



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



Pil-Gon Kim ^a, Ji-Yeon Roh ^a, Yongseok Hong ^b, Jung-Hwan Kwon ^{a,*}

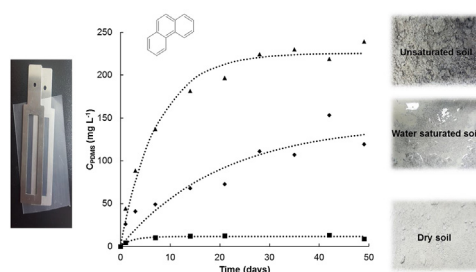
^a Division of Environmental Science and Ecological Engineering, Korea University, 145 Anam-ro, Seongbuk-gu, Seoul 136-713, Republic of Korea

^b Department of Environmental Engineering, Daegu University, 201 Daegudae-ro, Gyeongsan-si, Gyeongsangbuk-do 38453, Republic of Korea

HIGHLIGHTS

- Effects of soil water saturation on sampling equilibrium and kinetic were observed.
- In dry soil, $K_{\text{sampler/soil}}$ values were much lower than those in wet soils.
- Changes in properties of soil organic matter via wetting affected $K_{\text{sampler/soil}}$.
- Varying $K_{\text{sampler/soil}}$ 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



ARTICLE INFO

Article history:

Received 22 March 2017

Received in revised form

27 May 2017

Accepted 29 May 2017

Available online 31 May 2017

Handling Editor: Keith Maruya

Keywords:

Equilibrium passive sampling

Partition coefficient

Sampling kinetics

Soil water saturation

Polydimethylsiloxane (PDMS)

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 ($K_{\text{sampler/soil}}$) 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 $K_{\text{sampler/soil}}$ 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 $K_{\text{sampler/soil}}$ 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.

© 2017 Published by Elsevier Ltd.

1. Introduction

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

* Corresponding author.

E-mail address: jungchwankwon@korea.ac.kr (J.-H. Kwon).

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 pre-determined 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 ($K_{\text{sampler/soil}}$) as well as the uptake rate constants (k_u) were determined using nonlinear regression. The dependence of $K_{\text{sampler/soil}}$, 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 $125 \text{ }\mu\text{m}$ were purchased from Shielding-Solutions, Inc. (Great Notley, UK) and then cut into rectangular sheets ($10 \text{ mm} \times 42 \text{ mm}$). 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 $2 \times 8 \text{ mm} \times 40 \text{ mm}$ 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 ($\text{H}_2\text{Al}_2\text{Si}_2\text{O}_8 \cdot \text{H}_2\text{O}$) 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

Download English Version:

<https://daneshyari.com/en/article/5746181>

Download Persian Version:

<https://daneshyari.com/article/5746181>

[Daneshyari.com](https://daneshyari.com)