Chemosphere 325 (2023) 138419

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Development of an *in situ* equilibrium polydimethylsiloxane passive sampler for measuring volatile organic compounds in soil vapor

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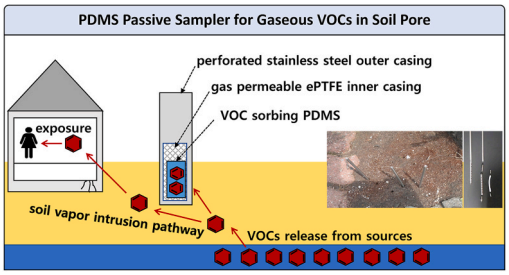
HIGHLIGHTS

- An equilibrium passive sampler was developed to measure VOCs in the soil vapor.
- C_{gas} and C_{water} in soil pores can be accurately deduced from C_{PDMS}.
- To evaluate the passive sampler, active sampling was performed simultaneously.
- Tests were conducted to observe the effects of soil components on passive sampling.
- A holder for the sampler made of stainless steel was used for field applications.

GRAPHICAL ABSTRACT



ARTICLE INFO

Handling Editor: Keith Maruya

Keywords:
Passive sampling
Volatile organic compounds
Equilibrium partition coefficient
Soil vapor
Vapor intrusion
Polydimethylsiloxane

ABSTRACT

An equilibrium passive sampler made of polydimethylsiloxane (PDMS) fiber was developed to measure volatile organic compounds (VOCs) in soil vapor. Expanded polytetrafluoroethylene (ePTFE) was used to protect PDMS from pollution and direct contact with soil components. For all tested VOCs, equilibrium was reached after 7 days at 5 °C. The equilibrium partition coefficients of VOCs between PDMS, gas, and water were measured at three different temperatures. The analyte concentrations in PDMS exposed to gas and water separately were almost the same, which suggests that C_{gas} and C_{water} in soil pores can be accurately deduced from C_{PDMS} after equilibrium at various temperatures. To evaluate the passive sampler, active sampling measurements were performed simultaneously. Concentrations of VOCs deduced from the passive sampler were consistent with the concentrations measured by active sampling near the 1:1 line. Tests with artificial soils were conducted to observe the effects of soil components on passive sampling. The results suggest that the effect of water saturation can be ignored; in other words, the developed passive sampler can be applied in the vadose zone, which has fluctuating water saturation. With a holder for the sampler made of stainless steel, the developed *in situ* passive sampler can measure VOCs in contaminated soil vapor. The developed passive sampler was proven to be an alternative for measuring VOCs in soil vapor, which can be helpful for soil risk assessment and for observing the diffusion of VOCs in contaminated sites.

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https://doi.org/10.1016/j.chemosphere.2023.138419
Received 4 November 2022; Received in revised form 10 March 2023; Accepted 13 March 2023
Available online 14 March 2023
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1. Introduction

Underground leakage of storage tanks and fuel spills can cause volatile organic compound (VOCs) contamination in soil and groundwater (Huang et al., 2014; Alharbi et al., 2018; Feng et al., 2020). From these contaminated sources, VOCs migrating continuously via diffusion and advection in soil vapor can invade buildings; this phenomenon is called vapor intrusion (Fitzpatrick and Fitzgerald, 2002; Rivett et al., 2011; Soucy and Mumford, 2017; Bekele et al., 2018; Ma et al., 2020). Vapor intrusion is considered to be the most likely potential pathway for human exposure to contaminated soil (ITRC, 2007; Ma and Lahvis, 2020). Human exposure to VOCs by vapor intrusion can pose severe human health risks (Belpomme et al., 2007; Chang and Chen, 2008; Petry et al., 2014).

Estimation of potential vapor intrusion risk is assessed from VOCs contents in soil vapor, which has been commonly estimated from soil concentration assuming equilibrium (Ministry of Ecology and Environment of China, 2014; Ministry of Environment of Korea, 2015; Ma and Lahvis, 2020). As uncertainties in the prediction of soil vapor VOCs concentrations from soil concentrations have been shown in many studies (Swartjes, 2011; Zhang et al., 2018), direct soil vapor sampling is preferred (USEPA, 2015). Soil vapor sampling is widely based on active sampling, which utilizes a power pump (ASTM, 2006). For example, Tedlar bags, canisters, and thermal desorption tubes have been used to collect soil vapor. However, they can have problems related to vacuum and flow in low-permeability soils and leak prevention (Gschwend et al., 2022). Additionally, active sampling is unsuitable for detecting relatively long-term, fluctuating concentrations (Seethapathy et al., 2008). Passive sampling is an alternative method for this purpose. Passive sampling acts without power, because it is based on the molecular diffusion of chemicals (Lewis and Mulik, 1985; Zabik et al., 1992; Górecki and Namieśnik, 2002). Passive sampling is easier to use and lower in cost (Salim and Górecki, 2019; Liang et al., 2021).

Passive sampling can be used with two different uptake phases: the linear uptake phase and the equilibrium phase (Zabiegała et al., 2010; Wania and Shunthirasingham, 2020). In the case of a passive sampler operating with a linear uptake phase, the mass uptake rate in a passive sampler can be translated into soil vapor VOCs content (McAlary et al., 2014). Unfortunately, gaseous VOCs transport in soil pores can be retarded by soil components, particularly water (Park et al., 1997; Kim et al., 2001, 2005). Retardation in soil can be problematic because it can affect the passive sampling rate in the linear uptake phase. The equilibrium passive sampler can neglect the retardation effect because retardation has no effect on the equilibrium partition coefficient. Because retardation in soil can extend the time to reach equilibrium, methods like using reference chemicals or deploying polymers differentiated by thickness are recommended to confirm whether equilibrium has been reached (Fernandez et al., 2009; Morales-McDevitt et al., 2021). Polymers, such as polyethylene, polymethyl methacrylate, and polyoxymethylene, are commonly used as sorbent phases in equilibrium passive samplers in soil (Apell and Gschwend, 2014; Enell et al., 2016; Lao et al., 2016; Qian et al., 2017). Among them, polydimethylsiloxane (PDMS) has been previously used for equilibrium passive sampling of hydrophobic organic chemicals in soil, such as polycyclic aromatic hydrocarbons (Kim et al., 2017, 2022; Kim and Kwon, 2020). Owing to its high affinity for organic chemicals, PDMS is also used for the passive sampling of VOCs in indoor air and groundwater (Seethapathy and Górecki, 2011; Nam et al., 2016; Lin et al., 2020). However, to the best of our knowledge, there have been no studies using PDMS as an adsorbent for the passive sampling of VOCs in soil vapor.

In this study, we developed an *in situ* equilibrium PDMS passive sampler. Nine VOCs, including benzene, toluene, p-xylene, and ethylbenzene, were selected for the experiment. To develop the passive sampler which can be applied in various VOCs, a total of 9 VOCs with a range of Henry's constants (KH; from 0.052 to 0.682) were chosen (Bonifacio et al., 2017). These chemicals have potential health risks, such as carcinogenicity (Belpomme et al., 2007). To protect PDMS from pollution and direct contact with soil components, the PDMS fiber was inserted into an expanded polytetrafluoroethylene (ePTFE) cylinder, which is only gas-permeable. The times for the nine VOCs to reach equilibrium between PDMS, gas, and water were tested to determine sufficient days for the application of the equilibrium passive sampler in soil media. Equilibrium partitioning coefficients between PDMS, gas, and water at 5 °C, 14 °C, and 25 °C were measured to translate the VOCs concentrations in PDMS to VOCs concentrations in soil media. To verify the accuracy of the developed passive sampler, measurements by the active sampling headspace of the vials were compared simultaneously. The effects of the soil components, water saturation, and organic matter on passive sampling were observed. Finally, a stainless steel sampler holder was used for the field tests.

2. Materials and methods

2.1. Theory

Fig. S1 shows the conceptual diagram of the test, where K_H is dimensionless Henry's law constant, VOCs in the gas phase are C_{gas}, VOCs in the water phase are C_{water}, VOCs in PDMS soaked in water are C_{PDMSw}, and VOCs in PDMS floating in the air are C_{PDMSg}, the equilibrium partition coefficient of VOCs between PDMS and gas is K_{PDMSg}, and the equilibrium partition coefficient of VOCs between PDMS and water is K_{PDMSw}. Assuming that VOCs in the three different phases are in equilibrium, K_H can be given by

$$K = \frac{K_{PDMSw}}{K_{PDMSg}} = \frac{\frac{C_{PDMSw}}{C_{water}}}{\frac{C_{PDMSg}}{C_{gas}}} = \frac{C_{gas}}{C_{water}} \quad (1)$$

After spiking water with the VOCs in the test vial, the mass balance in the test vial can be derived as

$$M_{total} = C_{water} \times V_{water} + C_{gas} \times V_{gas} + C_{PDMSg} \times V_{PDMSg} + C_{PDMSw} \times V_{PDMSw} \quad (2)$$

where M_{total} is the mass of the spiked VOCs, V_{water} is the volume of water, V_{gas} is the volume of the gas, V_{PDMSg} is the volume of PDMS in gas phase, V_{PDMSw} is the volume of PDMS in water phase. Assuming that the VOCs in the three different phases are in equilibrium, C_{PDMSw}, and C_{PDMSg} are the same. Then, the equation can be simplified as

$$C_{water} = \frac{M_{total} - (C_{PDMS} \times V_{PDMS}) \times 2}{V_{water} + K_H \times V_{gas}} \quad (3)$$

After *in situ* equilibrium PDMS passive sampling, C_{gas} and C_{water} in the soil pores were obtained from C_{PDMS}.

2.2. Chemicals

For model VOCs, benzene (BZN), 1,2-dichloroethane (DCA), trichloroethene (TCE), toluene (TOL), tetrachloroethene (PCE), chlorobenzene (CBZ), ethylbenzene (EBZ), p-xylene (PXY), 1,3-dichlorobenzene (DCB) were selected and purchased from Sigma-Aldrich (Milwaukee, WI, USA). Table S1 lists their chemical properties.

2.3. Passive sampler

PDMS was selected as a model polymer. PDMS was purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA) (ID 0.5 mm x OD 1 mm). Fibers of PDMS were cut to 1 cm, then cleaned with methanol and n-hexane for one day. To contact PDMS fiber only with air, 1 cm cut PDMS fibers were inserted into expanded PTFE tubes (Huizhou Besteflon Industries Co. Ltd.) (ID 2 mm × OD 4 mm), which are only gas permeable. The tubes were cleaned by Soxhlet extraction for 12 h with a mixture of 50 mL n-hexane and 50 mL acetone. The PTFE caps of 2 mm

diameter were used to seal. After PTFE caps are tightly fitted, PTFE tape was used to seal.

2.4. Time to reach equilibrium between PDMS, gas, and water

The time taken to reach equilibrium between the three phases was measured. The VOCs were spiked into distilled water to attain 5 mg L^{-1}. Thirty milliliters of the solution was placed in a 40 mL vial. All the vials were placed in an incubator at 5 °C in the dark. As shown in Fig. S2, two PDMS fibers connected to a wire were placed in a vial. The wire fixes the PDMS fiber so that one end is exposed to air and the other is exposed to solution. After 6, 12, 24, 48, 96, 168, and 240 h, the PDMS fibers were removed and extracted with 2 mL of dichloromethane for 24 h. Details of the instrumental analyses are provided in the supporting information. The tests were performed in triplicate. For *in situ* passive sampling, PDMS fibers were inserted into ePTFE tubes to block contact between the soil and PDMS. Triplicate tests were repeated with two PDMS fibers inserted into the ePTFE tubes, as shown in Fig. S2.

Assuming that the VOCs in vials were preserved, the VOCs in PDMS (μg g^{-1}) were described by the following equation:

$$C_{PDMS} = C_{eq} \times \left(1 - e^{-kt}\right) \quad (4)$$

where C_{eq} is the C_{PDMS} at equilibrium, k is the elimination rate constant [hr^{-1}], and t is the time [h]. Time-dependent measurements of C_{PDMS} and C_{PDMS} inserted into an ePTFE tube in the gas and water phases were used to determine C_{PDMS} at equilibrium.

2.5. Equilibrium partition coefficients between PDMS, gas, and water

The equilibrium partition coefficients between PDMS and gas, and the values between PDMS and water were measured at 5 °C, 14 °C, and 25 °C. The nine VOCs were spiked into distilled water for 1, 2, 3, 4, 5, and 6 mg L^{-1}. Thirty milliliters of the solution was put in a 40 mL vial. All vials were placed in an incubator at 5 °C, 14 °C, and 25 °C in the dark. As shown in Fig. S2, two PDMS fibers, connected with a wire and inserted into ePTFE tubes, were placed in a vial. The wire fixes the PDMS fiber so that one end is exposed to air and the other is exposed to solution. After 10 d, the PDMS fibers were removed and extracted with 2 mL of dichloromethane for 24 h. The tests were performed in triplicates.

Henry's law constants for VOCs at 5 °C, 14 °C, and 25 °C were measured. To find enough time to achieve equilibrium between the water and air, 30 mL of the 50 mg L^{-1} spiked solution with nine VOCs was placed in four 40 mL vials at 25 °C. After 1, 3, 5, and 24 h, the headspace of the vials (100 μL) was extracted using a gas-tight syringe. The concentrations of VOCs in the syringe and C_{gas} in the vial were measured using GC-MS. As shown in Table S2, the concentrations of VOCs in the syringe after 1, 3, 5, and 24 h were similar each other. Results suggest that 24 h are enough to achieve equilibrium. The nine VOCs were spiked into distilled water to attain 10, 50, and 70 mg L^{-1}. Thirty milliliters of the solution was placed in a 40 mL vial. All vials were placed in an incubator at 5 °C, 14 °C, and 25 °C in the dark. After 24 h, the headspace of the vials (100 μL) was extracted using a gas-tight syringe. The concentrations of VOCs in the syringe and C_{gas} in the vial were measured using GC-MS. C_{water} at equilibrium was calculated by subtracting measured mass of VOCs in gas from spiked mass of VOCs. Dimensionless Henry's law constants for VOCs at 5 °C, 14 °C, and 25 °C were calculated by the ratio of C_{gas} and C_{water}. The tests were performed in triplicate.

2.6. Verification of passive sampler

To validate the performance of the PDMS passive sampler, C_{gas} measured by passive sampling and C_{gas} measured by active sampling were deployed simultaneously, and the results were compared. We validated the sampler for the gas phase only, but not the water phase, because the PDMS passive sampler was developed to measure VOCs in soil vapor. In addition, inserted PDMS in ePTFE tube contacts with only gaseous VOCs. The nine VOCs were spiked into distilled water to attain 10, 30, 50, and 70 mg L^{-1}. Thirty milliliters of the solution was placed in a 40 mL vial. All the vials were placed in an incubator at 25 °C in the dark. As shown in Fig. S2, two PDMS fibers connected to a wire were placed in a vial. The wire fixes the PDMS fiber so that one end is exposed to air and the other is exposed to solution. After 10 d, the PDMS fibers were removed and extracted with 2 mL of dichloromethane for 24 h. The headspace of the vials (100 μL) was extracted using a gas-tight syringe. The concentrations of VOCs in the syringe and C_{gas} in the vial were measured using GC-MS. The tests were performed in triplicate.

2.7. Effects of soil components on passive sampling

The effects of the soil components like organic matter, and water on passive sampling were observed. Silicon sand, purchased from Kyung In Material (Republic of Korea), was used as sand. Humic, purchased from Black Earth Humic LP (Alberta, Canada), was used as surrogate organic matter. In a 12 mL vial, 10%, 20%, and 40% (w/w) water-saturated sand and 10% water-saturated artificial soils made with sand and organic matter (3 and 6%) were added. In all vials tested, 1 g of sand was added. For artificial soils made with 3% and 6% organic matter, 0.03 g and 0.06 g of organic matter were added, respectively. After 10 μL of each of the nine VOCs was spiked in each vial, 1 cm of cut PDMS fiber inserted into ePTFE was deployed in the soil. All the vials were placed in an incubator at 25 °C in the dark. After 10 d, the PDMS fibers were removed and extracted with 2 mL of dichloromethane for 24 h.

2.8. Field application

To enable the deployment of a passive sampler in soil, a stainless steel sampler holder was used. Fig. S3 shows the passive sampler and sampler holder made of stainless steel. PDMS (25 mm) was inserted into a 50 mm ePTFE and sealed with caps. The passive sampler was inserted into a 60 mm sampler holder, which has 28 holes for penetrating gas, and then sealed with a 15 mm stainless steel circular cone cap for deployment in soil and a 500 mm stainless steel cylinder holder with a diameter of 5 mm. A site contaminated with VOCs, especially TCE and PCE, around the Iksan National Industrial Complex (35°56′33″ N 126°58′29″ E), Iksan, Republic of Korea, was selected for the field test. A park, far away from the contaminated site, was selected as the background. In the contaminated sites, three tree beds at intervals within 50 cm of each other were selected as sampling sites. One tree bed was selected as the sampling site in the park. For each site, three passive samplers were deployed at intervals of 10 cm from each other. Fig. S4 shows the deployment of the passive samplers. After 10 days, passive samplers were extracted with a solid adsorption tube made of Tenax (Tenax-TA® tubes, KnR, Republic of Korea) for 24 h. Because VOCs are quickly lost from PDMS, removed PDMS was put in tube (4-4 HBZ, UNION Tech CO., LTD, Republic of Korea) made of stainless steel which can be used to seal the solid adsorption tube immediately to minimize the losses. Because tenax in adsorption tube has much higher sorption capacity for VOCs than PDMS, all VOCs in PDMS were transferred to adsorption tube after 24 h. After that, the solid adsorption tube was measured using TD-GC MS (APK 2350, KnR, Republic of Korea). C_{PDMS} and K_{gas} were used to obtain the C_{gas}.

2.9. Quality assurance and quality control

The spiked masses of VOCs were recovered in the experiments. The nine VOCs were spiked into distilled water for 1, 2, and 3 mg L^{-1}. Thirty milliliters of the solution was put in a 40 mL vial. All vials were placed in an incubator at 25 °C in the dark. After 10 days, The headspace of the vials (100 μL) was extracted using a gas-tight syringe. The 0.8 mL of water in the vials was extracted with 0.8 mL of dichloromethane

(Bonifacio et al., 2017). The concentrations of VOCs in the syringe and dichloromethane were measured using GC-MS. Measured masses are shown in Table S3. As shown in Table S4, the spiked masses of VOCs were recovered for 89% on average after 10 days. The nine VOCs were not detected in blank PMDS extracts. However, BZN, TOL, EBZ and PXY were detected in blank solid adsorption tube. The measured mass of those chemicals in blank solid adsorption tube was considered in field application. To determine the method detection limit (MDL), seven solid adsorption tubes were spiked with 5 μL of a 100 μg L^{-1} solution of nine VOCs in dichloromethane and measured using TD-GC MS (Glaser et al., 1981). The standard deviation of the measured samples was multiplied by 3.14 to define MDL, as shown in Table S5.

3. Results and discussion

3.1. Time to reach equilibrium between PDMS, gas, and water

The time required for the nine VOCs to reach equilibrium between PDMS, gas, and water was tested to determine sufficient days for the application of the equilibrium passive sampler in soil media. The uptake of VOCs by PDMS and PDMS inserted into ePTFE in gas and water is shown in Figs. S5 and S6. The units of C_{PDMSw} and C_{PDMSg} are shown in μg g^{-1}, which means μg of VOCs in g of only PDMS coating. Fig. 1 compares C_{PDMS} at equilibrium in the gas and water phases. In the case of C_{PDMS} without ePTFE at equilibrium, the R^2 and slope of the linear regression were 1.00 and 1.02, respectively. In the case of C_{PDMS} inserted into ePTFE at equilibrium, the R^2 and slope of the linear regression were 0.97 and 1.00 respectively. Regardless of the ePTFE tubes, C_{PDMSw} and C_{PDMSg} seemed to be almost the same at equilibrium, which suggests that VOCs in the three different phases are in equilibrium. Therefore, as suggested in theory, equation (3) can be applied. The results suggest that C_{gas} and C_{water} in the soil pores can be deduced from the C_{PDMS} after equilibrium.

Table S6 shows obtained C_{PDMS} at equilibrium and k. Equation (4) can be derived as

$$\frac{C_{PDMS}}{C_{eq}} = \left(1 - e^{-kt}\right) \tag{5}$$

Table S7 shows the calculated time required for the nine VOCs to reach 90 and 99% equilibrium between PDMS, gas, and water with equation (5) and obtained k. As expected, VOCs with higher affinity for PDMS require more time to reach equilibrium between the gas and PDMS because VOCs which partition more strongly into the PDMS require longer to reach equilibrium (Greenwood et al., 2007). For example, BZN reached 90% of equilibrium in 8.7 h, whereas DCB required 164 h to reach 90% of equilibrium without ePTFE. When PDMS was inserted into ePTFE, the time required to reach equilibrium between the gas and PDMS increased. For example, BZN reached 90% of equilibrium in 26 h. As shown in Fig. 2, for all tested VOCs, the time to reach 90% of equilibrium was less than 4 d at 5 °C when PDMS was inserted into ePTFE. As octanol water partition coefficients (K_{OW}) of VOCs increased, the time to reach 90% of equilibrium tended to increase. This can be seen in our previous study (Kim et al., 2017). For example, uptake rate constant of PDMS for phenanthrene was at least 10 times higher than corresponding value of benzo [a]pyrene in various water saturated soils (Kim et al., 2017). For all tested VOCs, the time to reach 99% of equilibrium was less than 7 d at 5 °C when PDMS was inserted into ePTFE. As the molecular diffusion coefficient increases with temperature, the time to reach equilibrium is less than 7 d at temperatures higher than 5 °C. When deploying the developed passive sampler in field soil at temperatures higher than 5 °C, the results imply that 7 days is sufficient for the application of an equilibrium passive sampler in soil media, because inserted PDMS in ePTFE tubes only contacts with gaseous VOCs. However, the true time required to reach equilibrium from an infinite source of VOCs such as soil could be underestimated from the values of k derived from the fitting of curves because the uptake into the PDMS of particularly the less volatile VOCs significantly accelerates the equilibration process (Greenwood et al., 2007). In addition, permeability of soil can affect the time to reach equilibrium (McAlary et al., 2014). Therefore, methods like using reference chemicals or deploying polymers differentiated by thickness are recommended to confirm whether equilibrium has been reached (Fernandez et al., 2009; Morales-McDevitt

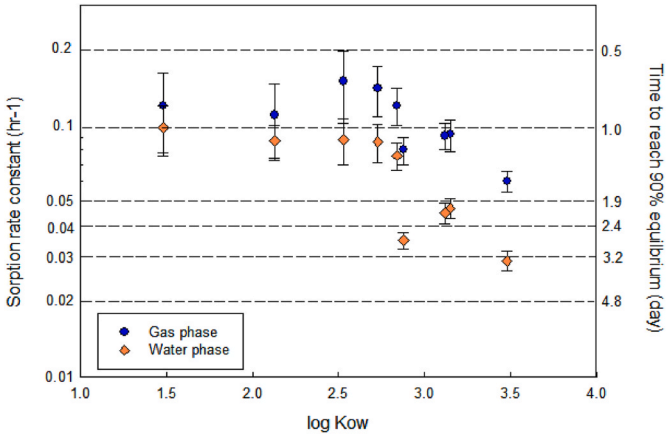

Fig. 2. Log K_{OW} dependent log k (hr^{-1}) and time to reach 90% equilibrium (day) in water and gas phases when PDMS was inserted into ePTFE.

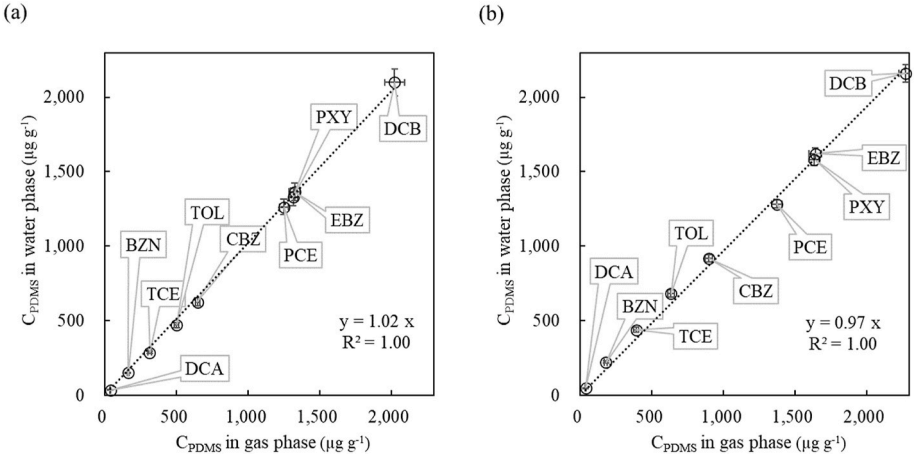

Fig. 1. (a) Linear relationship of C_{eq} in water phase and gas phase. (b) Linear relationship of C_{eq} of PDMS inserted into ePTFE in water phase and gas phase.

et al., 2021).

3.2. Equilibrium partitioning coefficients between PDMS, gas, and water

Equilibrium partitioning coefficients between PDMS, gas, and water at 5 °C, 14 °C, and 25 °C were measured to translate the VOCs concentrations of PDMS to VOCs concentrations in soil media, such as soil water and gas. Table 1 shows the measured log K_{PDMSg} and log K_{PDMSw} of the VOCs at 5 °C, 14 °C, and 25 °C. The measured VOCs concentrations of PDMS in the gas and water phases at 5 °C, 14 °C, and 25 °C are shown in Table S8. The measured Henry's law constants at 5 °C, 14 °C, and 25 °C, as shown in Table S9, were used to obtain log K_{PDMSg} and log K_{PDMSw}. The measured Henry's law constants in this study were similar to the values from the CRC Handbook of Chemistry and Physics, as shown in Table S1. For example, the measured value of BZN was 1.77 times lower. The measured value for the PCE was 5.8 times lower, which was the largest difference. The headspace of the vial was extracted to measure *C*gas. Owing to the high volatility of VOCs, C_{gas} can be underestimated by VOC leakage during extraction. This could be the reason for the lower measured values in this study. Using known VOCs doses in water, Henry's law constants and measured PDMS concentrations in the gas and water phases were used to obtain C_{gas} and C_{water} using equation (3). The calculated C_{gas} and C_{water} were used to obtain log K_{PDMSg} and log K_{PDMSw} of VOCs at 5 °C, 14 °C, and 25 °C.

The measured K_{PDMSg} of the nine VOCs was highly related to the vapor pressure and K_{OW} of the VOCs. The measured K_{PDMSg} seemed to increase with K_{OW}, as shown in Fig. S7. The R^2 value of the correlation between.

K_{PDMSg} and K_{OW} was 0.96. K_{PDMSg} can be derived as

$$K_{OW} = 0.26K_{PDMSg} + 230 \quad (6)$$

Additionally, the measured log K_{PDMSg} appeared to increase with (log vapor pressure)$^{-1}$ as shown in Fig. 3a. The R^2 of correlation between log K_{PDMSg} and the (log vapor pressure)$^{-1}$ was 0.93.

Log K_{PDMSg} can be derived as

$$\log K_{PDMSg} = 9.9(\log\ vapor\ pressure)^{-1} + 0.19 \quad (7)$$

The R^2 value of the multiple regression analysis between K_{PDMSg}, vapor pressure, and K_{OW} was 0.998. The *p*-values of the vapor pressure and K_{OW} were 0.015×10^{-5} and 0.059×10^{-2}, respectively. K_{PDMSg} can be predicted as

$$K_{PDMSg} = 58.38 + 0.83K_{OW} + \frac{2256036}{vapor\ pressure} \quad (8)$$

In addition to the nine VOCs, K_{PDMSg} for the target VOCs can be estimated using the vapor pressure and K_{OW} of VOCs using equation (8). In the case of log K_{PDMSw}, the measured K_{PDMSw} appeared to increase with K_{OW}, as shown in Fig. 3b. The R^2 value for the correlation between log K_{PDMSw} and log K_{OW} was 0.96. K_{PDMSw} can be derived as

$$\log K_{PDMSw} = 0.89 \log K_{OW} - 0.57 \quad (9)$$

K_{PDMSw} for the target VOCs can be estimated using the log K_{OW} of VOCs using equation (9). The error of slope and intercept were 0.22 and 0.69 respectively.

Table S10 lists the ratios of C_{PDMSw}, and C_{PDMSg} at different temperatures. Fig. S8 shows the correlation of the C_{PDMS} inserted into ePTFE in the water and gas phases at 5 °C, 14 °C, and 25 °C. The C_{PDMS} inserted into ePTFE in the water and gas phases was highly correlated at 5 °C, 14 °C, and 25 °C. For all nine VOCs, the R^2 values of the correlation between C_{PDMS} inserted into ePTFE in the water and in the gas phases were more than 0.98 at 5 °C, 14 °C, and 25 °C. The ratios of C_{PDMSw} and C_{PDMSg} at higher temperatures tended to be lower because the Henry's law constants increased. For example, the ratios of $C_{PDMSw,}$ and C_{PDMSg} for BZN at 5 °C, 14 °C, and 25 °C were 1.27, 0.89, and 0.8, respectively. Henry's law constants for BZN at 5 °C, 14 °C, and 25 °C were 0.068, 0.117, and 0.132, respectively. These results suggest that C_{gas} and C_{water} in the soil pores can be obtained from C_{PDMS} at various temperatures.

3.3. Verification of passive sampler

To verify the developed passive sampler, a comparison between measurement by the active sampling headspace of vials and measurement by passive sampling was carried out simultaneously. Fig. S9 and Table S11 show the C_{gas} measured by passive sampling and C_{gas} measured by active sampling at different concentrations. For all tested VOCs, the C_{gas} measured by both passive sampling and active sampling had strong linear relationships to the concentrations of the solution inserted into the vials. For example, the R^2 values of all nine VOCs for the correlation between C_{gas} measured by passive sampling and the concentrations of the solution were greater than 0.996. The R^2 values of all nine VOCs for the correlation between C_{gas} measured by active sampling and the concentrations of the solution were more than 0.977. The results showed that passive sampling was slightly more accurate at detecting VOC concentrations than active sampling used in this study. Table S12 lists the ratios of C_{gas} measured by active sampling to that measured by passive sampling at different concentrations. For all the tested VOCs, the ratio of C_{gas} measured by active sampling to the C_{gas} measured by passive sampling ranged from 0.85 to 2.5. The differences between C_{gas} measured by passive sampling and C_{gas} measured by active sampling were not related to the chemical properties and concentrations of the VOCs in vials. For all tested VOCs, C_{gas} measured by active sampling was on average 1.62-fold higher than C_{gas} measured by passive sampling. Fig. 4 compares C_{gas} measured by active sampling with that measured by passive sampling. They were very similar; nearly 1:1. Mean squared error between C_{gas} measured by passive sampling and C_{gas} measured by active sampling was 2.52. Generally, the difference between the measurement by passive sampling and "true" concentrations could be within a factor of three (Harner et al., 2006; Bohlin et al., 2007). Development of more accurate technique to measure VOCs in soil vapor is needed.

3.4. Effects of soil components on passive sampling

To observe the effects of soil components, such as sand, organic

Table 1
Measured K_{gas} and K_{water} of VOCs at 5 °C, 14 °C, and 25 °C. Values in parentheses mean standard deviations (n = 18).

Temperatures	25 °C		14 °C		5 °C	
Partition coefficients	K_g (L kg^{-1})	K_w (L kg^{-1})	K_g (L kg^{-1})	K_w (L kg^{-1})	K_g (L kg^{-1})	K_w (L kg^{-1})
BZN	230 (±55)	22 (±3.6)	270 (±32)	28 (±2.0)	430 (±130)	31 (±3.2)
DCA	580 (±210)	6.3 (±0.71)	560 (±190)	7.2 (±1.2)	940 (±480)	7.6 (±0.91)
TCE	450 (±110)	34 (±6.0)	590 (±90)	49 (±4.2)	1100 (±430)	54 (±5.5)
TOL	1300 (±220)	63 (±9.5)	1600 (±220)	84 (±6.5)	2600 (±630)	93 (±8.7)
PCE	1600 (±270)	170 (±28)	2200 (±220)	270 (±28)	8000 (±1900)	540 (±61)
CBZ	2100 (±270)	80 (±12)	3400 (±540)	120 (±11)	4900 (±2000)	82 (±7.5)
EBZ	3200 (±630)	200 (±27)	4500 (±330)	270 (±24)	2600 (±500)	77 (±7.0)
XYL	3100 (±670)	180 (±25)	4700 (±370)	260 (±27)	13,000 (±2600)	370 (±35)
DCB	11,000 (±3610)	300 (±37)	18,000 (±6000)	470 (±48)	58,000 (±13,000)	530 (±43)

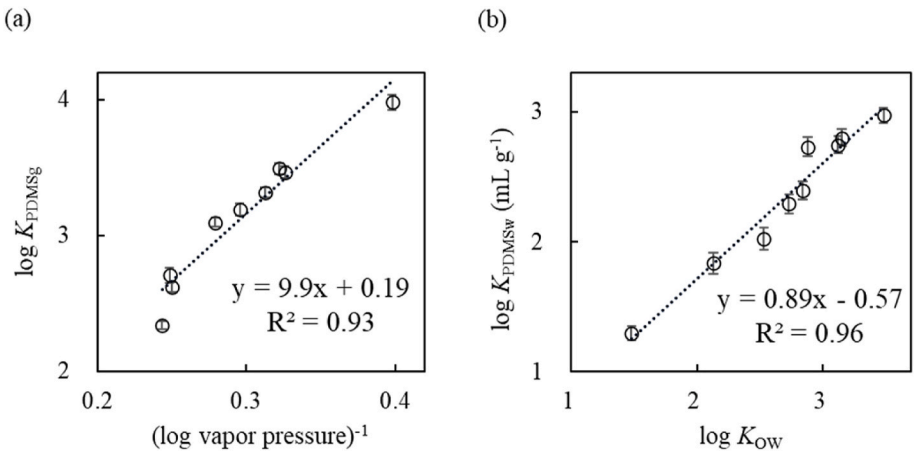

Fig. 3. (a) Correlation of measured log K_{PDMSg} with corresponding (log vapor pressure)$^{-1}$. (b) Correlation of measured log K_{PDMSw} with corresponding log K_{OW} values.

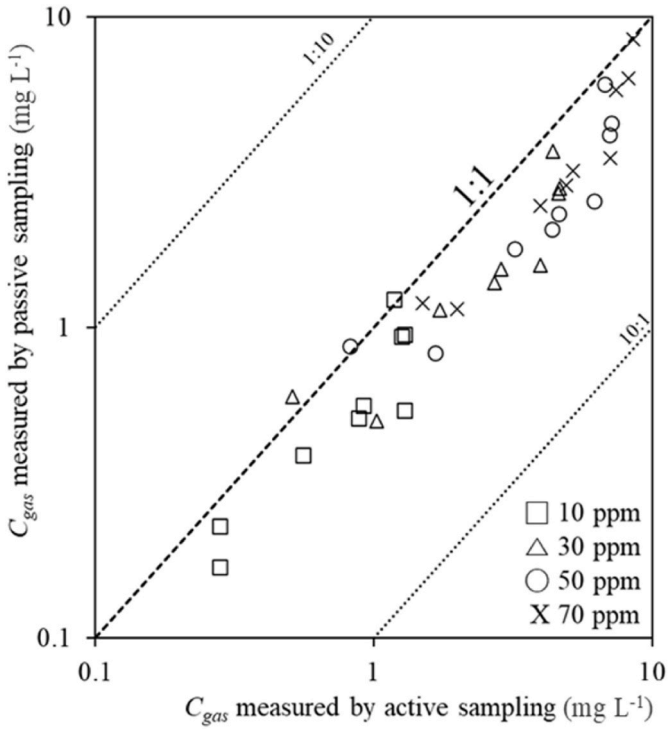

Fig. 4. Comparison of C_{gas} measured by passive sampling and active sampling in different concentrations, 10 ppm (□), 30 ppm (△), 50 ppm (○) and 70 ppm (x) solution inserted into vials.

matter, and water, laboratory tests were conducted using artificial soils in closed vials containing known quantities of the nine VOCs. Table S13 lists the C_{gas} values measured by passive sampling. Fig. 5a shows the effect of water saturation on passive sampling. Except for BZN and TCE, C_{gas}, deduced from the PDMS concentration slightly decreased with water saturation. As the water saturation increased, the dissolution of VOCs in the water increased. Therefore, C_{gas} decreases with water saturation. The differences between C_{gas} deduced from the PDMS concentration in 10% and 40% saturated soils were lower than 1.41-fold for all nine VOCs. This suggests that the effects of water saturation on passive sampling can be ignored. Fig. S10 shows the linear relationships between C_{gas} and vapor pressures of the nine VOCs in 10%, 20%, and 40% saturated soils. The measured C_{gas} values of the nine VOCs were related to the vapor pressure. The R^2 values of the correlation between C_{gas} and vapor pressure were more than 0.89 in 10%, 20%, and 40% saturated soils, because of the different volatilities of the nine VOCs. The slopes of the linear relationships between C_{gas} and vapor pressure were 0.032, 0.033, and 0.032 in 10%, 20%, and 40% saturated soils, respectively, which suggests that the effect of water saturation on passive sampling can be ignored. Therefore, the developed passive sampler can be applied in the vadose zone, which has fluctuating water saturation.

Fig. 5b shows the effect of organic matter on passive sampling. C_{gas} deduced from the PDMS concentration tends to decrease with increasing organic matter in soil because the sorption of VOCs to organic matter is one of the most significant processes determining the fate of VOCs in soils (Chiou et al., 1983; Pignatello and Xing, 1995; Chefetz et al., 2000). However, the larger VOCs like DCB showed no trend of decreasing C_{gas} with increasing organic matter content. The water saturating process may lead to conformational change of organic matter and swells the volume of SOM (Liu and Lee, 2006) and this swelling may create inner sorption sites that can host relatively smaller molecules. In case of smaller molecules, SOM volume contributed more significantly on sorption capacity (Kim et al., 2017). For larger VOCs like DCB, 10% saturation may not be enough to swell SOM creating inner sorption sites.

3.5. Effect of temperature on sorption of passive sampler

The thermodynamic sorption capacity of the passive sampler was evaluated using Van't Hoff equation (Zhang et al., 2014)

$$ln\ K_{PDMS,gas\ or\ water} = -\frac{\triangle H^{\circ}}{RT} + \frac{\triangle S^{\circ}}{R} \quad (10)$$

where R is the gas constant [8.314×10^{-3} kJ mol^{-1} K^{-1}], $\triangle H^{\circ}$ and $\triangle S^{\circ}$ are the changes in enthalpy and entropy in the sorption of VOCs on the passive sampler, respectively, and T [K] is the temperature. Van't Hoff plots of VOCs are shown in Fig. S11. Table 2 shows obtained $\triangle H^{\circ}$ from the linear plot. All $\triangle H^{\circ}$ values were negative, suggesting that the exothermal sorption of VOCs was inversely dependent on temperature. To evaluate the spontaneity of sorption, Gibbs free energy changes ($\triangle G^{\circ}$) were calculated.

$$\triangle G^{\circ} = \triangle H^{\circ} - T\triangle S^{\circ} \quad (11)$$

and shown in Table S14. Regardless of the temperature, all $\triangle G^{\circ}$ values were negative, suggesting that the sorption of VOCs to the passive sampler was spontaneous at all tested temperatures. As expected, all $\triangle G^{\circ}$ values in gas were more negative than those in water at 5 °C, 14 °C, and 25 °C, which suggests that the sorption of VOCs to the passive sampler is more spontaneous in the gas phase at all tested temperatures.

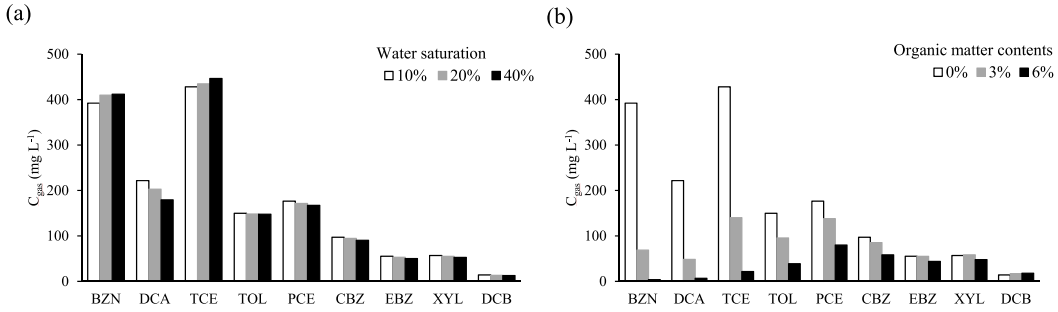

Fig. 5. (a) C_{gas} measured by passive sampling in 10%, 20%, and 40% water-saturated artificial soils made with sand. (b) C_{gas} measured by passive sampling in 10% water-saturated artificial soils made with 0%, 3%, and 6% organic matter and sand.

Table 2
Enthalpy changes in sorption of 9 VOCs on passive sampler.

	△H° (kJ mol^{-1}) in gas	△H° (kJ mol^{-1}) in water
BZN	−19	−12
DCA	−20	−6.6
TCE	−28	−17
TOL	−23	−14
PCE	−54	−39
CBZ	−27	−22
EBZ	−43	−17
XYL	−51	−26
DCB	−60	−20

The tendency of $\triangle G^{\circ}$ to be more negative for more hydrophobic VOCs suggests that van der Waals forces play an important role in the sorption process (Piatt et al., 1996; Chefetz et al., 2000). For example, the average $\triangle G^{\circ}$ values for DCB at 5, 14, and 25 °C in gas were 1.8 times more negative than that of BZN.

3.6. Field application

A stainless steel sampler holder was used to deploy the passive sampler in the field soil. Table 3 lists the results of the field tests. For the test in the field, the method for extraction of PDMS was changed from solvent extraction to thermal desorption to increase the detection capacity. Adsorbed VOCs in PDMS were totally extracted by thermal desorption as shown in Table S15. Except for TCE and PCE, the concentrations of VOCs in soil vapor deduced from C_{PDMS} were similar between the contaminated sites and the background. For TCE and PCE, concentrations of VOCs in soil vapor deduced from C_{PDMS} were high, whereas values in the background were undetected. As the contaminated sites were polluted, especially with TCE and PCE, this allowed the results to be reliable. These results suggest that the developed passive sampler is appropriate for field applications.

4. Conclusions

In this study, an *in situ* equilibrium PDMS passive sampler was developed for measuring VOCs in soil pores. The developed passive sampler has some advantages over existing methods. First, the developed equilibrium passive sampler can neglect the retardation effect because retardation does not affect the equilibrium partition coefficient although methods to confirm whether equilibrium has been reached are recommended. Second, the ePTFE tube was used as a barrier to block the direct contact between the PDMS and soil compartment except for gas, and the measurement error could be minimized. For all tested VOCs, the differences between C_{gas} measured by passive sampling and that measured by active sampling were lower than 2.5-fold. Furthermore, it was demonstrated that the effect of water saturation on passive sampling can be ignored, meaning that the developed passive sampler can be applied in the vadose zone, which has fluctuating water saturation. For further study, soil risk assessment in contaminated sites is being progressed with measurement of VOCs in soil pores using the developed passive sampler. Additionally, vertical and horizontal diffusion from the source in the contaminated site is being studied. Attenuation from the source through the soil pore gas to the indoor and outdoor air is also being measured. Further study about effects of additional processes such as desorption, local depletion and resupply on passive sampling in soil is needed.

Table 3
Measured concentrations of VOCs in gas (ug m^{-3}) in field soil vapor by passive sampling. Values in parentheses mean standard deviations.

C_{gas} (ug m^{-3})	Contaminated site 1	Contaminated site 2	Contaminated site 3	Park
BZN	1400 (±230)	1100 (±44)	1500 (±540)	ND
DCA	ND	ND	ND	ND
TCE	110 (±21)	ND	140 (±14)	ND
TOL	260 (±190)	250 (±230)	81 (±6.2)	15 (±1.7)
PCE	1700 (±360)	500 (±300)	490 (±56)	ND
CBZ	ND	ND	ND	ND
EBZ	ND	ND	ND	ND
XYL	10 (±3.4)	10 (±4.7)	6.0 (±0.10)	0.88 (±0.20)
DCB	ND	ND	ND	ND

Credit author statement

JaeKyuoung Moon: Data curation, Investigation, Writing – review & editing. **Pil-Gon Kim**: Conceptualization, Investigation, Writing – original draft. **Keum Young Lee**: Data curation, Investigation. **Jung-Hwan Kwon**: Conceptualization, Writing – review & editing. **Yongseok Hong**: Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

This work was supported by Subsurface Environment Management Projects funded by the Korea Environmental Industry and Technology Institute, South Korea (Project Number:2020002440005).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2023.138419.

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