} may be the more relevant parameter in terms of environmental chemistry point of view of PAH phase distribution processes, ecotoxicologists, regulators and decision makers may often be more interested in the actual exposure level, as expressed by C_{bioacc} .

As discussed above, the SBE method can be used as a depletive method to quantify bioaccessibility if SCR (Eq. 3) is larger than one, which means that the product of $K_{D,silicod}$ and $m_{silicod}$ is greater than the respective product of the soil sample. Figure 2 depicts f_{bioacc} vs $\log_{10}SCR$, as determined for individual PAHs in the 35 different soils.

Figure 2: Bioaccessible fractions (f_{bioacc}) of 16 individual US EPA PAHs in the 35 experimental soils vs. their corresponding sorption capacity ratio (SCR; note logarithmic scale). Points within the two shaded areas represent data obtained under depletive conditions ($\text{SCR} > 1$; for details, see text). Points inside the white area represent data that were gathered under insufficient depletion conditions ($\text{SCR} < 1$). Data were grouped by their octanol-water (K_{OW}) partitioning coefficients. The fractions $> 100\%$ ($N=5\%$) were set to 100% .

Figure 2 shows that more than half of the data (57%) were gathered under depletive conditions ($\text{SCR} > 1$). Only 12% of the data were obtained at $\text{SCR} > 10$, though, where it can be assured that the silicone rod fully acted as an infinitive sink. Consequently, the f_{bioacc} values obtained in these cases can be considered as robust. For those soils or analytes, where the f_{bioacc} results were obtained at $1 < \text{SCR} < 10$, the SBE method may not have provided sufficient sink capacity and f_{bioacc} may therefore

have been slightly underestimated. In the remaining cases, the depletion criterion was not fulfilled, and consequently, f_{bioacc} was even lower.

In general, C_{bioacc} and f_{bioacc} were successfully quantified for samples with relatively high PAH concentrations and when K_D values did not exceed 10^6 L kg^{-1} (SI, Figure S5). This combination of high PAH content and low sorption characterises the highest exposure and risk scenarios, where bioaccessibility measurements are most urgently needed. In contrast, it was more difficult to obtain valid bioaccessibility measurements for combinations of low PAH content and high K_D values, simply because it was difficult to obtain a sufficiently high SCR ratio. The earlier reported challenge for bioaccessibility measurements of PAHs due to capacity constraints is thus not limited to pure carbonaceous geosorbents such as soot or biochar, but also applies to many historically polluted soils. A large part of those results obtained with $\text{SCR} < 1$ exhibited K_D values higher than 10^6 L kg^{-1} (SI, Figure S5). Compounds with such elevated K_D are characterised by a low mobility; in this case, the K_D is the ruling factor that renders bioaccessibility difficult to quantify.

The sorptive capacity of the applied SBE method is much higher than cyclodextrin extractions, which would provide insufficient sorptive capacity for a much larger fraction of PAH and soil combinations. While the contaminant trap (Mayer et al., 2016) can provide much higher sorptive capacity, it is unfortunately not suited to directly measure bioaccessible fractions, and thus it remains a real challenge to measure bioaccessibility for high K_D situations, simply because it is difficult to provide a sufficient SCR. In principle we could improve the SCR of the system by increasing the mass of the silicone rod. Mayer et al. (2016) (Mayer et al., 2016) tested this option, increasing the mass ratio between sink and sample from 240 up to 9600 $\text{g}_{\text{sink}} \text{ g}_{\text{sample}}^{-1}$. Although these conditions provided a sufficient sink capacity, they were

not feasible in practise (30 m of silicone rods), and prone to artefacts due to the use of a possibly non-representative small amount of sample (0.025 g). In general, we stress that depletive conditions are not only determined by the favourable mass ratio of PS to sample (ideally $m_{PS}/m_s \rightarrow \infty$, where m_s is the mass of the solid (Smedes et al., 2012)), but also by the K_D of historically contaminated soils or sediments. Therefore, it must be quantified and taken into account during the adaptation and validation of the method for any given set of samples.

In some cases, and particularly for LMW PAHs, f_{bioacc} was as high as 100%, or even above (Figure 2). One reason for this artefact might be that the extraction conditions to determine C_{tot} were not always exhaustive in the first place. Another reason might be that extended wetting during SBE may have removed soluble or hydrophilic soil constituents (Hale et al., 2012), which possibly masked PAHs during C_{tot} determination in absence of a suitable solvent mediator.

3.2.2. Bioaccessibility estimates obtained under depletive conditions

Under depletive conditions ($SCR > 1$), C_{bioacc} of individual PAHs ranged from 0.50 to 17280 $\mu\text{g kg}^{-1}_{dw}$ (median = 37.43 $\mu\text{g kg}^{-1}_{dw}$) and are presented in Figure 3 against their corresponding C_{tot} .

In the following, we restrict the discussion of bioaccessibility data to those obtained under depletive criteria sink conditions. The other data are included in the SI Figure S6 (semi-transparent circles), but not interpreted any further.

In the second hypothesis (chapter 2.6) test, the ANOVA revealed again that the source of contamination and the K_{OW} values significantly influenced f_{bioacc} ($p < 9.5E-14$). Soils contaminated with skeet materials had the lowest f_{bioacc} (on average, 15%; Figure 3A), which corresponds to their highest K_{OC} values. Intermediate f_{bioacc} of 28%

447 and 41%, respectively, were obtained from those soils that received PAHs from other
 448 pyrogenic sources such as traffic road-side and urban garden soils (Figures 3B and
 449 3C). Higher f_{bioacc} were observed in soils from rural areas (on average, 63%) and
 450 forest (78%) (Figures 3D and 3E). Rural soils receive LMW PAHs (i.e., those
 451 quantified here) primarily via atmospheric transport in the gas phase from long-range
 452 transport sources. Such speciation facilitates phase transfer processes, specifically
 453 desorption forced by the SBE method, because it is not limited by, for example,
 454 physical entrapment in or retarded diffusion from co-emitted particles. The highest
 455 f_{bioacc} (on average, 73%) was observed for PAHs originating from the petrogenic
 456 source (Figure 3F). Similar to the C_{free} results (see above), this can be explained with
 457 the rubbery-like carbon material in this sample.

458
 459 Figure 3: Bioaccessible (C_{bioacc}) vs. total concentrations (C_{tot}) for the 16 US EPA
 460 PAHs in the 35 experimental soils. Results are arranged by source of contamination or

specific soil use types. A: skeet soils (N=9), B: traffic soils (N=12), C: urban garden soils (N=6), D: rural soils (N=6), E: forest soil (N=1) and F: petrogenically contaminated soil (N=1). Data were obtained under (quasi-) depletive sink conditions (SCR > 1; for details, see text). Data were grouped by their octanol-water (K_{OW}) partitioning coefficients. The three black lines represent 1:1 (thick solid lines), 1:10 (thin solid lines) and 1:100 (dashed lines) relations, i.e., bioaccessible fractions (f_{bioacc}) of 100%, 10% and 1%, respectively.

Several studies with contaminated soils and sediments that used SBE or Tenax[®] under infinitive sink conditions showed that bioaccessibility was higher than with only cyclodextrin solution (Gouliarmou et al., 2013; Li et al., 2015; Hong et al., 2016; Ruby et al., 2016). In other studies, the addition of either silicone rods or Tenax[®] were both found to increase the extraction of PAH from contaminated soil by factors of 1.3- 3.1 and 4.4, respectively, compared to the same experiment without the sink material (Collins et al., 2013; Li et al., 2015). Results similar to those of our study were obtained in the only other study using the SBE method with silicone rod in a soil where atmospheric deposition of soot was the main source of PAH contamination (Gouliarmou et al., 2013). There, f_{bioacc} results from a kindergarten soil ranged from 6 to 50% for the ΣPAH_{16} . A case of high bioaccessibility of PAHs in petrogenic-contaminated sediments was recently investigated using the Tenax[®] method (Hong et al., 2016); results were in line with those presented here.

3.3. Added value of bioaccessibility parameters for risk assessment

With regard to risk assessment and legislation, the presented data suggests that analysis of bioaccessibility by chemical proxies such as the SBE method may not

provide a better basis than C_{tot} . In case of low C_{tot} (i.e., uncontaminated soils), freely dissolved concentrations and bioaccessibility will never be an issue, even when a large fraction of the total is bioaccessible (which is still a matter of interest from a mechanistic and environmental chemistry point of view, though). In case of high C_{tot} (i.e. contaminated soils), bioaccessible concentrations, in most cases, will also be rather high, even when the fraction of bioaccessible PAH is low; therefore, such sites will usually require exposure reduction measures anyway. More meaningful applications of proxies for the assessment of soil PAH bioavailability include the evaluation of *in situ* remediation measures such as sorbent amendment to reduce PAH exposure and mobility in contaminated soils or sediments, or the substitution of living organisms in exposure experiments.

4. Conclusions and Outlook

To the best of our knowledge, this is the first paper that used the SBE method to investigate a large number of historically contaminated soils for bioaccessibility of PAHs. In general, the method proved feasible for soil samples with relatively high PAH concentrations and when K_D values did not exceed 10^6 L kg^{-1} . In contrast, the method did not always provide sufficient sink capacity when a low PAH content demanded a larger sample mass and K_D values exceeded 10^6 L kg^{-1} . Therefore, quality assurance and control parameters such as SCR should routinely be determined to critically evaluate the gathered data and avoid misinterpretation. When the SBE is properly applied, these results showed that they mirrored the influence of pollution source or soil type.

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- 697

1 **Highlights**

- 2 - Sufficient passive sampling sorption capacity is crucial for quality assurance
- 3 - Pollutant source type dominated K_D and bioaccessible concentrations
- 4 - Lowest bioaccessible fractions (15% on average) were found in skeet
- 5 contaminated soils
- 6 - Petrogenic polluted soil had the highest bioaccessible fractions (71% on
- 7 average)

8