



Sorption of PAHs and PAH derivatives in peat soil is affected by prehydration status: the role of SOM and sorbate properties

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Abstract

Purpose Sorption of organic compounds to soil largely determines their mobility and bioavailability in ecosystems. It is well known that molecular properties of the organic sorbates affect the sorbed amounts and sorption kinetics. But also changes in the hydration status of soils alter the physicochemical and sorptive properties of soil organic matter (SOM), which is the main sorbent for organic compounds in soils. This study elucidates the effects of varying SOM prehydration status on sorption of PAHs and PAH derivatives in peat soil.

Materials and methods For sorption experiments, topsoil samples of a peat soil with 51% SOM were adjusted to water contents of 15, 30, and 50% (w/w based on dry soil mass) and conditioned for different water contact times of up to 2 years at one constant water content. Sorption kinetics and isotherms of naphthalene, three naphthalene derivatives, phenanthrene, and pyrene to these samples were investigated in batch experiments. Effects of the sorbates' properties and SOM hydration on sorption were analyzed.

Results and discussion Sorption to the peat soil was nonlinear and varied among sorbates and differently prehydrated soil samples. Sorbate polarizability, molecular volume, and weight increased the sorbed amount. Sorption kinetics were two-phased with a fast and a slow sorbing fraction. Hydroxyl groups in sorbates acting as H-donor or acceptor led to an increase of the slow sorbing fraction. Increasing total water contents, amounts of non-freezable water in SOM, increasing pore sizes, and decreasing hydrophobicity of SOM decreased the total sorbed amount and the fast sorbing fraction while increasing the slow sorbing fraction. The latter effects increased with increasing polarity and dipole moment of the sorbate. The SOM matrix rigidity varied with prehydration status; higher SOM matrix rigidity led to non-ideal sorption processes, namely, higher sorption nonlinearity and slower sorption.

Conclusions The study revealed the effects and interplay of SOM prehydration status and molecular properties of the sorbates on sorption of PAHs and PAH derivatives. As sorbed amounts may decrease and become non-ideal upon aging at the presence of water, estimations of the mobility of organic compounds in the environment need to consider SOM prehydration status in high organic soils.

Keywords Sorption kinetics · Sorption isotherms · Hydration history · Non-freezable water · Differential scanning calorimetry · ¹H-NMR

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Abbreviations

DMM	Dual mode model
DSC	Differential scanning calorimetry
EDMM	Extended dual mode model
¹ H-NMR	Proton nuclear magnetic resonance
HPLC	High performance liquid chromatography
LOD	Limit of detection
NAP	Naphthalene
2NME	2-Methylnaphthalene
27NOL	Naphthalene-2,7-diol

2NOL	Naphthalene-2-ol
PAH	Polycyclic aromatic hydrocarbon
peat HR	Peat soil from Heudorfer Ried
PHE	Phenanthrene
PYR	Pyrene
SOM	Soil organic matter
TSKM	Two-stage kinetic model
WaMB	Water molecule bridge

1 Introduction

Sorption of xenobiotics in soils determines their mobility and bioavailability in ecosystems. The most important sorbent for organic, non-polar xenobiotics is soil organic matter (SOM) (Schwarzenbach and Westall 1981). Soil OM may be characterized as polydisperse, supra-molecular assemblies of monomers to macromolecules. It is comprised of a continuum from biomolecules to highly transformed or carbonaceous compounds with polymer-like properties and exhibits high spatial and chemical heterogeneity (Chen et al. 2003; Schaumann 2006; Senesi et al. 2009). Moreover, the sorbed xenobiotics exhibit a broad range of physicochemical properties that vary among individual compounds (Doucette 2003). The sorbates' different properties further add to the structural heterogeneity of SOM, resulting in a high overall variability of xenobiotics sorption to SOM.

Additionally, the natural variation in hydration and dehydration of field soils leads to temporal variation in SOM structure and surface properties (Nanda et al. 2018; Diehl et al. 2014a, b; Schaumann 2005). Several studies revealed the substantial sorbate-dependent effects of hydration on xenobiotic sorption (e.g., Borisover et al. 2017; Kim et al. 2017; Chen et al. 2012; Ochsner et al. 2006; Roy et al. 2000). For instance, phenol sorption in Pahokee peat increased by a factor of up to 17 when raising the water content from low to intermediate (Graber et al. 2007). In contrast, naphthalene sorption to soil increased more than twofold upon drying (Liu and Lee 2006), and, correspondingly, desorption of naphthalene and further polycyclic aromatic hydrocarbons (PAHs) from soil increased upon hydration (Thiele and Brümmer 1998). The various authors explained the effects of hydration-induced changes in SOM on a molecular scale by link solvation and sterical and/or structural changes. Structural changes of SOM and related effects on xenobiotic sorption were conceptually explained by the presence and convertibility of different domains in SOM termed as condensed and expanded (Chen et al. 2012; Huang et al. 1997; LeBoeuf and Weber 1999; Weber et al. 1992) or rigid and flexible (“glassy” and “rubbery”) domains (Huang et al. 2003; Pignatello et al. 2006; Xia and Pignatello 2001; Schaumann and LeBoeuf 2005; Chen et al. 2008). Chefetz and Xing (2009) concluded that structural characteristics of the sorbent, such as rigidity of alkyl domains

and accessibility of both alkyl and aromatic domains, are more sorption-determining than composition-related characteristics.

Such structural SOM characteristics were often determined in terms of “SOM rigidity” or “flexibility” (Schaumann and LeBoeuf 2005; Chen et al. 2008). The SOM rigidity varies as SOM interacts with compounds that act as plasticizer and antiplasticizer on the SOM matrix (Chen et al. 2008). At high water contents, water has a plasticizing effect on SOM, increasing SOM flexibility due to swelling (Hurrass and Schaumann 2007; Schaumann et al. 2003). At low water contents, water has an antiplasticizing effect because water molecule bridges (WaMBs) are formed that cross-link humic substances by hydrogen bonds upon aging, thereby increasing SOM rigidity (Schaumann and Thiele-Bruhn 2011; Schneckenburger et al. 2012; Ondruch et al. 2017). Water molecules in WaMBs do not contribute to swelling of SOM as was determined by ¹H-NMR-relaxometry (Schaumann and LeBoeuf 2005; Schaumann and Bertmer 2008). In general, three types of water are found in peat soil, non-freezable water, freezable-bound water, and freezable bulk-like water. Non-freezable water apparently contributes to the formation of WaMBs, stabilizing a SOM domain that relates to the WaMB transition at T₁* in differential scanning calorimetry (DSC). Freezable-bound water may form an additional water domain in SOM that results in a decreased water repellency of peat samples and relates to a higher temperature step transition at T₂* in DSC measurements (Schneckenburger et al. 2012). After hydration, SOM matrix rigidity increases with increasing water contact time at constant hydration conditions (Hurrass and Schaumann 2007; Schneckenburger et al. 2012) upon physicochemical aging and WaMB formation (Diehl et al. 2014a, b). In peat, SOM rigidity developed non-uniformly with increasing water content, and the rate of physicochemical aging during water contact strongly depended on the water content (Schneckenburger et al. 2012). Effects of hydration on the SOM matrix can be longer-lasting (Ritsemá and Dekker 2003; Kučerik et al. 2014).

First results indicated an influence of prehydration of SOM on subsequent sorption of organic chemicals even if the hydration status had been drastically changed over the short term, e.g., in batch experiments (Schneckenburger et al. 2012). However, a detailed analysis is still missing of how SOM properties, evolving during hydration, affect subsequent sorption and how these effects depend on molecular properties of the sorbate.

The present study investigates the effects of SOM long-term prehydration on sorption of PAHs and PAH derivatives with respect to the sorbates' molecular properties. The PAHs are of special interest due to their high persistence in the environment and their toxicity and cancerogenicity to humans. They are formed by incomplete combustion of organic compounds, mainly of fossil fuels. The major part of PAH emissions can be attributed to human sources, nowadays mainly to

motorized traffic (Meijer et al. 2008; Abdel-Shafy and Mansour 2016). To this end, peat from a Histosol was equilibrated at water contents of 15, 30, and 50% and water contact times of 2 to 116 weeks (> 2 years). An earlier study reported on the resulting changes in physicochemical properties of SOM outlasting re-hydration events (Schneckenburger et al. 2012). Selected soil samples from these experiments were used to investigate the sorption isotherms and kinetics of six PAHs and PAH derivatives: naphthalene, phenanthrene, pyrene, naphthalene-2-ol, naphthalene-2,7-diol, and 2-methylnaphthalene. This selection was done, in order to relate differences in sorption behavior to molecular properties of the respective sorbates such as polarity and molecular size and weight, as well as to physicochemical properties of SOM that varied upon hydration such as SOM matrix rigidity, wettability, and SOM pore size.

2 Materials and methods

2.1 Soil

Peat soil material (peat HR) was sampled from a Eutric Histosol at the Heudorfer Ried, a fen in southwest Germany (47°54' 08.37"N, 8°57' 00.39"E). The grassland at the Heudorfer Ried has been extensively used during the last 120 years. Due to melioration, i.e., lowering of the water table well below ground surface, any further growth of the fen peat was interrupted. No other disruption such as mud application occurred, though. The recent plant community is typical for wet meadows, i.e., *Molinietalia caeruleae* (Oberdorfer). The topsoil (0–20 cm) peat material used was strongly decomposed and pedogenically altered. According to FAO guidelines, the peat was qualified as hemic to sapric, and the degree of decomposition and humification was determined as D5.1 to D5.2, “moderately” to “very strong” (Jahn et al. 2006). The pH in 0.01 M CaCl₂ solution was 5.8. The content of SOM was 51.4%, and percentages of the mineral size classes of the total sample were 30% sand, 8.5% silt, and 10% clay. The maximum water holding capacity of the field-fresh sample was 200% (w/w). Further information on the sampled site is given in the Electronic supplementary material.

2.2 Hydration pretreatment of soil sample

Peat HR was adjusted gravimetrically to three different water contents of 15% (air-dry state), 30%, and 50% w/w based on dry soil mass. Samples were stored in desiccators at a temperature of 20 °C ± 1.0 °C at constant relative air humidities of 54, 75, and 97%, respectively, ensuring constancy of adjusted water contents in peat HR throughout the water contact time. Relative air humidities were adjusted by using saturated solutions of CaNO₃ (54%), NaCl (76%), and K₂SO₄ (97%) as described previously (Schneckenburger et al.

2012). Water contact times for prehydration ranged from a few hours to about 2 years. The following combinations of water content and hydration time were selected for this study: 15% water content (2, 8, 40, and 116 weeks), 30% water content (2 weeks), and 50% water content (2 and 8 weeks). That selection was done based on results reported by Schneckenburger et al. (2012) in order to best cover prehydration-induced variations in SOM structure and associated water.

Microbial alteration or degradation of soil material was low at the respective water contents. This was checked in samples incubated for prehydration through analysis of microbial respiration and UV-Vis spectra of SOM NaOH extracts (further information provided in Electronic supplementary material). UV-Vis spectra of peat HR incubated for 18 weeks at 50% water content did not significantly differ from samples stored in an air-dry state (Fig. S2), indicating the absence of microbial changes in SOM composition. Furthermore, microbial respiration was determined in selected samples. Low respiration rates of 0.67 μg CO₂-C g⁻¹ h⁻¹ were determined during 14-day incubation of peat HR. Extrapolating these respiration rates to a water contact time of 2 years would yield as a worst case degradation of < 2% of the 265 g SOC kg⁻¹ of soil (Data not shown).

2.3 Characterization of moisture effects on soil organic matter

Moisture effects on SOM were analyzed by differential scanning calorimetry (DSC), ¹H-NMR relaxometry, and the sessile drop method for determination of the contact angle (CA) after 30 ms as a measure of SOM wettability. From DSC thermograms, characteristics of the water molecule bridge transitions (WaMB transitions) and the amount of freezable and non-freezable water were determined. The WaMB transition temperature T₁* was taken as a measure of SOM rigidity. ¹H-NMR relaxometry revealed relative changes in pore size upon hydration, and the sessile drop method revealed the peat-water contact angle. More detailed information on the methodology of SOM characterization and the properties of the samples was reported earlier (Schneckenburger et al. 2012).

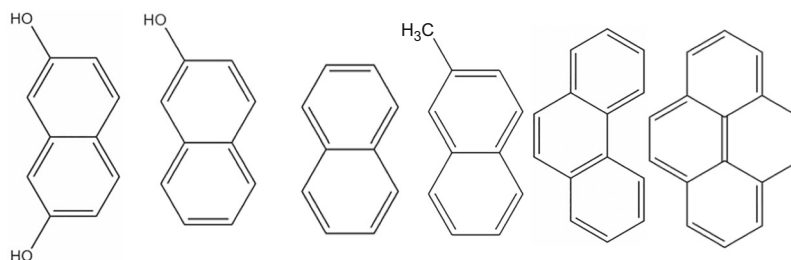
2.4 Model sorbates

Model sorbates were naphthalene-2,7-diol (27NOL), naphthalene-2-ol (2NOL), naphthalene (NAP), 2-methylnaphthalene (2NME), phenanthrene (PHE), and pyrene (PYR). The PAHs, 2NOL, and 2NME were purchased from Sigma-Aldrich (Steinheim, Germany) and 27NOL from Merck (Darmstadt, Germany). Sorbate properties are listed in Table 1. Sorbates were selected to cover (i) a range in polarity, reflected by their hydrogen-bond donor/acceptor properties and dipole moment (Table 1, 27NOL, 2NOL, NAP, 2NME), and (ii) a range in hydrophobicity (K_{ow}) and molecular weight and volume (Table 1, NAP, 2NME, PHE, PYR).

Table 1 Molecular and physicochemical properties and structural formulas of the six PAH and PAH derivatives used for sorption experiments

Compound Name		Naphtha- lene-2,7- diol	Naphtha- lene-2-ol	Naphtha- lene	2-Methyl- naphtha- lene	Phenan- threne	Pyrene
Abbreviation		2,7NOL	2NOL	NAP	2NME	PHE	PYR
CAS ^a		582-17-2	135-19-3	91-20-3	91-57-6	85-01-8	129-00-0
Chemical formula		C ₁₀ H ₈ O ₂	C ₁₀ H ₈ O	C ₁₀ H ₈	C ₁₁ H ₁₀	C ₁₄ H ₁₀	C ₁₆ H ₁₀
Purity		>98%	99.0%	99.7%	98.6%	99.5%	>99%
Molecular mass	M (g mol ⁻¹)	160.17	144.17	128.17	142.20	178.23	202.26
Molar volume	V _m (cm ⁻³) ^a	120.40	121.98	123.55	139.80	157.67	161.98
Molecular volume	V _{mol} (Å ³) ^b	142.14	133.65	125.17	142.00	168.48	184.13
Density	ρ (g cm ⁻³) ^a	1.33	1.18	1.04	1.02	1.13	1.25
Aqueous solubility	S (μmol L ⁻¹) ^a	6240	5240	242	173	6.45	0.668
Octanol-water part. coeff. logK _{ow}	logK _{ow} ^a	1.90	2.70	3.30	3.86	4.46	4.88
Polarizability	P (Å ³) ^a	18.97	18.23	17.48	19.39	24.55	28.73
Dipole-moment	μ (10 ⁻³⁰ Cm) ^b	1.78	1.41	0.00	0.327	0.0095	0.00
H-bond donor/acceptor	H _{da} ^a	2 / 2	1 / 1	0 / 0	0 / 0	0 / 0	0 / 0
logK _{OC} ^c		3.68	3.30	3.26	3.47	4.32	4.84
logK _{min} ^d				-0.56		0.58	0.34

Structural formula

^a ChemSpider database (www.chemspider.com)^b Molecular calculations using HyperChem 7.0 or from www.chemicalize.org^c Predicted values from US EPA EPISuite™^d Data on sorption to various clay minerals and pedogenic oxides compiled from Gładysz-Plaska et al. (2017), Meng et al. (2020) and Müller et al. (2007) as well as literature cited therein

2.5 Sorption experiments

Sorption of the model compounds to peat HR was investigated in customary batch experiments according to OECD guideline 106, in glass centrifuge tubes (kinetics, 70 mL; isotherms,

20 mL) with Teflon-lined screw caps in 0.01 M CaCl₂ solution at a soil-to-solution ratio of 1:20. Before use, the centrifuge tubes were flushed with acetone and heated at 130 °C for 3 h to minimize PAH sorption to the glass walls. Soil samples were completely wetted for 16 h before spiking the model

compounds. This ensured complete hydration and swelling of the soil's mineral phase so that effects of prehydration of the mineral phase were negligible for sorption experiments. All experiments were performed in triplicate. Sorbates were dissolved in methanol and spiked to the batch samples, yielding final methanol concentrations of 0.04 to 0.2 vol%. Methanol does not affect sorption up to at least 0.5 vol% (Guo et al. 2010).

Sorption kinetics were investigated at initial concentrations of $10 \mu\text{mol L}^{-1}$ at sorption time steps of 0.5, 1.0, 2.0, 4.0, 6.0, 8.0, 24, and 48 h with 2.5 g dry soil equivalent in 50 mL 0.01 M CaCl_2 . Sorption kinetics were investigated using NAP and the three NAP derivatives. At each time step, aliquots of 0.5 mL were taken from the batch samples using a glass syringe. Resulting reductions in batch solution volume were considered in the calculations. Preliminary experiments revealed that the selected soil/solution ratio and a contact time of 48 h were suited to reach sorption equilibrium. Increasing the contact time to 72 h did not yield any further significant increase in sorption (data not shown).

Isotherms of short-term sorption and desorption were determined using 0.5 g dry soil equivalent in 10 mL 0.01 M CaCl_2 at initial concentrations of 2, 5, 10, 20, 50, and $100 \mu\text{mol L}^{-1}$ (NAP and NAP derivatives) and 0.2, 0.5, 1.0, 2.0, 5.0, and $10.0 \mu\text{mol L}^{-1}$ (PHE, PYR) after 1 h of end-over-end shaking. A sorption time of 1 h was selected in order to characterize the fast sorbing fraction. Consequently, the short-term sorption does not represent a thermodynamic equilibrium state. Supernatants were collected after centrifugation of batch samples at $2000 \times g$ for 15 min with a Heraeus Multifuge X3R Centrifuge (Thermo Fisher Scientific, Osterode, Germany). Aliquots and supernatants, respectively, were passed through a $1 \mu\text{m}$ glass fiber filter ($\text{Ø}15 \text{ mm}$; Macherey-Nagel, Düren, Germany) and subsequently analyzed.

The total recovery rates of the complete experimental procedure ranged from 68 (PYR) to 100% (2NOL). Microbial degradation of the sorbates in batch experiments was negligible during 48 h as was shown in batch experiments in sterile vs. microbially reactivated samples (Fig. S1 in Electronic supplementary material). Furthermore, the pH values and C/N ratios of batch solutions remained constant during 200 h (8.3 days), indicating insignificant microbial activity in batch tubes (Table S6 in Electronic supplementary material). We determined 72 kinetic curves (four xenobiotics at six hydration treatments and three replicates) and 48 sorption and desorption isotherms (six xenobiotics at four hydration treatments).

2.6 Analysis of PAHs and PAH derivatives

Aliquots of supernatants from the batch were analyzed with an Agilent 1200 Series high performance liquid chromatography (HPLC) system with fluorescence detection (Agilent

Technologies, Inc., Waldbronn, Germany) and a 250-4 LiChrospher PAH stationary phase (Merck, Darmstadt, Germany). The flow rate of the methanol-water mobile phase was 0.8 mL min^{-1} . Retention times and excitation and emission wavelengths are given in Table S1. Fluorescence quenching, e.g., by sorption of PAHs and PAH derivatives to dissolved organic matter, was proven to be insignificant in preliminary experiments (Fig. S3). Linear calibration within the concentration range of the experiments was done using external standards obtained from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Limits of detection (LOD) were calculated, based on intensities of noise (I_{Noise}): $\text{LOD} = 5 \times I_{\text{Noise}}$. The LODs were 10 pmol for NAP, 5 pmol for the NAP derivatives, and 1 pmol for PHE and PYR.

2.7 Sorption models and statistical analyses

Sorption kinetics were evaluated with a two-stage kinetic model (TSKM) (Schneckenburger et al. 2012) that combines a Langmuir-type equation (also used in Michaelis-Menten kinetics) accounting for a fast sorbing fraction approaching equilibrium quite fast and a root function term accounting for slow sorption (Eq. (1)). The Langmuir-type term is based on bond energetics and derives from the Langmuir kinetic model (Pignatello 2000). The second term derives from the parabolic rate law, and it corresponds to the fractional power equation with an exponent of 0.5 (Sparks 1999) and can be taken as a measure for one-dimensional diffusion within the investigated concentration range.

$$c_s(t) = c_{s,\text{eq}} * t / \left(\frac{1}{k_1} + t \right) + 2 * k_2 * t^{0.5} \quad (1)$$

In Eq. (1), c_s ($\mu\text{mol kg}^{-1}$) is the concentration of the solute sorbed to the soil at the time t , and $c_{s,\text{eq}}$ ($\mu\text{mol kg}^{-1}$) is the equilibrium concentration of the fast sorbing fraction with k_1 (h^{-1}) as fast sorption rate constant. The parameter k_2 ($\mu\text{mol kg}^{-1} \text{ h}^{-0.5}$) is the overall slow or diffusion rate. The latter term mathematically approaches infinity, where a mass balance is impossible and an equilibrium concentration of the slow sorbing fraction does not exist. Thus, the equation is valid for the actual investigated concentration range and sorption times but may not be extrapolated.

Sorption isotherms were best described by the Freundlich model (Eq. (2)).

$$c_s(c_w) = K_F * c_w^n \quad (2)$$

where c_s ($\mu\text{mol kg}^{-1}$) is the concentration of xenobiotics in the solid phase (soil or peat), c_w ($\mu\text{mol L}^{-1}$) is the concentration of xenobiotics in the aqueous phase, K_F ($\mu\text{mol}^{1-n} \text{ L}^n \text{ kg}^{-1}$) is the Freundlich coefficient, and n is the dimensionless Freundlich exponent. Sorption hysteresis was expressed by hysteresis

indices (H_I), i.e., the ratios $K_{F,desorb}/K_{F,sorb}$ and n_{desorb}/n_{sorb} . The model equations were fitted to the data using Origin 7.0 (OriginLab Corporation, Northampton, MA, USA) and applying nonlinear least squares fitting, using the Levenberg-Marquardt algorithm.

Statistical analyses were done in R (version 2.8.1). Two-sided, paired Wilcoxon tests were applied to determine statistical significance in differences between data groups at a confidence level of 0.05. Data sets were correlated by linear Pearson and Spearman correlation analyses.

3 Results and discussion

3.1 Sorption kinetics and isotherms

Kinetics and isotherms averaging all hydration treatments of the peat HR soil sample are exemplarily shown in Fig. 1 a and b. Data points denote experimental values; lines represent the fits using the two-stage kinetic model and the Freundlich isotherm model (Eqs. (1) and (2)) that fitted the data best with coefficients of determination (R^2) from 0.839 to 1.000. Fitting parameters and statistical data of isotherms and sorption kinetics are provided in Tables S2 and S3.

Sorption kinetics of naphthalene and its three derivatives (Fig. 1a) were initially fast ($c_{s,eq}$, k_1 , Eq. (1)) followed by a slow sorption process (k_2 , Eq. (1)) and were consequently well-described for all sorbates and for all treatments by the two-phase sorption kinetics model (Table S2). More than 90% of the sorbed amount was reached within 1 h, and rate coefficients of the fast sorbing fraction (k_1 16.9–38.7 h⁻¹, average of all prehydration treatments) were considerably larger than rate coefficients of the slow sorbing fraction (k_2 0.35–1.10 $\mu\text{mol kg}^{-1} \text{h}^{-0.5}$, average of all prehydration treatments). Sorption kinetics varied between sorbates and the prehydration status of soil. From the error

bars in Fig. 1a, it can be seen that differences were clearly larger between sorbates and lesser affected by the prehydration treatments.

Sorption isotherms were largely nonlinear. As it was found for the kinetics, also sorption varied between sorbates and soil samples of different prehydration status. Also variations in sorption were dominated by the differences in sorbates, exceeding those among prehydration treatments. Sorption isotherms of NAP and NAP derivatives were mostly nonlinear with a mean Freundlich exponent n of 0.76 ± 0.07 , ranging from 0.60 to 0.92, whereas isotherms of PHE were almost linear at short prehydration times of 2 weeks ($n = 1.04 \pm 0.10$) and nonlinear at longer prehydration times of 8 weeks ($n = 0.83 \pm 0.09$ (Fig. 1b, Table S3)). In the case of PYR, n was not significantly different from 1, suggesting linearity for all prehydration treatments. Concentration-based sorption hysteresis occurred for all sorbates, as exemplified by 2NME in Fig. 1b (full data shown in Table S3). In high organic soils, such as peat HR, linear sorption was expected: Sorption linearity occurs in SOM with high polyamorphous alkyl (e.g., poly(m)ethylene) content (Chefetz and Xing 2009) and for SOM constituents such as cellulose and hemicellulose that loosen up by strong interactions of polar moieties with water, enabling the partitioning of organic sorbates (Chen et al. 2012). All these components are especially present in peat that represents an especially complex mixture of chemical substances (Hammond et al. 1985; Zhrebtsov et al. 2009). Furthermore, peat contains bitumens with typical contents in the range of 3–4% (Motorin and Iglovikov 2018) and linear partitioning will dominate PAH sorption to this fraction as well (Tan et al. 2016).

However, the slow sorption, nonlinearity, and hysteresis of sorption observed in the peat HR soil sample indicate the involvement of non-ideal sorption mechanisms in sorption of NAP and NAP derivatives to peat HR. This encompasses

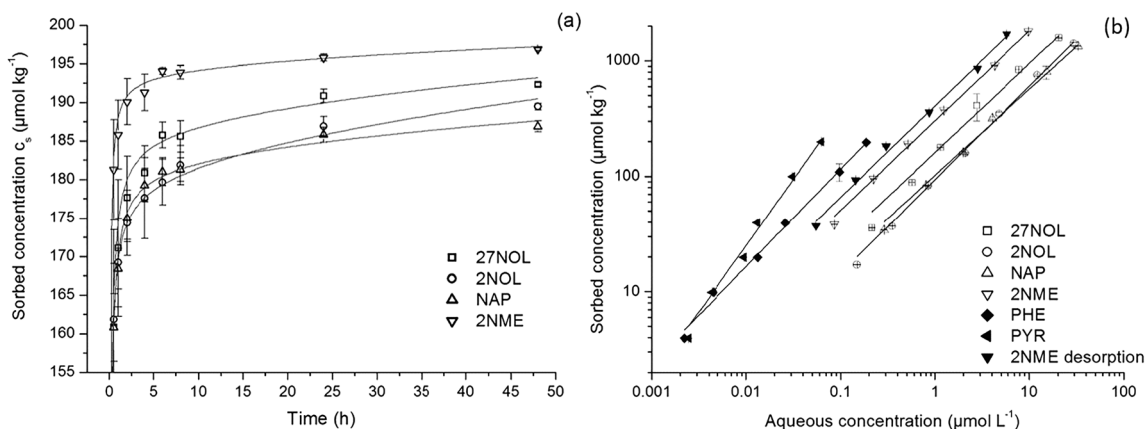


Fig. 1 Sorption kinetics (a) and sorption isotherms (b) of naphthalene-2,7-diol (27NOL), naphthalene-2-ol (2NOL), naphthalene (NAP), and 2-methylnaphthalene (2NME). Short-term, non-equilibrium sorption isotherms were recorded at sorption and desorption times of 1 h. Data points represent mean values of all hydration treatments. Lines indicate fits with

(a) the two-stage kinetic model (TSKM) and (b) the Freundlich isotherm model, respectively. Error bars denote standard deviations. Fitting parameters for single data (each compound at each hydration treatment) are given in Tables S2 and S3

surface-site-limited Langmuir-type adsorption including sites with different surface energies, hole-filling processes, and slow diffusion (Pignatello 2000; Pignatello and Xing 1996), causing irreversibility of sorption. It must be noted that the soil sample used for this model experiments comprised a relevant mineral fraction with 10% clay in the total sample. Sorption of PAHs also occurs to mineral surfaces and in respective microporous systems (Meng et al. 2020; Müller et al. 2007), e.g., via cation- π interactions between π donors and exchangeable cations accumulated at mineral surfaces (Zhu et al. 2004). However, the compilation of partitioning coefficients in Table 1 (K_{OC} vs. K_{min}) shows that sorption of PAHs to the mineral phase is by magnitudes lower than SOM, which will especially apply for a peat soil with 51% SOM compared with a terrestrial soil with about 5% SOM. A similar preference for sorption to SOM must be expected for the PAH derivatives (Novosad et al. 2005).

The results indicate that both linear and nonlinear processes were involved, which is related to sorbate properties on the one hand, for instance hydroxylation of PAH derivatives (see Section 3.1), and properties of the soil, especially of SOM on the other hand, for instance characteristics of the SOM matrix (see Section 3.2). The dual mode model (Xing and Pignatello 1997; Yu and Bi 2016) and the dual reactive domain model (Huang et al. 1997), which account for both partitioning and non-ideal sorption, were tested but did not yield a superior data fit compared with the Freundlich isotherm (Schneckenburger 2012).

3.2 Effects of sorbate properties on sorption

Figure 2 shows parameters of sorption kinetics (Fig. 2a, b, c) and sorption isotherms (Fig. 2d, e, f) to the peat HR soil sample. Boxplots show mean values and standard deviations of the sorption parameters and include all hydration treatments of the data given in Table S2 and S3 (kinetics, five hydration treatments, each with three replicates, 15 data points; isotherms, four hydration treatments, one fitting replicate, three experimental replicates, 12 data points). The kinetic parameters $c_{s,eq}$ (Fig. 2a), k_1 (Fig. 2b), and K_F (Fig. 2d) represent the fast sorption process within the first 6 h.

The sorbed amount in the fast fraction $c_{s,eq}$ and K_F increased among the non-polar sorbates with increasing hydrophobicity and molecular size and weight in the order NAP < 2NME < PHE < PYR (Fig. 2a, d). Comparability of K_F values of the sorbates was given due to nonsignificant differences in isotherm nonlinearity n (Fig. 2e).

Furthermore, the sorbed amount increased slightly with hydroxyl substitution (significant increase NAP < 27NOL, Fig. 2a, d). Sorption of the hydroxylated NAP derivatives 2NOL and 27NOL was lower than that of the methylated compound 2NME. This indicates lower sorption of polar sorbates at comparable molecular weights (dipole moments μ :

NAP 0.0, 2NME 0.33, 2NOL 1.41, 27NOL 1.78; Table 1). These observations confirmed the well-known increase in the sorbed amount with increasing sorbate hydrophobicity (e.g., Guo et al. 2010). The octanol-water partition coefficient, K_{ow} , and the aqueous solubility, S , explained the increase in sorption of the non-polar compounds (NAP, 2NME, PHE, PYR; $r = 0.95$, $p < 0.0001$) but would underestimate sorption of hydroxylated NAP derivatives, indicating that hydroxyl groups contributed specifically to the fast sorption process. The polarizability of the sorbate, corresponding to molecular size and the level of hydroxyl substitution, was strongly correlated with $\log K_F$ ($r = 0.95$, $p < 0.0001$) and $c_{s,eq}$ ($r = 0.71$, $p < 0.001$). The fast sorption rate constant k_1 was significantly highest for 2NME among the naphthalene derivatives (Fig. 2a). Thus, polarizability was the best measure for fast sorption and earlier reported to be a general measure for molecular reactivity (Tesconi and Yalkowsky 2000). The impact of sorbate polarizability on sorption of PAHs and hydroxyl derivatives was previously experimentally confirmed (Chen et al. 2005).

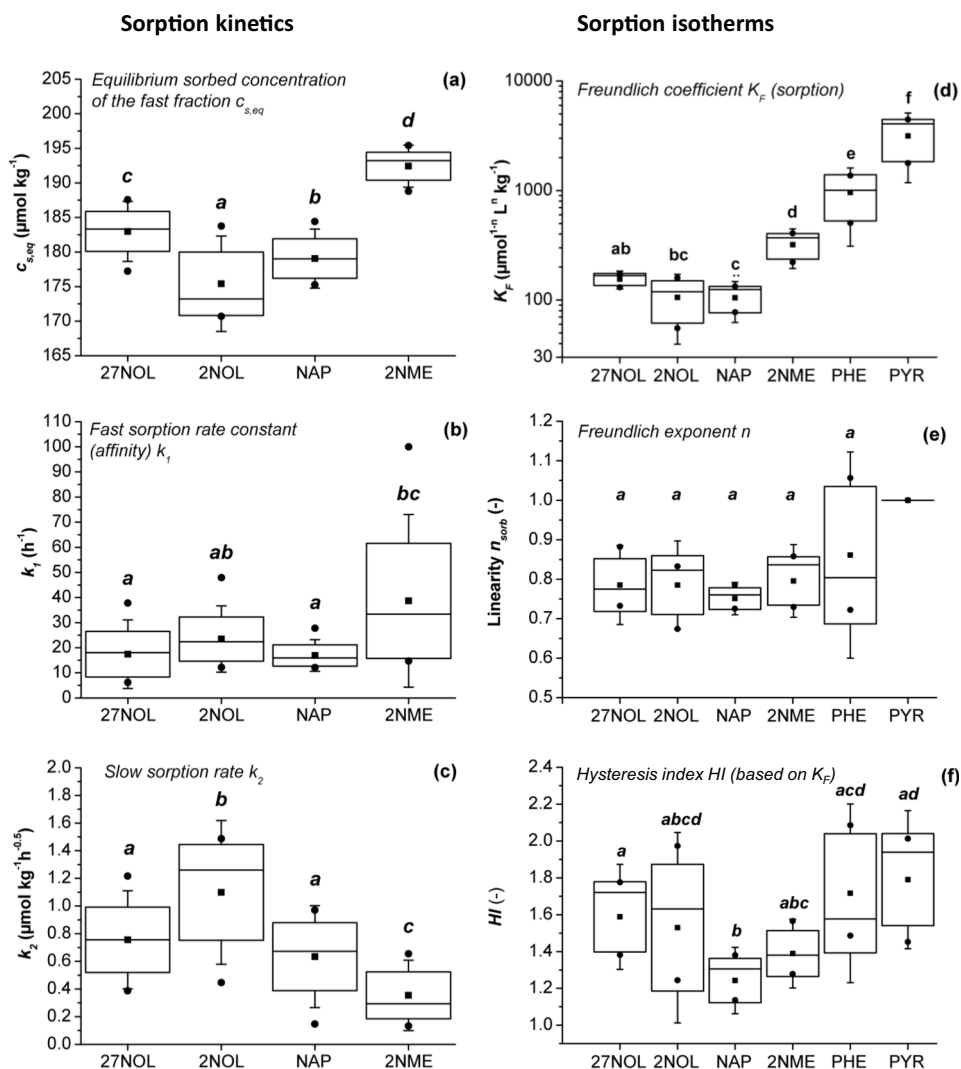
Sorption of NAP and NAP derivatives to the peat HR soil sample did not differ significantly among sorbates and was clearly nonlinear (Fig. 2e). It may be noted that the here investigated short-term sorption is typically more linear (Pan et al. 2006) as it was found for PYR in this study. Sorption hysteresis was lowest for NAP and showed increasing trends both with molecule size and degree of substitution (Fig. 2f). This points to chemical or physical-mechanical trapping in the SOM matrix of the larger, thus less mobile sorbates. Trapping of organic sorbates was previously observed to occur in rigid SOM (Pignatello and Xing 1996); see also Section 3.3.

In contrast, the slow sorption rate k_2 was lowest for 2NME ($0.35 \mu\text{mol kg}^{-1} \text{h}^{-0.5}$) and highest for 2NOL ($1.1 \mu\text{mol kg}^{-1} \text{h}^{-0.5}$), increasing in the order 2NME < NAP < 27NOL < 2NOL (Fig. 2c). Slow sorption is apparently mostly related to the steric or chemical hindrance and resistance, respectively, of the matrix to molecular diffusion (Pignatello 2000; Pan et al. 2006), where both transport processes and (ad)sorption processes play a role and may not be distinguishable (Sparks 1998). The matrix resistance depends on size and chemical properties of functional groups of the sorbates. It was shown that polar interactions such as hydrogen bonding and electron donor-acceptor interactions between the sorbates and acceptor groups within organic material affect the retardation of hydroxynaphthalenes in SOM and of PHE in biofilms, slowing down the diffusion process (Brusseau and Rao 1991; Wang et al. 2019).

3.3 The effect of prehydration of soil on sorption of PAH

Prehydration of the peat HR soil sample and more precisely of its SOM strongly affected sorption of PAHs. Figure 3 shows

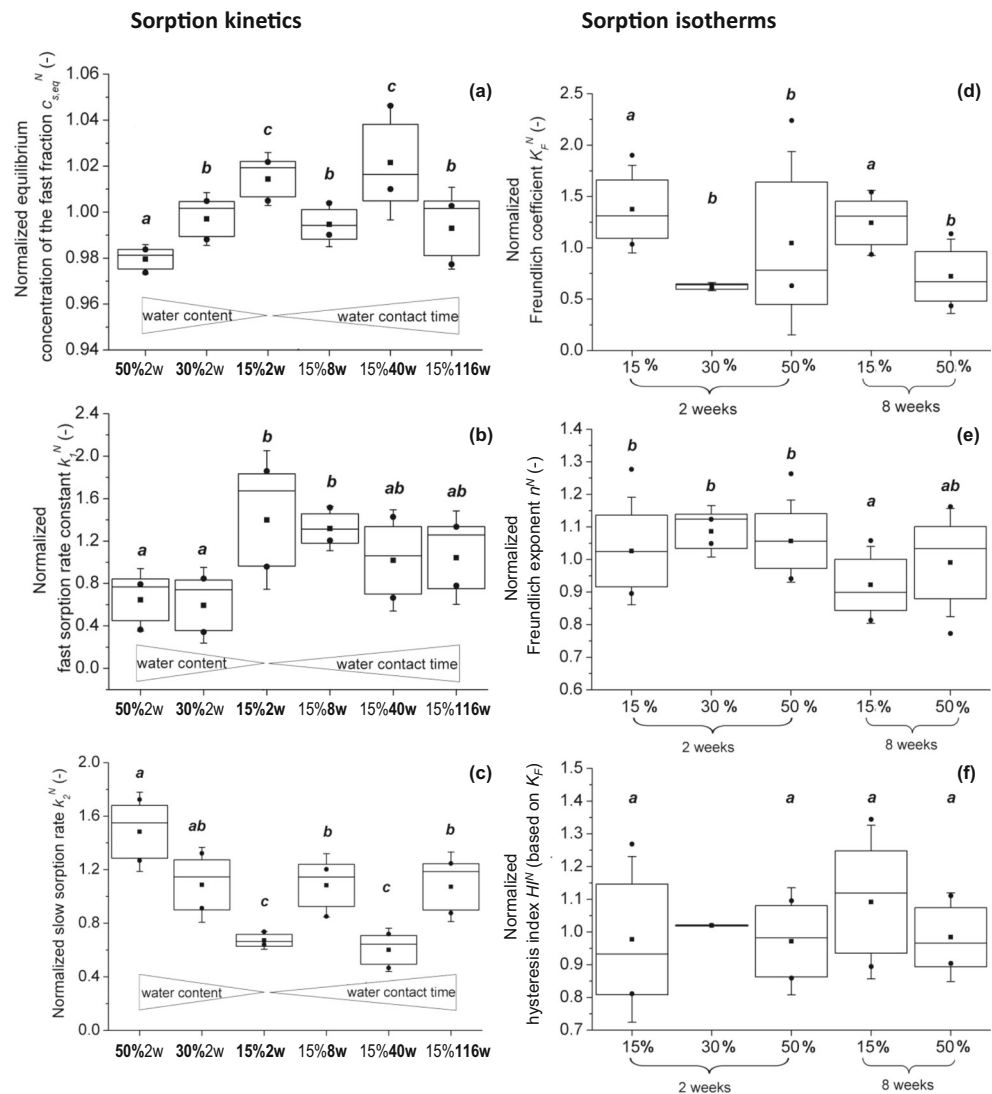
Fig. 2 Sorption parameters of naphthalene-2,7-diol (27NOL), naphthalene-2-ol (2NOL), naphthalene (NAP), 2-methylnaphthalene (2NME), phenanthrene (PHE), and pyrene (PYR) averaged overall prehydration treatments (3 to 15 data points). Displayed are coefficients of sorption kinetics modeled using the two-stage kinetic model (TSKM) and of sorption isotherms modeled using the Freundlich equation, i.e., **a** the equilibrium sorbed concentration of the fast sorbing fraction ($c_{s,eq}$), **b** the rate constant of the fast (k_1) and **c** of the slow sorbing phase (k_2), **d** the Freundlich coefficient (K_F) and **e** the Freundlich exponent (n) of the adsorption, and **f** the hysteresis index (HI) calculated for the difference in K_F of ad- and desorption. Differences at a significance level of $p < 0.05$ are indicated by lowercase letters. The box range represents the standard deviation (σ) and the line subdividing the box the median. The mean value is displayed as a filled square and the minimum and maximum values as filled circles. The whisker range corresponds to 1.5σ . Detailed data are given in Tables S2 and S3



the effects of water contents and water contact times (prehydration status) on sorption based on z-normalized data that were averaged for all sorbates. The z-normalization reveals the relative positive and negative effects of water content and hydration time on sorption, where 1 corresponds to 100%. Results for 27NOL, 2NOL, NAP, and 2NME were averaged for sorption kinetics (Fig. 3a, b, c), and results for 27NOL, 2NOL, NAP, 2NME, PHE, and PYR were averaged for sorption isotherms (Fig. 3d, e, f). On average of all sorbates, values of K_F at 50% prehydration water content were only 2/3 of those at 15%, while values of n slightly increased by a mean factor of 1.1. That effect was approximately the same level for adsorption and desorption. An increase of the prehydration water contact time from 2 to 8 weeks slightly reduced K_F of adsorption by an overall factor of 0.85, whereas alteration in K_F of desorption as well as the Freundlich exponents n was less (overall factor 0.96) (see Table S3).

Effects of the prehydration at different water content on SOM properties were reported by Schneckenburger et al. (2012). In brief, they found that increasing water content (15, 30, 50%) strongly alters various SOM properties and prehydration water contents are significantly correlated ($p < 0.05$) with the determined properties as follows. Increasing water content results in increased pore size or swelling of SOM, determined by the relaxation time T_2 in $^1\text{H-NMR}$ (Pearson correlation coefficient $r = 1.0$); increases SOM wettability, determined by the contact angle (CA; $r = -0.96$); and increases freezable water (fw) in SOM, determined by the area of the melting peak in DSC ($r = 0.98$), as well as non-freezable water (nfw), determined by the difference of water content and freezable water ($r = 0.93$), and the WaMB transition width in DSC ($r = 0.92$). The latter was reported to represent microscale variability in SOM (Weber et al. 2001) and is thus tentatively interpreted as SOM matrix heterogeneity. (For detailed Pearson

Fig. 3 Parameters of sorption kinetics (a–c) and isotherms (d–f) of six PAHs and PAH derivatives in dependence on the water content (15, 30, 50%) and contact time used for prehydration (2, 8, 40, 116 weeks) of peat HR. Sorption parameters shown are based on z-normalized data that were averaged for all six sorbates. Normalized sorption parameters are denoted with superscript ^N and become dimensionless. Deviations from 1 show relative hydration effects within the range of hydration treatments tested. For further details on the six PAHs and derivatives, respectively, the sorption coefficients, and the type of data shown by the boxplot, see legend of Fig. 2. Differences at a significance level of $p < 0.05$ are indicated by lowercase letters. Detailed data are given in Tables S2 and S3



and Spearman rank correlation parameters and respective significances, see Tables S4 and S5.)

The increase in SOM heterogeneity, pore sizes, and non-freezable water content resulted in a significant decrease of the sorbed amount ($c_{s,eq}$, K_F) and the fast sorbing fraction ($c_{s,eq}$, k_1) of PAHs and PAH derivatives, while the slow sorbing fraction (k_2) increased (Fig. 3a–d and Table S5). High matrix heterogeneity particularly decreased the fast sorption rate k_1 ($r = -0.69$, Fig. 3b, Table S5), indicating that more variable sorption sites internal to a porous SOM matrix favor slow sorption processes (Xing and Pignatello 1996). Furthermore, non-freezable water chemically interacts with soil sorption sites (Schaumann 2005; Kučerík et al. 2018). It is deduced that competition of non-freezable bound water and organic sorbates for sorption sites further limited fast sorption as it was reported by Graber and Borisover (2005). In contrast, slow sorption was positively affected particularly by freezable water ($r = 0.69$) (Fig. 3b, Table S5), indicating that transport in bulk pore water contributes to the slow sorption process and

diffusion-driven sorption induced by swelling of SOM increases (k_2 , Fig. 3c).

Also the water contact time affected SOM properties. When it was increased from 2 to 8, 40, and 116 weeks, also the *SOM matrix rigidity*, determined by the WaMB transition temperature T_1^* in DSC, increased ($r = 0.84$; Table S5). Matrix rigidity—for polymer matrices also referred to as matrix glassiness—is a measure of how rigid or flexible molecular moieties are within a molecular matrix (Hurrass and Schaumann 2005). With increasing matrix rigidities (T_1^*), short-term sorption isotherms became more nonlinear ($r = -0.40$; Fig. 3e, Table S5), indicating that non-ideal sorption processes were induced. Sorption of non-polar sorbates in flexible, amorphous matrices or SOM (also referred to as rubbery domains) follows the mechanism of linear partitioning, i.e., absorption respectively dissolution of a sorbate into a bulk solid phase (Pignatello and Xing 1996; Xia and Pignatello 2001; Xing and Pignatello 1996). Longer prehydration times alter SOM towards a more condensed and porous structure

(Xing and Pignatello 1997). The corresponding hole-filling mechanism of solute sorption leads to slower and more non-linear sorption, while solutes have a moderately greater affinity for holes than for the dissolution process that is postulated to occur at higher water contents and shorter prehydration times (Xing and Pignatello 1997; Xia and Pignatello 2001). Effects of prehydration on overall sorption hysteresis were not significant, though. In comparison, Ondruch et al. (2019) reported hampered desorption of phenol with increasing WaMB stability.

3.4 Differences in hydration effects among the sorbates

Increasing water content decreased the total sorbed amount $c_{s,eq}$ of all sorbates and increased the slow sorbing fraction k_2 in the sequence 2NME < NAP < 2NOL < 27NOL, indicating that the effect increased with sorbate polarity. This again points to a competition for polar sorption sites in the SOM matrix (Graber and Borisover 2005) and supports the hypothesis that water may especially disrupt the sorptive interactions of polar moieties of the sorbent molecules (Chen et al. 2012). The effect of water content was significant for all sorbates ($R^2 = 0.56–0.96$, $p < 0.05$). The same trends were observed for the effects of freezable and non-freezable water; both affected the polar sorbates 27NOL and 2NOL more strongly than non-polar sorbates NAP and 2NME. Furthermore, decreasing wettability (CA) of the SOM matrix with aging decreased slow sorption of the polar sorbates 27NOL and 2NOL more effectively than that of the non-polar sorbates NAP and 2NME, indicating a lower availability of non-favored polar sorption sites.

Matrix rigidity T_I^* was positively yet not significantly correlated with the fast fraction and negatively with the slow fraction, indicating that fast hole-filling is a likely dominant sorption mechanism in rigid matrices, whereas slow diffusion is impeded. Significant differences between the polar (27NOL, 2NOL) and non-polar sorbates (NAP, 2NME) could not be observed based on available data and may need further research. Sorption of xenobiotics in peat HR was well predicted by a parametric sorption model based on data reported in this publication and in Schneckenburger et al. (2012), including SOM matrix properties and sorbate descriptors as parameters. The parametric sorption model is presented in Schneckenburger (2012).

4 Conclusions

Prehydration times of up to 2 years at water contents from an air-dry state (15% w/w) to 50% (w/w) in a high organic soil significantly affect sorption of PAHs and PAH derivatives. Several physicochemical properties of the

model soil changed with hydration. According to the literature, changes in these properties are related to soil organic matter (SOM). We found correlations of changes in SOM properties with sorption kinetics and sorption isotherms of six PAH and PAH derivatives. The effects on sorption depend on the molecular properties of the sorbates on one hand and on SOM matrix rigidity, soil water content, and content of non-freezable water on the other hand. Water content most strongly influences the sorption process due to changes in pore sizes (swelling) and wettability of SOM. These factors retard and decrease sorption of polar sorbates more strongly than of non-polar sorbates. It is concluded that polar sorbates compete for sorption sites with water molecules. This suggests that hydration status particularly affects sorption of polar organic chemicals which may also account for pharmaceuticals and modern pesticides. Water contact time increases the rigidity of the soil/SOM matrix and increases isotherm nonlinearity showing that specific sorption rather than partitioning is the dominant sorption process for non-polar as well as more polar PAH derivatives.

Prehydration effects do not change sorption by orders of magnitudes. Yet, it is conceivable that, in field soil, a significant exceedance of limit concentrations of dissolved xenobiotics might be triggered by the hydration status of SOM. We suggest to consider detailed hydration effects on sorption, mobility, and bioavailability of xenobiotics in sorption models in order to improve their reliability for the risk assessment in the environment. Further research is indicated here.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have no conflicts of interest.

Human and animal rights and informed consent The research presented did not involve human participants or animals.

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