Chapter 4

Freely dissolved pore water concentrations and sorption coefficients of PAHs in spiked, aged and field-contaminated soils

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Abstract

Freely dissolved aqueous concentrations in the soil pore water represent an important aspect of bioavailability and risk assessment of contaminated soils. Pore water concentrations of hydrophobic organic compounds are difficult to assess, so risk assessors generally estimate these concentrations from total soil concentrations using equilibrium partitioning (EqP) models. Strong sorption to soot, coal and weathered oil, as well as so-called aging effects hampers a good estimation of these pore water concentrations. Various chemical methods like Supercritical Fluid Extraction (SFE), Tenax extraction and equilibrium partitioning based extraction methods have been developed to measure site specific bioavailable, bioassessable, or freely dissolved concentrations in contaminated soils.
In this study, a negligible depletion, partitioning based, sampling technique was validated and applied to measure free concentrations of polycyclic aromatic hydrocarbons (PAHs) in spiked, aged and field-contaminated soils. Detailed kinetic studies were performed to select appropriate equilibration times. Freely dissolved aqueous concentrations in the pore water were compared to total concentrations, and sorption coefficients were calculated. Results show that EqP-models from literature can predict sorption coefficients of freshly spiked and lab-aged soils with an accuracy of less than a one order of magnitude. The effects of aging (up to 550 days) are rather minor, leading to an increase in the sorption coefficient of less a factor 3. Contrastingly, pore water concentrations of field-contaminated soils are often highly overestimated. Freely dissolved concentrations in the pore water were up to more than two orders of magnitude lower than what was expected from EqP-models, and consequently, risks can be highly overestimated with these models. The partitioning based sampling technique used in this study is a simple and sensitive tool to measure pore water concentrations, and could therefore be applicable in site-specific risk assessment of field-contaminated soils.

Introduction

Hydrophobic organic chemicals like polycyclic aromatic hydrocarbons (PAHs) are common micro-pollutants in soils (*115*). PAHs are produced by incomplete combustion processes and can be of natural and anthropogenic origin. Industrial soils of manufacturing gas plants, petroleum refineries and wood preservation plants tend to have very high PAH-concentrations up to thousands of milligrams per kilogram soil. Freely dissolved concentrations in the pore water and sorption coefficients are two important and relevant entities in the analysis and discussion of bioaccessibility and bioavailability.
The generic environmental risk assessment procedures of organic chemicals like PAHs in soils are based on total soil concentrations or pore water concentrations estimated from total soil concentrations and organic carbon normalized partition coefficients (*17,*

35, 37, 110, 116). These partition coefficients are generally based on experiments with freshly spiked standard soils and sediments. They do not consider so-called aging effects, where sorption may slowly increases in time, due to for example slow diffusion of compounds into micro-pores or inflexible organic materials (*3, 7, 117-119*). Besides that, these models also disregard the heterogeneity of the organic carbon in soil. Standard tests soils and sediments usually contain lower amounts of strong sorbing matrices like soot, coal or tar than are found at contaminated industrial sites (*112, 120-124*) and in those cases the matrix itself is often the main source of PAHs. Aging effects as well as and strong sorption these matrices will lead to higher sorption coefficients and lower pore water concentrations in field sediment and soil. Higher sorption may lead to a reduction in the bioavailability and bioaccessibility, and subsequently to lower risks.

Various chemical techniques have been developed to study bioaccessibility and bioavailability. One series of approaches is focused on extraction only the weakly bound fraction in soil and sediment. Several solvents (mixtures) (*125, 126*) and sorbents like Tenax (*108, 127-129*) or XAD-2 (*130*) are used for this purpose. Supercritical Fluid Extraction (SFE) is somewhat similar, but this method uses a highly pressurized gas (CO_2) in the liquid phase (*131*).

Other approaches focus on the freely dissolved concentrations in the pore water. Freely dissolved aqueous concentrations can be determined by equilibrium dialysis (*54*), by a gas purge method (*24, 132, 133*), or by negligible-depletive passive samplers such as semi permeable membrane devices (SPMD) (*20, 22, 26, 134*), poly(oxymethylene) solid phase (POM) (*28*), polymer coated glass sheets or fibers (*27, 29, 34, 57*). These passive samplers are equilibrated with the contaminated soil or sediment, and free aqueous concentrations can be calculated with known partition coefficients between the passive sampler and water. If the sampler is not at steady state yet, kinetic data are needed to estimate freely dissolved concentrations. As pointed out by Mayer et al. (*33*) equilibrium based methods are often more reliable.

The objective of this study was to measure pore water concentrations and soil sorption coefficients in freshly spiked soils, and to study how aging affects these concentrations. Similar studies were performed in a series of contaminated field soils, to determine site-specific sorption coefficients and to analyze the variability in these sorption coefficients. Poly(dimethylsiloxane) coated glass fibers were applied as passive samplers to measure free aqueous pore water concentrations in the different soils. For the development of the method, fiber-water sorption coefficients were measured for a broad range of PAHs, and detailed kinetic studies were performed in soil suspensions. Furthermore, the results will be shortly discussed in relation to the risk assessment of contaminated soils.

Experimental Section

Chemicals, fibers, solvents and soils

Phenanthrene (Phe), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF) and benzo[ghi]perylene (BghiP) used for spiking soils were all purchased at Sigma Aldrich Chemie BV (Zwijndrecht, The Netherlands). Disposable glass fibers with a core diameter of 110 μm and a 28.5μm poly(dimethylsiloxane) (PDMS) coating (volume 12.4 μl/m) were obtained from Poly Micro Industries (Phoenix, AZ). Acetonitrile, acetone, methanol, ethylacetate (Lab-Scan, Dublin, Ireland) and n-hexane (Baker BV, Deventer, The Netherlands) used, were of analytical grade. Highly pure de-ionized water (R ≥18 MΩ) was prepared by a Millipore water purification system, equipped with organic free kit (Millipore Waters, Amsterdam, The Netherlands). Table 1 shows the origin and organic carbon contents of the five clean field soils and six contaminated field soils that were used in this study.

Table 1: The organic carbon (OC) content and the total PAH concentrations of the selected test soils. See Table A and B fore more detailed information on the PAH concentrations in the soils.

Soil	*% TOC (ref)*	*Additional information on the soils*	*ΣPAH mg/kg soil (dw)*
		Clean soils used for spiking studies	
Askov	1.39 (*135*)	Sandy loam soil (Denmark)	113.9 [a]
Borris-2	1.67 (*135*)	Sandy loam soil (Denmark)	105.4 [a]
Kettering	2.09 (*135*)	Sandy clay loam soil (UK)	105.4 [a]
Waschbach	2.29 (*135*)	Silt loam soil (Austria)	105.4 [a]
Norway	5.49 (*135*)	Forest soil (Norway)	105.4 [a]
		Contaminated soils	
Andujar-B2	3.3 (*136*)	Railway station site, air dried clayish silt 2003 (Spain)	4560
E6068-K	4.7 (*136*)	Industrial soil, piled since 1994, straw and sewage sludge added (Denmark)	332.1
K3840	1.2 (*136*)	Gasoline station site, sand soil piled since 2000 (Denmark)	16.7
Olst-J	4.1 (*136*)	Industrial soil (The Netherlands)	16.0
Skaegen	1.97 (*135*)	Sandy soil contaminated with tar by fishnet dipping (Denmark)	522
TP44	3.0[b]	Soil from a gas manufacturing plant (UK)	1020

[a] Nominal concentration spiked to the clean soils.

[b] CO_2-analysis after CO_3 removal by Jordforsk (Centre for Soil and Environmental Research, Norway).

Sorption isotherms to PDMS

Fiber water partitioning were determined with a relatively new method that is based on the depletion of pre-loaded fibers with selected amounts of water (*137*). The advantage

of this method is that it avoids difficulties that are often encountered with spiking of aqueous solutions with hydrophobic chemicals. The PDMS coated fibers were cut into 5.0 or 3.0 cm pieces and cleaned by heating at 275°C for 16 hr under a constant helium flow of 30-35 mL/min. Clean fibers were "loaded" by exposing them to a 1:1 methanol-water mixture (~6.2 µL PDMS in 5 mL methanol-water) spiked with seven PAHs at seven concentration levels. The loaded fibers were placed in three different volumes of water (6.2, 38 and 102 mL), to obtain three different volume water / volume PDMS ratios (11000, 102000 and 272000). The concentration of sodium azide (NaN_3, Merck, Amsterdam, The Netherlands) in these solutions was 10 mM in order to inhibit bacterial degradation. The flasks were shaken for 28 d (which is sufficient to reach equilibrium (*137*)) in the dark at 20 ± 1°C. PAH in the loaded and water-exposed fibers were extracted with 0.20 to 20 mL acetonitrile. Initial concentrations in the PDMS coating ranged from 0.7 to 5440 mg/L, 1.0 to 2380 mg/L, 0.5 to 1620 mg/L, 0.5 to 79 mg/L, 0.5 to 105 mg/L, 0.6 to 63 mg/L and 0.5 to 14 mg/L, for Phe, Fla, Pyr, BaA, BbF, BkF and BghiP, respectively. Aqueous concentrations were estimated by a mass-balance approach, assuming that all compounds depleted from the fiber were dissolved in the aqueous phase (Equation 1),

$$\frac{C_f}{C_{f\,(initial)}} = \frac{1}{1 + \frac{V_{aq}}{V_f * K_f}} \qquad (1)$$

where $C_{f\ (initial)}$ is the initial concentration in the loaded fiber, C_f and C_{aq} are the concentrations in the PDMS and aqueous phase at equilibrium, V_f and V_{aq} are the volumes of the PDMS and aqueous phase, and K_f is the fiber (PDMS)-water partition coefficient. In this approach it is assumed that the mass balance is 100%. Furthermore, aqueous concentrations were determined in a selection of the test vials (n= 13), by extraction a sample of the aqueous phase was extracted with n-hexane three times. Subsequently, the hexane was evaporated under a gentle stream of nitrogen, while adding acetonitrile.

Spiking and analyzing soils

All soils (Table 1) were stored at 4°C until use. Clean field soils were spiked according to Brinch and coworkers (*138*) with some adaptations. Before spiking, the clean soils were dried at 25 ±1°C until a constant weight (2-4 days) and gently grounded and sieved (1 mm mesh size). A sub-sample of 10% was spiked with the selected PAHs dissolved in acetone (soil / acetone ratio = 2 / 1 (w/v)) and was mixed by hand. After evaporation of the acetone (overnight at room temperature), the sub-sample (10%) was mixed with the rest (90%) of the soil, and shaken thoroughly for 1 hour with a one-dimensional shaker. After mixing, water (10 mM sodium azide) was added to ~60% of the water holding

capacity, and the soil was incubated for three weeks at 20 ±1°C. Final soil concentrations varied from 7.2 - 28.9 mg/kg per compound (Appendix II, Table A).
Total concentrations of spiked and field-contaminated soils were determined after a 16-hour ethylacetate soxhlet-extraction using 45 mL ethylacetate per 2 grams of soil. The field-contaminated soils were gently grounded and homogenized before extraction. The ethylacetate extraction has shown similar results as classical n-hexane / acetone extractions (*100*). Furthermore, a second soxhlet extraction of the field-contaminated Skaegen soil recovered less than 0.5% of the initially extracted PAHs. The initial extraction was therefore considered exhaustive. Additional information on the PAH concentrations of the field-contaminated soils can be found in Table B of Appendix II.

Exposing fibers to soil
Figure 1 gives a schematic picture of the fiber exposure. One to three thermally cleaned fibers (5 cm long, 0.62 µL PDMS) were exposed to 2 g (ww) aliquots of spiked or field-contaminated soil in 7 mL amber vials with 2 mL 10 mM sodium azide solution. The field-contaminated soils were gently grounded and sieved (1 mm mesh size) before fiber exposure. The vials were shaken on a "rock and roller" shaker (Snijders Scientific, Tilburg, The Netherlands). Exposed fibers were gently wiped with a wet tissue, and extracted with acetonitrile.

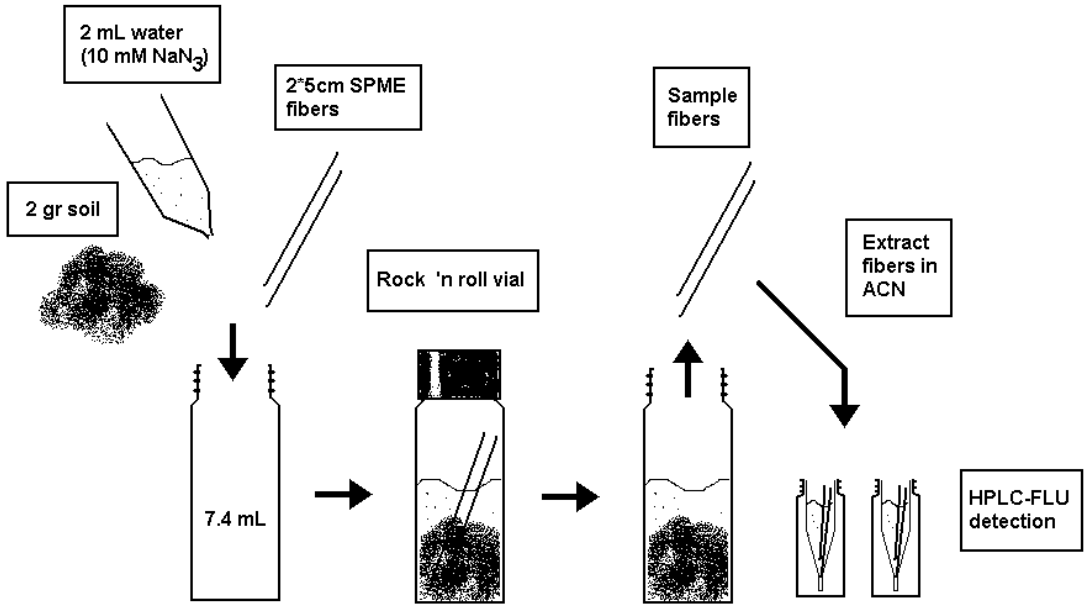

Figure 1: A schematic picture of negligible depletion passive samplers to measure freely dissolved aqueous concentrations of contaminants in soil.

The uptake kinetics of the fiber in the soil system was determined by analyzing fibers that were exposed to Askov soil spiked with Phe Fla, Pyr, BaA, BbF, BkF and BghiP, and field-contaminated Skaegen and TP44 soil for a variety of exposure times varying

between 0.5 and 7778 h. Equilibrium concentrations in the fiber ($C_{f(\infty)}$) and rate constants (k) were estimated from concentrations in the fiber in time ($C_{f(t)}$) with a one-compartment model using Graphpad Prism™ 3.0 (San Diego, CA):

$$C_{f(t)} = C_{f(\infty)} * (1 - e^{-k * t}) \quad (2)$$

If sorption to the fiber is the rate-limiting step, the rate constant k is equal to the elimination rate constant of the fiber ($k_{e\text{-fiber}}$). Based on this study, a minimum exposure time of 72 h was chosen.

Free aqueous concentrations (C_{aq}) in the soil pore water were calculated by dividing the concentration in the fiber at equilibrium ($C_{f(\infty)}$) by the fiber-water partition coefficient (K_f).

$$C_{aq} = \frac{C_{f(\infty)}}{K_f} \quad (3)$$

Analysis of samples

The quantification of PAH-mixtures in soil extracts, fiber extracts and water extracts were performed with a standard solution containing 16 PAHs (Supelco, Bellefonte, CA, selected by the EPA) in acetonitrile. The system consisted of a Shimadzu DGU 14A Degasser (Den Bosch, The Netherlands), a Spark Marathon autosampler (Emmen, The Netherlands), a Gynkotek p580 HPG HPLC pump (Gemering, Germany) and a Jasco FP-920 fluorescence detector (Maarssen, The Netherlands). Separation was performed using a Supelcosil (Supelco, Bellefonte, CA) LC-PAH column (length 100 mm, ø 4.6 mm, particles 3 μm) that was operated at 26°C. All analyses were performed with a flow rate of 1000 μL/min and an injection volume of 20 μL. The compounds were separated using gradient elution starting with 40% H_2O for two minutes followed by an increase of the acetonitril-fraction to 100% in 9.5 minutes, where it was kept for another 7.5 minutes before returning to the initial solvent composition for 6 minutes. The excitation and emission wavelengths (nm) of naphthalene were 221/337, fluorene was analyzed at 227/315, phenanthrene, anthracene, fluoranthene and pyrene were analyzed at 255/405 or 240/405, benz[a]anthracene and chrysene were analyzed at 277/393 or 271/386, while benzo[b]fluoranthene, benzo[k]fluoranthene and benz[a]pyrene concentrations were determined at 260/420 and benzo[ghi]perylene and dibenz[ah]anthracene at 295/425. Chromatograms were analyzed using Chromcard version 1.21 (Milan, Italy), and corrected by hand if necessary.

Results and discussion

Partitioning to PDMS at different concentrations

The relation between the concentration in the PDMS coating of the fiber (C_f, µg/L) and the aqueous phase (C_{aq} µg/L) was fitted by a Freundlich isotherm (Equation 4).

$$C_f = K_f * C_{aq}^{\ n} \tag{4}$$

The K_f is the ratio between concentrations in the fiber coating at an aqueous concentration of 1 µg/L, and n is the parameter that determines the sorption linearity. The obtained n-values did not significantly differ from 1.0 ($n_{Freundlich}$ values varied from 0.98 to 1.07), so the sorption to the PDMS material is concentration-independent, and a single K_f could be calculated. The data and the fits are shown in Figure 2, and the obtained partition coefficients are listed in Table 2.

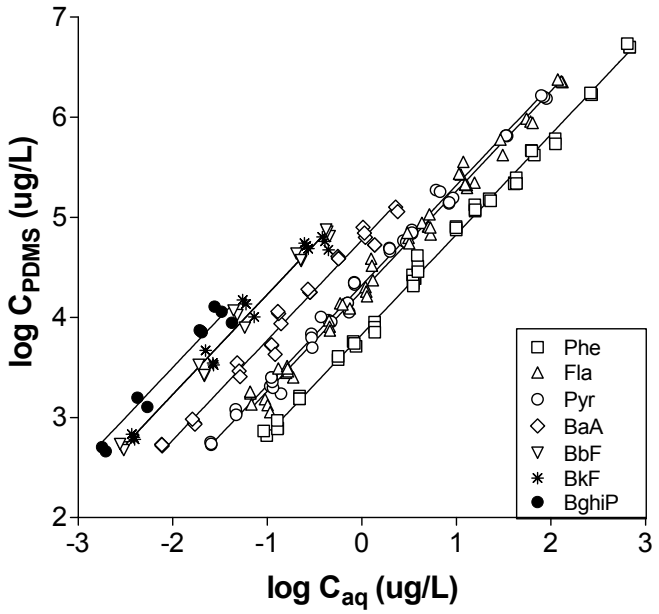

Figure 2: The concentrations in the fiber coating (log C_f) vs. the aqueous concentration (log C_{aq}). Aqueous concentrations are estimated using a 100% mass balance approach.

Table 2 also shows K_f values calculated from measured aqueous concentrations. These values are slightly higher (0.11 ± 0.04 log units) than the values obtained with the 100% mass balance approach, since recoveries varied from 87 to 95%. The corresponding fits of these data are shown in Appendix II, Figure A. Furthermore, it can be observed that obtained partition coefficients were very similar to literature values (*73, 137*) and a log K_{OW} based QSAR developed by Mayer et al. (*70*) (Figure 3).

Table 2: The PDMS-water partition coefficients (K_f) of a series of PAHs.

Comp.[a]	*log K_{OW} (ref)*	*Data from this study*		*Data from literature*			*log K_f Selected*[e]
		log K_f (SE, n) 100% MB[b]	*log K_f (SE, n) Measured C_{aq}*[c]	*log K_f Data from ref (73)*	*log K_f (SE) Data from ref (137)*	*log K_f (SD, n) Data from Jonker et al*[d]	
Naph	3.33 (*99*)			2.91			2.91
Flu	4.18 (*104*)			3.72			3.72
Phe	4.56 (*104*)	3.83 (0.01, 50)	3.88 (0.01, 13)	3.98	3.86 (0.03)	3.84 (0.04, 4)	3.83
Anth	4.63 (*139*)			4.17		3.84 (0.04, 4)	3.84
Fla	5.16 (*104*)	4.26 (0.01, 49)	4.35 (0.02, 13)	4.52	4.40 (0.02)	4.20 (0.03, 4)	4.26
Pyr	5.22 (*139*)	4.32 (0.01, 44)	4.41 (0.01, 13)	4.63	4.41 (0.04)	4.27 (0.02, 4)	4.32
BaA	5.91 (*99*)	4.77 (0.02, 28)	4.92 (0.01, 13)		4.92 (0.03)	4.77 (0.03, 4)	4.77
Chr	5.81 (*99*)			5.19		4.69 (0.03, 4)	4.69
BbF	6.20 (*140*)	5.23 (0.02, 15)	5.36 (0.02, 12)		5.28 (0.04)	5.21 (0.04, 4)	5.23
BkF	6.20 (*140*)	5.23 (0.03, 15)	5.37 (0.03, 13)		5.29 (0.04)	5.25 (0.04, 4)	5.23
BaP	6.13 (*99*)					5.24 (0.04, 4)	5.24
BghiP	6.85 (*139*)	5.50 (0.04, 10)	-[f]		5.39 (0.03)	5.08 (0.04, 4)	5.50
DahA	6.20 (*140*)					4.83 (0.04, 4)	4.83

[a] Abreviations of compounds: naphtalene (Naph), fluorene (Flu), phenanthrene (Phe), anthracene (Anth), fluoranthene (Fla), pyrene (Pyr), benz[a]anthracene (BaA), chrysene (Chr), benzo[b]fluoranthene (BbF), benzo[k]fluoran-thene (BkF), benz[a]pyrene (BaP), benzo[ghi]perylene (BghiP), dibenz[ah]anthracene (DahA).

[b] Partition coefficients were calculated assuming a 100% mass balance (Figure 2).

[c] Partition coefficients were calculated assuming with measured aqueous concentrations (Figure A, Appendix II).

[d] Unpublished results of M. T. O. Jonker and S. A. van der Heijden.

[e] These selected K_f values have been used in all further calculations.

[f] Aqueous concentrations were not quantifiable; therefore partition coefficients could not be calculated.

The constant K_f over a broad range of concentrations (4 orders of magnitude for phenanthrene), up to solubility in the aqueous phase and up to very high concentrations in the PDMS phase (ΣPAH >10000 mg/L), gives strong evidence that the sorption to the

30 μm PDMS of the disposable fibers is a partitioning process. Similar conclusion were also drawn by Mayer et al. (*70*), Poerschmann et al. (*73*) and Vaes et al. (*71*).

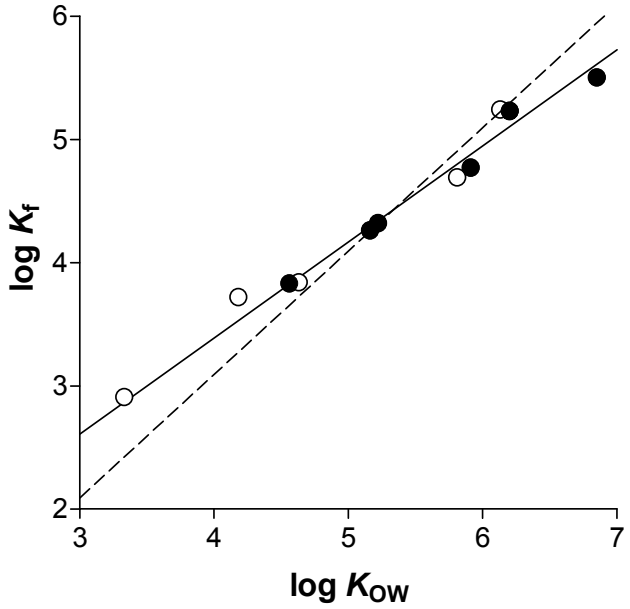

Figure 3: The PDMS partition coefficient (log K_f) plotted against the log K_{OW}. The solid symbols are the partition coefficients obtained in this study and the open symbols are selected partition coefficients from literature (see Table 2). The solid line represents the fit of the data obtained in this study (log K_f = 0.78 * log K_{OW} + 0.56) and the broken line is a log K_f – log K_{OW} relationship from Mayer et al. (*70*) obtained for a series of hydrophobic compounds (log K_f = log K_{OW} - 0.91).

Uptake kinetics of the fiber in a soil suspension: Askov and TP44 soil

The kinetics of the fiber exposure in soil was studied, since the concentration in the fiber can only be used to estimate the freely dissolved concentration in the pore water correctly when the soil, pore water and fiber are at equilibrium (*27, 30*). Figure 4 shows the uptake profile of the fibers exposed to Askov soil spiked with seven PAHs, at 10-30 mg/kg per compound, and the field-contaminated TP44 soil. It can be observed that concentrations in the fibers reached a steady state within the first three days for the Askov soil (aged for 21 (4a) and 553 (4b) days) and the TP44 soil (4c). A one-compartment model was fitted through the data (Equation 2), and equilibrium concentrations in the fiber ($C_{f(\infty)}$) and elimination rate constants (k_e) were determined. Table 3 lists the calculated elimination rate constants of the experiments with these soils. It can be observed that the rate constants measured in the TP44 soil and the freshly spiked and aged Askov soil are similar.

Table 3: Organic carbon normalized sorption coefficients (K_{OC}) and elimination rate constants (k_e) of spiked (aged) Askov soil and field-contaminated TP44 and Skaegen soil.

Compound	*Spiked Askov soil*				*TP44 soil*		*Skaegen soil*		
	aged for 21 days		*aged for 553 days*						
	log K_{OC} (SE, n)	*log $k_{e\text{-}fiber}$ (SE, n)*	*log K_{OC} (SE, n)*	*log $k_{e\text{-}fiber}$ (SE, n)*	*log K_{OC} (SE, n)*	*log $k_{e\text{-}fiber}$ (SE, n)*	*log K_{OC} (SE, n)*	*log $k_{e\text{-}fiber}$ (SE, n)*	*log $k_{e\text{-}slow}$ (SE, n)*
Phe	4.31 (0.05, 43)	0.170 (0.032, 59)	-[a]	-[a]	5,20 (0.01, 42)	0.140 (0.031, 42)	5.14 (0.11, 17)	0.046 (0.070, 59)	-2.677 (0.045, 59)
Anth					5,23 (0.01, 39)	0.074 (0.022, 39)	5.31 (0.12, 17)	-0.070 (0.057, 59)	-2.765 (0.044, 59)
Fla	4.89 (0.05, 43)	-0.099 (0.016, 59)	-[a]	-[a]	6,14 (0.01, 42)	-0.198 (0.011, 42)	6.05 (0.12, 17)	-0.313 (0.029, 55)	-2.907 (0.050, 55)
Pyr	5.03 (0.05, 42)	-0.128 (0.016, 59)	-[a]	-[a]	5,94 (0.01, 42)	-0.244 (0.010, 42)	6.14 (0.12, 17)	-0.264 (0.036, 59)	-2.993 (0.042, 59)
BaA	5.73 (0.05, 35)	-0.450 (0.005, 56)	5,94 (0.03, 43)	-0.521 (0.044, 45)	6,81 (0.01, 39)	-0.690 (0.005, 39)	6.91 (0.11, 17)	-0.437 (0.029, 59)	-3.050 (0.061, 59)
Chr					6,71 (0.01, 39)	-0.725 (0.004, 39)	6.47 (0.23, 17)	-0.209 (0.176, 59)	-3.314 (0.041, 59)
BbF	6.43 (0.05, 31)	-0.774 (0.003, 59)	6,70 (0.02, 43)	-0.836 (0.014, 45)	7,52 (0.01, 39)	-0.941 (0.002, 39)	7.71 (0.14., 17)	-0.375 (0.096, 59)	-3.096 (0.123, 59)
BkF	6.39 (0.05, 31)	-0.817 (0.003, 59)	6,59 (0.01, 43)	-0.889 (0.007, 47)	7,55 (0.01, 39)	-1.014 (0.002, 39)	7.67 (0.13, 17)	-0.604 (0.015, 59)	-3.033 (0.111, 59)
BaP					7,59 (0.01, 39)	-0.981 (0.002, 39)	7.85 (0.17, 17)	-0.172 (0.093, 59)	-3.283 (0.140, 59)
BghiP	6.94 (0.05, 27)	-1.099 (0.002, 59)	7,22 (0.02, 43)	-1.180 (0.004, 47)	8,08 (0.01, 36)	-1.248 (0.001, 36)	8.15 (0.35, 17)	-0.632 (0.030, 52)	-3.648 (0.440, 52)
DahA					7.33 (0.01, 33)	-1.365 (0.002, 33)	7.41 (0.47, 17)	-[a]	-[a]

[a] Quantification of compound of insufficient quality for determination of kinetic parameters.

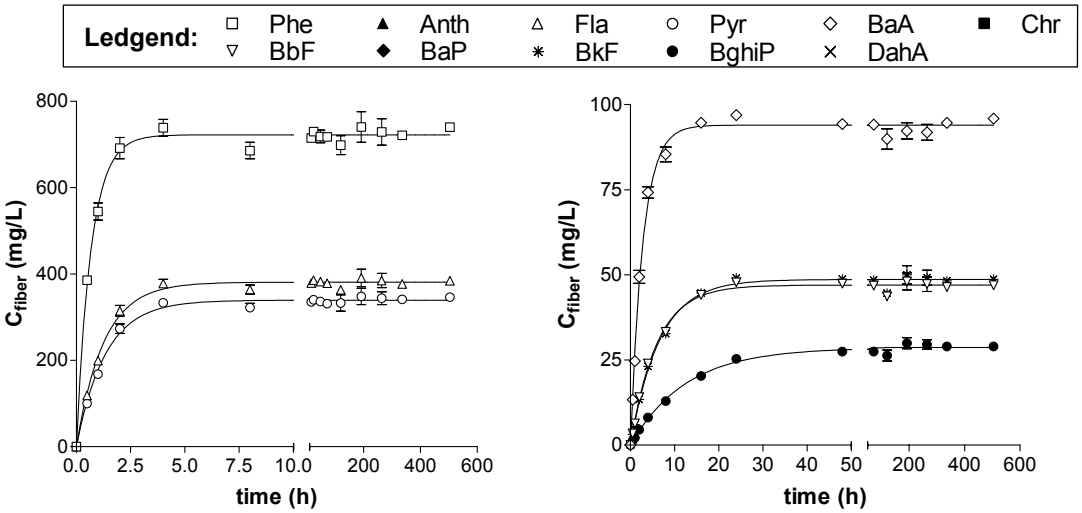

Figure 4a: Uptake profiles of fibers exposed to spiked Askov soil after 21 days. The lines in represent the fits of Equation 2.

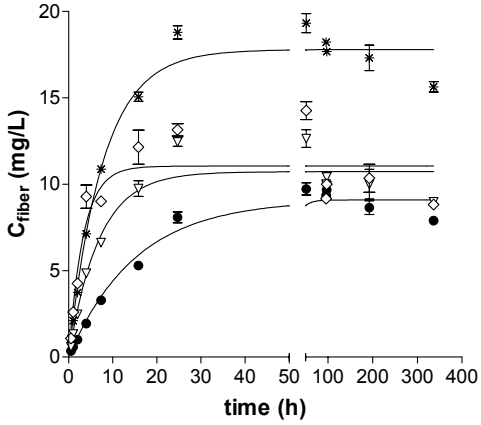

Figure 4b: Uptake profiles of fibers exposed to spiked Askov soil after 553 days of aging. The lines represent the fits of Equation 2.

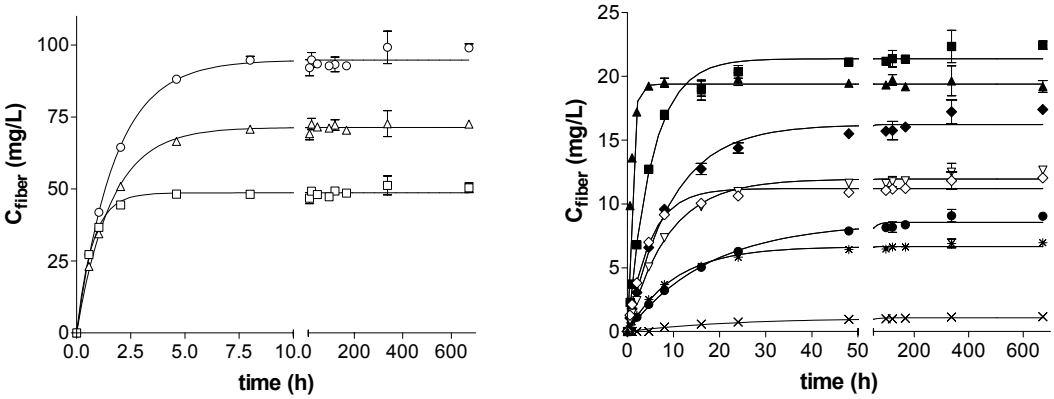

Figure 4c: Uptake profiles of fibers exposed to field-contaminated TP44 soil. The lines represent the fits of Equation 2.

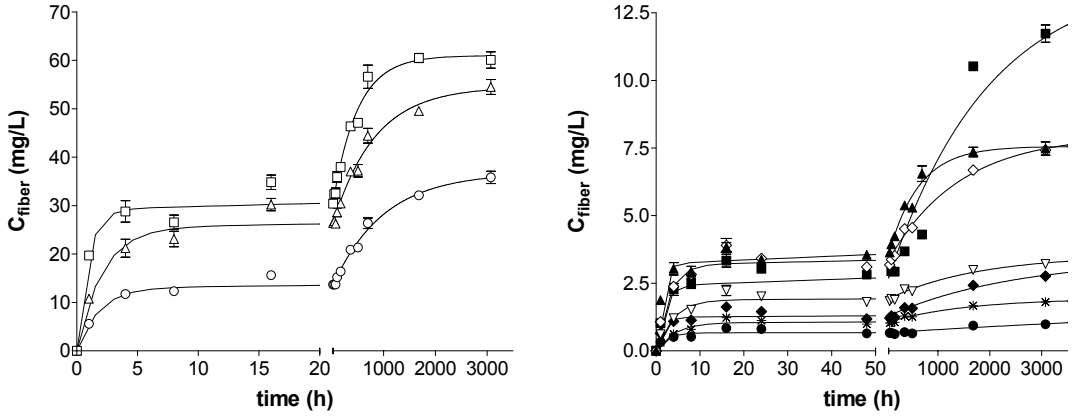

Figure 4d: Uptake profiles of fibers exposed to Skaegen soil. The lines in represent the fits of Equation 6.

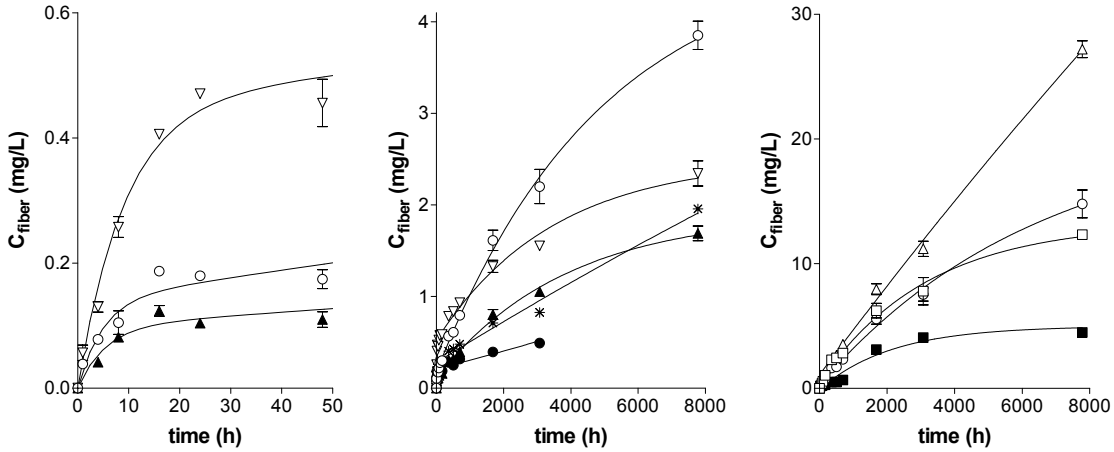

Figure 4e: Uptake profiles of fibers exposed to untreated Skaegen soil. The lines represent the fits of Equation 6.

The interpretation of this rate constant is not unambiguous because several kinetic processes occur in the exchange between soil, soil pore water and the fiber (see Figure 5 for a schematic overview). We strongly believe that, at least in these two soils, the fiber-water exchange is the rate-limiting step. Arguments for the validity of this assumption are, that the experimental data follow the one compartment model precisely (see Figure 4a, 4b & 4c), and that earlier studies, including modeling exercises, have shown that the flux from soil to water is usually too high to be rate limiting (*30, 108, 141*). If we assume that the fiber-water exchange is the rate-limiting step, Equation 2 can be rewritten as:

$$C_{f(t)} = \frac{k_{u-fiber}}{k_{e-fiber}} * C_{aq} * (1 - e^{-k_{e-fiber}*t}) \qquad (5)$$

In this equation, $k_{u\text{-fiber}}$ is the uptake rate constant from pore water to fiber, and $k_{e\text{-fiber}}$ is the elimination rate constant from the fiber to water. The ratio of the uptake rate constant and the elimination rate constant (k_u/k_e) is the fiber-water partition coefficient (K_f). A plot of the uptake and elimination rate constant versus the fiber partition coefficient will supply information about the rate-limiting step in the exchange process between fiber and water (*34, 142-145*). The $k_{u\text{-fiber}}$ will be constant if the diffusion in the aqueous phase around the fiber, also known as the unstirred boundary layer (UBL), is rate limiting. If the diffusion in the PDMS coating is rate limiting, the $k_{u\text{-fiber}}$ will increase linearly with increasing fiber water partition coefficients.

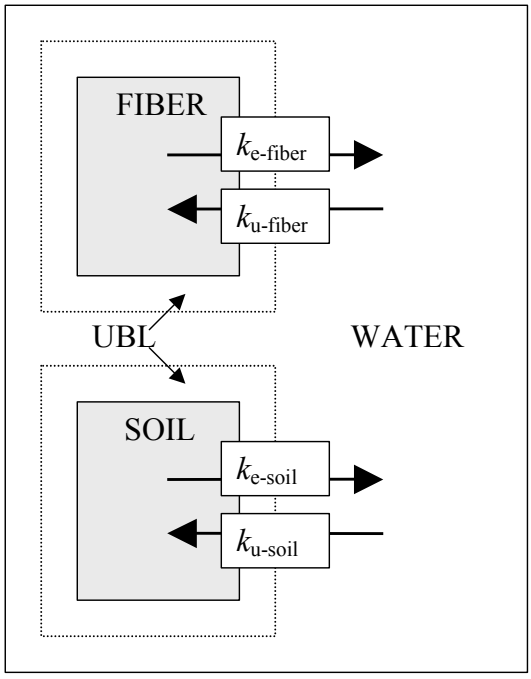

Figure 5: A schematic picture of the soil water fiber system, with uptake (k_u) and elimination (k_e) rate constants of the PDMS coated fiber and the sorbent in the soil. UBL stands for the unstirred boundary layer, a stagnant layer of water that surrounds the fiber or soil particle.

The shift from the rate limiting step from PDMS to the aqueous diffusion layer is often found at a K_f of 10^3 to 10^4 (*34, 143, 144*). However, this break point also depends on the agitation of the system and the surface to volume ratio of the fiber. Strong agitation can move the break point to a K_f above 10^5 (*48*). A plot of the uptake ($k_{u\text{-fiber}}$) and elimination ($k_{e\text{-fiber}}$) rate constant, versus the K_f is given in Figure 6a. The $k_{u\text{-fiber}}$ (h^{-1}) is constant at a level of $10^{4.3}$ at a $K_f > 10^{4.5}$ for the Askov and TP44 soil. This suggests that the diffusion in the UBL is rate limiting above this K_f. The reduction of the $k_{u\text{-fiber}}$ at a lower K_f can be attributed to a shift in the rate limiting process from diffusion in the UBL towards the diffusion in the PDMS coating.

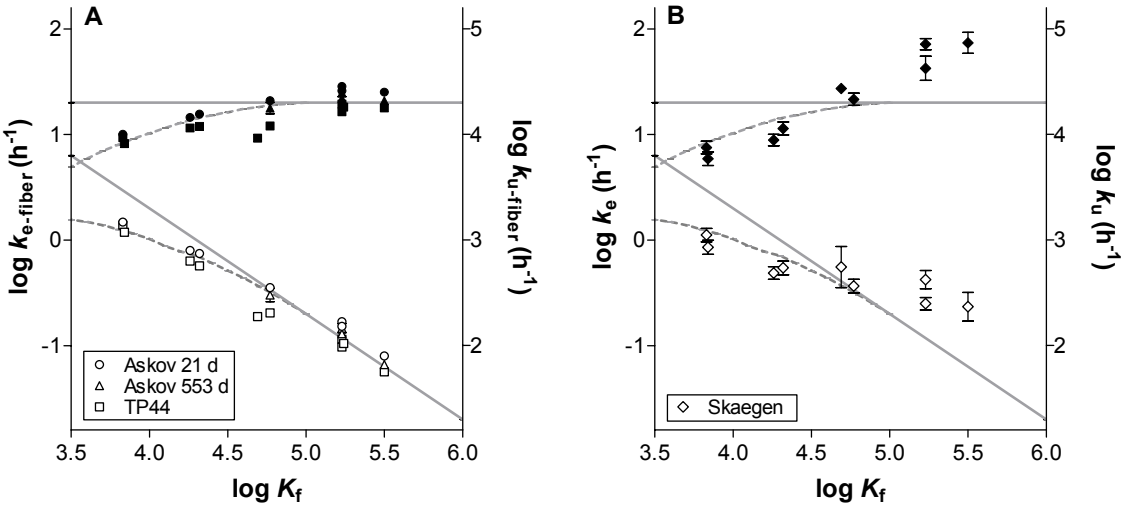

Figure 6: The elimination ($k_{e\text{-fiber}}$, open symbols, left Y-axes) and uptake ($k_{u\text{-fiber}}$, solid symbols, right Y-axes) and rate constants plotted against the fiber-PDMS partition coefficient (K_f). Figure 6a shows the data for the spiked Askov soil incubated for 21 and 553 days and the field-contaminated TP44 soil. Figure 6b shows the data for the field-contaminated Skaegen soil. Error bars represent standard errors.

The small but systematic variation in the $k_{u\text{-fiber}}$ (and $k_{e\text{-fiber}}$) observed between the Askov soil and TP44 soil (~0.14 ± 0.07 log units) can be due to different physical properties of the soil slurry (e. g. viscosity, dissolved organic matter (DOM) concentration). Differences in viscosity can affect the mixing of the soil slurry and the movement of the fiber in the soil slurry, thereby influencing the thickness of the UBL. This is difficult to quantify and therefore an excess of water (far beyond the water holding capacity) was added to create more standardized conditions. The presence of DOM in the aqueous diffusion layer may also affect the kinetics (*79, 96*). This phenomenon will become more important at increasing hydrophobicity. Figure 6a shows no clear increase of the $k_{u\text{-fiber}}$ above a K_f of $10^{4.5}$, therefore the contribution of DOM on the kinetics of the fiber is considered insignificant. This observation is in line with literature, where only very high DOM concentrations (>100 mg/L) affected the kinetics significantly (*79, 146*).

Uptake kinetics of the fiber in a soil suspension: Skaegen soil

The fiber uptake kinetics was also studied in Skaegen soil. The uptake profile of the fibers exposed to the Skaegen soil was different from the fibers exposed to the spiked Askov and field contaminated TP44 soil. A pseudo-equilibrium was reached within the first days of exposure, after which the concentration slowly increased over a period of weeks to months (Figure 4d). A two-phase uptake model distinguishes a "fast equilibrating fraction" (fef) and a "slow equilibrating fraction" (1-fef) of the final equilibrium level in the fiber. The kinetics of the fast equilibrating fraction was very similar to those in the spiked Askov soil and field contaminated TP44 soil. We therefore assume that the initial uptake represents the kinetics of the fiber-water exchange, described by the fiber elimination rate constant ($k_{e\text{-fiber}}$). The orders of magnitude slower

kinetics of the second, slow equilibrating fraction is described by a second elimination rate constant ($k_{e\text{-}slow}$) and might be related to slow desorption from the soil.

$$C_{f(t)} = C_{f(\infty)} * fef * (1 - e^{-k_{e-fiber} * t}) + C_{f(\infty)} * (1 - fef) * (1 - e^{-k_{e-slow} * t}) \quad (6)$$

Equation 6 was used to fit the concentrations in the fiber exposed to the Skaegen soil. The $k_{e\text{-}fiber}$ values are summarized in Table 3. Figure 6b shows both the $k_{e\text{-}fiber}$ values and the $k_{u\text{-}fiber}$ values (calculated by replacing $C_{f(\infty)}$ by C_{aq} * $k_{u\text{-}fiber}$ / $k_{e\text{-}fiber}$, see Equation 6). It can be observed that the $k_{e\text{-}fiber}$ values of the less hydrophobic PAHs (K_f <$10^{4.5}$) are comparable to the $k_{e\text{-}fiber}$ values of the other soils. Therefore, also the pseudo-equilibrium is limited by diffusion in the aqueous layer around the fiber. Both the $k_{e\text{-}fiber}$ and $k_{u\text{-}fiber}$ values of the more hydrophobic PAHs (K_f >$10^{4.5}$) are higher than the $k_{e\text{-}fiber}$ values of the other soils, resulting in a (up to 4 times) shorter equilibration time of the fiber. This is probably a result of the (temporary) depletion of the 2 mL soil pore water, since depleting the aqueous phase during uptake, leads to a reduction in equilibration times (*141*).
The slow uptake kinetics of the fibers exposed to the Skaegen soil is not typical for field soils. The other field soil (TP44) behaves similar to spiked soils, in the sense that the fiber-water exchange is the rate-limiting step for fiber-uptake in soil suspensions. The "abnormal" behavior in the Skaegen soil is likely due to the type of sorbent. The PAHs in this soil are mainly incorporated or captured in tar particles. The PAHs will diffuse very slowly out of this matrix (*147*) and a new equilibrium with the depleted fast desorbing fraction, the pore water and the fiber will be established very slowly. The observed equilibration times of several months are in line with slow diffusion / desorption rates found for tar, soot and coal matrices or soils and sediments contaminated with these materials (*128, 147, 148*).

Effects of soil pretreatment on uptake kinetics of exposed fibers in the Skaegen soil
The equilibrium kinetics of the fibers exposed to the Skaegen soil seemed to depend on the desorption rate of the soil. Grounding and sieving a soil breaks up organic matrices, enlarges their surface-volume ratio and affect the desorption rate of the contaminants from these matrices. In Figure 4d, the fibers were exposed to gently treated (grounded and sieved) Skaegen soil. Figure 4e shows the uptake profile of the fiber exposed to Skaegen soil that was untreated. It can be observed that the fast equilibrating fraction in this untreated soil was very small (BaA, BbF and BaP) or not even quantifiable (other compounds), and that steady state was not even fully reached after 324 days (7778 hours). Because the system was still far from equilibrium, steady state concentrations in the fibers could not be estimated accurately for the untreated Skaegen soil.
The observed effect of grounding and sieving clearly shows that pretreatment of soils may speed up the uptake into the SPME fiber. Similar effects might be observed for

uptake in organisms, and processes such as (bio)degradation and leaching might be affected. Therefore, pretreatment of soils in testing for risk assessment should be considered with great care.

Sorption coefficients of spiked aged soils

Kinetic studies have shown that a 2 to 3 d equilibration period is sufficient to equilibrate the soil-water-fiber system in those cases where desorption from the soil is not the rate limiting step. Therefore, a standard exposure time of 72 h was selected. Concentrations in the pore water were calculated from concentrations in the fiber after 72 h exposure ($C_{f(72)}$), and fiber-water partition coefficients (K_f) reported in Table 2. Organic carbon normalized soil sorption coefficients (K_{OC}) were calculated from measured pore water concentrations and measured total organic carbon normalized concentrations in the soil (C_{OC}).

$$K_{OC} = \frac{C_{OC}}{\frac{C_{f(72)}}{K_f}} \tag{7}$$

The soil concentrations were determined from samples that were taken at the start of the fiber exposure and are reported in Table C of Appendix II. Even though the soils were sterilized using 10 mM sodium azide, concentrations in soil decreased during the 553-day storage period. The concentrations of most of the PAHs in the soil remained constant, only the low molecular decreased significantly during storage. However, sorption coefficients could still be calculated at the different aging periods, because concentrations in soil were measured. Another, more critical, assumption is the stability of the test compound during the fiber exposure. In an additional study it was observed that the total concentration of the soils aliquots used to expose the fibers did not show a significant decrease during 504 hours of fiber exposure (95% to 99% was recovered after 504 h fiber exposure compared to 0.5 - 2 h fiber exposure (see Figure B of Appendix II).
Figure 7 shows the sorption coefficients of seven PAHs that were spiked to five clean field soils after different aging periods. Soil sorption coefficients were determined after 21, 240 and 553 days aging for the Askov soil and 18, 77 and 171 days for Borris-2, Kettering, Waschbach, and Norway soil, and plotted against the octanol water partition coefficient of the compounds. It can be observed that the sorption coefficients of the smaller PAHs are comparable to the QSAR-prediction of Karickhoff (*35*), and the sorption of the larger PAHs is slightly higher than predicted. The small deviation is most likely an effect of the overestimation of free pore water concentrations (due to binding of compounds to dissolved organic carbon), in the data Karickhoff used to develop this QSAR (*66, 149*). One of the objectives of our study was to analyze effects of aging on freely dissolved concentrations and sorption coefficients. The sorption coefficients only

slightly increase during the 177 or even 553 days aging periods (less than a factor 3). The small increase in sorption coefficients might be explained by slow absorption into so-called "hard" organic polymeric matrices or slow diffusion into micro-pores (*7*). The (relative) fraction that is strongly sorbed might be enlarged by degradation of more accessible fractions, resulting in a higher (apparent) sorption coefficient. This process is often thought to be responsible for the increased sorption coefficients and incomplete removal of contaminants from remediated contaminated sites (*150*).

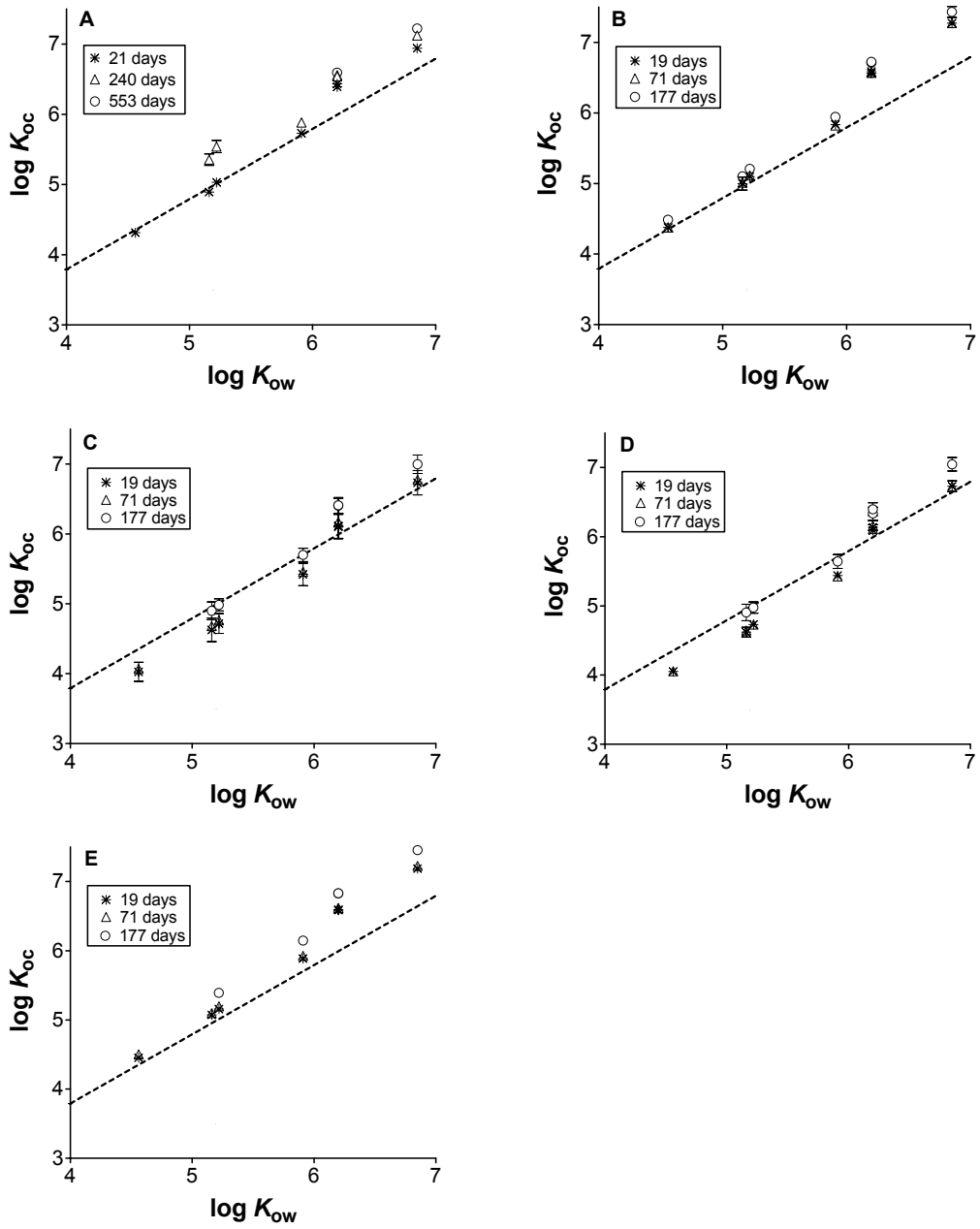

Figure 7: Organic carbon normalized sorption coefficients (log K_{OC}) plotted against the octanol water partition coefficient (log K_{OW}) for spiked Askov (a) soil aged for 21, 240 and 553 days, and the Borris-2 (b), Kettering (7c), Waschbach (d) and Norway (e) soil, aged for 19, 77 and 177 days. The sorption coefficients are only shown when less than 50% of the spiked concentration was recovered. The broken line represents: log K_{OC} = log K_{OW} - 0.21 of Karickhoff (*35*).

Concluding, the contact time of the selected compounds with the selected clean field soils have only a small effect on the sorption coefficient. A factor 3 reduction in freely dissolved concentration in pore water is not really high in light of the risk assessment process. These observations are in line with literature findings. Sorption coefficients of hydrophobic organic chemicals spiked to soils did not increase severely in time (*151, 152*), and bioavailability and extractability by mild solvents (*125, 126*) or Tenax (*153*), decreased only slightly (*153*).

Sorption coefficients of field-contaminated soils

Sorption coefficients were also determined for a series of field-contaminated soils. The chosen equilibration time of the fiber exposure to determine the aqueous concentration was 72-74 hours for all soils. This exposure is sufficient for laboratory-spiked soils and probably also for most of the field-contaminated soils. Only for the Skaegen soil, contaminated with tar, the exposure time is too short to reach steady state, leading to an overestimation of the sorption coefficient. Figure 8a shows the sorption coefficients of 5 field contaminated industrial soils. It can be observed that sorption coefficients of the field contaminated soils are variable, and sorption coefficients can be up to two orders of magnitude higher than what is expected from the log K_{OW} - log K_{OC} relationship of Karickhoff (*35*). In Figure 8b sorption coefficients of the Skaegen soil are plotted against the log K_{OW} of the compounds. The sorption coefficients were calculated from fibers exposed to untreated and treated Skaegen soil for 72 hours as well as by estimation of the equilibrium concentration calculated from uptake profiles (Figure 4d) of the treated soil. The sorption coefficients calculated from the 72 h exposure are generally 0.3 log units (a factor 2) higher than sorption coefficients calculated at equilibrium. The overestimation of sorption coefficients estimated from the fiber exposed to the untreated soil for 72 h is much more severe (one to two orders of magnitude).

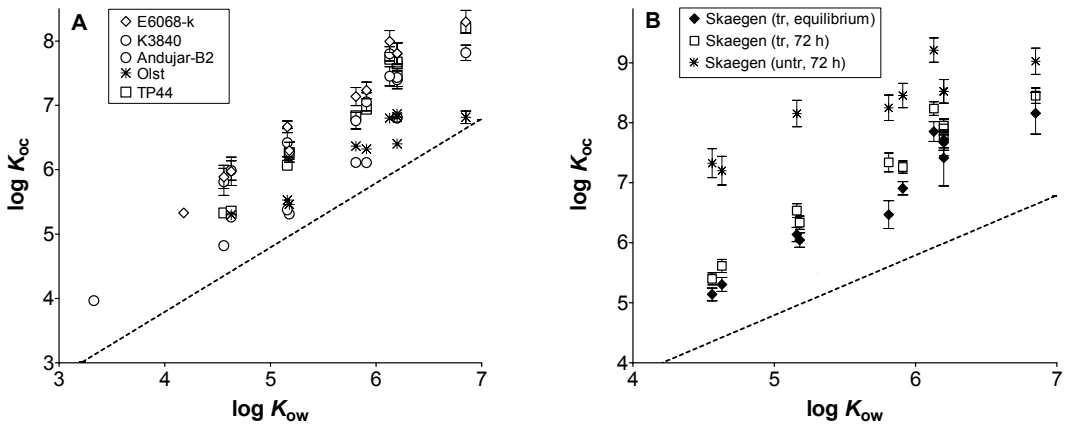

Figure 8: Organic carbon normalized sorption coefficients with their standard deviations (log K_{OC}) are plotted against the octanol water partition coefficient (log K_{OW}) for 6 field-contaminated soils. Figure 8a shows the sorption coefficients of five soils and Figure 8b the calculated sorption coefficients of treated and untreated Skaegen soil after 72 h and treated skaegen soil at equilibrium. The broken line represents a QSAR (log K_{OC} = log K_{OW} - 0.21) of Karickhoff (*35*).

Evaluation of the negligible depletion-SPME technique to measure freely dissolved concentration and sorption coefficients

Requirements for accurate measurements of freely dissolved pore water concentrations (and soil sorption coefficients) via a passive sampler such as the SPME fiber are: (i) the sampler is in equilibrium with the soil-water system, (ii) partition coefficients to the fibers are known, and (iii) the sampler may not affect the concentration in soil. The exposure time of the passive sampler is therefore crucial. Because elimination rate constants for the fiber-water exchange are related to the partition coefficient of the fiber (*30*), equilibration times can be predicted relatively easily. Adjusting the surface - volume ratio or the material (partition coefficient) of the passive sampler can change equilibration times to practical periods.

If, however, desorption of the soil becomes rate limiting, because compounds are sequestered in condensed organic matrices, the equilibration times become longer, and are more difficult to predict. Grinding and sieving a soil might increase desorption kinetics, by enlarging surface-volume ratios of the sorbing materials in the soil. However, it is the question whether or not these changes in the properties of the soil still will lead to realistic numbers from a risk assessment perspective. Another option is to increase the soil – passive sampler ratio, thereby increasing the desorption capacity of the soil compared to the amount sampled by the passive sampler. Furthermore, the larger this ratio the smaller the relative amount sampled by the passive sampler, so the smaller the effect of potential desorption nonlinearity of the test soil, and the closer the sorption coefficient is to the sorption coefficient in the field situation (*154*). In order to check whether desorption from soil is rate limiting, the uptake kinetics of a passive sampler should always be monitored in new samples by measuring concentrations at a (small) series of exposure times.

With the suggested adaptations, the pore water concentration and sorption coefficient can be determined. This pore water concentration might however be different from the field situation, since free concentrations in the field can also be affected by biological (and chemical) degradation and losses due to evaporation or leaching (*155-159*). If these processes are faster than desorption from the soil, free pore water concentrations will continuously be at a steady state below the chemical equilibrium as determined under sterile, controlled conditions in the laboratory. Especially soils with very slow desorption kinetics are prone to be affected by these processes. In vivo measurements of pore water concentrations using passive samplers might therefore be considered estimates of 'potential' pore water concentrations in the field. The pore water concentrations in the field might also be assessed by in situ exposure of passive samplers (*160*). This is however more difficult, especially in a soil, since exposure concentrations might vary in time, samplers are not agitated (leading to longer equilibration times, and possibly depletion of the local environment), and environmental conditions (temperature, the amount and chemical composition of the water in the soil) cannot be controlled.

Free concentrations and site-specific sorption coefficients in risk assessment

It is clear that simple generic modeling of sorption is not sufficient to estimate the risks of hydrophobic contaminants like PAHs in soil. In actual field samples, pore water concentrations can be much lower and soil sorption coefficients can be much higher than predicted by K_{OW}-based QSAR models. Therefore, site-specific risk assessment should be applied. The tool presented in this study can contribute to site-specific risk assessment by determining site-specific (potential) pore water concentrations and sorption coefficients. The proposed tool is relatively simple and cheap, and might therefore be implemented as a screening tool. If the results are pivotal, one can decide to expand the research to bioassays, and other tests.

It is beyond doubt that the presented technique is only valid for hydrophobic organic contaminants. The negligible depletion passive sampling approach needs development and testing before it can be applied for a wider range of organic (polar and ionizable) and possibly also inorganic compounds in soils (*33*).

Aknowledgements

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