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SEMIPERMEABLE MEMBRANE DEVICE-ASSISTED DESORPTION OF PYRENE FROM SOILS AND ITS RELATIONSHIP TO BIOAVAILABILITY

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Abstract—Desorption of pyrene from three different soils was studied using a semipermeable membrane device (SPMD)-assisted method to develop a new approach to predict bioavailability of hydrophobic organic compounds (HOCs) in soils. The results showed that pyrene desorption increased with reduction of soil organic matter content and elevation of pyrene concentration in unaged soils, and the 50-d desorption percentage was $52.2 \pm 3.6\%$, $76.3 \pm 1.5\%$, and $99.4 \pm 3.3\%$ for soils 1, 2, and 3, respectively, at an initial pyrene concentration of 10 mg/kg and $73.6 \pm 4.9\%$, $94.1 \pm 4.1\%$, and $98.3 \pm 4.9\%$, respectively, at an initial pyrene concentration of 100 mg/kg. Aging led to a reduction in SPMD-assisted desorption because of movement of pyrene molecules from easy-desorbing to difficult-desorbing sites. The pyrene 50-d desorption percentage from 180-d-aged soils reduced to $5.8 \pm 0.6\%$, $18.8 \pm 0.9\%$, and $34.2 \pm 3.1\%$ in soils 1, 2, and 3, respectively, at an initial pyrene concentration of 10 mg/kg and $43.9 \pm 2.9\%$, $54.3 \pm 4.7\%$, and $86.3 \pm 3.5\%$, respectively, at an initial pyrene concentration of 100 mg/kg. Dry and wet conditions during aging had different effects on aging-derived reduction of pyrene desorption, which was found, to our knowledge for the first time, to depend on pollutant concentration. The water to soil ratio during desorption had a significant effect on SPMD-assisted desorption dynamics. When this ratio changed from 10:1 to 1:1, desorption dynamics became more linear and slower, because when the ratio was low, the SPMD could not contact with soil particles well and the diffusion of pyrene from pore water into the SPMD might become the limiting step for SPMD accumulation of pyrene from soils. Good correlations were found between SPMD-assisted desorption and the biota-soil accumulation factor for both unaged and aged soils. The SPMD-assisted desorption is considered to be a reliable approach to predict the bioavailability of HOCs in soils.

Keywords—Bioavailability Semipermeable membrane device Desorption Aging Pyrene

INTRODUCTION

The combination state of hydrophobic organic chemicals (HOCs) in soils, which refers to the specific site at which the HOC molecules exist in soil particles and the binding force between the HOC molecules and the constituents of soil particles, is an important factor controlling their fate, reactivity, and bioavailability in the terrestrial environment. When HOCs enters soil, their combination state in soil differentiates greatly because of the high heterogeneity of soil particles. It has been proposed that HOC molecules exist in soil as three different combination states from the view of desorption and bioavailability: Some are combined with those easy-desorbing and available sites, some with difficult-desorbing and less available sites, and others with irreversible and nonavailable sites [1,2].

Consequently, only a portion of HOC molecules in soils is available for desorption and bio-uptake. Hence, the bioavailability of HOCs in soils is thought to be a more reasonable index than the total chemical concentration to reflect its real risk to the terrestrial ecosystem and to human beings [3,4]. Factors that influence the combination state of HOCs in soils will exert effects on their bioavailability, which are expected to include soil properties (soil organic matter [SOM] content and structure, clay content and particle size, etc.), molecular properties (water solubility, K_{ow} , and molecular size and structure) and contamination level, and other environmental factors (e.g., temperature and water content) [5–8]. Moreover, HOCs

become increasingly less available with longer contact time (i.e., aging) in soils [9–11], which implies that the combination state of the HOC has changed further during aging, with some of the HOC molecules moving from the easy-desorbing and available sites to the difficult-desorbing and less available sites—and even to the irreversible and nonbioavailable sites. Hence, complex factors control the combination state and, consequently, the bioavailability of HOCs in soils.

Therefore, the development of fast and accurate bioavailability measurements or predicting assays is an urgent need in eco-risk assessment. Bioassay using an earthworm uptake test is a traditional method to assess the bioavailability of HOCs in soils [12]; however, it is time-consuming, of low precision, and expensive. Attempts have been made to set up chemical approaches to predict bioavailability, such as organic solvent extraction with mild solvents [13], solid-phase extraction [14], digestive fluid extraction [15], and supercritical fluid extraction [16].

A semipermeable membrane device (SPMD) is an innovative, in situ approach for passively monitoring dissolved HOCs in aquatic systems [17]. With increasing frequency, SPMDs have been employed worldwide to monitor HOCs in a variety of media, such as marine water, freshwater, air, and sediment [18,19]. The low-density polyethylene membrane tubes of SPMD containing a thinly spread layer of neutral glycerol triolein inside are able to mimic organism use of HOCs. Dissolved lipophilic HOCs can pass through the membrane of the SPMD and accumulate in the internal lipid, which is similar to how HOCs are absorbed and accumulated by aquatic or terrestrial organisms. Thus, some studies used

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Table 1. Physicochemical properties of the tested soils (Tianjin, China)

Soil	Organic matter (%)	pH	Sand grain (%)	Silt (%)	Clay (%)	Texture
1	18.7	7.0	48.6	35.4	16.0	Sandy loam
2	4.1	7.1	66.0	22.4	11.6	Sandy loam
3	0.32	7.9	34.9	26.1	39.1	Clay loam

SPMD accumulation to predict the bioavailability of HOCs to aquatic organisms. A few, however, have reported on predicting the bioavailability of HOCs in soils or sediments using SPMD-assisted desorption [20,21]. Moreover, studies on predicting the bioavailability of HOCs by SPMDs in aged soils is still lacking.

Hence, the objectives of the present study were to establish SPMD-assisted procedures to study the desorption of HOCs in soils and to elucidate the effects of chemical concentration, soil properties, aging, and water content on SPMD-assisted HOC desorption. Moreover, we tried to explore the applicability of SPMD-assisted desorption as a method for predicting the bioavailability of HOCs by analyzing its correlation with earthworm bioaccumulation. A typical polycyclic aromatic hydrocarbon (PAH), pyrene, was used as a representative HOC in the present study, because PAHs are important pollutants in soils and have caused much concern as a result of their possible carcinogenicity.

MATERIALS AND METHODS

Chemicals and materials

Pyrene (purity, 98%) was purchased from Acros Corporation (Fairlawn, NJ, USA). Pyrene stock solution (1 g/L) was prepared in high-performance liquid chromatography (HPLC)-grade methanol. Acetonitrile used for the mobile phase in HPLC analysis and *n*-hexane used for extraction were of HPLC grade. Low-density polyethylene membrane tube was purchased from Environmental Sampling Technologies (St. Joseph, MO, USA), and glycerol triolein (chemically pure) was purchased from Sinopharm Shanghai Chemical Reagent (Shanghai, China).

Soil samples

Three soils were collected from various districts in Tianjin (China) and classified according to the U.S. Department of Agriculture Soil Classification Systems [22]. The soils were named soils 1, 2, and 3. The soils were air-dried at room temperature and then passed through a sieve (mesh size, 2 mm) before use.

Several physicochemical properties of the soils were determined according to the standard methods in China [23] (Table 1). Organic matter content was determined by potassium dichromate–outside heating method. The pH was measured in a 1:1 (w/w) soil–CaCl₂ water suspension. Water content was determined by heating the samples for 6 to 12 h at 105°C, and soil texture was measured by the densimeter method.

Semipermeable membrane device

The low-density polyethylene membrane tubes were first soaked in *n*-hexane for 3 d to remove polyethylene wax, additional agents, and other possible pollutants on the membrane tube. The *n*-hexane was changed once a day. Each low-density polyethylene tube was clipped to 4 cm in length, and one end

of the tube was heat-sealed by a plastic sealer. Then, 0.05 ml of glycerol triolein was added in the tube, and the other end of the tube was heat-sealed. The finished SPMDs were wrapped in aluminum foil and kept in a freezer at –20°C before use.

Preparation of unaged and aged soil samples

To obtain pyrene-contaminated soil samples, 30-g aliquots of soil were added to 100-ml, brown, wide-mouth bottles. A certain volume of pyrene–methanol solution was added to the soil samples to make up the final measured pyrene concentration of 10 ± 0.5 and 100 ± 5 mg/kg dry soil, respectively. A specific amount of 0.2% NaN₃ water solution was added to inhibit biological activity as well as to keep soil moisture at 30% (wet-wt basis). The bottles were placed into a ventilation cabinet for 4 h, and the samples were vigorously mixed for 6 s every 30 min to accelerate evaporation of the methanol and to mix the pyrene with the soil. Then, the bottles were tightly covered with silicone-backed Teflon® liners and kept in the dark at $25 \pm 1^\circ\text{C}$ overnight and for 180 d to obtain unaged and dry-aged soils, respectively. The loss during the contamination process was less than 8 and 5% for 10 and 100 mg/kg of pyrene, respectively, and the loss was accounted for by spiking an appropriate amount of pyrene stock solution.

To obtain wet-aged soils, the contaminated soils were mixed with a certain volume of 5 mmol/L of CaCl₂ aqueous solution (soil:water, 1:5 w/w) containing a specific amount of pyrene. The bottles were shaken for 48 h on a reciprocating shaker operated at 120 rpm and $25 \pm 1^\circ\text{C}$. Then, the bottles were tightly covered with silicone-backed Teflon liners and kept in the dark at $25 \pm 1^\circ\text{C}$ for 180 d. Primary experiments showed that more than 97% of the original pyrene was associated with the solid phase and that approximately 2% was lost because of wall adsorption. The loss has been accounted for by spiking an appropriate amount of pyrene stock solution.

SPMD-assisted desorption of pyrene

Six grams of the contaminated soils were suspended in Erlenmeyer beakers containing 60 ml of electrolyte solution (5 mmol/L of CaCl₂), and then one piece of the finished SPMD was added. The beakers were capped and shaken horizontally in a shaker operated at 120 rpm and $25 \pm 1^\circ\text{C}$. The SPMD-assisted desorption was conducted for 50 d, with regular sampling at 2, 4, 7, and 12 h as well as at 2, 4, 7, 12, 20, and 50 d. During sampling, the SPMD was taken out from the suspension, and a new SPMD was added to continue the desorption. The desorption tests were done in duplicate. The sampled SPMDs were treated according to the standard operating procedures recommend by the manufacturer [24] (<http://www.est-lab.com>). The SPMD was placed on a glass plate, and the residual moisture on the surface of the SPMD member was scrubbed away using absorbent cotton wetted with acetone followed by isopropanol. Then, the SPMD was placed on aluminum foil and air-dried at room temperature. Next, the SPMDs were dialyzed three times in 90 ml of *n*-hexane. The first dialysis lasted for 18 h, and the second and third dialyses both lasted for 6 h each. The dialysis solutions were combined, concentrated by rotary evaporation to near dryness, and re-dissolved in 1 ml of methanol. Recovery of pyrene from the SPMD by this extraction method was measured as $98.5 \pm 0.8\%$.

PAH analysis

Pyrene in the methanol was analyzed by HPLC (Waters 1525 Binary HPLC Pump, Millinium 32 station; Waters, Mil-

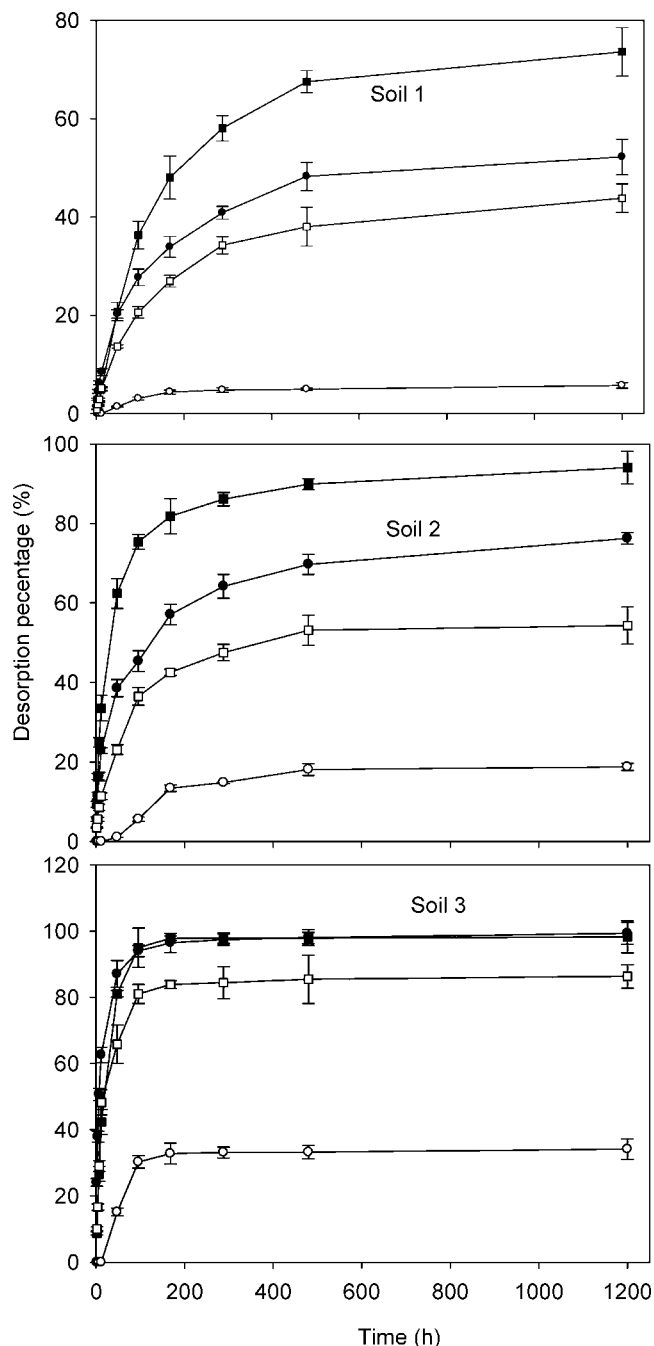


Fig. 1. Desorption dynamics of pyrene assisted by a semipermeable membrane device under different initial concentrations from unaged and aged soils: Unaged, 10 mg/kg (—●—); aged, 10 mg/kg (—○—); unaged, 100 mg/kg (—■—); and aged, 100 mg/kg (—□—).

ford, MA, USA) equipped with a fluorescence detector (Waters 2475 Multi λ fluorescence detector). A Waters Symmetry C_{18} column (Dublin, Ireland) was used. Acetonitrile–water (80:20 v/v) was used as the mobile phase, with a flow rate of 1.0 ml/min. Pyrene was detected by an excitation wavelength at 333 nm and an emission wavelength at 390 nm.

RESULTS

Desorption from different soils at different concentrations

The SPMD–assisted desorption of pyrene at two initial concentrations (10 and 100 mg/kg) from the three unaged and

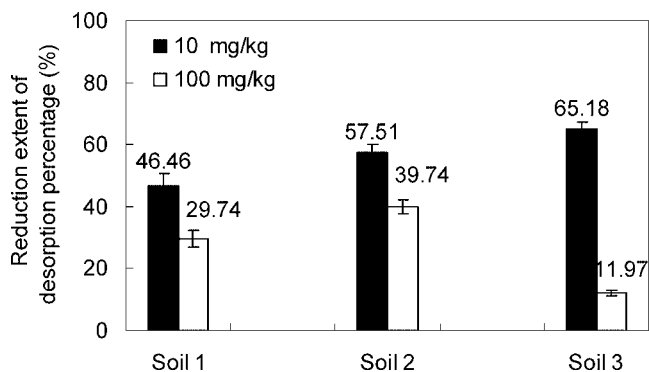


Fig. 2. Dry-aging influence on 50-d desorption percentages of pyrene assisted by a semipermeable membrane device.

aged soils is shown in Figure 1. The SPMD–assisted desorption included two stages: A fast-desorption stage, and a slow-desorption stage. For unaged soils, SPMD–assisted desorption varied markedly with soil type and with the initial concentration of pyrene. For unaged soils, the 50-d desorption percentage increased with the reduction of SOM content, and as the SOM content went down from 18.7% for soil 1 to 4.06% for soil 2 and to 0.32% for soil 3, the 50-d desorption percentage increased from $52.2 \pm 3.6\%$ to $76.3 \pm 1.5\%$ and to $99.4 \pm 3.3\%$, respectively, for pyrene at an initial concentration of 10 mg/kg. The desorption percentage was $73.6 \pm 4.9\%$, $94.1 \pm 4.1\%$, and $98.3 \pm 4.9\%$ for soils 1, 2, and 3, respectively, when the pyrene concentration was 100 mg/kg. When the pyrene concentration increased by 10-fold, desorption increased remarkably for soils 1 and 2 but did not change significantly for soil 3. The SOM in soil 3 was too little to hold many pyrene molecules, so the desorption percentage reached almost 100% for both levels.

Desorption after aging

Aging refers to the increase in contact time between the pollutant and soils. It has been found by vigorous extraction with organic solvents that the mass of HOCs in soils does not decrease after aging; rather, the combination state of the pollutants in soils changes so that it becomes less available to desorption, extraction, bio-uptake, and toxic effects [4].

Figure 1 compares the desorption dynamics of pyrene from unaged and dry-aged soils. It can be seen from Figure 1 that 180 d of aging caused a significant reduction ($p < 0.05$) in SPMD–assisted desorption of pyrene. The desorption percentage in 50 d decreased to $5.8 \pm 0.6\%$, $18.8 \pm 0.9\%$, and $34.2 \pm 3.1\%$ for aged soils 1, 2, and 3, respectively, for pyrene at an initial concentration of 10 mg/kg but decreased to $43.9 \pm 2.9\%$, $54.3 \pm 4.7\%$, and $86.3 \pm 3.5\%$, respectively, for pyrene at an initial concentration of 100 mg/kg. The extent of reduction in the 50-d desorption percentage because of aging, which is summarized in Figure 2, ranged from $12.0 \pm 0.9\%$ to $65.2 \pm 2.3\%$. The extent of reduction in the desorption percentage generally is greater at a lower pyrene concentration than at a higher pyrene concentration. The amount of the difficult-desorbing sites in a soil for a specific chemical is fixed and limited. Thus, the accessibility of pyrene molecules at lower concentration to these difficult-desorbing sites became higher during the aging process; hence, aging had more effect on low-level pollutants. Moreover, the extent of reduction in the desorption percentage increased with the reduction in the SOM content at a pyrene concentration of 10 mg/kg, which seems

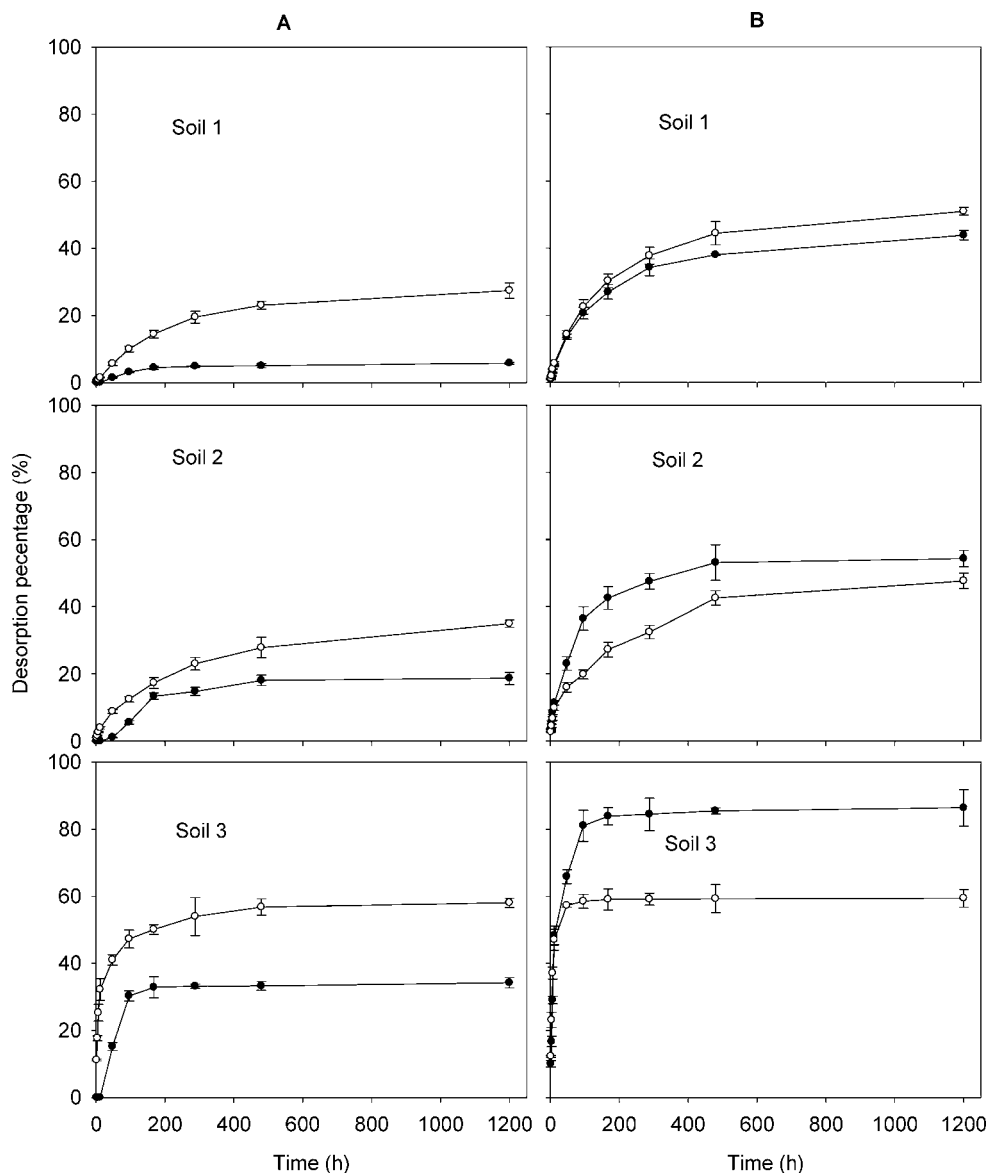


Fig. 3. Desorption dynamics of pyrene assisted by a semipermeable membrane device under different initial concentrations from wet- and dry-aged soils. (A) Initial pyrene concentration of 10 mg/kg. (B) Initial pyrene concentration of 100 mg/kg. Wet-aged (—●—); dry-aged (—○—).

to indicate that the combination state of the pollutant changed to a greater extent during aging in soils with a low SOM content. At a pyrene concentration of 100 mg/kg, however, an unexpected result occurred for soil 3—namely, the reduction of desorption in this soil was the lowest. This reveals that not only the SOM content but also the relative concentration of the pollutant together determine the aging-induced change of the pollutant's combination state.

Aging has been conducted under two different conditions, dry aging and wet aging, to observe whether the water content of the soil has an influence on the effect of aging. The dynamics of SPMD-assisted desorption of pyrene from soils that experienced dry aging and wet aging are shown in Figure 3 for pyrene concentrations of 10 and 100 mg/kg. The SPMD-assisted desorption of pyrene was significantly different ($p < 0.05$) after being aged under different conditions. For pyrene at an initial concentration of 10 mg/kg, the desorption percentages of pyrene in dry-aged soils were relatively greater for all three soils than were for those in wet-aged soils. For pyrene at an initial concentration of 100 mg/kg, however, the

desorption percentages in wet-aged soils 2 and 3 were greater. Hence, it could be concluded that water content does influence the aging-induced change in desorption and, moreover, that the influence of water content is quite different at different pollutant levels.

Desorption at different water content

The SPMD-assisted desorption of pyrene from the three unaged soils was conducted at two water contents (water:soil, 10:1 and 1:1) to find the effect of water content on diffusion of the pollutant from the soil into the SPMD (Fig. 4). It can be seen from Figure 4 that when the water to soil ratio was higher (10:1), SPMD-assisted desorption of pyrene proceeded quickly during the initial period of the desorption, and afterward, the desorption slowed gradually into a plateau. When the water to soil ratio was lower (1:1), the desorption rate became lower and the desorption dynamics more linear, which means that the desorption rate was constant during the experimental period.

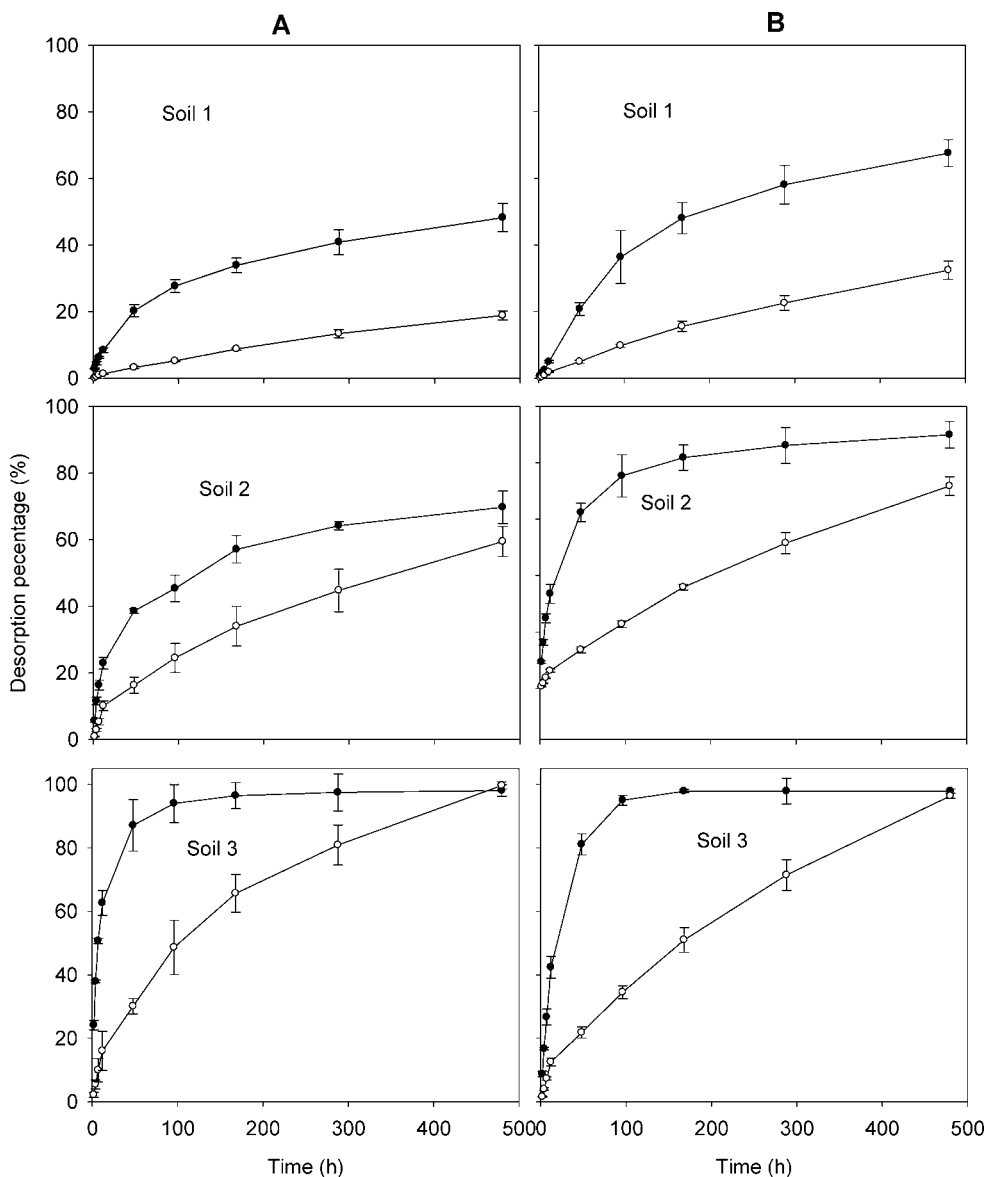


Fig. 4. Influence of water content on desorption dynamics of pyrene assisted by semipermeable membrane device from soils. (A) Initial pyrene concentration of 10 mg/kg. (B) Initial pyrene concentration of 100 mg/kg. Soil to water ratios: 1:10 (—●—); 1:1 (—○—).

DISCUSSION

The SPMD-assisted desorption can reflect the differences of pyrene combination states in soils. The SPMD-assisted desorption varied greatly when the parameters that are expected to influence the combination state of the pollutant changed. Four parameters—soil properties, pollutant concentration, water content, and contacting time and pattern—were tested in the present study.

Effects of soil property and pollutant concentration on pyrene desorption

Soil is a complex that has minerals and SOM as its two main constituents, with high heterogeneity. The soil mineral itself and its complex with organic matters possess lots of micro- to nanopores with different pore sizes and inner surface properties [25]. Moreover, structurally different domains of organic matter exist in soils, which have been proposed to divide into a relative soft and flexible structure, known as a rubbery domain, and a hard and rigid structure, known as a

glassy domain [26–28]. Sorption of HOCs in soils can occur by entering into relatively large pores or by physical adsorption through the weak binding force in the rubbery domain (i.e., easy-desorbing sites); on the other hand, sorption also can occur by embedding into relatively small pores or by chemical or internal adsorption through the strong binding force in the glassy domain (i.e., difficult-desorbing or irreversible sites). Hence, the apparent desorption rate of the same HOC in different domains of one soil can become quite different, which leads to the two or more stages in desorption dynamics [29,30]. It generally is accepted that pollutants combined to soils with a higher SOM content are more difficult to desorb [31]. In the present study, SPMD-assisted desorption can reflect the different combination states of pyrene in different soils: The 50-d percentage increased with the reduction of SOM, and desorption of the sorbed pyrene reached almost 100% on day 50 in soil 3, the SOM content of which was only 0.32%.

When the pyrene concentration increased by 10-fold, the desorption percentage increased significantly for soils 1 and 2

but did not change for soil 3. The quantity of the difficult-desorbing sites in soils, which is the key factor in determining the desorption percentage, is fixed and limited for a specific chemical. As the pollutant concentration in soils becomes higher, the difficult-desorbing sites may become saturated; hence, desorption into water solution could occur more quickly and easily. Chung and Alexander [7] investigated the effects of pollutant concentration on the bioavailability and residual level of pyrene in soils, and they also found that the residual pyrene percentage reduced with the increase of the initial pollutant concentration from 1.0 to 10 to 100 mg/kg soil. Those authors proposed that soil has a saturated capacity for HOC sorption. Gan et al. [32] obtained results similar to those of Chung and Alexander [7]. In the present study, no difference was found between the SPMD-assisted desorption percentages of pyrene from soil 3 at the two initial pyrene concentrations. We ascribe this to the fact that the 0.32% SOM content in soil 3 may be too little to hold even 10 mg/kg of pyrene. Hence, its desorption percentage reached almost 100% at this lower concentration, so no difference could be found when the concentration was elevated to 100 mg/kg. We think, however, that desorption will decrease if we reduce the pyrene concentration to a certain level.

Effect of aging on SPMD-assisted pyrene desorption

It has been reported that aging can lead to a reduction in mobility and availability to chemical reactions and biological processes of HOCs in soils [3,9–11]. In the present study, we found that SPMD-assisted desorption of pyrene decreased by 12.0 to 65.2% after 180 d of dry aging (Fig. 2) and that the extent of the reduction varied in different soils and at different initial concentrations. Aging allows pollutant molecules combined with the easy-desorbing sites to transfer to the difficult-desorbing sites, which leads to an increase of pollutant residual quantity during aging. Many of the HOC molecules can combine with the difficult-desorbing sites in soils with a high SOM content, such as soil 1, in which the difficult-desorbing sites are easily accessed even without aging. Hence, the percentage of pyrene molecules transferring from easy-desorbing to difficult-desorbing sites was lower during aging in soils with a high SOM content. On the other hand, when the SOM content is low, the difficult-desorbing sites become difficult to access without aging, and aging gives time for HOC molecules to find the difficult-desorbing sites. Hence, the change of combination state is great in soils with a low SOM content. This can explain why the aging-induced reduction in SPMD-assisted desorption of pyrene increased with the reduction of SOM content at an initial pyrene concentration of 10 mg/kg. Jin et al. [33] found that the bioavailability of naphthalene did not change significantly in a peat with a SOM content of 39.0% after 135 d of aging; however, it decreased by more than 60% in a soil with a SOM content of 2.4%.

When the initial concentration of pyrene was elevated to 100 mg/kg, the aging-induced reduction of the pyrene desorption percentage became smaller compared to that at a pyrene concentration of 10 mg/kg. We attribute this to the fact that the difficult-desorbing sites became limited in the face of the relatively high concentration of the pollutant. Jin et al. [33], however, did not find an obvious difference in the extent of aging-induced reduction when studying the effect of aging on the bioavailability of naphthalene at two levels, 2 and 20 mg/kg, using a soil with a SOM content of 2.4%. Hence, it can be concluded that the extent of aging-induced reduction

in the mobility and bioavailability of HOCs might be determined both by the SOM content and by the relative concentration level.

We further checked the extent of reduction in desorption in the three soils at 100 mg/kg of pyrene, and we found that the reduction of desorption was $29.7 \pm 2.6\%$ in soil 1, $39.7 \pm 2.2\%$ in soil 2, and $12.0 \pm 0.9\%$ in soil 3. An unexpected result occurred for soil 3, which was attributed to the fact that the SOM content in soil 3 was extremely low and its difficult-desorbing sites were quite limited, especially for higher initial concentrations of pyrene. Hence, even given enough contact time, many of the pyrene molecules could not access the difficult-desorbing sites.

A few studies have found that the water content of soil during aging influences the effects of aging. We have found that butanol extraction of pyrene reduced to greater extent after aging in a dry soil than it did in the same soil with a 15% water content (unpublished data). In the present study, we found that water content had a different influence on the aging-induced reduction of desorption at the two pyrene concentrations. Desorption was reduced to a greater extent after wet aging compared to dry aging in all three soils with 10 mg/kg of pyrene and in soil 1 with 100 mg/kg of pyrene, whereas the opposite result occurred for pyrene at a concentration of 100 mg/kg in soils 2 and 3. When the pyrene concentration was low, the SOM in soils could provide enough active binding sites, and water and pyrene molecules were likely to be sorbed in inorganic mineral and SOM, respectively. As a result, competition of water molecules did not occur. Under this situation, the existence of water during aging (i.e., wet aging) favored the transport of pyrene molecules into the interior SOM, which led to increased sequestration. This also was true for pyrene at 100 mg/kg in soil 1 because of that soil's relatively high SOM content. When the pyrene concentration was high, the SOM in soils 2 and 3 could not provide enough binding sites, and pyrene had to compete with water molecules for the active binding sites on inorganic minerals [34,35], which are likely to be occupied by a thin film of water molecules [36]. Hence, pyrene can find fewer binding sites in wet-aged soils during aging, and its desorption percentage was relatively higher than that in dry-aged soils.

Effect of water content on SPMD-assisted pyrene desorption

When the water to soil ratio increased from 1:1 to 10:1, the 20-d desorption percentages of pyrene in soils 1, 2, and 3 were enhanced by $29.4 \pm 2.9\%$, $10.3 \pm 0.4\%$, and $-1.60 \pm 0.7\%$, respectively, for an initial pyrene concentration of 10 mg/kg and by $35.1 \pm 1.3\%$, $18.2 \pm 1.5\%$, and $1.49 \pm 0.1\%$, respectively, for an initial pyrene concentration of 100 mg/kg. The pyrene desorption percentage went up with the increase in water content, which is in accordance with findings in the literature [36]. When the water to soil ratio is high, soil particles are well dispersed in water, which allows the desorbing pyrene easy access to the SPMD, and the limiting step of the desorption is thought to be the diffusion of pyrene inside the soil particles and the release of sorbed pyrene from soil particles into water. Hence, the desorption dynamics were well divided into two stages: A fast-desorbing stage, and a slow-desorbing stage. When the water to soil ratio is low, the soil particles are aggregated, which makes reaching the SPMD difficult for the desorbed pyrene molecules, and the rate-lim-

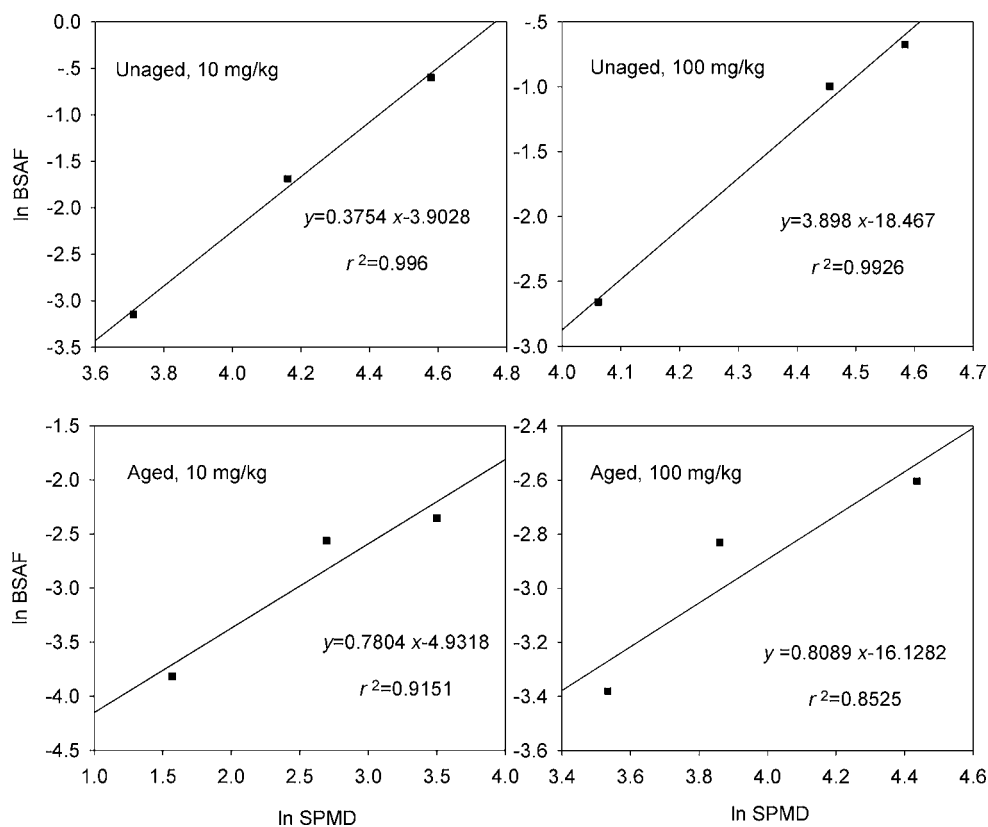


Fig. 5. Correlation between ln SPMD (natural logarithm of 12-d desorption percentage assisted by a semipermeable membrane device) and ln BSAF (natural logarithm of biota–soil accumulation factor) of pyrene in unaged and aged soils in different series. Dots in the figures are data points observed using different soils. Lines represent correlation relationship; their corresponding correlation coefficients also are given.

iting step becomes the transport of the pollutant in pore water. Thus, the apparent desorption rate became constant.

Characterization of bioavailability by SPMD–assisted desorption

To evaluate whether SPMD–assisted desorption can be used as a method to predict bioavailability, the present study investigated the relationships between biota–soil accumulation factors (BSAFs) and the SPMD–assisted desorption percentages of pyrene for unaged and aged soils. The BSAFs were reported previously in literature by Sun and Li [2] and were obtained through a 12-d earthworm accumulation test using the same soils that had experienced the same spiking and dry-aging process as used in the present study. When the initial concentration of pyrene was 10 mg/kg, the BSAFs were 0.043, 0.185, and 0.549 in unaged soils 1, 2, and 3, respectively, and decreased to 0.022, 0.077, and 0.095, respectively, after aging. The 12-d SPMD–assisted desorption percentage of pyrene was 40.9, 64.2, and 97.5% in soils 1, 2, and 3, respectively, which decreased to 4.8, 14.8, and 33.2%, respectively, after dry-aging. Based on the above data, the correlation coefficient (r^2) between ln SPMD (the natural logarithm of the SPMD–assisted desorption percentage of pyrene) and ln BSAF (natural logarithm of biota–soil accumulation factor) was 0.996 and 0.915 in unaged and aged soils, respectively (Fig. 5). When the initial concentration of pyrene was 100 mg/kg, the BSAF was 0.070, 0.369, and 0.509 in unaged soils 1, 2, and 3, respectively, which decreased to 0.034, 0.059, and 0.074, respectively, after aging. The 12-d SPMD–assisted desorption percentage of pyrene was 58.1, 86.1, and 97.9% in soils 1, 2, and 3, respectively, which decreased to 34.3, 47.5, and 84.4%, respectively,

after aging. Accordingly, the correlation coefficient (r^2) between ln SPMD and ln BSAF was 0.993 and 0.853 in unaged and aged soils, respectively (Fig. 5). Hence, good relationships between ln SPMD and ln BSAF existed in different series.

We have tried to set up a uniform linear correlation equation using all available data; however, the correlation is not as good ($r^2 = 0.518$) (Fig. 6). It should be acknowledged that SPMD uptake of sorbed pollutant is not the same process as biotransformation by earthworms. The comparison of the relationships between SPMD–assisted desorption and BSAF at the two concentrations revealed that when the pyrene concentration was elevated 10-fold, SPMD–assisted desorption increased, whereas the BSAF did not increase significantly, especially for soils with a lower SOM content. This means that when the available pyrene concentration is high enough, the limiting step for the uptake of sorbed pyrene by earthworms might be from the earthworm side. The U.S. National Research Council [1] has defined bioavailability as the bioavailability process, which includes release of sorbed pollutant, transport of bound or free pollutant to biological membrane, passing of pollutant across biological membrane, and transport of pollutant to the target biomolecule in the organism. According to this definition, the biologically related processes are critical to the bioavailability when the transports outside the organism are quick enough. The capacity of the SPMD is greater than that of the earthworms, however, and the SPMD is not as easily saturated as the earthworms are. Hence, data for the 100 mg/kg group generally are at the lower right side compared to those for the 10 mg/kg group in Figure 6. The correlation coefficients became acceptable when we divided the data into two series based on their concentration ($r^2 = 0.709$ and 0.702 for a pyrene

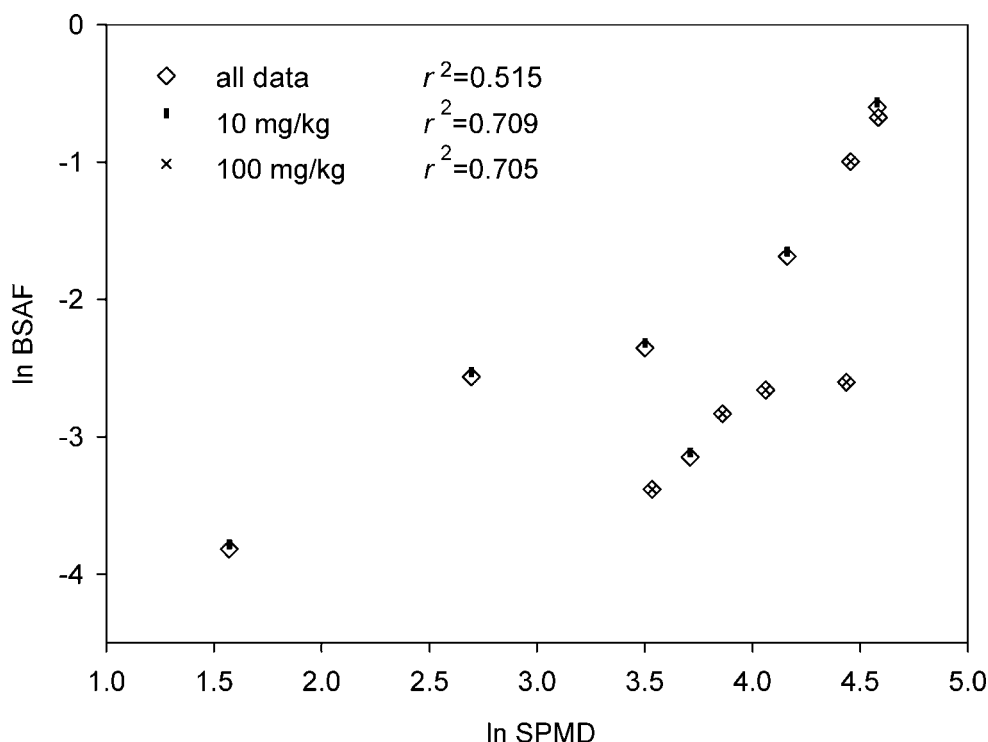


Fig. 6. Correlation between \ln SPMD (natural logarithm of 12-d desorption percentage assisted by a semipermeable membrane device) and \ln BSAF (natural logarithm of biota-soil accumulation factor) of pyrene in unaged and aged soils. Dots in the figure are data points observed using different soils, and r^2 represents the corresponding correlation coefficient.

concentration of 10 and 100 mg/kg, respectively). Moreover, it is thought that the relationship between SPMD-assisted desorption and biological uptake could be improved if the length of the SPMD tube and the amount of lipid inside are chosen so that it has an uptake capacity similar to that of the objective organism. Leppänen and Kukkonen [37] found that the SPMD could simulate the biological uptake of HOCs when absorption through the skin of the animal was the major uptake approach of the HOC.

CONCLUSION

In the present paper, we found that the SPMD-assisted method is a good way to study the combination state, desorption, and bioavailability of HOCs in soils.

Soil organic matter content, initial concentration of the pollutant, aging and its pattern, and water content of the soil strongly influence the SPMD-assisted desorption percentage of pyrene. For unaged soils 1, 2, and 3, the 50-d desorption percentage of pyrene was $52.2 \pm 3.6\%$, $76.3 \pm 1.5\%$, and $99.4 \pm 3.3\%$, respectively, at an initial pyrene concentration of 10 mg/kg and $73.6 \pm 4.9\%$, $94.1 \pm 4.1\%$, and $98.3 \pm 4.9\%$, respectively, at an initial pyrene concentration of 100 mg/kg, which reversed with SOM. The effect of SOM on the SPMD-assisted desorption is attributed to the fact that soil with a higher SOM content could provide more active binding sites, in which the sorbed pyrene becomes difficult to desorb. As the pyrene concentration in soil became higher, the percentage of pyrene combined with the easy-desorbing sites increased; consequently, the desorption percentage of pyrene also increased.

Aging made the desorption rate and extent decrease because of the movement of pollutant molecules to the difficult-desorbing sites, which are inaccessible to SPMD desorption. After 180 d of aging, the pyrene desorption percentage decreased

from between 52.2 and 99.4% to between 5.8 and 34.2% for the three soils at an initial pyrene concentration of 10 mg/kg and from between 73.6 and 98.3% to between 43.9 and 86.3% at an initial pyrene concentration of 100 mg/kg. Generally, the reduction in the extent of desorption, which represents the quantity of pyrene molecules that have moved from easy-desorbing to difficult-desorbing sites, is greater at lower pollutant concentration and in soils with a lower SOM content. An unexpected result occurred for soil 3 at a pyrene concentration of 100 mg/kg, because the difficult-desorbing sites in soil 3 are so few in the face of a high level of pyrene that even during aging, few pyrene molecules could access them. It was found, to our knowledge for the first time, that when the pollutant does not have to compete with water molecules for soil minerals, aging under the wet condition reduces desorption to a greater extent, because water is favorable to the transport of pollutant into soil particles. When water is a competitor, however, the opposite is true. Dry-aged soils enhance sequestration of the pollutant compared to wet-aged soils, which in turn leads to lower desorption.

In addition, when the water to soil ratio in SPMD-assisted desorption decreased from 10:1 to 1:1, pyrene desorption dynamics became more linear. We concluded that this occurred because the rate-limiting step had changed from the inner particle diffusion at a high water content to the transport in pore water at a low water content. On day 20, the desorption percentage decreased by $29.4 \pm 2.9\%$ and $35.1 \pm 1.3\%$ in soil 1 and by $10.3 \pm 0.4\%$ and $18.2 \pm 1.5\%$ in soil 2 for pyrene at a concentration of 10 and 100 mg/kg, respectively. The 20-d desorption percentage did not vary significantly in soil 3, however, even though the desorption dynamics were quite different under the two conditions.

The good correlations between SPMD-assisted desorption and the BSAF indicate that SPMD could simulate the uptake

of HOCs from soils by organisms. The SPMD-assisted desorption is expected to become a rapid method to assess the bioavailability of HOCs in soils.

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