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Effects of soil water saturation on sampling equilibrium and kinetics of selected polycyclic aromatic hydrocarbons

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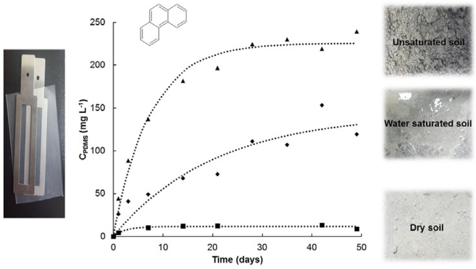
HIGHLIGHTS

- Effects of soil water saturation on sampling equilibrium and kinetic were observed.
- In dry soil, $K_{sampler/soil}$ values were much lower than those in wet soils.
- Changes in properties of soil organic matter via wetting affected $K_{sampler/soil}$.
- Varying $K_{sampler/soil}$ and Henry's law constants of chemicals influenced k_u values.
- Results in this study provide a helpful insight on passive sampling in unsaturated soils.

GRAPHICAL ABSTRACT



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ABSTRACT

Passive sampling can be applied for measuring the freely dissolved concentration of hydrophobic organic chemicals (HOCs) in soil pore water. When using passive samplers under field conditions, however, there are factors that might affect passive sampling equilibrium and kinetics, such as soil water saturation. To determine the effects of soil water saturation on passive sampling, the equilibrium and kinetics of passive sampling were evaluated by observing changes in the distribution coefficient between sampler and soil ($K_{sampler/soil}$) and the uptake rate constant (k_u) at various soil water saturations. Polydimethylsiloxane (PDMS) passive samplers were deployed into artificial soils spiked with seven selected polycyclic aromatic hydrocarbons (PAHs). In dry soil (0% water saturation), both $K_{sampler/soil}$ and k_u values were much lower than those in wet soils likely due to the contribution of adsorption of PAHs onto soil mineral surfaces and the conformational changes in soil organic matter. For high molecular weight PAHs (chrysene, benzo[*a*]pyrene, and dibenzo[*a*,*h*]anthracene), both $K_{sampler/soil}$ and k_u values increased with increasing soil water saturation, whereas they decreased with increasing soil water saturation for low molecular weight PAHs (phenanthrene, anthracene, fluoranthene, and pyrene). Changes in the sorption capacity of soil organic matter with soil water content would be the main cause of the changes in passive sampling equilibrium. Henry's law constant could explain the different behaviors in uptake kinetics of the selected PAHs. The results of this study would be helpful when passive samplers are deployed under various soil water saturations.

1. Introduction

Many hydrophobic organic chemicals (HOCs) such as polycyclic aromatic hydrocarbons (PAHs) are ubiquitous contaminants in

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soils. For the evaluation of environmental risks of HOCs, it is important to know their bioavailability in soils (Alexander, 2000; Lamoureux and Brownawell, 1999; Loonen et al., 1997). It is well known that measuring the total concentration of HOCs using whole extraction of soil may overestimate the bioavailable concentration.

The freely dissolved concentration of HOCs in soil pore water is thought to explain the bioavailability of HOCs. With a predetermined distribution coefficient between passive sampling material and water, the freely dissolved concentration of HOCs in soil pore spaces is calculated indirectly by measuring the concentration of the HOCs in sampling phase at equilibrium (e.g., Ter Laak et al., 2006; Hong and Luthy, 2008). The advantages of passive sampling for the evaluation of bioavailability of HOCs have been discussed in earlier literature. For example, Gomez-Eyles et al. (2012) compared passive sampling with extraction using a mild solvent and cyclodextrin and showed that passive sampling was more appropriate to predict the measured accumulation of PAHs in earthworms and in rye grass. Enell et al. (2016) compared passive sampling with a soil leaching test (Gamst et al., 2007) and concluded that passive sampling better predicted the freely dissolved concentration of PAHs in soil. Because of the advantages of passive sampling, it has also been used to evaluate the effectiveness of various soil amendment methods for reducing risks of HOCs (Hale et al., 2012; Marchal et al., 2014; Scherr et al., 2009; Stefaniuk and Oleszczuk, 2016). Although the total concentration of HOCs remained unchanged by soil amendments, it is expected that risks caused by HOCs are reduced by lowering the freely dissolved concentration (Marchal et al., 2014; Stefaniuk and Oleszczuk, 2016).

Most studies evaluating bioavailability of HOCs using passive sampling were conducted in sediments (e.g., Apell and Gschwend, 2014; Fernandez et al., 2014; Mayer et al., 2013) or at fixed values of soil water content (Enell et al., 2016; Gomez-Eyles et al., 2012; Hong and Luthy, 2008; Li et al., 2013; Scherr et al., 2009; Stefaniuk and Oleszczuk, 2016; Ter Laak et al., 2006). For unsaturated soils, however, the presence of an additional phase (i.e., soil air) might affect passive sampling equilibrium and kinetics and water content of soil is highly variable depending on the environmental conditions of contaminated sites. Thus, bioavailability or the freely dissolved fraction might be affected by soil water content, which changes the physical state of soils. As an extreme case, dry soils have a much stronger binding capacity than wet soils, because of increased adsorption capacity of mineral surfaces via drying (Chiou and Shoup, 1985; Goss et al., 2004; Rutherford and Chiou, 1992). Surface adsorption of HOCs onto mineral surfaces increases the apparent distribution coefficients between soil and air. Wetting of mineral surfaces reduces the adsorption capacity because hydrated surfaces inhibit the adsorption of HOCs. In addition, soil water content affects the properties of soil organic matter (Liu and Lee, 2006; Roy et al., 2000). It has been suggested that drying processes shrink organic matter and break polar interactions such as hydrogen bonding, making organic matter more hydrophobic because hydrophobic surfaces are exposed (Liu and Lee, 2006). Thus, it is likely that the sorption capacity of soils for HOCs changes with the degree of soil water saturation. These changes may affect the passive sampling equilibrium and kinetics. Nevertheless, to our best knowledge, there has been no research on the quantitative evaluation of the water saturation effects on passive sampling kinetics and equilibrium in soils.

In this study, the effects of soil water saturation on passive sampling equilibrium and kinetics were evaluated for seven selected PAHs using polydimethylsiloxane (PDMS) as a sampling material. Changes in the accumulation of PAHs in PDMS samplers from artificial soils spiked with PAHs were measured at various water saturations. Using a two-compartment model for passive sampling, equilibrium partition coefficients between PDMS and soil ($K_{sampler/soil}$) as well as the uptake rate constants (k_u) were determined using nonlinear regression. The dependence of $K_{sampler/soil}$, k_u, and the logarithm of the organic carbon-water partition coefficient (log K_{oc}) for PAHs on soil water content was assessed quantitatively and discussed.

2. Experimental

2.1. Chemicals

For model PAHs, phenanthrene (98%), anthracene (99%), fluoranthene (98%), pyrene (99%), chrysene (100%), benzo[*a*]pyrene (96%), and dibenzo[*a*,*h*]anthracene (100%) were chosen to cover wide range of physicochemical properties (i.e., molecular weight, hydrophobicity, and Henry's law constant) as well as their occurrence in soils. Model PAHs and solvents were purchased from Sigma-Aldrich (St. Louis, MO, USA), Supelco (Bellefonte, PA, USA), or Fluka (Buch, Switzerland) and all their purities were over 98%. All organic solvents used were ACS grade. Some important chemical properties of the selected PAHs are summarized in Table 1.

2.2. Passive sampler

PDMS sheets with density of 1.16 g cm^{-3} and thickness of 125 μm were purchased from Shielding-Solutions, Inc. (Great Notley, UK) and then cut into rectangular sheets (10 mm × 42 mm). These custom-cut PDMS sheets were cleaned by submerging them in *n*-hexane (*n*-hexane:PDMS = 150:1 [v/v]) for one day and then air-drying. This procedure was repeated using methanol, and the cleaned PDMS sheets were stored in methanol until use. One PDMS sheet was inserted into a custom-made aluminum sampler housing with an exposed sampling surface area of 2 × 8 mm × 40 mm for passive sampling experiments (Fig. S1, Supplementary Material).

2.3. Artificial soil

The artificial soil used in the passive sampling studies was composed of 75% sand, 20% clay, and 5% organic matter. Silicon dioxide (SiO_2) with an average particle size of 2 mm was used as the sand, and kaolin ($H_2Al_2Si_2O_8 \cdot H_2O$) was chosen as the model clay. Both silicon dioxide and kaolin were purchased from Fisher Scientific (Loughborough, UK). Peat moss, purchased from Lambert (Rivière-Ouelle, Canada), was used as the surrogate soil organic matter. When mixing the three soil components, bigger debris present in the peat moss was removed by a 2 mm sieve, and SiO_2 and kaolin were mixed without any further treatment after purchase. Although air drying does not remove soil moisture completely, 0% water saturated soil was defined as air dried soil under an ambient relative humidity (ca 50%) in this study. Water saturation of test soil was adjusted by wetting the air dried soil. Levels of water saturation of test soils were adjusted to 0%, 5%, 10%, 25%, 50%, 75%, and 100% for the passive sampling experiments.

2.4. Passive sampling experiments

In a glass box, 1 kg of soil was placed, spiked with 285 mL of methanol solution containing 10 mg of each PAH, and mixed thoroughly by hand. Spiked soil samples were placed in a fume hood for 3 days to allow complete evaporation of methanol from the soil. Loss of PAHs during the evaporation of methanol was found to be negligible by checking the initial concentration of each

Table 1
Chemical properties of the selected PAHs in this study.

Chemicals	log K_{ow}[a]	log $K_{PDMS/w}$[b]	log K_{oc}[c]	H (Pa m^3 mol^{-1})[d]	D_a (10^{-6} m^2 s^{-1})[e]	D_w (10^{-10} m^2 s^{-1})[e]
Phenanthrene	4.52	3.87	4.61	5.61	5.93	6.7
Anthracene	4.50	3.98	4.89	6.33	5.93	6.7
Fluoranthene	5.20	4.32	5.11	2.98	5.73	6.36
Pyrene	5.00	4.36	5.51	2.44	5.73	6.42
Chrysene	5.86	4.74		0.60	5.26	5.85
Benzo[*a*]pyrene	6.35	5.09	7.16	0.16	5.12	5.66
Dibenzo[*a,h*]anthracene	6.75	5.47	7.56	0.0015[f]	2.02[f]	5.18[f]

[a] Sangster Research Laboratory. LOGKOW-A databank of evaluated octanol water partition coefficient (log P). (http://logkow.cisti.nrc.ca/logkow/index.jsp expired on October 3, 2014).
[b] Measured using the ABL permeation method reported by Kwon et al. (2007).
[c] Measured log K_{oc} values using Aldrich humic acid by Kim and Kwon (2010).
[d] Determined using the diffusion in air and water boundary layers determined by Lee et al. (2012).
[e] Calculated values from Lee et al. (2012).
[f] Values taken from US EPA Soil Screening Level data (USEPA, 1996).

PAH. Except for 0% saturated soil, in which six passive samplers were deployed, nine passive samplers were deployed per soil saturation level. Each passive sampler was deployed vertically with the entire sampling area submerged in the test soil. Spacing between samplers was at least 1.5 cm not to interfere each other. The passive samplers were removed from the soils after predetermined time intervals. For the 5%, 10%, 25%, 50%, 75%, and 100% water saturated soils, the concentrations of the samplers were measured after 1, 3, 7, 14, 21, 28, 35, 42, and 49 days. For the 0% saturated soil, the concentrations in the samplers were measured after 1, 7, 14, 21, 42, and 49 days. During the experiments, glass boxes containing artificial soils spiked with PAHs and passive samplers were closed to maintain the level of water saturation of the soils. All glass boxes were kept in an incubator at 25 °C and in the dark. After the experiments, the remaining soil water content was checked for all soils. Although the glass box contained approximately 1 L headspace and it was sealed with a polypropylene lid having high sorption capacity for PAHs (Lee et al., 2014), loss of PAHs due to evaporation and sorption to the lid was found to be negligible due to high distribution coefficient between soil and water and/or that between soil and air as shown below. The concentrations of spiked PAHs were also checked for a soil with 25% water saturation as an example, to confirm the experimental conditions were maintained. Two samples of 5 g of spiked wet soil were Soxhlet extracted for 12 h using 100 mL of a mixture of *n*-hexane and acetone (50:50), and the extracts were subjected to HPLC analysis to determine PAH concentrations. PAHs accumulated in the PDMS were extracted using 4 mL of acetonitrile for, at least, 1 day at 25 °C and 150 rpm in a shaking incubator.

2.5. Determination of partition coefficients, uptake rate constants, and organic carbon-water partition coefficients

Because selected PAHs have sufficiently high organic carbon-water distribution coefficients (K_{oc}) and low Henry's law constants (Table 1), PAHs concentration in soil would not change due to dissolution to pore water regardless of the degree of water saturation, evaporation to headspace and sorption to surfaces. Assuming that PAH concentrations in soils did not change significantly over time during the passive sampling experiments, the changes in the concentration of a PAH in a PDMS sampler ($C_{sampler}$) is described by a differential equation:

$$\frac{dC_{sampler}}{dt} = k_u C_{soil} - k_e C_{sampler} \tag{1}$$

The analytical solution for Equation (1) is

$$\begin{aligned} C_{sampler} &= C_{soil} K_{sampler/soil} \left[1 - e^{-k_e t} \right] \\ &= C_{soil} K_{sampler/soil} \left[1 - e^{-\frac{k_u}{K_{sampler/soil}} t} \right] \end{aligned} \tag{2}$$

where C_{soil} is the concentration of a PAH in soil [mg kg^{-1}], $K_{sampler/soil}$ is the partition coefficient between sampler [kg L^{-1}] and soil, k_u is the uptake rate constant [kg L^{-1} d^{-1}], and k_e is the elimination rate constant from the sampler [d^{-1}]. Time-course measurements of $C_{sampler}$ at different levels of water saturation were used to determine both $K_{sampler/soil}$ and k_u. Nonlinear least squares regression was conducted using the nls function using the Gauss-Newton algorithm in the R software (R Development Core Team, 2016).

The distribution coefficient between soil and water (K_d) was calculated using determined $K_{sampler/soil}$ and the values of partition coefficient between PDMS and water ($K_{PDMS/w}$) obtained using the aqueous boundary layer permeation method (Kwon et al., 2007). The organic carbon-water partition coefficient (K_{oc}) was then obtained by dividing K_d by the mass fraction of soil organic carbon content (f_{oc}; 0.023 in this study).

2.6. Instrumental analyses

The selected PAHs were analyzed using an HPLC system equipped with a quaternary gradient pump (Waters 600E, Milford, MA, USA), an auto sampler (Waters 717+), and a multiwavelength fluorescence detector (Waters 2475). The total flow rate of the eluent was 1 mL min^{-1}. The wavelengths of excitation/emission were 260/352 nm for phenanthrene; 260/420 nm for anthracene, pyrene, chrysene benzo[*a*]pyrene, and dibenzo[*a,h*]anthracene; and 260/460 nm for fluoranthene. Concentration in the passive sampler extracts was quantified using a calibration curve obtained from independently prepared external standards.

3. Results and discussion

3.1. Kinetic experiments

To confirm that the experimental conditions were maintained throughout, water saturation was checked after each experiment (Table S1, Supplementary Material). Triplicate analyses showed that the initial conditions were maintained to the end of the tests. As shown in Table S2 (Supplementary Material), the remaining concentrations of all selected PAHs were between 8 and 10 mg kg^{-1}

based on dry weight, indicating that the initially spiked concentration was maintained.

Fig. 1 shows the uptake kinetics for two of the selected PAHs, phenanthrene and benzo[*a*]pyrene, by the samplers in the soils with water saturations of 100, 25, and 0%. For both of these PAHs, the concentrations in the samplers at plateau for the dry soil (0%) were much lower than those for the 100 and 25% saturated soils. However, the effects of the water saturating process were very different on phenanthrene and benzo[*a*]pyrene. The amount of phenanthrene taken up by a passive sampler was smaller at greater soil water saturation, whereas the trend is somewhat the opposite for benzo[*a*]pyrene. All kinetic experimental results for other PAHs at various water saturation are shown in Fig. S2–S8 (Supplementary Material). Except for benzo[*a*]pyrene at 100% water saturated soil, standard errors for all fitted partition coefficients in Fig. 1 and Fig. S2–S8 were less than 20%, suggesting that the kinetic model explains the experimental results well.

3.2. Effects of water saturation on distribution coefficients

Table 2 summarizes all $K_{sampler/soil}$ and k_u values obtained, along with their standard errors of regression. For dry soils (0% water saturation), both $K_{sampler/soil}$ and k_u values for all the selected PAHs were much lower than those values obtained from soils containing at least some water (Fig. 1, Fig. S2 and Table 2). The lower values of $K_{sampler/soil}$ in dry soils could be explained by higher distribution coefficients between soil and pore air because the partition coefficient between PDMS and air is only slightly affected by the absorption of pore water in PDMS (Sprunger et al., 2007). It has been acknowledged that water sharply reduces the adsorption capacity of mineral surfaces for organic compounds (Chiou and Shoup, 1985; Goss et al., 2004; Rutherford and Chiou, 1992). For example, Chiou and Shoup (1985) observed that increasing relative humidity of Woodburn soil containing 1.9% organic matter from 0 to 90% reduced sorption capacity of dry soil by two orders of magnitude for benzene and chlorinated benzenes. This agrees with the measured $K_{sampler/soil}$ in this study. Water saturation reduced sorption capacity of dry soil about one order of magnitude for relatively low hydrophobic PAHs (i.e., phenanthrene, anthracene, fluoranthene and pyrene) and almost two orders of magnitude for more hydrophobic PAHs (i.e., benzo[*a*]pyrene and dibenzo[*a*,*h*]anthracene). In addition, the water saturating process may lower the hydrophobicity of soil organic matter by changing the molecular conformation and volume of organic matter, thus exposing hydrophilic functional groups (Liu and Lee, 2006).

The effects of water saturation on the $K_{sampler/soil}$ values for all the selected PAHs can be seen in Fig. 2. Interestingly, the $K_{sampler/soil}$ slightly decreased with increasing water saturation for low molecular weight PAHs (i.e., phenanthrene, anthracene, fluoranthene, and pyrene) (Fig. 2a–d). For example, the $K_{sampler/soil}$ values for phenanthrene and anthracene at 5% water saturation were greater than those at 100% water saturation by factors of 1.5 (±0.3) and 1.7 (±0.2), respectively. On the other hand, changes in the $K_{sampler/soil}$ values showed an opposite tendency for higher molecular weight PAHs (Fig. 2e–g). For benzo[*a*]pyrene and dibenzo[*a*,*h*]anthracene, the $K_{sampler/soil}$ values at 100% water saturation were greater than those at 5% water saturation by factors of 2.2 (±1.2) and 6.0 (±2.0), respectively. The increased $K_{sampler/soil}$ values for the higher molecular weight PAHs with increasing water saturation should be due to the decrease in the sorption capacity of soil organic matter with increasing water saturation. It has been observed that the sorption capacity of soil organic matter such as humic acid increased with reduced water content (Liu and Lee, 2006; Roy et al., 2000). However, increased sorption capacity of soil organic matter at lower water saturation cannot explain the observed slight decrease in the $K_{sampler/soil}$ values for low molecular weight PAHs (phenanthrene, anthracene, fluoranthene, and pyrene) with increasing water saturation. The water saturating process may lead to conformational change of organic matter and swells the volume of organic matter (Liu and Lee, 2006) and this swelling may create inner sorption sites that can host relatively smaller molecules, as the partition coefficient between cyclodextrin and water was higher for PAHs of smaller molecular size (Kim and Kwon, 2010). The observed trend for low molecular weight PAHs in this study may be attributable to the compensation of the two competing effects of water saturation although further studies are required.

The changes in K_{oc} with increasing soil water saturation are shown in Fig. 3, and the obtained values of K_{oc} are listed in Table S3 (Supplementary Material). Opposite trends were observed for low molecular weight PAHs (Fig. 3a) and for high molecular weight PAHs (Fig. 3b). For 100% saturated soil, the calculated K_{oc} values in this study were close to but slightly lower than those obtained from our earlier study using dissolved Aldrich humic acid (Kim and Kwon, 2010) (Table 1).

3.3. Effects of water saturation on the uptake rate constants

Fig. 4 shows the effects of water saturation on the k_u for the selected PAHs. Low molecular weight PAHs (phenanthrene, anthracene, fluoranthene, and pyrene) exhibited similar tendencies in $K_{sampler/soil}$ values in that their k_u values decreased with increasing water saturation (Fig. 4a–d). For example, the k_u values

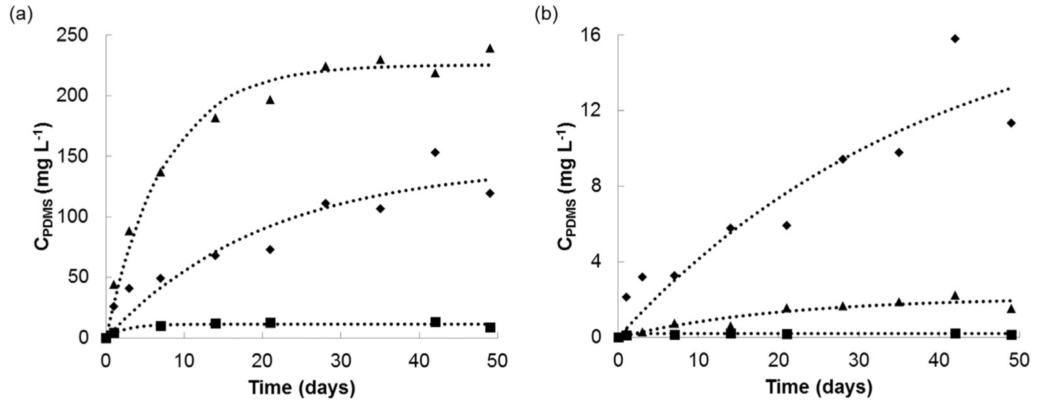

Fig. 1. Changes in concentration of phenanthrene (a) and benzo[*a*]pyrene (b) in PDMS passive samplers with sampling time for 100% (◆), 25% (▲), and 0% (■) saturated soils. Dotted lines show the best-fit curves per Equation (1).

Table 2
Uptake rate constants (k_u) and partition coefficients between sampler and soil ($K_{sampler/soil}$) for the selected PAHs at various water saturations.

Chemicals	k_u (kg L^{-1} day^{-1})							$K_{sampler/soil}$ (kg L^{-1})						
	100%	75%	50%	25%	10%	5%	0%	100%	75%	50%	25%	10%	5%	0%
Phenanthrene	0.80 (±0.20)	0.65 (±0.21)	1.87 (±0.34)	3.45 (±0.33)	4.37 (±0.38)	3.30 (±0.64)	0.54 (±0.24)	16.17 (±2.78)	17.07 (±5.24)	17.66 (±1.01)	25.44 (±0.67)	22.80 (±0.46)	23.77 (±1.22)	1.31 (±0.09)
Anthracene	1.24 (±0.29)	1.22 (±0.46)	2.70 (±0.56)	5.12 (±1.06)	5.84 (±1.49)	5.73 (±1.15)	0.68 (±0.50)	13.04 (±1.08)	12.94 (±1.68)	15.57 (±0.77)	23.59 (±1.08)	21.73 (±1.15)	21.48 (±0.90)	0.97 (±0.11)
Fluoranthene	0.40 (±0.11)	0.27 (±0.08)	0.50 (±0.10)	0.65 (±0.06)	0.88 (±0.07)	0.73 (±0.10)	0.095 (±0.007)	10.90 (±3.06)	7.80 (±2.43)	8.51 (±0.93)	12.14 (±0.64)	11.68 (±0.42)	13.36 (±1.06)	0.93 (±0.03)
Pyrene	0.47 (±0.14)	0.36 (±0.08)	0.50 (±0.08)	0.64 (±0.12)	0.92 (±0.10)	0.74 (±0.08)	0.11 (±0.03)	6.21 (±0.79)	4.05 (±0.35)	5.66 (±0.34)	7.53 (±0.55)	7.85 (±0.24)	8.75 (±0.35)	0.70 (±0.04)
Chrysene	0.15 (±0.04)	0.15 (±0.04)	0.13 (±0.03)	0.071 (±0.016)	0.101 (±0.017)	0.11 (±0.02)	0.024 (±0.005)	4.34 (±1.12)	1.85 (±0.21)	1.72 (±0.17)	1.38 (±0.21)	2.07 (±0.24)	2.62 (±0.37)	0.16 (±0.01)
Benzo[*a*]pyrene	0.049 (±0.014)	0.054 (±0.017)	0.056 (±0.016)	0.011 (±0.003)	0.022 (±0.002)	0.017 (±0.003)	0.025 (±0.013)	1.94 (±0.85)	0.56 (±0.06)	0.39 (±0.03)	0.22 (±0.041)	0.56 (±0.06)	0.87 (±0.28)	0.020 (±0.001)
Dibenzo[*a,h*]anthracene	0.042 (±0.012)	0.077 (±0.030)	0.12 (±0.05)	0.084 (±0.093)	0.013 (±0.003)	0.011 (±0.003)	0.0026 (±0.0021)	1.15 (±0.33)	0.39 (±0.04)	0.28 (±0.02)	0.046 (±0.005)	0.18 (±0.02)	0.19 (±0.03)	0.029 (±0.009)

Values in parentheses are standard errors obtained by nonlinear regression using Equation (1).

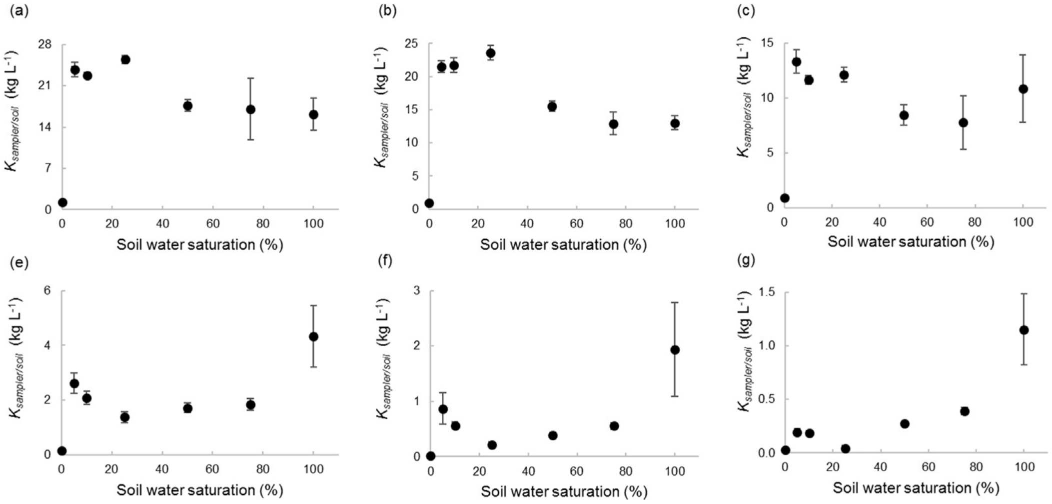

Fig. 2. Partition coefficient between sampler and soil ($K_{sampler/soil}$) at various soil water saturations for phenanthrene (a), anthracene (b), fluoranthene (c), pyrene (d), chrysene (e), benzo[*a*]pyrene (f), and dibenzo[*a,h*]anthracene (g). Error bars represent the standard errors.

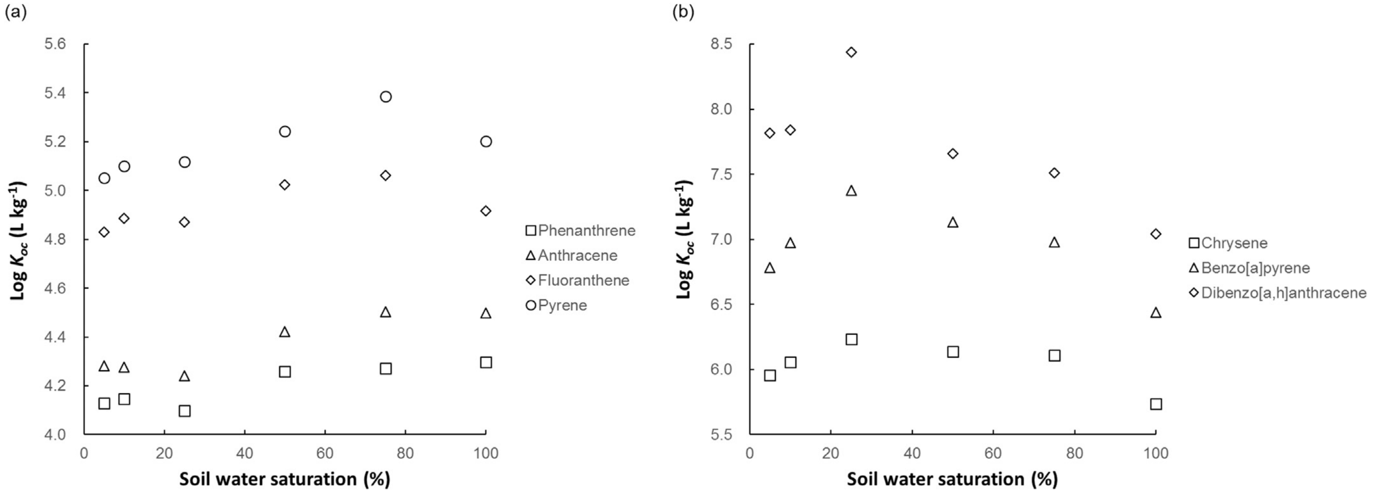

Fig. 3. Organic carbon-water partition coefficient (K_{oc}) for various water saturated soils for phenanthrene, anthracene, fluoranthene, and pyrene (a) and chrysene, benzo[*a*]pyrene, and dibenzo[*a,h*]anthracene (b).

for phenanthrene and anthracene at 5% water saturation were greater than those at 100% water saturation by factors of 4.1 (±1.3) and 4.6 (±1.4), respectively. As was the case with $K_{sampler/soil}$ values for high molecular weight PAHs (chrysene, benzo[*a*]pyrene and

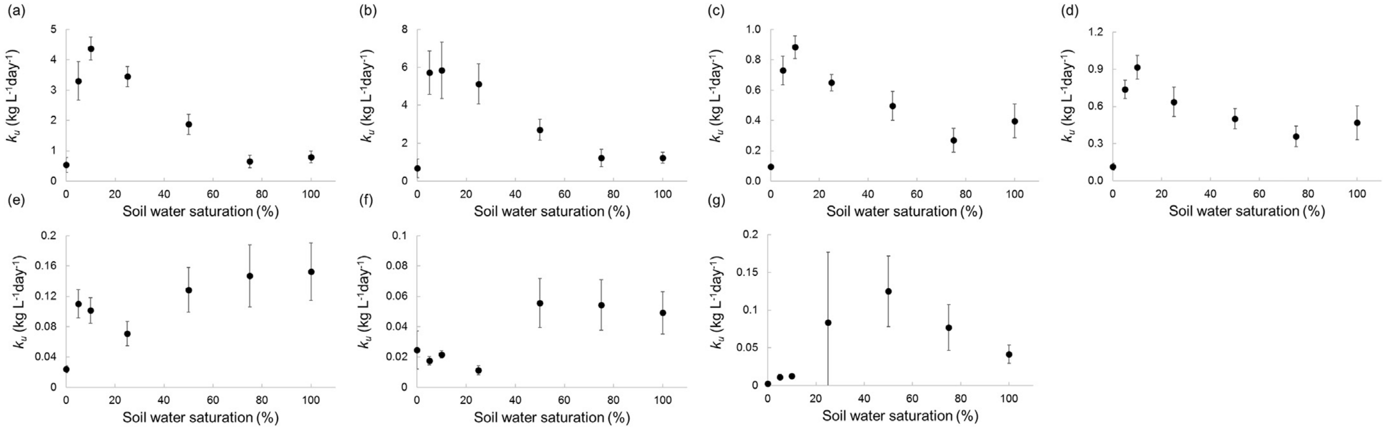

Fig. 4. Uptake rate constant (k_u) for various soil water saturations for phenanthrene (a), anthracene (b), fluoranthene (c), pyrene (d), chrysene (e), benzo[*a*]pyrene (f), and dibenzo[*a*,*h*]anthracene (g). Error bars represent the standard errors.

dibenzo[*a*,*h*]anthracene), the k_u values for such show an increasing tendency with increasing water saturation (Fig. 4e–g). For benzo[*a*]pyrene and dibenzo[*a*,*h*]anthracene, the $K_{sampler/soil}$ values at 100% water saturation were greater than those at 5% water saturation by factors of 2.9 (±1.0) and 3.8 (±1.5), respectively.

In isothermal and isobaric conditions, molecular diffusion in air and in water is the predominant transport mechanism in soil pore space (Scanlon et al., 2001). If molecular diffusion is the dominant mechanism of mass transfer, the mass transfer resistance is determined by the molecular diffusion coefficients in air (D_a) and in water (D_w), Henry's law constant, and the thickness of the diffusion boundary layers. For the model PAHs, the calculated diffusion coefficients in air are bigger than those in water by approximately four orders of magnitude (values are shown in Table 1). If one assumes that the boundary layer thickness in air is not significantly different from that of water in soil pores, the relative contribution in mass transfer resistance would be determined by the Henry's law constants of PAHs (values are shown in Table 1). According to this assumption, the ratio of the mass transfer resistance in water to that in air is computed by D_aH/D_wRT, where R is the gas constant and T is temperature. For phenanthrene, the ratio under ambient conditions is approximately 20. Higher mass transfer resistance through pore water can explain the decrease in the k_u of phenanthrene with increasing soil water saturation (Fig. 4a). On the other hand, the ratio for benzo[*a*]pyrene is estimated at only 0.58. Because of higher mass transfer resistance in air, the k_u of benzo[*a*]pyrene increased with increasing soil water saturation (Fig. 4b).

4. Conclusions

Effects of soil water saturation on passive sampling equilibrium and kinetics were evaluated by observing changes in $K_{sampler/soil}$ and k_u at various soil water saturations. The significantly higher binding capacity of dry soil was explained by the increased adsorption to soil mineral surfaces. The effects of soil water saturation differed for the selected PAHs. For low molecular weight PAHs, the $K_{sampler/soil}$ and k_u decreased with increasing soil water saturation, whereas they increased with increasing soil water saturation for high molecular weight PAHs. These observations would be helpful in determining sampling time for equilibrium sampling as well as the bioavailability of HOCs in soils when passive sampling is used under field conditions. Bioavailability of HOCs is likely to be affected by a factor of approximately two because of the changes in K_{oc} values, although further investigation is needed.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.chemosphere.2017.05.170.

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