Journal of Hazardous Materials 448 (2023) 130933

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Determination of partition coefficients of phthalic acid esters between polydimethylsiloxane and water and its field application to surface waters

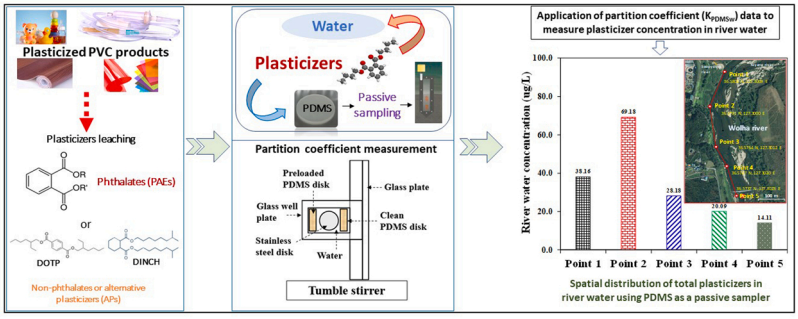
Rishikesh Bajagain [a], Pil-Gon Kim [b], Jung-Hwan Kwon [b], Yongseok Hong [a,*]

[a] Department of Environmental Engineering, Korea University Sejong Campus, 2511 Sejong-ro, Sejong City, 30019, South Korea
[b] Division of Environmental Science and Ecological Engineering, Korea University, Seoul 02841, South Korea

HIGHLIGHTS

- Polydimethylsiloxane (PDMS)-water partition coefficients for PAEs are measured.
- log K_{PDMSw} linearly correlated with log Kow values up to 8 and then deviated.
- Decrease in temperature resulted an increase in log K_{PDMSw} values for all PAEs.
- Partitioning process is affected by ionic strength, but DOM has no significant effect.
- Plasticizer concentration in river water was measured using partition coefficient data.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Feng Xiao

Keywords:
Phthalates
Passive sampling
Kinetic permeation method
PDMS-water partition coefficient

ABSTRACT

Phthalic acid esters (PAEs) or phthalates are endocrine-disrupting chemicals and among the most frequently detected hydrophobic organic pollutants, which can be gradually released from consumer products into the environment (e.g., water). This study measured the equilibrium partition coefficients for 10 selected PAEs, with a wide range of logarithms of the octanol-water partition coefficient (log K_{ow}) from 1.60 to 9.37, between poly (dimethylsiloxane) (PDMS) and water (K_{PDMSw}) using the kinetic permeation method. The desorption rate constant (k_d) and K_{PDMSw} for each PAEs were calculated from kinetic data. The experimental log K_{PDMSw} for the PAEs ranges from 0.8 to 5.9, which is linearly correlated with log K_{ow} values up to 8 from the literature ($R^2 >$ 0.94); however, it slightly deviated for the PAEs with log K_{ow} values greater than 8. In addition, K_{PDMSw} decreased with the temperature and enthalpy for PAEs partitioning in PDMS-water in an exothermic manner. Furthermore, the effects of dissolved organic matter and ionic strength on the partitioning of PAEs in PDMS were investigated. PDMS was used as a passive sampler to determine the aqueous concentration of plasticizers in river surface water. The results of this study can be used to evaluate the bioavailability and risk of phthalates in real environmental samples.

* Corresponding author.
E-mail address: yongseokhong@korea.ac.kr (Y. Hong).

https://doi.org/10.1016/j.jhazmat.2023.130933
Received 21 November 2022; Received in revised form 18 January 2023; Accepted 31 January 2023
Available online 1 February 2023
0304-3894/© 2023 Elsevier B.V. All rights reserved.

Environmental Implication

This study investigated the partitioning of phthalates between poly(dimethylsiloxane) (PDMS) and water. Phthalates are considered as hazardous chemicals since they are endocrine disruptors, and also related to decreased fecundity, pregnancy loss, and adverse obstetric outcomes. PDMS is widely used as passive sampler to measure the concentration of hydrophobic chemicals. The present study measured the partition coefficient of phthalates between PDMS and water and various environmental factors associated with the partitioning process. Furthermore, the obtained data were applied to measure the freely dissolved concentration of plasticizers in river water. The results will be useful for estimating various exposure risk to PAEs.

Data Availability

Data will be made available on request.

1. Introduction

Phthalic acid esters or phthalates (PAEs) are one of the emerging and ubiquitous hydrophobic organic pollutants in the environment, as they are most frequently detected in air, water, solids, foods, beverages, and dusts [1–4]. They are detected in urine samples of young girls and pregnant women and possibly migrate from ingestion, inhalation, and adsorption sources [5,6]. They are endocrine disruptors and are associated with decreased fecundity, pregnancy loss, liver toxicity, and adverse obstetrical outcomes [1,7,8]. It has been reported that premature breast development in young girls, human breast cancer, and the current reduction in the male ratio might be partly due to the increase in exposure to PAEs, which might persist in human body tissues for long periods [9].

Plasticizers are additives that have been extensively used for the softening of plastic products (10–70 % by mass of plastic additive), and approximately 80 % or more of plasticizers are used in polyvinyl chloride (PVC) [10–12]. PAEs have been the most commonly used plasticizers in PVC products since the 1920s and constitute over 85 % of the plasticizers produced every year [11,13,14]. Lower-molecular-weight PAEs (LPAEs) are used in personal care products, pesticides, lubricants, and paint solvents, whereas higher-molecular-weight PAEs (HPAEs) are widely used in PVC and food packaging materials [6,15]. LPAEs in plastics have been replaced by HPAEs or other alternative plasticizers (APs) such as terephthalates, adipates, benzoate esters, citrates, and trimellitates [16–20]; however, the consumption of PAEs is expected to remain high in the future [3].

The mass of plastic waste is increasing every year [10,21] and could have several environmental, economic, and social impacts on terrestrial and marine environments [7]. As plasticizers (PAEs or APs) are not chemically bound to polymers, they can be gradually released from the products and migrate into the air, water, skin, and environment or enter the food chain, leading to health and ecological risks [16,22–30]. Therefore, the risks posed by plastic-based contaminants in the environment should be evaluated. However, knowledge of the freely dissolved concentration in water and sediment is required for risk assessments because the movement and bioaccumulation of contaminants are driven by these media [31]. Therefore, it is necessary to investigate the kinetics of PAEs released into water and sediments. Nevertheless, the measurement of the water soluble concentration of hydrophobic organic chemicals is difficult because of their low concentrations and large pore water volume is needed to determine the sediment pore water concentration [32,33]. In addition, the problem of incomplete phase separation between particle-bound and dissolved contaminants makes challenging in determining the dissolved analytes [33]. PAEs in aqueous-based samples (water, milk, beverages, urine, and serum) are usually quantified using liquid-liquid extraction (LLE) or solid-phase extraction (SPE) methods, which generally require a large sample and solvent volume (up to liters) and require sample preconcentration and multiple extractions [4,34–38]. These methods are expensive, labor-intensive, time-consuming, and sample contamination may occur during analysis; thus, they are not environmentally friendly and less practical [4,34], requiring alternative methods to resolve these complications.

Passive sampling methods are simple and promising for the direct measurement of exposure to hydrophobic organic chemicals [32,39–41]. The absorption-based passive sampling method is a good alternative to traditional sampling methods, which can be used to quantify dissolved concentrations in sediments or biota with a low detection limit and can provide time-integrated data [31,42,43]. The concentrations of organic pollutants monitored by passive sampling methods are agreed well (with less variation) with those from traditional methods (for example water-column sampling method followed by total solvent extraction), thus passive samplers have been encouraging as a scientifically robust tools for assessing exposure [44–47]. Various passive samplers such as low-density polyethylene (LDPE) [33], polyoxymethylene (POM) [48], polydimethylsiloxane (PDMS) [49] or other silicone rubbers [50–52], and Tenax [53] have been developed to determine freely dissolved concentrations. Among them, PDMS is most popular sorbent to evaluate the fate of hydrophobic organic pollutants because of heat resistance, very inert and reproducible, which reduces the losses of unstable and/or polar analytes due to irreversible sorption, and the materials are consistent across the manufacturers [39,40,52,54–57]. In addition, PDMS has shown better performances in terms of lower transport resistance and partition coefficients with high organic contaminant sorption capacity, having ease of fabrication/operation and low cost [51,56,58]. To evaluate the fate of hydrophobic organic pollutants, the partition coefficients of the target compounds between PDMS and water (K_{PDMSw}) should be known [54,58], which can be used to convert the data from the sampler to aqueous phase concentration [59,60].

In this study, PDMS was used as a passive sampler to quantify the aqueous concentration of the PAEs. Although solid-phase microextraction (SPME) using PDMS was carried out to determine the PAEs in aqueous samples [4,61,62], the K_{PDMSw} values for PAEs are scarce in the literature, which necessitates the determination of these values to conduct passive sampling for estimating the phthalate concentration. Smedes (2018) measured the partition coefficients between silicone rubber and aqueous solutions for various organic chemicals, including PAEs; however, a large volume of water (up to 10 L) and a longer time (3 months) were used for the experiment [60]. To shorten the equilibration time and water volume, Kwon et al. (2007) successfully demonstrated a simple kinetic aqueous boundary layer (ABL) permeation method and determined the K_{PDMSw} values for various organic chemicals (with log K_{ow} in the range of 4.05–6.90), including polycyclic aromatic hydrocarbons (PAHs) [54]. They suggested that this method could be applied to measure K_{PDMSw} for even more hydrophobic chemicals within a few days. Furthermore, the accurate measurement of K_{PDMSw} can be affected by various environmental factors, such as temperature, presence of dissolved organic matter (DOM), and salt concentration [60]. Thus, this study aimed to determine the K_{PDMSw} for various PAEs (LPAEs to HPAEs) using the ABL permeation method under various environmental conditions.

The objective of this study was to determine the K_{PDMSw} for 10 selected PAEs (with a wide range of log K_{ow} values, i.e., 1.60–9.37) using the ABL permeation method. The effects of temperature and enthalpy of the PAEs partitioning process, as well as the effects of DOM and ionic strength on K_{PDMSw}, were also investigated. In addition, we studied the correlation between the partition coefficients of the phthalates and their physicochemical properties. The obtained K_{PDMSw} values were used to measure the freely dissolved concentration of plasticizers in real

environmental samples, using PDMS as a passive sampler. The results of this study can be used for risk assessment of exposure to PAEs.

2. Materials and methods

2.1. Reagents and materials

All reagents used in the present study were of analytical grade. Phthalates and other chemicals purchased from Alfa Aesar included dimethyl phthalate (DMP, Germany, 99 %), diethyl phthalate (DEP, India, 99 %), dibutyl phthalate (DBP, USA, 99+ %), diisobutyl phthalate (DIBP, Japan, 99 %), di-n-pentyl phthalate (DNPP, Great Britain, 98 %), benzyl butyl phthalate (BBP, Great Britain, 98 %), di(2-ethylhexyl) phthalate (DEHP, Colombia, 98+ %), dicyclohexyl phthalate (DCP, Japan, 99+ %), di-n-octyl phthalate (DNOP, Japan, 98 %), benzyl benzoate (BB, India, 99+ %), and tetrahydrofuran (THF, USA, 99.7+ %). Diisononyl phthalate (DINP, 99+ %) was purchased from Sigma-Aldrich (Netherlands) and bis(2-ethylhexyl) terephthalate (DOTP, 97 %) from Acros Organics (USA). The physicochemical properties of phthalates used in the present study are summarized in Table S1. Certified reference materials (CRM 113-03-006) for different phthalates were purchased from the Korea Research Institute of Standards and Science (KRISS). The DOM stock solution (Suwannee River DOM, International Humic Substance Society) was obtained. Dichloromethane (DCM, 99.8 %) and n-hexane were obtained from Daejung (Korea, 96 %) and methanol from Sigma-Aldrich (Daejung, 99.5 %).

The PDMS disk used in this study was prepared from a 1 mm thick PDMS sheet (HSW Co., Ltd., Korea). The custom-cut PDMS disks (6-mm diameter) were cleaned using methanol, n-hexane, and methanol for 24 h each and stored in methanol until use. The method details to prepare clean and phthalate-loaded PDMS disks are described elsewhere (Text S1). In a similar way, this study also prepared clean PDMS disks from other four commercial PDMS sheets, which were obtained from following suppliers; 0.1 mm thick PDMS (HSW Co., Ltd., Korea); 0.1 mm thick PDMS (Kureha Elastomer Co., Ltd., Japan); 0.1 and 0.81 mm thick PDMS (CS Hyde, USA).

2.2. Determination of K_{PDMSw} for PAEs by kinetic ABL permeation method

To determine the partition coefficients for PAEs between PDMS and water (K_{PDMSw}), the kinetic aqueous boundary layer (ABL) permeation method was employed [54]. Briefly, a preloaded PDMS disk (6-mm diameter) and a clean PDMS disk of the same size were separated by 160 μL of deionized (DI) water in a simple ABL permeation reactor, and a 5 mm stainless steel disk was placed in the water (Fig. S1). The preloaded PDMS disk serves as a donor and a clean PDMS disk as an acceptor. The device was covered with a glass plate with sealed tape and placed on a magnetic stirrer at 300 rpm. After stirring at different time intervals, both PDMS disks (donor and acceptor) were removed carefully using clean metal forceps, rinsed with DI water, wiped with a tissue, and analyzed for PAEs separately. The experiment was conducted at 25 °C with 3–4 replicates.

The detailed theory and mathematical background for calculating the partition coefficients of phthalates between PDMS and water (K_{PDMSw}) are described in Text S2, as suggested previously [54]. In brief, the partition coefficient between PDMS and water (K_{PDMSw}) is defined as;

$$K_{PDMSw} = \frac{C_{PDMS}}{C_w} \quad (1)$$

where, C_{PDMS} and C_w are the PAEs concentrations in PDMS sampler and water, respectively. For the highly hydrophobic compounds with high K_{PDMSw}, it is difficult to monitor the change in concentration of donor disk within short time of experiment. Thus, the monitoring for depletion of concentration in the donor PDMS should be avoided. However, the concentration in the acceptor disk can be monitored accurately against the initial concentration of zero as shown in Eq. 2;

$$C_{PDMS,acceptor} = \frac{C_0}{2}[1 - \exp(-k_d t)] \quad (2)$$

$$\ln\left(1 - \frac{2C_{PDMS,acceptor}}{C_0}\right) = -k_d t \quad (3)$$

where, $C_{PDMS,acceptor}$ (mol m^{-3} PDMS) is the concentration in acceptor PDMS; C_0 is the initial concentration in the preloaded PDMS disk, and t is time (in s). Eq. 3 is obtained by rearranging Eq. 2 to obtainin the desorption rate constant (k_d) easily by measuring $C_{PDMS,acceptor}$. The desorption rate constant (k_d) is determined by using a linear regression between ln (1–2$C_{PDMS,acceptor}/C_0$) and t. Then, the K_{PDMSw} for different phthalates can be calculated by using Eq. 4;

$$k_d = \frac{k_a}{K_{PDMSw}} \cong \frac{D_w}{\delta_w}\frac{A}{V_{PDMS}K_{PDMSw}} \quad (4)$$

where, k_a ($m_w^3/m_{PDMS}^3 s^{-1}$) and k_d (s^{-1}) are the absorption and the desorption rate constants, respectively; D_w is aqueous diffusion coefficient of the solute in water (m^2/s) which is calculated using molecular weight (Table 1), V_{PDMS} is the volume of PDMS (m^3), A is the interface area (m^2), and δ_w is the ABL thickness (in m) which is set to 12.5 μm as reported in the literature [54].

Furthermore, various environmental variables, such as temperature, organic matter, minerals, and salts, can also affect the accurate measurement of K_{PDMSw} [60]. Thus, the variables considered in this study were temperature, DOM, and ionic strength variation (see details in Text S3) at different magnitudes under environmental relevance, as suggested elsewhere [63–65]. Each experiment was conducted in triplicate.

2.3. Field application of PDMS passive sampler

Passive sampler deployment was carried out in the Wolha River on July 19–26 2022 at Jochiwon-eup, Sejong-si, South Korea. The passive sampler was prepared using a pre-cleaned PDMS sheet (36-mm × 12-mm × 1-mm) sandwiched between two stainless steel frames, and the frames were clipped with nalclips. Then, the passive sampler was tied with a wire and deployed for 7 days by placing it approximately 20 cm below the water surface. Sampling was performed in triplicate. We have prepared five sets of five different kinds of PDMS passive samplers (i.e., 0.1 mm thick PDMS (Korea), 0.1 mm thick PDMS (Japan), 0.1 mm thick PDMS (USA), 0.81 mm thick PDMS (USA), and 1 mm thick PDMS (Korea)). Each set of samplers consisted of five types of PDMS with three replicates, that is, 15 PDMS samplers per set. Five sets of PDMS samplers were deployed in the surface water at five different locations of the river (Fig. 1). As such, the first set of samples was deployed upstream (before the confluence of the river with wastewater effluent), and the second set was deployed at the confluence of wastewater effluent and river. The third, fourth, and fifth sets of passive samplers were deployed downstream of the river following second set (about 250 m distance between each set of samplers, total distance of ~1000 m). The samplers were deployed for one week. Furthermore, field control samplers from the same preparation batch were used to evaluate possible background contamination during cleaning, transportation, extraction, and analysis. The control samplers were then stored in aluminum foil, brought to the laboratory, and kept for 7 days in at ambient laboratory temperature for seven days. After seven days, the field and control samplers were retrieved, rinsed with DI water and tissue, and extracted for phthalate concentration.

2.4. Extraction and analysis of phthalates

The PAEs in PDMS were extracted ultrasonically [22] and analyzed

Table 1
Summary of logarithm of PDMS-water partition coefficients (log K_{PDMSw}) for 10 phthalates measured in this study, calculated enthalpy of partitioning, aqueous diffusion coefficients, and literature log K_{ow} and log K_{pw} values.

Phthalate	Abbreviation	Molecular weight (g/mol)	[a] D_w (m^2s^{-1})	[b] log K_{ow}	[c] log K_{PDMSw} (This study)	[d] log K_{pw} (Smedes, 2018)	[e] ΔH (KJ/mole)
Dimethyl phthalate	DMP	194.18	6.41	1.60	0.84 ± 0.05[f]	2.54	-13.22
Diethyl phthalate	DEP	222.24	5.82	2.47	1.62 ± 0.07[f]	3.23	-14.42
Diisobutyl phthalate	DIBP	278.34	4.96	4.11	3.95 ± 0.20	4.03	-31.24
Dibutyl phthalate	DBP	278.34	4.96	4.50	4.03 ± 0.18	4.64	-33.52
Benzyl butyl phthalate	BBP	312.36	4.57	4.73	4.22 ± 0.17	5.20	-40.91
Di-n-pentyl phthalate	DNPP	306.40	4.64	5.62	4.98 ± 0.16	NA	-38.34
Dicyclohexyl phthalate	DCP	330.42	4.39	6.20	4.77 ± 0.14	5.67	-36.35
Di(2-ethylhexyl) phthalate	DEHP	390.56	3.90	7.60	5.93 ± 0.36	4.61	-39.72
Di-n-octyl phthalate	DNOP	390.56	3.90	8.10	5.68 ± 0.13	6.07	-30.77
Diisononyl phthalate	DINP	418.61	3.71	9.37	5.87 ± 0.35	5.11	-40.20

[a] D_w: aqueous diffusion coefficient calculated using Eq. S7 (Supplementary Material); [b] log K_{ow}: logarithm of 1-octanol/water partition coefficient obtained from literature [70]; [c] log K_{PDMSw}: logarithm of PDMS/water partition coefficient obtained in this study (n = 3–4); [d] log K_{pw}: logarithm of polymer (silicone)/water partition coefficient from the literature [60]; [e] obtained from log K_{PDMSw} vs 1/T curves; [f] measured by shaking method; NA: data not available.

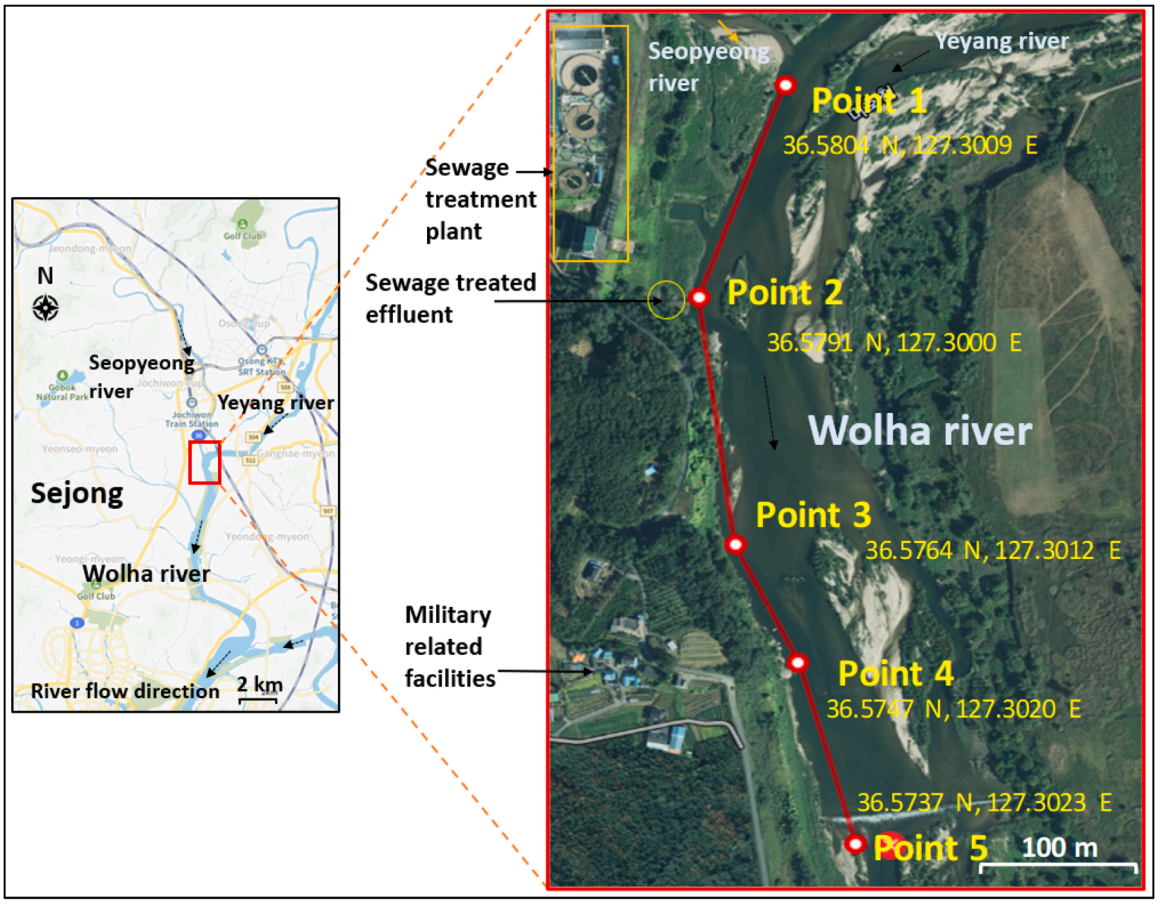


Fig. 1. Geographical map of Sejong city (South Korea) showing different sampling sites located in the Wolha river site. The sampling locations in river are labeled Point 1 to Point 5, and wastewater is released from the sewage treatment plant to the river at Point 2.

using a gas chromatograph (Agilent 6890 N GC) coupled with a mass spectrometer (Agilent 5973 MSD) and DB–5 capillary column (Agilent, 30 m × 250 μm × 0.25 μm), as described elsewhere (Text S4). As suggested in literatures, benzyl benzoate (BB) was used as the internal standard for phthalate analysis in PDMS and calibration standard samples, which is considered as universal internal standard for analytical determination of phthalates in environmental samples [66–69]. A typical chromatogram for 10 phthalates and benzyl benzoate in TIC mode is shown in Fig. S2. Table S2 presents the retention time, qualifying, and quantification of ions for each phthalate and non-phthalate. The overall percentage recoveries of different phthalates in PVC CRM using this method ranged from 84.2 % to 100.8 %, which are obtained from the relationships between certified and measured values (see Table S3). The initial concentration of PAEs in the donor PDMS disk ranged between 684.9 (DMP) and 115,500 (DINP) mmol m^{-3} (see Table S4 for all PAEs). In addition, the mass balance between the donor and acceptor was mostly between 80.9 ± 1.5 % and 103.1 ± 4.2 % (Table S5). The calibration blank and method blank (clean PDMS) samples were also analyzed routinely and no PAEs were detected, which confirmed no background contamination during analysis.

2.5. Analysis

The data were entered into Excel file (Microsoft Office Excel, 2019)

to calculate descriptive statistics (mean and standard deviation, SD). These data were used in one-way ANOVA analysis, and the significant differences of the mean values at $p < 0.05$ were determined using the Tukey (honestly significant difference) test using Origin Pro 8.5 software. Box plot diagrams were created using Origin Pro 8.5.

3. Results and discussion

3.1. Kinetics of phthalates partitioning into PDMS and water

The PAEs released from the donor PDMS to water were measured using acceptor PDMS as a passive sampler. Thus, the phthalates in the acceptor PDMS were monitored as a function of experimental time. Fig S3 shows the concentration of PAEs released from the donor PDMS to the acceptor PDMS over time during the partitioning experiments. The results showed that the concentration of all PAEs in the acceptor PDMS gradually increased with time, suggesting an increase in the PAEs released from the donor PDMS to water over time. However, the release kinetics reached an equilibrium within a certain time interval (48–72 h). To obtain thermodynamic equilibrium between water and PDMS, sufficient experimental time is required [54].

The normal and linearized scaled permeation kinetics from the donor PDMS to the acceptor PDMS disk are presented in Fig. 2 (see Fig. S4 and Fig. S5; Supplementary Material for all the PAEs). The dashed lines in these curves are the best fits at equilibrium using Eqs. 2 and 3, which describe the predicted kinetics of different PAEs. The release kinetics of DMP and DEP using the ABL method are not presented here because they are highly soluble in water compared to other PAEs. The results showed that the $2\,C_{PDMS,acceptor(t)}/C_0$ ratio, which represents the release of phthalates from the donor PDMS to the acceptor PDMS, was higher for lower molecular PAEs than for higher molecular PAEs (Fig. S4). It was found that the $2C_{PDMS,acceptor}/C_0$ value for DIBP, having the lowest K_{PDMSw} using ABL method, was 0.54 at 48 h, whereas it was only 0.0069 for DEHP, which has the highest K_{PDMSw}. A similar trend was observed when the permeation kinetic results of the different phthalates were plotted using a linearized scale [ln $(1–2C_{PDMS,acceptor(t)}/C_0)$ vs. time] (Fig. S5). At equilibrium, the fraction of DIBP and DBP concentration in the acceptor PDMS disks with respect to their initial donor PDMS concentration was more than 25 %, while it was very low for DEHP, DNOP, and DINP (below 0.5 %). The BBP, DCP, and DNPP had moderate acceptor PDMS fractions of 17.8 %, 6.9 %, and 4.9 %, respectively. The low acceptor PDMS concentrations for more hydrophobic PAEs are attributed to the lower water solubility of PAEs with higher molecular weights than that of PAEs with low molecular weights. The increase in carbon number and the presence of branched or cyclic alkyl groups in the phthalate parent structure may contribute to the increase in hydrophobicity of the PAEs derivatives. Overall, it can be said that the sorption of PAEs in PDMS is significantly higher and faster than their desorption into water, and thus PDMS can be used as a passive sampler to determine freely dissolved phthalates in aqueous samples.

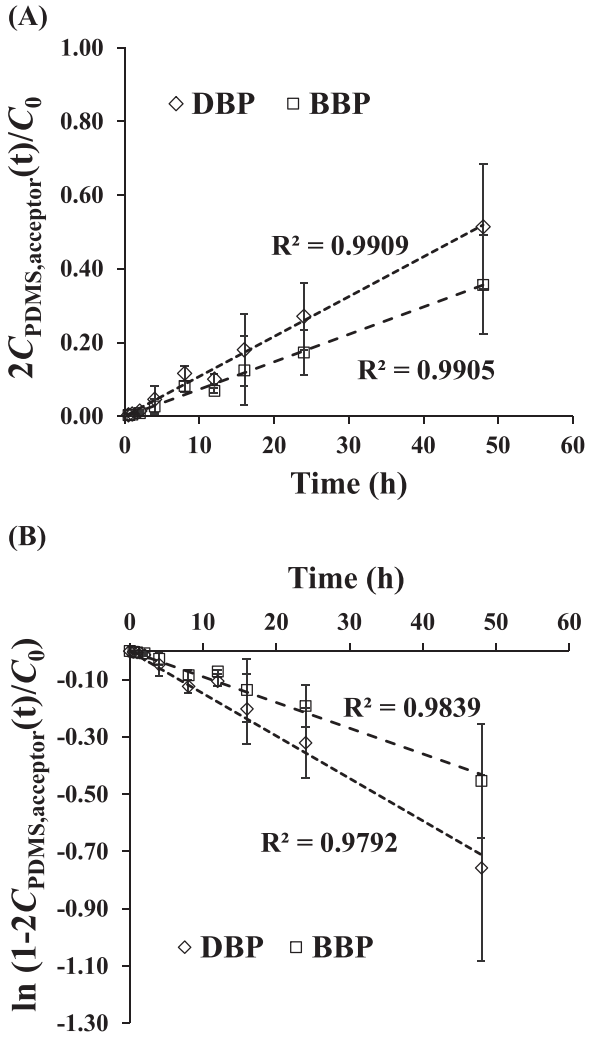


Fig. 2. Permeation kinetics of DBP and BBP as examples using (A) normal scale [$2C_{PDMS,acceptor(t)}/C_0$ Vs time] and (B) linearized scale [ln $(1–2C_{PDMS,acceptor(t)}/C_0)$ Vs time]. Dashed lines denote best fit using Eqs. 2 and 3, respectively, and error bars represent the standard deviation of three replicates (n = 3).

3.2. Partition coefficients of phthalates

In this study, we calculated the PDMS-water partition coefficients (K_{PDMSw}) for different PAEs using kinetic partitioning data and desorption rate constants (k_d) obtained from the ABL permeation method (Eq. 4). The k_d values were estimated from the slope of the linear regression lines obtained from the linearized scale plots of ln $(1 - 2\,C_{PDMS,acceptor(t)}/C_0)$ and time (t) using Eq. 3. In addition, the K_{PDMSw} values for LPAEs with high water solubility (DMP and DEP) were also measured using the conventional shaking method because the K_{PDMSw} values for these PAEs were found to be unexpectedly higher (logarithm of PDMS water partition coefficient, log K_{PDMSw} ~3.50) than the K_{ow} values obtained using the ABL method. For this, a precleaned PDMS disk (6–mm × 1–mm) was introduced into a 4 mL glass vial containing an aqueous solution of DMP and DEP at known concentrations (below water solubility) with zero headspace and placed in an end-over-end tumbler at 30 rpm. After 48 h, the PDMS was analyzed for PAEs, and the K_{PDMSw} was calculated using their concentrations in PDMS and water by assuming no mass loss during experiment. Using the conventional shaking method, the K_{PDMSw} values for DMP and DEP were lower than the log K_{ow} values, indicating that the ABL method may overestimate the K_{PDMSw} values for less hydrophobic chemicals (log K_{ow}<2.50) tested in this study. The log K_{PDMSw} values determined in this study, calculated aqueous diffusion coefficients (D_w), logarithm of 1-octanol water coefficient (log K_{ow}) [59], and logarithm of polymer (silicone)-water partition coefficients (log K_{pw}) [60] from the literature for different phthalates are summarized in Table 1.

The correlation between log K_{PDMSw} obtained from this study and log K_{ow} are presented in Fig. 3 and Fig. S6. A linear correlation was obtained when the data were plotted between log K_{ow} and log K_{PDMSw}, and the slope of the linear regression was close to unity (~0.85) with a good correlation coefficient value (R^2 >0.94) for the first eight PAEs (log K_{ow}<7.60); then, it slightly deviated (for DNOP and DINP with high log Kow>8.10) from the ideal linear regression line and showed a non-linearity. The experimental log K_{PDMSw} values for PAEs generally increase from 0.84 (DMP) to 5.93 (DEHP) with increasing log K_{ow} up to eight PAEs investigated in this study (log K_{ow} = 7.60). Thereafter, the log K_{PDMSw} remained almost constant for DNOP (5.68) and DINP (5.87).

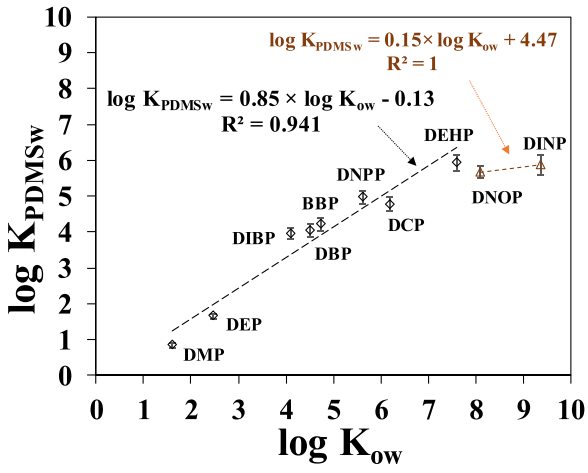


Fig. 3. Relationship between logarithm of log K_{PDMSw} obtained in this study and log K_{ow} reported in the literatures for different phthalates. Error bars represent the standard deviation of 3–4 replicates, and solid lines represent the linear regression models.

This may be due to the highly hydrophobic nature of DEHP, DNOP, and DINP, with log K_{ow} values of 7.60, 8.10, and 9.37, respectively. They also have similar water solubility (<2.5 × 10^{-5} g/L), vapor pressure (<5.4 × 10^{-7} mmHg), and molecular mass (390.6–418.6 g/mole) (Table S1), which may result in similar partitioning into PDMS and water. The presence of branched or cyclic alkyl groups in high-molecular-weight phthalates may contribute to the increase in their hydrophobicity. In addition, Fig. S6 shows a good logarithmic correlation (R^2 >0.97) when the log K_{ow} values were plotted with log K_{PDMSw} for all PAEs tested in this study. Using these simple regression curves, the PDMS-water partition coefficients for various phthalates (other than 10 PAEs tested in this study) or other plasticizers could be calculated. For the practical purpose, this study suggests that the logarithmic regression curve could be considered when estimating the K_{PDMSw} and thereby aqueous concentration of a wide range of PAEs (log K_{ow} =1–10 or more), whereas the linear regression lines could be used if the PAEs range between 1 and 8. The greater the affinity of target chemical (more hydrophobic PAEs) to the PDMS sampler, the greater the partition coefficient between PDMS and water, and the greater capacity of the PDMS for that chemical.

Furthermore, this study also plotted log K_{PDMSw} obtained in this study versus literature log K_{pw}, log K_{pw} versus log K_{ow} for phthalates, and the logarithm of partition coefficients of PAHs between PDMS and 1:1 methanol-water mixture (log $K_{PDMS/m-w}$) versus log K_{ow} reported in various studies [60,71] (see Fig. S7). When the literature partition coefficient data were plotted against log K_{ow}, the slopes were found to be much lower (~0.3) than those obtained in this study (Fig. S7) [60,71]. In the ABL method, DMP and DEP showed unexpectedly higher log K_{PDMSw} values (3.46–3.58) than log K_{ow} although all other phthalates had smaller log K_{PDMSw} values than log K_{ow}. However, the partitioning of DMP and DEP using a conventional shaking method were calculated as 0.84 and 1.62, respectively, and these results are more likely. This indicates that the ABL method is limited to PAEs or other organic chemicals with log K_{ow} values of ≥3. Nam et al. [64] found that the partition coefficients between dissolved BTEX (benzene, toluene, ethylbenzene, xylene) and PDMS were lower than K_{ow}, and those values for polyoxymethylene (POM) were higher than K_{ow} in the case of less hydrophobic chemicals (i.e., K_{ow}<3). Smedes also obtained higher polymer water partition coefficients (log K_{pw}) for DMP and DEP than for log K_{ow} [60]. There is also a linear relationship between log K_{PDMSw} obtained in this study and log K_{pw} reported in the literature, with a relatively lower correlation coefficient (Fig. S7). The kinetic ABL permeation method may overestimate the K_{PDMSw} values for compounds with log K_{PDMSw} < 4.0 [54]. However, ABL permeation method is advantageous over conventional methods; for e.g., with this method, the equilibration time is shortened (48–72 h) even for highly hydrophobic chemicals (log K_{ow} up to 9.37 tested in this study), and a very small water volume (160 μL) is sufficient to obtain the equilibrium partitioning relationships between the passive sampler (i.e., PDMS) and water [54]. Conventional methods generally require large volume of water (up to liters) and long experimental time (up to months) to attain an equilibrium for hydrophobic chemicals [60].

Table S6 lists the partitioning of PAEs between water and the different types of PDMS obtained from various suppliers using the conventional shaking method. In this method, a PDMS disk preloaded with PAEs (6-mm×1-mm, Korea, same as in the ABL method) and a precleaned PDMS from different companies from Korea, Japan and USA (see Table S6; 6-mm diameter but 0.1, 0.81, and 1-mm thick) were kept in a 20-mL glass vial containing pure water with zero headspace and shaken in a tumbler for 185 h at 30 rpm and 25 °C. K_{PDMSw} was calculated using the PAE concentration in the acceptor, donor, and preloaded PDMS disks. Fig. S8 shows good linear correlations (R^2 >0.99, slope range 0.86–1.04) between the partition constants obtained from the shaking method for all PDMS and ABL permeation methods. The partition coefficient values can be used for the determination of phthalate concentrations in real environmental samples using PDMS as a passive sampler.

3.3. Factors affecting partitioning of PAEs

3.3.1. Effect of temperature

In this study, we evaluated the effect of temperature on the partition coefficients of phthalates. The K_{PDMSw}, in general, KPDMSw decreases with an increase in temperature within the experimental temperature range tested (Table S7). The shift in log K_{PDMSw} values showed that the distribution of phthalates between the PDMS phase and the aqueous phase is temperature-dependent. The log K_{PDMSw} values for different PAEs were increased by 0.07–0.25 log units when the temperature was decreased from 25 ℃ to 15 ℃; a further decrease in temperature from 15 to 4 ℃ resulted in an increase in log K_{PDMSw} values by 0.11–0.48 log units. Similarly, when the temperature was increased from 25° to 40°C, the log K_{PDMSw} value for various phthalates decreased by 0.10–0.46 log units. The overall variation in log K_{PDMSw} in the temperature range of 4–40 °C was relatively more pronounced for the higher molecular phthalates (>0.7 units) than for lower molecular phthalates (<0.7 units). This suggest that partitioning of PAEs between PDMS and water is more affected by temperature for the PAEs with higher number of carbon atoms in the chain, and highly hydrophobic nature, while that for the PAEs with lower number of carbon atoms (e.g. DMP, DEP) are less affected by temperature. The results might imply that the partitioning of less hydrophobic PAEs between PDMS and water could be occurred with similar extent regardless of temperature. With increase in temperature, the aqueous solubility of PAE molecules is increased due to increase in kinetic energy of molecules which allows the water molecules to more effectively dissolve the PAE molecules and thereby decrease in K_{PDMSw} values. But, the less hydrophobic PAE molecules would have higher solubility at all temperature range tested. Similar results have been reported in the literature, in which the partition coefficients of BTEX between the polymer and environmental phases decreased with temperature [64]. The results of this study can be used during the actual sampling of environmental samples to obtain accurate data by extrapolating the K_{PDMSw} values at different temperatures of interest.

The enthalpy for the partitioning of PAEs in PDMS and water was also calculated within the experimental temperature range, and the results are presented in Table 1 and S7. The enthalpy (ΔH) of the partitioning process was estimated from the slope of the linear regression lines (Eq. S8) plotted between log K_{PDMSw} and the inverse of temperature (1/T), with a good correlation coefficient (R^2 = 0.87–0.99) for all PAEs

(Fig. S9). The thermodynamic data showed that the chemical partitioning of PAEs in PDMS is exothermic, which involves the release of energy, as proven by the decrease in K_{PDMSw} with increasing temperature [64]. In general, the enthalpy of phthalate partitioning is increased (ranged from −13.2 to −40.9 KJ/mole) with the molecular weight of compounds, and those values for DMP and DEP are found to be lowest i.e., −13.2 and − 14.4 KJ/mole, respectively. The large change in enthalpy for the PAEs indicates that partitioning is essentially an enthalpy-driven process [72]. This shows that the water released from the hydrophobic environment to the bulk water is due to an enthalpy-driven hydrophobic association [64,73]. The contribution of enthalpy-driven partitioning process for large hydrophobic molecules is higher as compared to the small molecules [74]. The enthalpy change is higher for more hydrophobic PAEs, indicating that more energy is released when the partitioning of highly hydrophobic PAEs occurs between water and PDMS. This phenomenon is lower for less hydrophobic PAEs (e.g., DMP and DEP) because they have a low enthalpy change due to their higher water solubility.

3.3.2. Effect of dissolved organic matter

The DOM present in soil or sediment matrices in the form of proteins and membrane vesicles can reduce the freely dissolved concentrations of hydrophobic organic chemicals (HOCs), thereby altering the partitioning process because they can sorb HOCs [64]. Many studies have explored the interaction between DOM and PDMS [64,75,76], but the interaction between DOM-containing PAEs and PDMS remains unexplored. This study found that the presence of DOM generally reduced the freely dissolved aqueous concentration of all PAEs to a small extent, thereby slightly increasing the K_{PDMSw} values. Table S8 shows that the log K_{PDMSw} values for all PAEs increased with DOM concentration at certain DOM levels, and a further increase in DOM did not significantly facilitate log K_{PDMSw}. It was found that the log K_{PDMSw} for less hydrophobic PAEs (log K_{ow} 4–5) increased from 0 to 1 mg/L DOM and that for more hydrophobic PAEs (log $K_{ow} > 5$) increased up to 10 mg/L. In addition, the increase in log K_{PDMSw} was more pronounced for the more hydrophobic PAEs (DEHP, DNOP, and DINP) than for the less hydrophobic PAEs. In contrast, the log K_{PDMSw} values for DMP and DEP decreased slightly when DOM was added to the water and remained constant within the DOM concentration tested (see Table S8). Overall, the log K_{PDMSw} values did not change significantly with the DOM concentration tested in this study (0.1–10 mg/L).

Nam et al. also found that the presence of DOM did not significantly affect the PDMS or POM-water partition coefficients of less hydrophobic compounds (log $K_{ow} < 3$) [64]. It has been reported that the release of DBP from PVC to aqueous solutions increases with fulvic acid concentration [22]. However, the sorption of PAEs in the acceptor PDMS disk may have been slightly impeded by the presence of DOM, even though the PAE desorption from the donor PDMS disk might have increased to a small extent. This is because DOM has a strong ability to bind hydrophobic chemicals, thereby reducing its freely dissolved aqueous concentration [75]. Further investigation is needed to clarify the effect of DOM on the partitioning of PAEs in PDMS and water, with or without PDMS as a passive sampler (i.e., acceptor PDMS).

3.3.3. Effect of ionic strength

Salt is also an important matrix present in soil, and the thermodynamic equilibrium is often affected by the activity of chemicals in the salt solution, resulting in the alteration of the equilibrium partitioning constants [64]. Thus, this study also investigated the effect of ionic strength on the partitioning of PAEs between PDMS and water, and the results are presented in Table S9. In general, the log K_{PDMSw} was increased when the ionic strength increased from 0 to 0.5 M and then remained almost constant. However, the log K_{PDMSw} values for DMP and DEP slightly decreased when a low amount of NaCl was added to water (up to 0.01 M) and slightly increased with increasing salt concentration (1.0 M). Results showed that the log K_{PDMSw} values for PAEs were increased by 0.68–1.40 log units (except DMP and DEP) with the increase in ionic strength tested in this study (0–1 M NaCl). Similar results have been reported in the literature, in which the partition coefficients of organic chemicals increased with ionic strength [64,77]. This may be due to the salting-out effect, which causes an increase in the hydrophobicity of the chemicals, and the hydrophobic compounds tend to be excluded from the aqueous phase by associating more with ionic species [77].

Moreover, the Setschenow constant (k_s) values, the measure of the change in aqueous solubility as a function of ionic strength, were calculated and are presented in Table S10. There was no strong correlation between k_s and K_{PDMSw} values; however, when only considering more hydrophobic PAEs (except DMP and DEP), the k_s values decreased with increasing log K_{PDMSw}, suggesting a smaller effect of ionic strength on more hydrophobic PAEs. This may be due to the weaker interaction of more hydrophobic PAEs in the aqueous solution. In addition, the k_s values (0.18–0.58) calculated in this study are found in the range of data reported in various studies [64,77].

3.3.4. Relation between log K_{PDMSw} and physicochemical properties of PAEs

The relationships between the partitioning coefficients of the various PAEs in PDMS and water (K_{PDMSw}) and their physicochemical properties were also studied (see Fig. S10). In general, log K_{PDMSw} was found to decrease with increasing vapor pressure and solubility in water. A similar trend was observed when plotting log K_{PDMSw} against the desorption rate constant and aqueous diffusion coefficient. However, a reverse trend was observed when log K_{PDMSw} was plotted against the molecular mass of phthalates, such that the partitioning of phthalates in PDMS water increased with their molar mass. An increase in molar mass generally increases the hydrophobicity of the chemical, thereby increasing the partition coefficients. Moreover, no clear correlation was found between log K_{PDMSw} and density/boiling points.

3.3.5. Environmental implication of this study: passive sampling using PDMS

The concentration of target contaminants is usually very low, so that it is difficult to detect them with existing analytical techniques (e.g. liquid-liquid extraction or solid phase extraction) unless a large sample (water) volume is extracted with sample preconcentration. In addition, the contaminant concentration measured by passive samplers are found to be similar to that obtained from traditional methods, with good agreement and less variability [44–47,64]. This study also demonstrated the experimental analysis of plasticizers (PAEs or non-PAEs) to test the applicability of PDMS for passive sampling in real environmental fields. Five different types of PDMS passive samplers were deployed in the Wolha River at five sampling locations (Fig. 1), and the concentrations of plasticizers sorbed by PDMS were measured. The freely dissolved concentrations of the plasticizers at the river sites are presented in Fig. 4. Six types of plasticizers were found in the field sample, of which five were PAEs (i.e., DMP, DBP, BBP, DEHP, and DNOP) and one was a non-phthalate plasticizer, that is, di(2-ethylhexyl) terephthalate (DOTP). The concentration of DOTP was estimated from the partition coefficient obtained from the trendline equation of log K_{PDMSw} versus log K_{ow} plot with the literature log K_{ow} value [70] (see Fig. 3). DMP was detected at the highest concentration (μg/L) in river water because it is highly soluble in water, whereas other chemicals were found at low concentrations (ng/L), followed by DBP≈BBP, DEHP, and DOTP≈DNOP. The ranges of plasticizer concentrations detected in river water are presented in Table S11. The range of DBP concentration in this study was found to be similar with the Asan Lake (Korea) concentration reported in a literature [7]. In the present study, DEHP was found in lower concentration, while DMP and DNOP concentrations are higher than that in the literature. Interestingly, the trend for all chemicals in the river water was found to be similar, and the concentration suddenly increased when moving from upstream of the river (point 1) to sampling

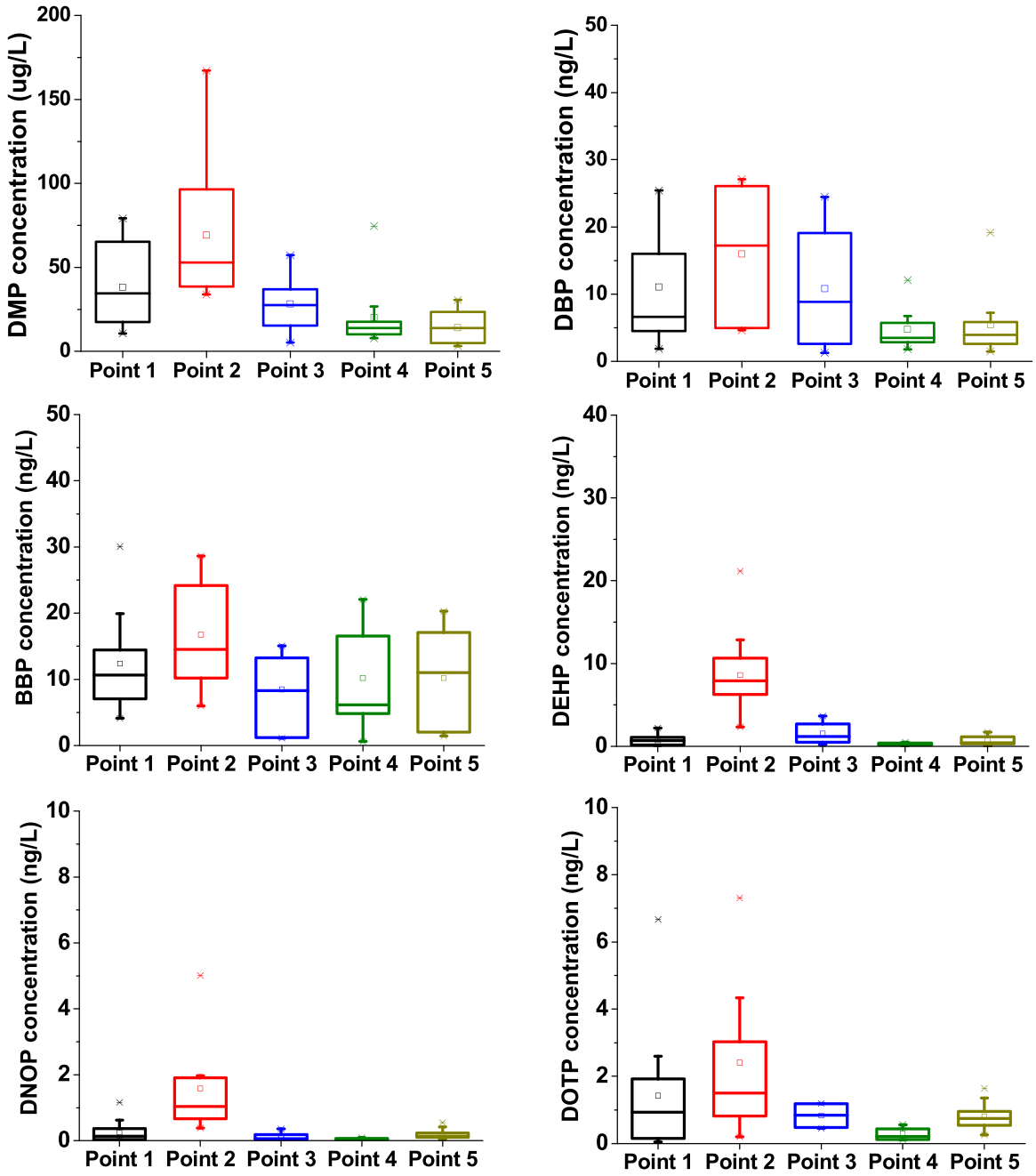


Fig. 4. Concentration of plasticizers measured in surface river water at five sampling points (as shown Fig. 1) using five different types of PDMS with triplicate sampler (n = 15) as a passive sampler at Jochiwon, Sejong-si, Korea.

point 2 and then gradually decreased downstream from point 2 to point 4 and remained almost constant at point 5 with a very low concentration. The highest change (10-folds) from point 1–2 was found for DEHP, which showed that DEHP is the most widely used plasticizer and is thus released from effluent at higher concentrations. This is because the wastewater produced from the sewage treatment plant was released at sampling point 2, where the highest concentration of chemicals was detected; therefore, the wastewater was diluted by upstream river water.

The spatial distributions of total plasticizers concentration ($\sum_6$ plasticizers) in the Wolha river water are shown in Fig. 5. The $\sum_6$ plasticizers concentrations in river water tend to increase 2-folds when moving from upstream (point 1) to the confluence with sewage treatment plant effluent (point 2) and then gradually decreased moving to downstream (point 2 to point 5) where some tributaries or channels were flowing into the river from the agricultural land. The results indicate that the effluents from the sewage treatment plant located in the point 2 might be the potential sources of plasticizers in water. Overall, the results of this study showed that the aqueous concentration of plasticizers could be measured at very low concentrations (even below ng/L) by a simple passive sampling method using PDMS and partition coefficient values for chemicals.

This study provides details on the kinetics and thermodynamic equilibrium partitioning of hydrophobic compounds (PAEs) on an equilibrium sampler (PDMS) under various environmental variables. The results of this study can be used to estimate the kinetics of plasticizer released from products (e.g., PVC microplastics) into water. Accurate determination of the fate and bioavailability of PAEs in environmental samples (such as surface and sediment pore waters), along with risk assessment, can be performed by applying PDMS as a passive sampler deployment. In future research, the chemical partitioning of various

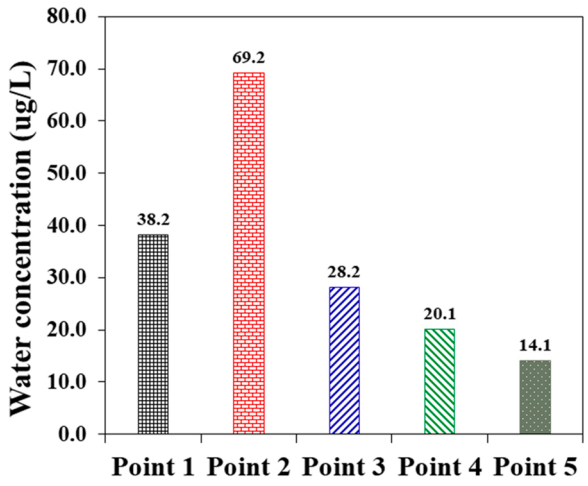


Fig. 5. Spatial distribution of $\sum_6$ plasticizers concentration in river water using PDMS passive sampler. Sewage treated effluent being is released into Wolha river at point 2.

plasticizers (e.g., phthalates or non-phthalates) in PDMS (or PVC) and water could be estimated.

4. Conclusions

This study investigated the chemical partitioning of hydrophobic PAEs in PDMS and water over a few days using a kinetic ABL permeation method. A good linear correlation was obtained between the experimental log K_{PDMSw} values and the literature log Kow values ($R^2 > 0.94$). In addition, log K_{PDMSw} values for different environmental variables (temperature, DOM, and ionic strength) were estimated. The partitioning of PAEs in PDMS-water is decreased with increasing temperature, and the process was found to be exothermic. In general, the salt concentration facilitates the log K_{PDMSw} values, whereas DOM has a smaller effect on partitioning. In addition, the log K_{PDMSw} values correlated with various physicochemical properties of phthalates. The partitioning results obtained in this study were used to evaluate the concentration of plasticizers at real sites (rainwater drainage effluent and surface river water) using PDMS as a passive sampling device. The results of this study can be used to estimate freely dissolved concentrations of hydrophobic compounds in environmental samples. In the future, phthalate released from plastic products to the environment and exposure/toxicity assessment based on these compounds can be performed using PDMS as a passive sampler.

CRediT authorship contribution statement

Rishikesh Bajagain: Conceptualization, Methodology, Formal analysis, Data curation, Investigation, Writing – original draft, Visualization; **Pil-Gon Kim:** Methodology; **Jung-Hwan Kwon**: Methodology, Writing - review & editing; **Yongseok Hong**: Conceptualization, Writing - review & editing, Supervision; Validation; Funding acquisition, Project administration; Resources. All authors have approved the final article.

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.

Acknowledgements

This research was supported by Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education, South Korea (grant number: 2021R1I1A3058765) and by Subsurface Environment Management Projects through the Korea Environmental Industry and Technology Institute funded by the Ministry of Environment, South Korea (Project Number: 2020002440005).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2023.130933.

References

[1] Grindler, N.M., Vanderlinden, L., Karthikraj, R., Kannan, K., Teal, S., Polotsky, A.J., et al., 2018. Exposure to phthalate, an endocrine disrupting chemical, alters the first trimester placental methylome and transcriptome in women. Sci Rep 2018 81 (8), 1–9. https://doi.org/10.1038/s41598-018-24505-w.

[2] Gao, D.W., Wen, Z.D., 2016. Phthalate esters in the environment: a critical review of their occurrence, biodegradation, and removal during wastewater treatment processes. Sci Total Environ 541, 986–1001. https://doi.org/10.1016/J.SCITOTENV.2015.09.148.

[3] Hu, R., Zhao, H., Xu, X., Wang, Z., Yu, K., Shu, L., et al., 2021. Bacteria-driven phthalic acid ester biodegradation: current status and emerging opportunities. Environ Int 154, 106560. https://doi.org/10.1016/J.ENVINT.2021.106560.

[4] V. Vinod, A.P.S., Harathi, P.B., 2022. A critical review on extraction and analytical methods of phthalates in water and beverages. J Chromatogr A 1675, 463175. https://doi.org/10.1016/J.CHROMA.2022.463175.

[5] Sugeng, E.J., Symeonides, C., O'Hely, M., Vuillermin, P., Sly, P.D., Vijayasarathy, S., et al., 2020. Predictors with regard to ingestion, inhalation and dermal absorption of estimated phthalate daily intakes in pregnant women: The Barwon infant study. Environ Int 139, 105700. https://doi.org/10.1016/J.ENVINT.2020.105700.

[6] Berger, K.P., Kogut, K.R., Bradman, A., She, J., Gavin, Q., Zahedi, R., et al., 2018. Personal care product use as a predictor of urinary concentrations of certain phthalates, parabens, and phenols in the HERMOSA study, 29 J Expo Sci Environ Epidemiol 2018 (291), 21–32. https://doi.org/10.1038/s41370-017-0003-z.

[7] Lee, Y.M., Lee, J.E., Choe, W., Kim, T., Lee, J.Y., Kho, Y., et al., 2019. Distribution of phthalate esters in air, water, sediments, and fish in the Asan Lake of Korea. Environ Int 126, 635–643. https://doi.org/10.1016/J.ENVINT.2019.02.059.

[8] Gkrillas, A., Dirven, H., Andreassen, M., Papadopoulou, E., Hjertholm, H., Husøy, T., 2020. Risk assessment of phthalates based on aggregated exposure from foods and personal care products and comparison with biomonitoring data. EFSA J 18, e181105. https://doi.org/10.2903/J.EFSA.2020.E181105.

[9] Li, X., Zeng, Z., Chen, Y., Xu, Y., 2004. Determination of phthalate acid esters plasticizers in plastic by ultrasonic solvent extraction combined with solid-phase microextraction using calix[4]arene fiber. Talanta 63, 1013–1019. https://doi.org/10.1016/J.TALANTA.2004.01.006.

[10] Hahladakis, J.N., Velis, C.A., Weber, R., Iacovidou, E., Purnell, P., 2018. An overview of chemical additives present in plastics: Migration, release, fate and environmental impact during their use, disposal and recycling. J Hazard Mater 344, 179–199. https://doi.org/10.1016/J.JHAZMAT.2017.10.014.

[11] B. Amato, S. Karl, C. Ng, Phthalate plasticizers, (2001). http://wwwcourses.sens.buffalo.edu/ce435/2001ZGu/Phthalate_Plasticizers/PhthalatePlasticizersReport.htm (accessed July 23, 2022).

[12] M. Gilbert, Relation of Structure to Chemical Properties, in: M. Gilbert (Ed.), Brydson's Plast. Mater. Eighth Ed., Eighth Edi, Butterworth-Heinemann, 2017: pp. 75–102. https://doi.org/10.1016/B978-0-323-35824-8.00005-0.

[13] Lindström, A., Hakkarainen, M., 2006. Environmentally friendly plasticizers for poly(vinyl chloride)—improved mechanical properties and compatibility by using branched poly(butylene adipate) as a polymeric plasticizer. J Appl Polym Sci 100, 2180–2188. https://doi.org/10.1002/APP.23633.

[14] A. Lindström, Environmentally friendly plasticizers for PVC: Improved material properties and long-term performance through plasticizer design, Fiber- och polymerteknologi Fibre and Polymer Technology, 2007.

[15] Runkel, A.A., Mazej, D., Snoj Tratnik, J., Tkalec, Ž., Kosjek, T., Horvat, M., 2022. Exposure of men and lactating women to environmental phenols, phthalates, and DINCH. Chemosphere 286, 131858. https://doi.org/10.1016/J.CHEMOSPHERE.2021.131858.

[16] Qadeer, A., Kirsten, K.L., Ajmal, Z., Jiang, X., Zhao, X., 2022. Alternative plasticizers as emerging global environmental and health threat: another regrettable substitution? Environ Sci Technol 56, 1482–1488. https://doi.org/10.1021/acs.est.1c08365.

[17] Y. Wang, H. Qian, Phthalates and Their Impacts on Human Health, Healthc. 2021, Vol. 9, Page 603. 9 (2021) 603. https://doi.org/10.3390/HEALTHCARE9050603.

[18] Nehring, A., Bury, D., Ringbeck, B., Kling, H.W., Otter, R., Weiss, T., et al., 2020. Metabolism and urinary excretion kinetics of di(2-ethylhexyl) adipate (DEHA) in

four human volunteers after a single oral dose. Toxicol Lett 321, 95–102. https://doi.org/10.1016/J.TOXLET.2019.12.006.
[19] Vieira, M.G.A., Da Silva, M.A., Dos Santos, L.O., Beppu, M.M., 2011. Natural-based plasticizers and biopolymer films: a review. Eur Polym J 47, 254–263. https://doi.org/10.1016/J.EURPOLYMJ.2010.12.011.
[20] LCSP, Phthalates and Their Alternatives: Health and Environmental Concerns, Lowell, MA 01854, 2011. https://www.sustainableproduction.org/downloads/PhthalateAlternatives-January2011.pdf.
[21] Jambeck, J.R., Geyer, R., Wilcox, C., Siegler, T.R., Perryman, M., Andrady, A., et al., 2015. Plastic waste inputs from land into the ocean. Sci (80-) 347, 768–771. https://doi.org/10.1126/science.1260352.
[22] Yan, Y., Zhu, F., Zhu, C., Chen, Z., Liu, S., Wang, C., et al., 2021. Dibutyl phthalate release from polyvinyl chloride microplastics: influence of plastic properties and environmental factors. Water Res 204, 117597. https://doi.org/10.1016/J.WATRES.2021.117597.
[23] Clausen, P.A., Liu, Z., Kofoed-Sørensen, V., Little, J., Wolkoff, P., 2012. Influence of temperature on the emission of Di-(2-ethylhexyl)phthalate (DEHP) from PVC flooring in the emission cell FLEC. Environ Sci Technol 46, 909–915. https://doi.org/10.1021/ES2035625.
[24] Thomson, B., 2009. Exposure to endocrine-disrupting chemicals in food. Endocr-Disrupting Chem Food 211–258. https://doi.org/10.1533/9781845695743.3.211.
[25] Navarro, R., Perrino, M.P., Tardajos, M.G., Reinecke, H., 2010. Phthalate plasticizers covalently bound to PVC: plasticization with suppressed migration. Macromolecules 43, 2377–2381. https://doi.org/10.1021/MA902740T.
[26] Peijnenburg, W.J.G.M., 2008. Phthalates. Encycl. Ecol 2733–2738. https://doi.org/10.1016/B978-008045405-4.00419-5.
[27] Gao, D., Li, Z., Wang, H., Liang, H., 2018. An overview of phthalate acid ester pollution in China over the last decade: Environmental occurrence and human exposure. Sci Total Environ 645, 1400–1409. https://doi.org/10.1016/J.SCITOTENV.2018.07.093.
[28] Net, S., Sempéré, R., Delmont, A., Paluselli, A., Ouddane, B., 2015. Occurrence, fate, behavior and ecotoxicological state of phthalates in different environmental matrices. Environ Sci Technol 49, 4019–4035. https://doi.org/10.1021/ES505233B.
[29] Sajiki, J., Yonekubo, J., 2003. Leaching of bisphenol A (BPA) to seawater from polycarbonate plastic and its degradation by reactive oxygen species. Chemosphere 51, 55–62. https://doi.org/10.1016/S0045-6535(02)00789-0.
[30] Hou, H., Min, Y., Liu, X., Wang, P., Zhou, Z., Liu, D., 2021. Occurrence and migration of phthalates in adhesive materials to fruits and vegetables. J Hazard Mater 418, 126277. https://doi.org/10.1016/J.JHAZMAT.2021.126277.
[31] Sumner, N.R., Guitart, C., Fuentes, G., Readman, J.W., 2010. Inputs and distributions of synthetic musk fragrances in an estuarine and coastal environment; a case study. Environ Pollut 158, 215–222. https://doi.org/10.1016/J.ENVPOL.2009.07.018.
[32] Yates, K., Davies, I., Webster, L., Pollard, P., Lawton, L., Moffat, C., 2007. Passive sampling: partition coefficients for a silicone rubber reference phase. J Environ Monit 9, 1116–1121. https://doi.org/10.1039/B706716J.
[33] Booij, K., Hoedemaker, J.R., Bakker, J.F., 2003. Dissolved PCBs, PAHs, and HCB in pore waters and overlying waters of contaminated harbor sediments. Environ Sci Technol 37, 4213–4220. https://doi.org/10.1021/ES034147C.
[34] Serôdio, P., Nogueira, J.M.F., 2006. Considerations on ultra-trace analysis of phthalates in drinking water. Water Res 40, 2572–2582. https://doi.org/10.1016/J.WATRES.2006.05.002.
[35] Jara, S., Lysebo, C., Greibrokk, T., Lundanes, E., 2000. Determination of phthalates in water samples using polystyrene solid-phase extraction and liquid chromatography quantification. Anal Chim Acta 407, 165–171. https://doi.org/10.1016/S0003-2670(99)00829-6.
[36] Hadjmohammadi, M.R., Fatemi, M.H., Taneh, T., 2012. Coacervative extraction of phthalates from water and their determination by high performance liquid chromatography. J Iran Chem Soc 2011 81 (8), 100–106. https://doi.org/10.1007/BF03246206.
[37] Salazar-Beltrán, D., Hinojosa-Reyes, L., Ruiz-Ruiz, E., Hernández-Ramírez, A., Luis Guzmán-Mar, J., 2017. Determination of phthalates in bottled water by automated on-line solid phase extraction coupled to liquid chromatography with uv detection. Talanta 168, 291–297. https://doi.org/10.1016/J.TALANTA.2017.03.060.
[38] Sibali, L.L., Okonkwo, J.O., Mccrindle, R.I., 2013. Determination of selected phthalate esters compounds in water and sediments by capillary gas chromatography and flame ionization detector. J Environ Sci Heal Part A Toxic/Hazard Subst Environ Eng 48, 1365–1377. https://doi.org/10.1080/10934529.2013.781884.
[39] Vrana, B., Allan, I.J., Greenwood, R., Mills, G.A., Dominiak, E., Svensson, K., et al., 2005. Passive sampling techniques for monitoring pollutants in water. TrAC Trends Anal Chem 24, 845–868. https://doi.org/10.1016/J.TRAC.2005.06.006.
[40] Posada-Ureta, O., Olivares, M., Delgado, A., Prieto, A., Vallejo, A., Irazola, M., et al., 2017. Applicability of polydimethylsiloxane (PDMS) and polyethersulfone (PES) as passive samplers of more hydrophobic organic compounds in intertidal estuarine environments. Sci Total Environ 578, 392–398. https://doi.org/10.1016/J.SCITOTENV.2016.10.194.
[41] Lohmann, R., Booij, K., Smedes, F., Vrana, B., 2012. Use of passive sampling devices for monitoring and compliance checking of POP concentrations in water. Environ Sci Pollut Res 2012 196 19, 1885–1895. https://doi.org/10.1007/S11356-012-0748-9.
[42] Pintado-Herrera, M.G., Lara-Martín, P.A., González-Mazo, E., Allan, I.J., 2016. Determination of silicone rubber and low-density polyethylene diffusion and polymer/water partition coefficients for emerging contaminants. Environ Toxicol Chem 35, 2162–2172. https://doi.org/10.1002/ETC.3390.
[43] Poiger, T., Buser, H.R., Balmer, M.E., Bergqvist, P.A., Müller, M.D., 2004. Occurrence of UV filter compounds from sunscreens in surface waters: regional mass balance in two Swiss lakes. Chemosphere 55, 951–963. https://doi.org/10.1016/J.CHEMOSPHERE.2004.01.012.
[44] Rojo-Nieto, E., Muz, M., Koschorreck, J., Rüdel, H., Jahnke, A., 2019. Passive equilibrium sampling of hydrophobic organic compounds in homogenised fish tissues of low lipid content. Chemosphere 220, 501–504. https://doi.org/10.1016/J.CHEMOSPHERE.2018.12.134.
[45] Burgess, R.M., Lohmann, R., Schubauer-Berigan, J.P., Reitsma, P., Perron, M.M., Lefkovitz, L., et al., 2015. Application of passive sampling for measuring dissolved concentrations of organic contaminants in the water column at three marine superfund sites. Environ Toxicol Chem 34, 1720–1733. https://doi.org/10.1002/ETC.2995.
[46] Perron, M.M., Burgess, R.M., Suuberg, E.M., Cantwell, M.G., Pennell, K.G., 2013. Performance of passive samplers for monitoring estuarine water column concentrations: 2. Emerging contaminants. Environ Toxicol Chem 32, 2190–2196. https://doi.org/10.1002/ETC.2248.
[47] Alvarez, D.A., Stackelberg, P.E., Petty, J.D., Huckins, J.N., Furlong, E.T., Zaugg, S.D., et al., 2005. Comparison of a novel passive sampler to standard water-column sampling for organic contaminants associated with wastewater effluents entering a New Jersey stream. Chemosphere 61, 610–622. https://doi.org/10.1016/J.CHEMOSPHERE.2005.03.023.
[48] Jonker, M.T.O., Koelmans, A.A., 2001. Polyoxymethylene solid phase extraction as a partitioning method for hydrophobic organic chemicals in sediment and soot. Environ Sci Technol 35, 3742–3748. https://doi.org/10.1021/ES0100470/ASSET/IMAGES/LARGE/ES0100470F00005.JPEG.
[49] Mayer, P., Vaes, W.H.J., Hermens, J.L.M., 2000. Absorption of hydrophobic compounds into the poly(dimethylsiloxane) coating of solid-phase microextraction fibers: High partition coefficients and fluorescence microscopy images. Anal Chem 72, 459–464. https://doi.org/10.1021/AC990948F/ASSET/IMAGES/MEDIUM/AC990948FE00003.GIF.
[50] Booij, K., Smedes, F., Weerlee, E.M.Van, 2002. Spiking of performance reference compounds in low density polyethylene and silicone passive water samplers. Chemosphere 46, 1157–1161. https://doi.org/10.1016/S0045-6535(01)00200-4.
[51] Rusina, T.P., Smedes, F., Klanova, J., Booij, K., Holoubek, I., 2007. Polymer selection for passive sampling: a comparison of critical properties. Chemosphere 68, 1344–1351. https://doi.org/10.1016/J.CHEMOSPHERE.2007.01.025.
[52] Wennrich, L., Vrana, B., Popp, P., Lorenz, W., 2003. Development of an integrative passive sampler for the monitoring of organic water pollutants. J Environ Monit 5, 813–822. https://doi.org/10.1039/B303497F.
[53] Cornelissen, G., Rigterink, H., ten Hulscher, D.E.M., Vrind, B.A., van Noort, P.C.M., 2001. A simple Tenax® extraction method to determine the availability of sediment-sorbed organic compounds. Environ Toxicol Chem 20, 706–711. https://doi.org/10.1002/ETC.5620200403.
[54] Kwon, J.H., Wuethrich, T., Mayer, P., Escher, B.I., 2007. Dynamic permeation method to determine partition coefficients of highly hydrophobic chemicals between poly(dimethylsiloxane) and water. Anal Chem 79, 6816–6822. https://doi.org/10.1021/AC0710073.
[55] Angel, D.M., Gao, D., Delay, K., Lin, E.Z., Eldred, J., Arnold, W., et al., 2022. Development and application of a polydimethylsiloxane-based passive air sampler to assess personal exposure to SARS-CoV-2. Environ Sci Technol Lett 9, 153–159. https://doi.org/10.1021/ACS.ESTLETT.1C00877.
[56] Baltussen, E., Cramers, C.A., Sandra, P.J.F., 2002. Sorptive sample preparation - a review. Anal Bioanal Chem 373, 3–22. https://doi.org/10.1007/S00216-002-1266-2.
[57] Niu, L., Henneberger, L., Huchthausen, J., Krauss, M., Ogefere, A., Escher, B.I., 2021. pH-Dependent partitioning of ionizable organic chemicals between the silicone polymer polydimethylsiloxane (PDMS) and water. ACS Environ Au 2, 253–262. https://doi.org/10.1021/ACSENVIRONAU.1C00056.
[58] Zhu, T., Chen, W., Singh, R.P., Cui, Y., 2020. Versatile in silico modeling of partition coefficients of organic compounds in polydimethylsiloxane using linear and nonlinear methods. J Hazard Mater 399, 123012. https://doi.org/10.1016/J.JHAZMAT.2020.123012.
[59] Rusina, T.P., Smedes, F., Koblizkova, M., Klanova, J., 2010. Calibration of silicone rubber passive samplers: experimental and modeled relations between sampling rate and compound properties. Environ Sci Technol 44, 362–367. https://doi.org/10.1021/ES900938R.
[60] Smedes, F., 2018. Silicone–water partition coefficients determined by cosolvent method for chlorinated pesticides, musks, organo phosphates, phthalates and more. Chemosphere 210, 662–671. https://doi.org/10.1016/J.CHEMOSPHERE.2018.07.054.
[61] Alshehri, M.M., Ouladsmane, M.A., Aouak, T.A., ALOthman, Z.A., Badjah Hadj Ahmed, A.Y., 2022. Determination of phthalates in bottled waters using solid-phase microextraction and gas chromatography tandem mass spectrometry. Chemosphere 304, 135214. https://doi.org/10.1016/J.CHEMOSPHERE.2022.135214.
[62] Cao, X.L., 2008. Determination of phthalates and adipate in bottled water by headspace solid-phase microextraction and gas chromatography/mass spectrometry. J Chromatogr A 1178, 231–238. https://doi.org/10.1016/J.CHROMA.2007.11.095.
[63] Difilippo, E.L., Eganhouse, R.P., 2010. Assessment of PDMS-water partition coefficients: implications for passive environmental sampling of hydrophobic organic compounds. Environ Sci Technol 44, 6917–6925. https://doi.org/10.1021/ES101103X.

[64] Nam, G.U., Bonifacio, R.G., Kwon, J.H., Hong, Y., 2016. Kinetics and equilibrium partitioning of dissolved BTEX in PDMS and POM sheets. Environ Sci Pollut Res 23, 18901–18910. https://doi.org/10.1007/S11356-016-7098-Y.
[65] Bonifacio, R.G., Nam, G.U., Eom, I.Y., Hong, Y.S., 2017. Development of solid ceramic dosimeters for the time-integrative passive sampling of volatile organic compounds in waters. Environ Sci Technol 51, 12557–12565. https://doi.org/10.1021/ACS.EST.7B03678.
[66] Wang, H., Thaxton, K., 2009. Application Note 02100: Determination of Phthalate Compounds in Plastic Toys Using the Varian 225-MS Ion Trap Mass Spectrometerr 1–4. ⟨https://www.agilent.com/cs/library/applications/si-02100_phthalate_toys_225-ms_gcms_appn_v03.pdf⟩.
[67] Al-Natsheh, M., Alawi, M., Fayyad, M., Tarawneh, I., 2015. Simultaneous GC–MS determination of eight phthalates in total and migrated portions of plasticized polymeric toys and childcare articles. J Chromatogr B 985, 103–109. https://doi.org/10.1016/J.JCHROMB.2015.01.010.
[68] Ziembowicz, S., Kida, M., Koszelnik, P., 2018. Development of an analytical method for dibutyl phthalate (DBP) determination in water samples using gas chromatography. E3S Web Conf 44, 00200. https://doi.org/10.1051/E3SCONF/20184400200.
[69] Figueroa, L.E., Brown, M.C., Briscoe, T., Chisam, J., Lewis, D., Westover, J., et al., 2019. Synthesis of a potential new internal standard for the analytical Determination of Dibutyl Phthalate (DBP) and Monobutyl Phthalate (MBP) in water samples. Proc Okla Acad Sci 99, 114–119. ⟨http://156.110.192.75/ojs-2.4.8/index.php/OAS/article/view/7984⟩. accessed January 4, 2023.
[70] Pubchem, PubChem, (n.d.). https://pubchem.ncbi.nlm.nih.gov/ (accessed June 26, 2022).
[71] Ter Laak, T.L., Durjava, M., Struijs, J., Hermens, J.L.M., 2005. Solid phase dosing and sampling technique to determine partition coefficients of hydrophobic chemicals in complex matrixes. Environ Sci Technol 39, 3736–3742. https://doi.org/10.1021/es048406p.
[72] NASEM, Why Indoor Chemistry Matters, National Academies Press, Washington, DC, 2022. https://doi.org/10.17226/26228.
[73] Setny, P., Baron, R., McCammon, J.A., 2010. How can hydrophobic association be enthalpy driven? J Chem Theory Comput 6, 2866–2871. https://doi.org/10.1021/CT1003077.
[74] Haftka, J.J.H., Govers, H.A.J., Parsons, J.R., 2010. Influence of temperature and origin of dissolved organic matter on the partitioning behavior of polycyclic aromatic hydrocarbons. Environ Sci Pollut Res 17, 1070–1079. https://doi.org/10.1007/s11356-009-0263-9.
[75] Ter Laak, T.L., Busser, F.J.M., Hermens, J.L.M., 2008. Poly(dimethylsiloxane) as passive sampler material for hydrophobic chemicals: Effect of chemical properties and sampler characteristics on partitioning and equilibration times. Anal Chem 80, 3859–3866. https://doi.org/10.1021/AC800258J.
[76] Kramer, N.I., Van Eijkeren, J.C.H., Hermens, J.L.M., 2007. Influence of albumin on sorption kinetics in solid-phase microextraction: Consequences for chemical analyses and uptake processes. Anal Chem 79, 6941–6948. https://doi.org/10.1021/AC070574N.
[77] Jonker, M.T.O., Muijs, B., 2010. Using solid phase micro extraction to determine salting-out (Setschenow) constants for hydrophobic organic chemicals. Chemosphere 80, 223–227. https://doi.org/10.1016/J.CHEMOSPHERE.2010.04.041.