Pedosphere **33**(2): 365–371, 2023
doi: 10.1016/j.pedsph.2022.06.049
ISSN 1002-0160/CN 32-1315/P
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Published by Elsevier B.V. and Science Press

PEDOSPHERE

www.elsevier.com/locate/pedosphere

Effect of soil pH on the sorption capacity of soil organic matter for polycyclic aromatic hydrocarbons in unsaturated soils



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(Received April 29, 2021; revised June 23, 2021; accepted August 16, 2021)

ABSTRACT

Sorption by soil organic matter (SOM) is considered the most important process affecting the bioavailability of hydrophobic organic chemicals (HOCs) in soil. The sorption capacity of SOM for HOCs is affected by many environmental factors. In this study, we investigated the effects of soil pH and water saturation level on HOC sorption capacity of SOM using batch sorption experiments. Values of soil organic carbon-water partition coefficient (K_{OC}) of six selected polycyclic aromatic hydrocarbons (PAHs) were measured in an artificial soil under various soil pH and water saturation conditions. Passive sampling was used to measure K_{OC} with polydimethylsiloxane as the sampling material. Regardless of soil pH, K_{OC} increased with increasing soil water saturation level for lower-molecular-weight PAHs. In contrast, K_{OC} decreased with increasing soil water saturation level for higher-molecular-weight PAHs. Despite some fluctuations, K_{OC} tended to decrease with increasing soil pH at all water saturation levels. This indicates that earlier studies on the effects of soil pH on K_{OC} under saturated conditions could be extended to unsaturated soils. These K_{OC} tendencies were reproduced in three different natural soils, suggesting that the effects of soil water saturation level and pH might be generalized, at least for PAHs. The PAH sorption capacity of SOM was found to be resilient under dynamic soil pH conditions, which can be used to adjust the effects of soil pH.

Key Words: contaminated soil, hydrophobic organic chemical, partition coefficient, passive sampling, pollutant, soil water saturation level

Citation: Kim P G, Tarafdar A, Kwon J H. 2023. Effect of soil pH on the sorption capacity of soil organic matter for polycyclic aromatic hydrocarbons in unsaturated soils. *Pedosphere*. **33**(2): 365–371.

INTRODUCTION

Understanding the bioavailability of hydrophobic organic chemicals (HOCs) in HOC-contaminated soils is important for the evaluation of environmental risk and the prioritization of clean-up, monitoring, and remediation (Loonen *et al*., 1997; Lamoureux and Brownawell, 1999; Alexander, 2000; Tarafdar *et al*., 2018; Tarafdar and Sinha, 2018). Hydrophobic organic chemicals such as polycyclic aromatic hydrocarbons (PAHs) are pervasive soil pollutants. Sorption by soil organic matter (SOM) is considered the major consequential process affecting the bioavailability of HOCs in soil (Chiou *et al*., 1983; Pignatello and Xing, 1996; Onken and Traina, 1997; Chefetz *et al*., 2000; Tarafdar *et al*., 2020).

The sorption capacity of SOM for HOCs is influenced by many environmental parameters (Chiou and Shoup, 1985; Rutherford and Chiou, 1992; Roy *et al*., 2000; Liu and Lee, 2006; Wang *et al*., 2016; Kim *et al*., 2017; Bartolomé *et al*., 2018; Kim and Kwon, 2020). Among them, changes in soil water saturation levels can lead to dynamic changes in the soil organic carbon-water partition coefficient (K_{OC}). In our earlier study, K_{OC} elevated with enhanced soil water saturation for relatively low-molecular-weight PAHs; in contrast, the tendency was reversed for higher-molecular-weight PAHs (Kim *et al*., 2017). As soil water saturation fluctuates temporally, the ratio of HOC concentration in SOM to that in porewater is likely to change constantly.

Soil pH is another influential environmental parameter affecting the sorption capacity of SOM, which may change for many reasons. Soils can become more acidic through over-fertilization (Ullah *et al*., 2008; Liu *et al*., 2010; Savci, 2012) and acid precipitation (Sharma and Reddy, 2004; Du *et al*., 2012). For instance, the average pH of forest soils in selected locations in Korea has been consistently decreasing since 2010 (Lee and Koo, 2020). In the southern Jiangsu Province of China, the average soil pH decreased by 0.56 and 0.52 pH units in 1980–2000 and 2000–2015, respectively (Xie *et al*., 2019). Earlier experiments on the effect of soil pH on the sorption capacity of SOM for neutral HOCs showed higher HOC sorption by SOM at lower soil pH (Laor *et al*., 1998; Ertli *et al*., 2004; Ping *et al*., 2006; Li *et al*., 2010; Yang *et al*., 2013). For example, the K_{OC} for nonionic organic compounds decreased by approximately 35% as soil pH increased from 2.7 to 7.3 (Li *et al*., 2010), the sorption of phenanthrene by humic acids was greater at lower pH (Laor *et al*., 1998; Ping *et al*., 2006), and the sorption of phthalic acid esters by soil decreased with increasing soil

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pH (Yang *et al*., 2013) in saturated soils. However, it was recently demonstrated that soil water saturation can affect the sorption capacity of SOM. For example, the K_{OC} of benzo[a]pyrene in 25% saturated soil was almost nine times larger than that of 100% saturated soil, despite the same SOM used (Kim *et al*., 2017). Because soil pH and water saturation levels affect K_{OC}, it is necessary to understand the dynamic response of K_{OC} to the combination of these two influencing factors.

In this study, the effects of dynamic soil pH and water saturation conditions on the sorption capacity of SOM for PAHs were evaluated using a passive sampling technique. Polydimethylsiloxane (PDMS) was used as the sampling material, and an artificial soil was used for the experiment. Peat moss was selected as the model SOM, because it is traditionally used in agriculture and sorption experiments (Chefetz *et al*., 2000; Kim *et al*., 2017; Kim and Kwon, 2020) and has been recommended for use in the preparation of the artificial soil for soil bioaccumulation tests (OECD, 2010). The K_{OC} values of six selected PAHs were measured at a soil pH range of 4.0–8.5 and a soil water saturation range of 10%–100%. After the experiments, soils with pH 4.0 and 8.5 at 50% and 100% soil water saturation were adjusted to pH 5.2, and the K_{OC} values of the six selected PAHs were measured again to test whether the sorption capacity of SOM is resilient to changing soil pH. To observe the effects of soil water saturation and pH in natural soils, the K_{OC} values of the six PAHs were measured at two pH and two water saturation levels in three natural soils.

MATERIALS AND METHODS

Chemicals

Six PAHs, phenanthrene (98% purity), anthracene (99% purity), fluoranthene (98% purity), pyrene (99% purity), chrysene (100% purity), and benzo[a]pyrene (96% purity), were selected as model HOCs. The ACS grade organic solvents were procured from Supelco (Bellefonte, USA), Sigma-Aldrich (St. Louis, USA), and Fluka (Buch, Switzerland). NaOH (Samchun, Pyeongtaek, Korea) and HCl (Daejung, Siheung, Korea) were used to adjust soil pH.

Passive samplers

Polydimethylsiloxane sheets (10 mm × 40 mm, 125-μm thickness; Specialty Silicone Products, Inc., Ballston Spa, USA) were used for the model polymer of the passive sampler. Rectangular PDMS sheets were placed in n-hexane (n-hexane:PDMS = 150:1, volume:volume) for cleaning. After 24 h, they were air-dried. The cleaning process was repeated using methanol. The cleaned PDMS sheets were placed in a sampler holder made of aluminum (Fig. S1, see Supplementary Material for Fig. S1).

Artificial soil

An artificial soil, with 75% sand (SiO_2) (Fisher Scientific, Loughborough, UK), 20% kaolin clay ($H_2Al_2Si_2O_8 \cdot H_2O$) (Fisher Scientific), and 5% peat moss (Lambert, Rivière-du-Loup, Canada), was prepared as the model soil, according to OECD test guidelines (OECD, 2010). A blender was used to homogenize the peat moss, which was sieved (2 mm) before mixing with sand and clay.

The artificial soil (300 g) was placed in a sealed glass enclosure and spiked with methanol solution (90 mL) containing 1.12 mg of each PAH. The PAH concentrations in natural soil are generally lower than those spiked in this study, but the concentrations at polluted sites could be much higher (Bhatt *et al*., 2002; Eom *et al*., 2007). The PAH-spiked soil samples were subjected to thorough homogenization by hand. Mixed soil samples were air-dried for 3 d in a laminar flow cabinet to thoroughly volatilize methanol. After evaporating methanol, the soil pH was adjusted to 4.0, 5.2, 6.4, 7.5, and 8.5, using 1.0 mol L^{-1} NaOH or HCl solution. The water saturation levels of the mixed soil samples were calibrated to 10%, 20%, 50%, 75%, and 100%. Further details about adjusting soil water saturation and pH are provided in File S1 (see Supplementary Material for File S1).

Natural soils

Natural soils were collected at three different locations and were classified as sand (soils A and B) and sandy clay loam (soil C) (Whiting *et al*., 2005). The detailed locations, texture, total organic carbon content, and pH of the soils are provided in File S2 (see Supplementary Material for File S2). The soils were homogenized and sieved according to the method used for the artificial soil described above. Natural soil samples (300 g) were placed in glass enclosures, spiked with PAHs (3 mg of each PAH) containing methanol solution (120 mL), evaporated, and then adjusted to pH 6.0 and 8.5 using NaOH or HCl solution. Soil water saturation levels were adjusted to 10% and 75%. After the experiments, soil water saturation and soil pH were measured. Additional details are provided File S2.

Passive sampling experiments

Passive samplers were vertically embedded (5 samplers per 300 g soil) in a glass enclosure. The glass enclosures were all placed away from light in an incubator (25 °C). Soil water saturation level and concentrations of PAHs were maintained during the experiments (Kim *et al*., 2017). Embedded passive samplers were removed from the soils 7, 14, 21, 28, and 35 d after sampling. The PDMS sheets removed from the samplers were sunk in 4 mL of acetonitrile and placed in a shaker incubator for 1 d (150 r min^{-1}, 25 °C).

After the above experiments, the 50% and 100% saturated artificial soil with pH levels of 4.0 and 8.5 was adjusted to pH 5.2 using 1.0 mol L^{-1} NaOH or HCl solution. The passive sampling experiments were repeated, following the same protocols. After all experiments, maintenance of soil pH was tested as shown in Table SI (see Supplementary Material for Table SI).

Verification of partition coefficients, uptake rate constants and K_{OC}

Initial soil PAH concentrations were maintained throughout the experiments. Therefore, the time (t)-dependent PAH concentration in the PDMS sampler (C_{sampler}) can be expressed by the following differential equation:

$$\frac{\mathrm{d}C_{\text{sampler}}}{\mathrm{d}t} = k_{\text{u}}C_{\text{soil}} - k_{\text{e}}C_{\text{sampler}} \quad (1)$$

and the analytical solution for C_{sampler} is:

$$\begin{aligned} C_{\text{sampler}} &= C_{\text{soil}}K_{\text{sampler/soil}}\left(1-\mathrm{e}^{-k_{\text{e}}t}\right) \\ &= C_{\text{soil}}K_{\text{sampler/soil}}\left(1-\mathrm{e}^{-\frac{k_{\text{u}}}{K_{\text{sampler/soil}}}t}\right) \end{aligned} \quad (2)$$

where k_{u} is the uptake rate constant (kg L^{-1} d^{-1}), C_{soil} denotes the soil PAH concentration (mg kg^{-1}), k_{e} is the elimination rate constant from the sampler (d^{-1}), and $K_{\text{sampler/soil}}$ signifies the partitioning coefficient between the sampler and the soil (kg L^{-1}) (Kim *et al*., 2017). The PAH concentrations in the PDMS samplers were estimated using a high-performance liquid chromatography (HPLC) system (Waters, Milford, USA). Detailed procedures are provided in File S3 (see Supplementary Material for File S3). Time-dependent C_{sampler} was measured to obtain both $K_{\text{sampler/soil}}$ and k_{u} using the R nlsfit function (R Development Core Team, 2019).

Soil-water partition coefficient (K_{d}) was estimated using the obtained $K_{\text{sampler/soil}}$ and the PDMS-water partition constant ($K_{\text{PDMS/w}}$) from earlier citations (Table SII, see Supplementary Material for Table SII) (Kwon *et al*., 2007). Afterwards, the division of K_{d} by the mass fraction of the SOM in soil was used to estimate K_{OC} because the neutral HOC was predominantly absorbed by SOM (Onken and Traina, 1997; Chefetz *et al*., 2000).

RESULTS AND DISCUSSION

Effects of soil water saturation and pH on partition coefficients in the artificial soil

The PAH uptake by the passive samplers at various soil pH and water saturation levels is depicted in Fig. S2 (see Supplementary Material for Fig. S2). All the $K_{\text{sampler/soil}}$ and $\log K_{\text{OC}}$ estimates are listed in Tables SII and SIII (see Supplementary Material for Table SIII). As demonstrated in our earlier experiments (Kim *et al*., 2017), the effect of soil water saturation on the sorption capacity of SOM is retained across a wide range of soil pH. Other studies have also reported that soil water saturation affects SOM sorption capacity (Roy *et al*., 2000; Liu and Lee, 2006) and volume (Liu and Lee, 2006). These two effects create conflicting trends for chemicals, as shown in Fig. 1.

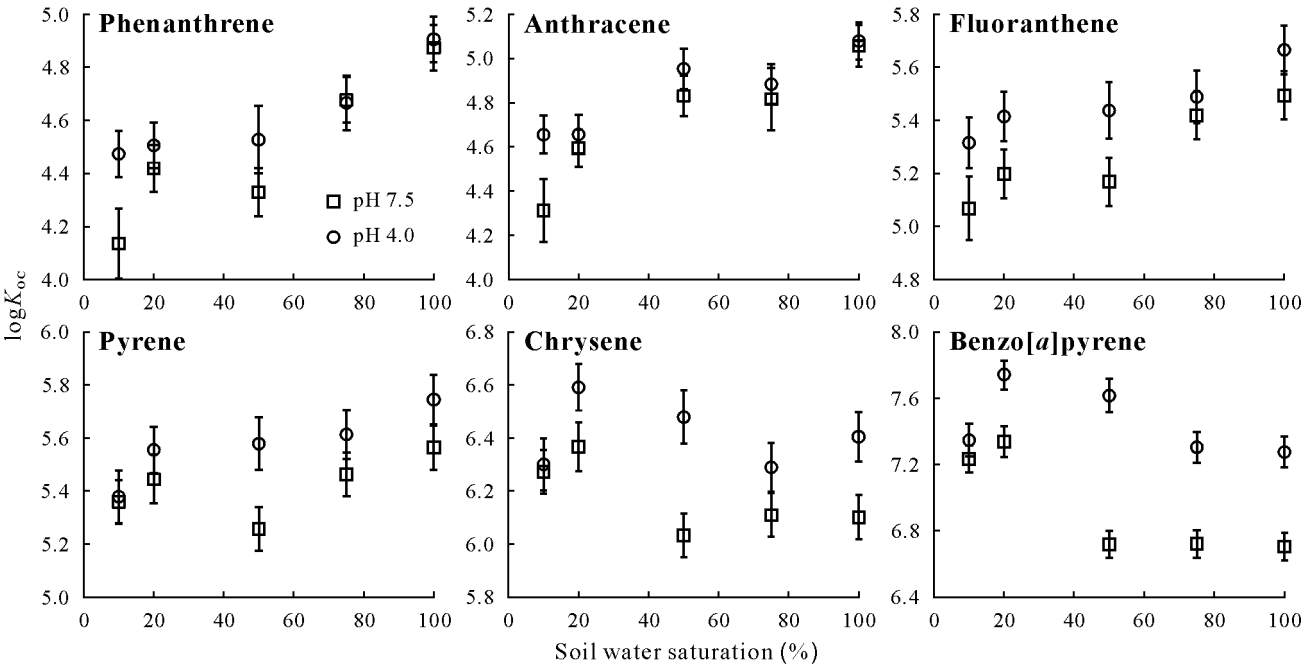


Fig. 1 Soil organic carbon-water partition coefficient ($\log K_{\text{OC}}$) of six selected polycyclic aromatic hydrocarbons under various soil water saturation levels at pH 7.5 and 4.0. Error bars signify standard errors of the means ($n = 5$).

Effect of soil water saturation on SOM volume is extremely important for lower-molecular-weight PAHs (Kopinke and Stottmeister, 1996). For higher-molecular-weight PAHs, the effect of soil water saturation on SOM sorption capacity is more important than its effect on SOM volume. For phenanthrene, anthracene, and fluoranthene, the differences in $\log K_{\mathrm{OC}}$ between 10% and 100% saturated soils tended to decrease with increasing soil pH (Fig. 1). For example, the increases in the $\log K_{\mathrm{OC}}$ of the fully saturated soil over that of 10% saturated soil were 447% and 171% at pH 7.5 and 4.0, respectively. Reduced soil pH (McCarthy *et al*., 1989; Schlautman and Morgan, 1993) and increasing soil water saturation (Kim *et al*., 2017) may loosen the structure of SOM. Thus, any decreases in $\log K_{\mathrm{OC}}$ due to lower soil water saturation would be mitigated at lower pH.

Effect of soil pH on SOM sorption capacity was observed at 10%, 20%, 50%, 75%, and 100% soil water saturation. $\frac{\Delta \log K_{\mathrm{OC}}}{\Delta \mathrm{pH}}$ values were negative for all PAHs, regardless of the level of soil water saturation. As soil pH increases, the net negative charge of organic soil also increases (Moayedi *et al*., 2011). Thus, increases in soil pH increased SOM polarity, and consequently, the affinity of SOM for HOCs decreased. This reduction in SOM sorption capacity for HOCs with increasing soil pH has been elucidated in earlier studies (Laor *et al*., 1998; Ertli *et al*., 2004; Ping *et al*., 2006; Li *et al*., 2010; Yang *et al*., 2013). When soil pH is adjusted to 8.5, dissolved organic matter (DOM) may increase (You *et al*., 1999). However, the effect of DOM is negligible. Because DOM has a strong affinity for HOCs, smaller molecules forming DOM still act like natural sorbents (Bondarenko and Gan, 2009). Therefore, only freely dissolved HOCs in porewater can diffuse into PDMS (Hawthorne *et al*., 2009), leading to an insignificant effect of DOM on the concentrations of freely dissolved HOCs in porewater. These dissolution effects could be involved in the changes of SOM structure that accompany pH changes.

However, in earlier studies, the effect of soil pH on SOM sorption capacity was only observed in fully water-saturated soils or soil solutions, suggesting that the effect of soil pH did not depend on water saturation (Laor *et al*., 1998; Ertli *et al*., 2004; Ping *et al*., 2006; Li *et al*., 2010; Yang *et al*., 2013). The decreases in K_{OC} with increasing soil pH seemed to be relatively small in the saturated soils; however, the tendency was not statistically significant (Fig. 1). The absolute values of $\frac{\Delta \log K_{\mathrm{OC}}}{\Delta \mathrm{pH}}$ for phenanthrene were 0.007 and 0.06 in 100% and 10% saturated soils, respectively. For phenanthrene, anthracene, and fluoranthene, the absolute values of $\frac{\Delta \log K_{\mathrm{OC}}}{\Delta \mathrm{pH}}$ in the 100% saturated soils were lower than those obtained from the unsaturated soils. The trend was the same for pyrene, chrysene, and benzo[a]pyrene, except in the 10% saturated soils.

In the unsaturated soils, as soil water saturation increased, the absolute values of $\frac{\Delta \log K_{\mathrm{OC}}}{\Delta \mathrm{pH}}$ also increased for pyrene, chrysene, and benzo[a]pyrene. The absolute values of $\frac{\Delta \log K_{\mathrm{OC}}}{\Delta \mathrm{pH}}$ for benzo[a]pyrene were 0.04 and 0.2 in the 10% and 75% saturated soils, respectively. Both increasing soil pH and water saturation levels reduced the SOM sorption capacity for HOCs. Therefore, any decreases in $\log K_{\mathrm{OC}}$ due to higher soil water saturation would be intensified at higher pH. However, these trends were inapplicable to the lower-molecular-weight PAHs, phenanthrene and anthracene, because SOM volume contributed more significantly in those cases.

A two-way analysis of variance (ANOVA) without replication was used to evaluate the effects of two independent variables, *i.e.*, soil pH and water saturation, on the sorption capacity of SOM for PAHs in soil. The K_{OC} values were dependent on both soil pH and water saturation (Table SII). For each ANOVA, a set of null hypotheses was established as follows: there are no significant differences in the average K_{OC} values grouped by the same soil water saturation level (θ_1), and there are no significant differences in the average K_{OC} values grouped by similar soil pH levels (θ_2). The hypotheses were applied to all the PAHs investigated.

From the ANOVA results, it was observed that almost all the F-statistic values were higher than the F-critical values, except for those pertaining to the effect of soil pH on phenanthrene, indicating that there was a difference in K_{OC} at a 5% level of significance (Table SIV, see Supplementary Material for Table SIV). Except for phenanthrene, the P values of the five PAHs for soil water saturation and pH were below the critical value of 0.05; hence, the null hypotheses were rejected. Therefore, the average K_{OC} values grouped by soil water saturation and pH were not the same for the five PAHs.

The null hypothesis (θ_2) was only accepted in the case of phenanthrene, as the F-statistic value of soil pH was lower than the F-critical value (Table SIV). For phenanthrene, the effect of soil water saturation on K_{OC} was significant, but the effect of soil pH was not significant ($P > 0.05$).

Insignificant effect of soil pH on the sorption of phenanthrene might be due to its lowest hydrophobicity among the tested PAHs. Additionally, the effect on SOM volume plays an important role in lower-molecular-weight PAHs. Soil pH and water saturation have different effects on SOM volume. This could be a secondary reason for the lower-molecular-weight PAHs. The average values of K_{OC} for PAHs grouped by soil water saturation and pH are shown in Figs. 2 and S3 (see Supplementary Material for Fig. S3). The effect of soil water saturation on K_{OC} was significant for all PAHs, whereas the effect of soil pH was non-significant for phenanthrene.

Effects of soil water saturation and pH on partition coefficients in natural soils

The PAH uptake of the passive samplers in the three

different natural soils are shown in Fig. S4 (see Supplementary Material for Fig. S4). All $K_{\text{sampler/soil}}$ values are listed in Table SV (see Supplementary Material for Table SV). The K_{OC} values obtained are listed in Table I.

As shown in Table I, the K_{OC} values are proportional to soil water saturation for the comparatively low-molecular-weight PAHs (*i.e.*, phenanthrene and anthracene). On the other hand, the trend was reversed for the higher-molecular-weight PAHs (*i.e.*, chrysene and benzo[a]pyrene) in all three natural soils at both soil pH 6.0 and 8.5. For example, the $\log K_{\text{OC}}$ values of phenanthrene were 5.18 and 4.47 at 75% and 10% soil water saturation, respectively, whereas the $\log K_{\text{OC}}$ values of benzo[a]pyrene were 7.12 and 7.26 at 75% and 10% soil water saturation, respectively, at pH 8.5 in soil A. To date, the influence of soil water saturation on the sorption capacity of SOM has only been demonstrated using artificial soil with peat moss as the SOM. The reproduction of a similar tendency in this study strengthens the hypothesis that the influence of soil water saturation on K_{OC} depends on the molecular size of HOCs in general. Further studies on diverse HOCs are needed to better understand this dynamic behavior and how various HOC and SOM properties are associated with the apparent partition coefficients at different soil water saturation levels.

Effect of pH on SOM sorption capacity was observed in the natural soils. For all the selected PAHs, the K_{OC} values decreased as soil pH increased (Table I). For example, the K_{OC} values of phenanthrene and benzo[a]pyrene were 52% and 141% lower at pH 8.5, respectively, compared to those at pH 6.0 in 75% saturated soil B. A reduction in SOM sorption capacity for HOCs with increasing soil pH was also observed in the natural soils (Table SV). Soil pH is a dynamic property that leads to fluctuations in the sorption capacity of natural SOM for HOCs. The approximate ranges of $\log K_{\text{OC}}$ within each range of soil pH are indicated by the margins of this natural fluctuation.

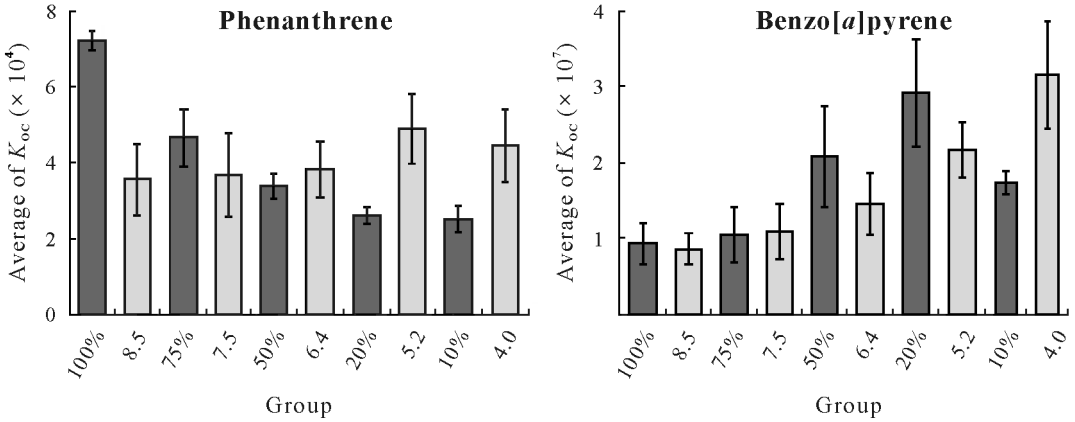


Fig. 2 Average values of soil organic carbon-water partition coefficient (K_{OC}) for phenanthrene and benzo[a]pyrene grouped by soil water saturation and pH. Data for anthracene, fluoranthene, pyrene, and chrysene are shown in Fig. S4 (see Supplementary Material for Fig. S4). Darker pillars indicate the average K_{OC} values grouped by soil pH for a given soil water saturation, and brighter pillars indicate the average K_{OC} values grouped by soil water saturation for a given soil pH. Error bars signify standard errors of the means ($n = 5$).

TABLE I

Soil organic carbon-water partition coefficient (K_{OC}) for six selected polycyclic aromatic hydrocarbons affected by soil water saturation (Ø) and pH in three natural soils

Soil	pH	Ø	$\log K_{\text{OC}}$					
			Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benzo[a]pyrene
		%						
A (sand)	8.5	75	5.18 (5.08, 5.26)[a)]	5.28 (5.18, 5.36)	5.17 (4.98, 5.36)	5.23 (5.08, 5.34)	6.18 (5.95, 6.32)	7.12 (7.01, 7.21)
		10	4.47 (4.37, 4.56)	4.75 (4.64, 4.83)	5.30 (5.19, 5.39)	5.44 (5.34, 5.52)	6.44 (6.33, 6.53)	7.26 (7.15, 7.35)
	6.0	75	5.22 (5.09, 5.32)	5.39 (5.29, 5.48)	5.33 (5.17, 5.45)	5.37 (5.25, 5.46)	6.49 (6.35, 6.60)	7.34 (7.23, 7.43)
		10	4.54 (4.44, 4.63)	4.79 (4.69, 4.87)	5.39 (5.27, 5.47)	5.53 (5.43, 5.61)	6.55 (6.44, 6.64)	7.37 (7.25, 7.47)
B (sand)	8.5	75	4.62 (4.47, 4.62)	4.89 (4.76, 4.99)	5.04 (4.91, 5.15)	5.14 (4.96, 5.27)	6.23 (6.09, 6.34)	6.55 (6.44, 6.64)
		10	4.37 (4.25, 4.46)	4.67 (4.57, 4.75)	5.15 (5.02, 5.25)	5.30 (5.17, 5.41)	6.45 (6.28, 6.58)	7.17 (7.04, 7.27)
	6.0	75	4.80 (4.67, 4.90)	5.10 (4.98, 5.20)	5.29 (5.12, 5.41)	5.37 (5.26, 5.45)	6.51 (6.39, 6.60)	6.94 (6.82, 7.03)
		10	4.49 (4.39, 4.58)	4.74 (4.64, 4.83)	5.34 (5.23, 5.43)	5.50 (5.40, 5.58)	6.73 (6.59, 6.73)	7.41 (7.29, 7.51)
C (sandy clay loam)	8.5	75	4.69 (4.58, 4.79)	4.96 (4.85, 5.04)	5.47 (5.36, 5.56)	5.39 (5.29, 5.48)	6.28 (6.16, 6.37)	6.81 (6.69, 6.90)
		10	4.53 (4.42, 4.62)	4.75 (4.64, 4.83)	5.32 (5.20, 5.40)	5.51 (5.40, 5.59)	6.30 (6.19, 6.39)	7.11 (6.99, 7.20)
	6.0	75	4.82 (4.70, 4.92)	5.10 (4.98, 5.19)	5.53 (5.41, 5.61)	5.58 (5.48, 5.66)	6.46 (6.35, 6.55)	7.20 (7.09, 7.29)
		10	4.56 (4.46, 4.64)	4.76 (4.66, 4.85)	5.38 (5.27, 5.47)	5.52 (5.42, 5.61)	6.50 (6.39, 6.59)	7.30 (7.18, 7.40)

[a)] Data in parentheses are 95% confidence limits estimated by error propagation.

Resilience in the sorption capacity of SOM under changing soil pH

After altering soil pH from 4.0 and 8.5 to 5.2 in 50% and 100% saturated soils, the K_{OC} values were used as indicators for the changes in SOM sorption capacity under changing soil pH (Table II).

All the measured values of $K_{sampler/soil}$ are listed in Table SVI (see Supplementary Material for Table SVI), and the PAH uptake of the passive samplers in the soils with adjusted pH are depicted in Fig. S5 (see Supplementary Material for Fig. S5). The acquired K_{OC} estimates are presented in Table II. For both saturated and unsaturated soils, the K_{OC} values seem to be resilient under changing soil pH. For example, the difference in the K_{OC} values for benzo[a]pyrene between the 100% saturated soils with pH values of 8.5 and 5.2 was 85%. After soil pH was adjusted from 8.5 to 5.2, the difference decreased to 44%. Likewise, the difference in the K_{OC} values for benzo[a]pyrene was 58% between the 100% saturated soils with pH values of 4.0 and 5.2. After soil pH was adjusted from 4.0 to 5.2, the difference in the K_{OC} values decreased to 28%. Although the values did not return to their original state, this observation supports the idea that SOM sorption capacity would recover during changes in soil pH.

The differences in the K_{OC} values between the different soil pH values were relatively larger in unsaturated soils (Table II). For example, the difference in the K_{OC} values for benzo[a]pyrene between soils with pH values of 8.5 and 5.2 was 270% in 50% saturated soil. After soil pH was adjusted from 8.5 to 5.2, the difference decreased to 28%. Likewise, the difference in the K_{OC} values for benzo[a]pyrene was 56% between 50% saturated soils with pH levels of 4.0, and 5.2. After soil pH was adjusted from 4.0 to 5.2, the difference decreased to 2%. Dynamic changes in soil pH can occur anytime, prompting alterations in the sorption capacity of SOM. Although further studies are required, the outcome of this study suggests that the sorption capacity is likely to change under the typical dynamic ranges of soil pH and water saturation.

CONCLUSIONS

Effects of soil water saturation level and pH on SOM sorption capacity observed in previous studies for six selected PAHs were reproduced across a wide range of pH and water saturation levels. Additionally, soil water saturation levels affected the $\frac{\Delta \log K_{OC}}{\Delta pH}$ values, depending on the molar volume of the PAHs. Increasing soil water saturation intensified the effect of soil pH on higher-molecular-weight PAHs at higher pH levels. This was not applicable to the lower-molecular-weight PAHs because SOM volume contributed more significantly in their case. The impacts of soil water saturation and pH in the artificial soil were consistently observed in the three natural soils. The dynamic changes in $\log K_{OC}$ under changing soil pH conditions were also found to be resilient, implying that $\log K_{OC}$ is a dynamic property and that the values obtained at one pH level can be used after correcting for pH effects using the $\frac{\Delta \log K_{OC}}{\Delta pH}$ relationship proposed in this study.

ACKNOWLEDGEMENT

This work was supported by the Subsurface Environment Management Projects funded by the Korea Environmental Industry and Technology Institute, Korea (No. 2020002440-005).

SUPPLEMENTARY MATERIAL

Supplementary material for this article can be found in the online version.

TABLE II

Soil organic carbon-water partition coefficient (K_{OC}) for six selected polycyclic aromatic hydrocarbons at two soil water saturation (Ø) levels (50% and 100%) and dynamic soil pH (5.2, from 4.0 to 5.2, and from 8.5 to 5.2)

Ø	pH	$\log K_{OC}$					
		Phenanthrene	Anthracene	Fluoranthene	Pyrene	Chrysene	Benzo[a]pyrene
%							
100	5.2	4.84 ± 0.087[a)]	5.04 ± 0.087	5.64 ± 0.087	5.66 ± 0.096	6.37 ± 0.106	7.08 ± 0.094
	From 8.5 to 5.2	$4.85 \pm 0.085 \rightarrow$ 4.86 ± 0.085	$5.01 \pm 0.082 \rightarrow$ 5.02 ± 0.083	$5.58 \pm 0.082 \rightarrow$ 5.58 ± 0.089	$5.64 \pm 0.084 \rightarrow$ 5.66 ± 0.083	$6.15 \pm 0.102 \rightarrow$ 6.31 ± 0.090	$6.81 \pm 0.089 \rightarrow$ 6.92 ± 0.091
	From 4.0 to 5.2	$4.91 \pm 0.085 \rightarrow$ 4.85 ± 0.085	$5.08 \pm 0.085 \rightarrow$ 5.04 ± 0.086	$5.67 \pm 0.093 \rightarrow$ 5.54 ± 0.095	$5.75 \pm 0.093 \rightarrow$ 5.61 ± 0.092	$6.41 \pm 0.090 \rightarrow$ 6.26 ± 0.098	$7.28 \pm 0.098 \rightarrow$ 6.97 ± 0.096
50	5.2	4.61 ± 0.082	4.77 ± 0.081	5.48 ± 0.088	5.57 ± 0.093	6.42 ± 0.094	7.42 ± 0.106
	From 8.5 to 5.2	$4.58 \pm 0.082 \rightarrow$ 4.71 ± 0.086	$4.69 \pm 0.108 \rightarrow$ 4.70 ± 0.084	$5.33 \pm 0.090 \rightarrow$ 5.31 ± 0.103	$5.30 \pm 0.117 \rightarrow$ 5.42 ± 0.118	$6.07 \pm 0.093 \rightarrow$ 6.50 ± 0.097	$6.86 \pm 0.105 \rightarrow$ 7.53 ± 0.107
	From 4.0 to 5.2	$4.53 \pm 0.127 \rightarrow$ 4.66 ± 0.086	$4.95 \pm 0.092 \rightarrow$ 4.83 ± 0.082	$5.44 \pm 0.106 \rightarrow$ 5.48 ± 0.120	$5.58 \pm 0.100 \rightarrow$ 5.55 ± 0.118	$6.48 \pm 0.142 \rightarrow$ 6.46 ± 0.090	$7.62 \pm 0.102 \rightarrow$ 7.42 ± 0.132

[a)] Values are means $\pm$ standard errors ($n = 5$); standard errors were obtained using Eq. 2 through non-linear regression.

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