RESEARCH ARTICLE



Kinetics and equilibrium partitioning of dissolved BTEX in PDMS and POM sheets

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Abstract Passive sampling of volatile organic chemicals from soil and groundwater is primarily important in assessing the status of environmental contamination. A group of low molecular weight pollutants usually found in petroleum fuels, benzene, toluene, ethylbenzene, and xylenes (BTEX) was studied for its kinetics and equilibrium partitioning with single-phase passive samplers using polydimethylsiloxane (PDMS) and polyoxymethylene (POM) as sorbing phase. PDMS (1 mm) and POM (0.076 mm) sheets were used for sorption of BTEX and concentrations were analyzed using GC-FID. The equilibrium absorption and desorption of PDMS in water was achieved after 120 min while POM sheets absorbed up to 35 days and desorbed in 7 days. The kinetic rate constants in PDMS is higher than in POM up to 3 orders of magnitude. Logarithms of partition coefficient were determined to be in the range of 1.6-2.8 for PDMS and 2.1-3.1 for POM. The results indicate that POM is a stronger sorbent for BTEX and has slower equilibration time than PDMS. The partitioning process for both polymers was found to be enthalpy-driven by measurement of K_d values at varying

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temperatures. K_d values increase at low temperature and high ionic strength conditions. Presence of other gasoline components, as well as dissolved organic matter, did not significantly affect equilibrium partitioning. A good 1:1 correlation between the measured and the predicted concentrations was established on testing the potential application of the constructed PDMS sampler on natural soils and artificial soils spiked with gasoline-contaminated water.

Keywords Passive sampling · BTEX · Volatile organic compounds · Polydimethylsiloxane (PDMS) · Polyoxymethylene (POM) · Kinetics · Equilibrium partitioning · Soil pollution · Groundwater pollution

Introduction

Volatile hydrocarbons benzene, toluene, ethyl benzene, and xylenes, collectively known as BTEX, are residues abundant in petroleum fuels (e.g., gasoline), and their toxicity and potential carcinogenicity are of recent concern. Among other fuel components, BTEX compounds have relatively high water solubility, and this property enables them to migrate easily into groundwater and drinking water supplies (Buddhadasa et al. 2002). Their extensive discharge into the environment through chemical spills, improper waste disposal, or leakage from underground storage tanks can lead to the contamination of groundwater (Aivalioti et al. 2012). It is therefore useful to analyze dissolved BTEX concentrations in soil and groundwater near fuel sources such as gasoline stations or petroleum storages in order to assess the degree of contamination.

Recent efforts on environmental analysis have developed a more accurate and more efficient method in determining dissolved organic pollutant concentrations in situ. Several literatures presented reviews on the different kinds of passive samplers for

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sediments and soil (Meyer et al. 2003; Rusina et al. 2007; See thapathy et al. 2008). The most useful sampler for determination of freely dissolved concentrations makes use of equilibrium passive sampling, in which the equilibrium concentration is measured by exposing the device on an environmental phase until thermodynamic equilibrium is established (Meyer et al. 2003). Among various kinds of passive samplers, single-phase passive samplers are recently employed because of their simplicity, low-cost, reusability, and comparable affinity for hydrophobic compounds (Rusina et al. 2007). These devices are usually constructed with single-phase polymeric materials such as polydimethylsiloxane (PDMS) and polyoxymethylene (POM). Studies on PDMS as a sorptive material are abundant because of its well-defined hydrophobicity for a very wide concentration range (Meyer et al. 2003; Ter Laak et al. 2008), while POM samplers are commonly used for sediment and aqueous phase systems because of its stability and higher affinity for most polar chemicals (Endo et al. 2011; Jonker and Koelmans 2001). To characterize a sampler, two major factors are needed to be considered: affinity of the sampler to the analyte and the rate of sampling (Ter Laak et al. 2008).

In sampling for contaminants, it is necessary to consider the time it takes to accumulate the sample concentration until equilibrium. Moreover, polymeric samplers allows desorption especially for volatile compounds. Therefore, information on both the absorption and desorption kinetics are essential. A very recent study on PDMS samplers on high molecular weight compounds have shown that volatile losses can significantly occur during field sampling when the sampling device is retrieved or exposed to air (Thomas and Reible 2015). This is especially true in analyzing highly volatile and low molecular weight compounds, and as such, the kinetic properties of the passive sampler must be studied.

The affinity of the sampler to the analyte is usually defined by a chemical-specific constant called partition coefficient (K_d) . Correlation of log K_d with log K_{ow} values represents the hydrophobicity of the compounds, and higher values means more hydrophobicity. For equilibrium passive samplers, a direct relationship can be established between the concentration of the analyte in the receiving phase (C_s) and the freely dissolved concentration of the analyte (C_w) which is related through the partition coefficient. It is important to determine the accurate K_d in order to obtain accurate measurements on freely dissolved analyte concentrations in the environmental phase (Endo et al. 2011).

In addition to the accurate measurement of partition coefficients, the effect of several environmental variables must be investigated in order to establish appropriate correlation of experimental K_d values to actual samples. Partition coefficients can vary as much as 65–85 % difference on various temperatures and ionic strengths (DiFilippo and Eganhouse 2010). Additionally, the presence of dissolved organic matter (DOM) may also affect the diffusion processes (Ter Laak et al.

2008). Such difference has corresponding effect on calculated analyte concentrations. Few studies thus far have taken K_d measurement for BTEX compounds considering the effects of temperature, ionic strength, and dissolved organic matter, and available data are mostly for high molecular weight organic compounds.

This study focuses on the partitioning of BTEX compounds in PDMS and POM and its potential application to in situ passive sampling in contaminated soil environment. The selected passive samplers, PDMS and POM, have been widely studied for its interaction with hydrophobic organic compounds (HOCs), but it is mostly with polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and chlorinated pesticides. Such compounds yield higher and more sensitive K_d values, less volatile, and thus easier to handle. However, investigations on HOCs with low molecular weight compounds such as BTEX are very few. It is therefore of interest to characterize the kinetics and partitioning of BTEX compounds using single-phase passive sampling devices and thus provide a milestone for in situ analysis of low molecular weight organic pollutants in soil environment.

Materials and methods

Chemicals, samplers, solvents, and instruments

Benzene, toluene, ethylbenzene, and *p*-xylene used for making stock solutions were all purchased from Sigma Aldrich Co. (USA). The methanol used as solvent was of HPLC grade, while an ACS grade methanol was used only for washing, and both were purchased from Acros Organics (USA). A 10,000 mg/L stock solution of BTEX was made using 0.1 % (v/v) methanol in water as solvent. All solutions are refrigerated to 4 °C. Dichloromethane used for gasoline extraction as well as general grade soils sand and kaolin were purchased from Fischer Scientific (UK). Sphagnum peat moss were acquired from Lambert Canada. For the polymers, PDMS and POM sheets were purchased from Specialty Silicone Products, Inc. (Ballston Spa, NY, USA) and CS Hyde Company (Lake Vila, IL, USA), respectively. The sheets were cut into circular disks with 1.6 cm diameter. A PDMS sheet is 1 mm thick and weighs 0.25 g, while a POM sheet is 76 μ m thick and weighs 0.025 g. Prior to every use, the PDMS and POM disks were cleaned by immersion in methanol for at least 1 day at room temperature and then oven-dried (50 °C) to remove impurities. A PDMS sampling device was constructed using a rectangular sheet fitted between stainless steel holders. Sodium chloride for salting out effect experiment was obtained from Acros Organics (USA). The instrument used to measure BTEX concentrations is a Shimadzu GC-2010 gas chromatograph with flame ionization detector (GC-FID). The column used for analysis was a 0.25-µm Agilent DB-5

(30 m × 0.25 mm) with 15.0 split ratio. Ultra-pure nitrogen is used as carrier gas with a constant flow of 3.0 mL/min. Both the injection and detector temperatures are at 260 °C. The oven was programmed at initial temperature of 50 °C for 2 min, followed by 4 °C/min increase to 85 °C, and then 40 °C/min to 225 °C, held to 2 min. The auto-injector device for liquid phase sampling was Shimadzu AOC-20i, adjusted to 2.5 μ L injection volume. Gas phase analysis of the head-space in vial by manual injection are sampled at 100 μ L using a 250- μ L gas-tight syringe.

Measurement of BTEX absorption and desorption

A clean polymer disk was placed into 40 mL amber glass vial, and then filled with 40 mL deionized water. The vial was spiked with 1 mg/L BTEX solution and then sealed using the mininert valve (Supelco, Inc., USA) for standard solutions and kinetics analysis, or the Teflon-coated silicone septum for equilibrium analysis. All vials were mixed using a tumble stirrer (38 rpm) until taken out for analysis. With PDMS, the vials were shaken for 1 day, while vials with POM were shaken for 35 days. These amounts of time were shown to be enough for equilibration. For absorption kinetics, the vials were analyzed after 1 day for PDMS and 35 days for POM. For the ionic strength analysis, aqueous sodium chloride with varying concentrations (0.001, 0.01, 0.1, 0.6, and 1.0 mol/L) was added to the sample solution. For the DOM effect, the concentrations of DOM added to the samples are 1.0, 3.0, 10, 30, and 100 mg/L. The samples were processed at room temperature, except for the temperaturedependence analysis wherein the vials were handled at varying temperatures: 4, 15, 25, and 40 °C. All samples were prepared in triplicates. The headspace of the vial was analyzed in GC-FID via manual injection, and then compared with calibration curves from that of freshly prepared standard solutions to quantify for the aqueous phase concentration. Following headspace sampling, the cap of the vial was opened and the PDMS and POM disks were taken out. The polymer disks were dried with tissue and BTEX compounds were extracted into 2 mL glass vial using 1 mL methanol. The aqueous phase extracts were analyzed in GC-FID using Shimadzu AOC-20i auto-injector. To analyze for the desorption kinetics, the polymer disks were instead placed on aluminum foil and allowed to evaporate for a corresponding desorption time until extraction with methanol. The concentration of BTEX extracted from the polymer using methanol was compared with the concentration acquired prior to extraction, and the percent extraction efficiency is calculated.

Absorption equilibrium in contaminated water for gasoline

The waster-washed gasoline was prepared separately from fresh gasoline by first filling a 2-L glass bottle with 1 L deionized water. One liter of fresh gasoline was carefully added on the top of the water surface. The bottle was sealed with a Teflon-coated cap and slowly stirred with a magnetic stir bar to ensure equilibrium in room temperature. After equilibration, the water-washed gasoline was extracted and then diluted into 40 mL amber glass vial. The dilution ratios are as follows: onefold (40 mL contaminated water), fivefold (8 mL contaminated water and 32 mL deionized water), tenfold (4 mL contaminated water and 36 mL deionized water). PDMS and POM disks were put into the vials and then sealed using the Teflon-coated silicone septum. The vials were mixed to ensure equilibrium in room temperature. All samples were triplicate prepared. The headspace of the vial was analyzed using GC-FID. Following headspace sampling, PDMS and POM disks were taken out and BTEX was extracted in a 2-mL vial with 1 mL methanol. To extract the BTEX from the gasolinecontaminated water, 1 mL dichloromethane (DCM) was added into the vial and then shaken for 1 day. After shaking, the inverted vials were centrifuged and DCM was extracted by using syringe and then placed into 2 mL vials. The aqueous phase extracts were analyzed with GC-FID via AOC-20i autoinjector.

Predicted BTEX concentration in soil contaminated with gasoline

Two types of soils were prepared: one using uncontaminated natural soil (NS) taken from a backyard mountain in Daegu University, South Korea, and the other was the artificial soil (AS) formulated according to OECD Guidelines section 3, No. 317 (OECD. 2010). The soil samples were weighed to 35 g and then placed into 50-mL glass vial which was filled with 35 mL water-washed gasoline. The vials were sealed using the Teflon-coated silicone septum. After 3 days, the PDMS passive samplers were inserted into the soil matrix and were left for 2 days. All samples were prepared in triplicates. Gas phase analysis was done in GC-FID and then related to the aqueous phase concentration. This was followed by methanol extraction of the PDMS sheets and aqueous phase analysis using AOC-20i auto-injector.

Calculation method

The main approach to the calculation of BTEX concentration is to measure its equilibrium concentration after volatilization into the headspace of the vial and calculate the concentration in the aqueous phase (C_w) and gaseous phase (C_g) in milligram per liter. The polymer absorbs BTEX until it is in equilibrium with the aqueous phase and gaseous phase in the system. The amount of freely dissolved concentration that was absorbed by the polymer can be determined by calculating for the concentration that was left on the aqueous solution. Henry's law relates the aqueous phase concentration with the gas phase concentration, allowing measurement in the headspace (Oomen et al. 2000). Involving the measurement of the equilibrium concentration in the gas phase requires the temperature-dependent Henry's law constant (H) and is given by the equation,

$$\log H = A - \frac{B}{T} \tag{1}$$

where A and B are values specific for an organic compound, and T is the temperature at which equilibration was carried out (Roberts 2001). This constant is thus an essential correction factor for water-to-air partitioning and its reciprocal is multiplied with $C_{\rm w}$ to obtain $C_{\rm g}$. A critical compilation of values for most organic compounds are available from literature (Roberts 2001). The total measured concentrations of BTEX in the aqueous and gaseous phases represent the amount that was not absorbed by the polymer. Thus, the theoretical amount of BTEX absorbed by the polymer can be obtained by a simple law of conservation of mass: subtract the total measured equilibrium concentration from the original amount of BTEX added to the solution. The amount of BTEX in the polymer (C_s) is then expressed as milligram BTEX per kilogram polymer. The partition coefficient can be calculated from the following equation:

$$K_{\rm d} = \frac{C_{\rm s}}{C_{\rm w}} \tag{2}$$

It was understood that BTEX can easily be extracted from the polymer using methanol. Methanol is extensively used for solid–liquid extraction of BTEX compounds in soils and sediments. The amount of extracted BTEX was quantified by analysis of the aqueous phase, and then compared with the previously calculated C_s to determine the percent extraction efficiency (ε). This is necessarily obtained since the analysis of freely dissolved BTEX by gas phase analysis may differ from aqueous phase analysis after extraction. Extraction efficiency values using this method were found to be >80 % for both PDMS and POM even at varying temperatures (Table S1). In actual sample calculations, the percent extraction efficiency must be added as a factor in order to accurately obtain the freely dissolved concentration of BTEX:

$$C_{\rm w} = \frac{C_{\rm s}}{K_{\rm d} \times \varepsilon} \tag{3}$$

Results and discussion

Absorption and desorption kinetics

To determine the time needed for the polymer to be equilibrated, the absorption and desorption kinetics were investigated. The concentration uptake kinetics of PDMS and POM sheets

were determined by calculating the concentration of BTEX adsorbed in the polymer as a function of time (Fig. 1). The graph shows that both polymers reach a constant concentration during the experiments. BTEX concentration in PDMS polymers achieved equilibrium after 120 min. The diffusion of BTEX on POM sheets were shown to have very slow process, attaining equilibrium after 35 days. This is a common property of POM absorption of hydrophobic organic compounds in which some studies suggest at least 28 days equilibrium time for PAHs and PCBs absorption (Endo et al. 2011; Jonker and Koelmans 2001). In PDMS, the equilibration time was achieved after merely 2 h, although the absorbed BTEX concentrations are noticeably lower than in POM polymer. This kinetic experiment implies that the time to achieve equilibrium for PDMS is shorter than in POM samplers and that it will be more practical to use PDMS if sampling time is limited. PDMS has been widely studied for its affinity and faster response towards highly hydrophobic compounds.

After reaching equilibrium, it can be observed that both polymers were able to absorb *p*-xylene the most, followed by ethyl benzene, toluene, and benzene. The low C_s values of both benzene and toluene can be attributed to the fact that they are less hydrophobic and have relatively higher solubility in water than in the polymer. Meanwhile, POM was able to absorb larger amounts until equilibrium, varying from 400 to 750 mg BTEX per kg polymer, whereas PDMS absorbed only as much as 40 to 130 mg/kg (Fig. 1). This is also reflected in



Fig. 1 The kinetics of dissolved BTEX absorption to \mathbf{a} 1 mm thick PDMS and \mathbf{b} 76 μ m thick POM sheets. Note that the time scales of PDMS and POM are minutes and days, respectively

the partition coefficients obtained for PDMS and POM which will be discussed in the later section.

While the polymers are able to absorb compounds, the diffusion process is reversible and a volatile analyte can desorb back into the atmosphere. This becomes a problem when, for example, the sampler is brought back to the laboratory for analysis, as desorption will cause a great loss of analyte from the sampler material. Therefore, desorption kinetics were studied in order to assess the rate in which the analyte is removed from the sampler. The absorbed analyte in the polymer were allowed to desorb to air and the concentration of BTEX was measured at different times (Fig. 2). The results show that PDMS easily desorbs BTEX with almost the same rate as its absorption (120 min), while POM desorbs faster than its absorption rate (7 days). Obviously, PDMS has rapid uptake kinetics but it also has very fast desorption which can be disadvantageous during field sampling. It also desorbs benzene and toluene faster than it can absorb. Thomas and Reible (2015) studied volatile losses of PAHs on PDMS fibers and concluded that compound loss are significant for lower molecular weight compounds. In one case, naphthalene, the most volatile PAH, has a desorption half-life of 12 min in at least 1060/1000 µm PDMS fiber. This can be circumvented, however, with the use of thicker PDMS, rapid onsite analysis, or operation at very low temperatures (Thomas and Reible 2015).

Quantitative results of the kinetic experiments can be best represented by calculation of their kinetic rate constants. Rate constants signify the quantity of change in concentration per unit time. The calculated rate constants can be found in



Fig. 2 The kinetics of a 1 mm thick PDMS and b 76 μ m thick POM sheets sorbed BTEX desorption to air. Note that the time scales of PDMS and POM are minutes and days, respectively

Tables 1 and 2. From the rate constants, it is observed that PDMS absorption and desorption are greater than that of POM by about 3 orders of magnitude. The results describes how fast PDMS and POM sheets were able to absorb and desorb BTEX. Within chemical groups, benzene consistently has the highest rate constant for both absorption and desorption. It can be inferred that a smaller molecule is absorbed and desorbed quickly due to less physical interaction with the polymer or the absence of steric hindrance when interacting with the polymer matrix. While the absorption processes for both polymers can be assumed to have first order kinetics, wherein its sorption rate is independent of the concentration and rather dependent on temperature (Levine 2009), the experimental aqueous phase concentrations (C_w) show a corresponding decrease with time (Fig. S1). Consequently, the kinetic model can be derived from the equation of analytical concentration of the compounds based on mass transfer processes (Kwon et al. 2009):

$$C_{\rm s} = \frac{K_{\rm d}C_{\rm w,0}}{1 + K_{\rm d}\frac{V_{\rm s}}{V_{\rm w}}} \left(1 - \exp\left(-\left(1 + K_{\rm d}\frac{V_{\rm s}}{V_{\rm w}}\right)k_{\rm a}t\right)\right)$$
(4)

where C_s is the absorbed BTEX mass on polymer in milligram/kilogram, K_d is the partition coefficient of compounds to the polymer in liter/kilogram, $C_{w,0}$ is the initial aqueous phase concentration in milligram/liter, V_s is the volume of the sampler in milliliter, V_w is the volume of the solution in milliliter, k_a is the absorption kinetic rate constant in days⁻¹, and t is the sampling time in days. Equation 4 shows that the changes are significant for PDMS since the sampler volume is not negligibly small compared with the aqueous phase volume. Thus, absorption rate constants are actually underestimated (Table 1) than general kinetic models when aqueous phase concentration is assumed to be constant. This is, however, not the case for desorption process and a general exponential equation can be fitted to calculate for the desorption kinetic rate constant (k_d):

$$C_{\rm s} = C_{\rm s,0}(-\exp(-k_{\rm d}t)) \tag{5}$$

where the units are the same as presented in Eq. 4. Nonetheless, this study has shown that both sorption processes are rapid and occurring exponentially and must be considered especially for in situ sampling.

Equilibrium partition coefficients

In comparing the obtained partition coefficients with a standard reference system, the logarithm of the experimental K_d was plotted against the logarithm of K_{ow} (Fig. 3). The log K_{ow} values were obtained from a well-established data for BTEX compounds (CRC Handbook of Chemistry and Physics 2005). Among the compounds studied, benzene has the Table 1 The first order absorption kinetic rate constants for dissolved BTEX sorption to 1 mm thick PDMS and 76 µm thick POM sheets

	$k_{\rm a} ({\rm day}^{-1})$			
	Benzene	Toluene	Ethylbenzene	<i>p</i> -Xylene
PDMS (1.0 mm thick)	61.2 ± 8.8	34.9 ± 10.9	17.6±13.7	16.8 ± 13.1
POM (76 µm thick)	0.11 ± 0.02	0.12 ± 0.03	0.10 ± 0.03	0.12 ± 0.03

lowest K_d value, followed by toluene, ethylbenzene, and pxylene. The presence of methyl group in toluene and ethyl groups in ethylbenzene and p-xylene contributes to the increase in hydrophobicity of these benzene derivatives. $K_{\rm d}$ values of POM are apparently greater than PDMS by about 1 log unit indicating that PDMS is a weaker sorbent than POM for BTEX compounds. It is also noticeable that the obtained $\log K_{\rm d}$ values does not fall precisely into 1:1 correlation with $\log K_{ow}$. The partition coefficients for PDMS are generally slightly lower than its K_{ow} values indicating a weak sorption of PDMS compared to *n*-octanol. For POM, $\log K_d$ is slightly higher than the log K_{ow} values. This further indicates that POM is more absorbing for less hydrophobic compounds (i.e., $K_{ow} > 3$) and the basis lies with its relatively polar structure. POM has weaker affinity to hydrophobic molecules and is more sensitive to polar organic compounds because of the presence of a hydrogen bonding acceptor (-CH₂O-) in its molecular structure (Endo et al. 2011). Compared with PDMS, POM can absorb more BTEX concentration due to its stronger affinity to less hydrophobic compounds, which are, in general, low molecular weight compounds. Thus, measurements for actual sampling will be biased if these obtained $K_{\rm d}$ values were not to be considered.

A linear fit of the form $\log K_d = a \log K_{ow} + b$ can be constructed from the double logarithmic plot and generate a single parameter linear free energy relationship (SP-LFER). Using SP-LFER, the free energy (ΔG) contributions for all partition processes are considered to be linearly related, and the only variable taken into account is of a single type of intermolecular interaction (Goss and Schwarzenbach 2001). The slope acan simply define the single parameter for the variance in intermolecular interactions, namely H-bonding and van der Waals interactions (Goss and Schwarzenbach 2001), as well as different factors that define the free energy costs of cavity formation (Schwarzenbach et al. 2003). BTEX compounds are structurally related, their structures vary only with the

position and presence of methyl or ethyl groups, and thus have relatively similar intermolecular interactions. As observed from the obtained SP-LFER equations (Table S2), the slope values are independent of temperature. In PDMS, the calculated slope slightly deviate (about 0.2 log units) from the average literature value (DiFilippo and Eganhouse 2010), while the slope in POM is considerably (about 0.7 log units) less than available literature value (Endo et al. 2011). The low slope values for POM (i.e., $K_d > K_{ow}$) suggests its exceptional property of having higher affinity for less hydrophobic or polar compounds.

Effect of temperature

One important environmental variable is temperature. In general, soil and groundwater environment operate at different temperatures, and the environmental temperatures of interest is around 0 to 40 °C (DiFilippo and Eganhouse 2010). It was generally observed that lowering the temperatures on which $K_{\rm d}$ measurements are taken resulted to higher log $K_{\rm d}$ values, within 0.2 log units for PDMS and 0.7 log units for POM. The obtained K_{d} values at varying temperatures are summarized in Table 3. The slight shift of values shows that the distribution of BTEX between the environmental phase and the polymer is temperature-dependent. This is in conjunction with the results of Chen and Pawliszyn (2004) where in the K_d of BTEX decreases with the temperature. The obtained data allows extrapolation of K_d values at different temperature of interest which should be considered when it comes to actual sampling in order to obtain more accurate calculations.

Partitioning processes between two phases has a general thermodynamics, which is mainly governed by free energy of transfer from the aqueous phase to organic phase (Goss and Schwarzenbach 2001). Moreover, it can be broken down into different free energies (ΔG) for vaporization, cavity creation, and solute interactions. Partitioning thermodynamics

Table 2The first orderdesorption kinetic rate constantsfor BTEX desorption from 1 mmthick PDMS and 76 μ m thickPOM sheets to air		$k_{\rm d} ({\rm day}^{-1})$	$k_{\rm d} ({\rm day}^{-1})$			
		Benzene	Toluene	Ethylbenzene	<i>p</i> -Xylene	
	PDMS (1.0 mm thick) POM (76 μm thick)	$\begin{array}{c} 134\pm12.4\\ 0.44\pm0.07\end{array}$	89.8 ± 9.4 0.42 ± 0.06	$\begin{array}{c} 60.6\pm4.7\\ 0.46\pm0.07\end{array}$	$\begin{array}{c} 62.9\pm4.4\\ 0.55\pm0.08\end{array}$	

Table 2 The



Fig. 3 The correlation of experimental log K_d at various temperatures versus log K_{ow} obtained from literature data for BTEX partitioning in **a** 1 mm thick PDMS and **b** 76 μ m thick POM sheets. A *dashed line* across the graph represents the 1:1 line

for interaction of high molecular weight compounds with fluidic membranes, such as phospholipids, is widely studied in literatures (Kwon et al. 2007; Setny et al. 2010). The enthalpy (ΔH) for the partitioning process can be calculated using the van't Hoff relation:

$$\log K_{\rm d} = -\frac{\Delta H}{2.303R} \frac{1}{T} + A \tag{6}$$

where *R* is the gas constant (8.314 J/mol-K), *T* is the temperature (in K), and *A* is a constant that describes the entropy if partition coefficients are molar fraction-based. From the enthalpy results listed in Table 4, the partitioning process is exothermic for both PDMS and POM within the experimental temperature range. This is true as K_d values were found to increase with a decrease in temperature. Thus, the partition processes for PDMS and POM entail a release of energy. In a computational study done by Setny et al. (2010), the enthalpy-driven hydrophobic association results from the release of water from the hydrophobic environment to the bulk water.

Effect of ionic strength and dissolved organic matter

The soil is a complex matrix of organic matter, minerals, as well as salts. Because passive sampling is driven by chemical potentials, the effect of strong long-range forces, such as ionic forces, is not entirely negligible. This behavior has long been established in Debye-Huckel's law (Levine 2009). Therefore, the activities of chemicals in a salt solution affect thermodynamic equilibrium and, in turn, the equilibrium constants. The experiment shows the effect of varying ionic concentrations on $\log K_{\rm d}$ (Fig. 4). An increase in the slope implies that increasing with the ionic strength affects the K_d values positively. This agrees with the theory on salting out effect, such that the aqueous phase tends to exclude out the hydrophobic chemicals by associating more with the ionic components, and thus decreasing the solubility of these chemicals in water. For 1 M ionic concentration, the K_d values shifted up to 0.2 log units. A study by Jonker and Muijs (2010) for PDMS-partitioning on most PAH compounds also showed an increase in $\log K_{\rm d}$ with increasing concentration of dissolved salt. Additionally, experimental results suggests that a steeper slope can be obtained with decreasing $\log K_{\rm d}$ value. The magnitude of change in K_d values with ionic strength can be quantified using Setschenow equation (Jonker and Muijs 2010):

$$\log\left(\frac{K_{\rm d}^{\rm s,i}}{K_{\rm d}^{\rm o}}\right) = k_{\rm s}I\tag{7}$$

where K_d^o is the original partition constant, $K_d^{s,i}$ is the partition constant in the presence of salts, k_s is the Setschenow constant, and *I* is the ionic strength. From the equation of the line, the slope represents the Setschenow constant which is a measure of the change in aqueous solubility as a function of ionic strength. The k_s values, listed in Table S3, slightly decrease with increasing K_d which suggests that a more hydrophobic compound, *p*-xylene in this case, is less affected by ionic strength. This might be due to the fact that a hydrophobic compound has weaker interactions in aqueous solutions and is less affected by strong ionic forces. Furthermore, k_s values are lower in POM than in PDMS. This is comparable to the results obtained by Jonker and Muijs (2010) in which they also found smaller change for POM partitioning than in PDMS for log K_d values at varying ionic strength.

Dissolved organic matter such as proteins and membrane vesicles can also be naturally found in soil matrices. Since they can sorb hydrophobic organic compounds, the freely **Table 3** The equilibrium partitioning coefficients (log K_d) between dissolved BTEX and PDMS/POM at 4, 15, 25, and 40 °C

Polymer	Temp (°C)	Benzene	Toluene	Ethylbenzene	<i>p</i> -Xylene
PDMS	4	1.87 ± 0.04	2.36 ± 0.03	2.76 ± 0.02	2.76 ± 0.04
	15	1.75 ± 0.16	2.34 ± 0.05	2.71 ± 0.02	2.70 ± 0.02
	25	1.64 ± 0.14	2.31 ± 0.14	2.66 ± 0.07	2.65 ± 0.07
	40	1.56 ± 0.26	2.23 ± 0.03	2.52 ± 0.03	2.50 ± 0.03
POM	4	2.84 ± 0.06	3.00 ± 0.12	3.10 ± 0.05	3.10 ± 0.06
	15	2.78 ± 0.04	2.94 ± 0.02	3.01 ± 0.03	3.01 ± 0.03
	25	2.64 ± 0.07	2.79 ± 0.04	2.90 ± 0.04	2.90 ± 0.07
	40	2.13 ± 0.13	2.34 ± 0.09	2.49 ± 0.05	2.47 ± 0.05

dissolved concentrations are reduced. Several literatures investigated the interaction of DOM with PDMS fibers (Kramer et al. 2007; Ter Laak et al. 2008). In this study, the log K_d values for both PDMS and POM were also constant in the presence of DOM concentrations from 1 to 100 mg/L (Fig. S2). As the literatures suggested, although equilibration time was found to significantly increase, the partitioning constants were not affected because organic matter, proteins for example, do not interact with the polymer nor provide additional source of the analyte (Kramer et al. 2007).

Equilibrium partitioning coefficients in gasoline-contaminated water

Gasoline is a complex mixture of hydrocarbons, including BTEX. To simulate the potential effects of gasoline concentration on K_d values, a gasoline-contaminated water was analyzed for its BTEX concentration and their partition coefficients were subsequently determined. Log K_d values graphed against varying dilution ratios of gasoline in water is presented in Fig. 5. The graph clearly shows that K_d is insignificantly affected by gasoline concentrations. This could also imply that partitioning of BTEX compounds is independent of the presence of other hydrophobic compounds in gasoline. While it was shown that K_d is affected by strong ionic interactions, no other similarly weak chemical interactions are influencing the partitioning of BTEX on both PDMS and POM polymers. The extent of dilution of gasoline contamination in water does not significantly change the

Chemical	PDMS		РОМ	
	ΔH (kJ/mole)	R^2	ΔH (kJ/mole)	R^2
Benzene	-23.1	0.949	-20.9	0.944
Toluene	-23.3	0.979	-20.9	0.950
Ethylbenzene	-16.9	0.989	-17.6	0.985
Xylene	-15.2	0.954	-17.2	0.988

equilibrium partitioning of BTEX to the samplers. Such implications are valuable in the determination of BTEX components from gasoline-contaminated environments.

Passive sampling of BTEX in natural and artificial soil

To test for the applicability and efficiency of the assembled sampler device, experimental analysis on actual soil samples spiked with gasoline-contaminated water was necessarily done. A simple sampler was made by exposing the polymer held in stainless steel case and then allowing the analytes from the soil to diffuse until equilibration. The freely dissolved concentration of BTEX contaminants in the soil was measured using only PDMS since its faster equilibration time than POM is an advantage in a laboratory-scale situation. The natural soil is a loamy soil type while the artificial soil was formulated from peat moss, kaolinite, and sand in 1:2:7 ratio. The results are presented in Fig. 6. Benzene levels are highest in both AS and NS, with NS absorbing higher amounts of benzene than in AS. In general, absorption in artificial soil is lower than in natural soil. This signifies that the artificial soil, having a different soil matrix, may have contained higher amounts of organic material or suspended particles which could have absorbed some of the analytes, causing a decrease in concentration. It has been concluded in literatures (Ter Laak et al. 2008) that the presence of other organic materials or suspended soil particles affect the kinetics and affinity of the contaminants to the sampler. These particles can sorb freely dissolved chemicals or facilitate transport through aqueous diffusion layers (Ter Laak et al. 2008). The predicted $C_{\rm w}$ was obtained from the gas phase analysis of the headspace of the vial which represents the freely dissolved BTEX concentration in a water-saturated soil matrix, while the concentration extracted from the PDMS sheets represents the measured $C_{\rm w}$ of BTEX absorbed by the sampling device. Moreover, a good correlation was obtained between the measured and predicted concentrations, and thus a reliable measurement of BTEX in soil or water phase can be made using the assembled sampling device.



Fig. 4 The effect of ionic strength on BTEX equilibrium partitioning to a 1 mm thick PDMS and b 76 μ m thick POM sheets. The equation of the lines are tabulated in Table S1

Environmental implications/conclusion

This study provided significant details on kinetics and thermodynamic equilibrium partitioning of low molecular weight compounds on two different equilibrium samplers, PDMS and POM. The partitioning kinetics shows that PDMS has faster rate of uptake and desorption, within 2 h, whereas POM reached equilibration after 35 days and desorbs completely after 7 days. While it is advantageous to use PDMS for its faster absorption, its exponential desorption creates drawbacks when applied to field sampling as BTEX is significantly lost at an impractical amount of time. Meanwhile, POM was able to absorb larger concentrations of BTEX until equilibration (up to 1200 mg/kg), as well as higher K_d values, which means POM is more sensitive and a stronger sorbent for BTEX measurements. The sorption processes for both PDMS and POM were shown to vary at different temperatures, with lower temperatures resulting to higher K_{d} values for both polymers. In a thermodynamic analysis, it was found out that the processes are enthalpy-driven, and partitioning is favorable at lower temperatures. Moreover, ionic strength was found to affect K_d values positively. The partitioning of BTEX to PDMS and POM thus increases in sampling, for example, at a colder environment and in saline environment such as those near estuaries and saltwater systems. Because 1:1 correlation with K_{ow}



Fig. 5 The BTEX equilibrium partitioning to \mathbf{a} 1 mm thick PDMS and \mathbf{b} 76 μ m thick POM sheets in a gasoline-contaminated water

was not observed, analysis at various temperatures and at different ionic strength was helpful for unbiased BTEX concentration calculations. Moreover, as the presence of other hydrophobic



Fig. 6 Comparing dissolved BTEX levels in 100 % saturated soil pore estimated by PDMS and POM and by direct measurement. Note that in the graph legend, *B*, *T*, *EB*, and *X* represent benzene, toluene, ethylbenzene, and xylene, respectively, and *NS* and *AS* represent natural and artificial soil, respectively

components in gasoline and that of dissolved organic matter do not significantly affect K_d measurements, an efficient passive sampling can be utilized in BTEX analysis from gasolinecontaminated environment. Applicability of the passive sampler was simulated using natural and artificial soils wherein the measured concentrations were in good correlation with the predicted concentration, signifying reliable measurements using the experimental parameters in this study. This study provides a groundwork for the future possibility of utilizing the studied passive samplers in field sampling of soil and groundwater.

For future research interests, other volatile organic pollutants can be analyzed such as methyl tert-butyl ether (MTBE), trichloroethylene (TCE), and perchloroethylene (PCE). Moreover, characterization of PDMS and POM, as well as of other polymers such as low density polyethylene (LDPE), must be specifically done to properly establish the variables that were studied in this paper. For example, the main partitioning processes depends on the diffusion properties of the compound in the polymer system. Hence, a study on diffusion properties of these polymers might be helpful to provide a better understanding on the partitioning processes with a contaminant.

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