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Development of an expanded polytetrafluorethylene dosimeter for the passive sampling of volatile organic compounds in air

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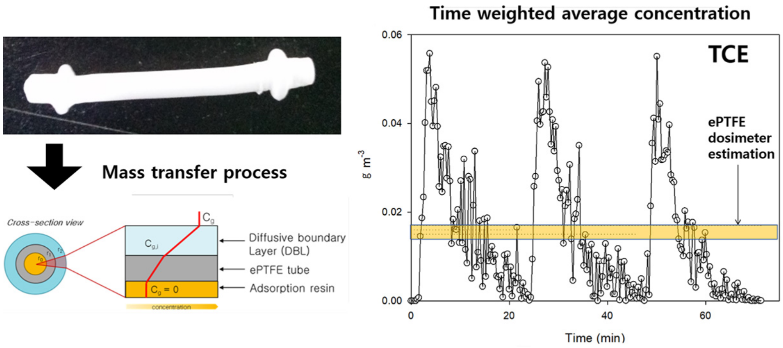
HIGHLIGHTS

- A passive sampler was developed to effectively concentrate VOCs in the air.
- Sampling rates were larger considering the mass of the absorbent.
- Appropriate sampling time and absorbed mass considering desorption were determined.
- A PTR-MS and sampler were deployed simultaneously under pulsed exposure to VOCs.
- The results confirm the high precision and accuracy of passive sampling.

GRAPHICAL ABSTRACT



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ABSTRACT

A passive sampler composed of a porous, hydrophobic, and gas-permeable expanded polytetrafluoroethylene (ePTFE) tube was developed to effectively concentrate volatile organic compounds (VOCs) in the air. The ePTFE dosimeter has larger sorbent mass normalized sampling rates (L h^{-1}) compared with literature. This result suggests that ePTFE dosimeter can effectively detect low level VOCs in less contaminated air, including indoors. The air boundary layer thickness can be neglected when the mass accumulated in sorbent is converted to gas phase VOCs concentrations. The vapor pressure dependent desorption of VOCs from the sorbent was observed and modeling results suggested that this could lead to the underestimation of VOCs concentrations in air. However, the determination of the appropriate sampling time and the consideration of desorption could overcome the underestimation. A proton transfer reaction quadrupole mass spectrometer and passive samplers were deployed simultaneously in a chamber under fluctuating VOCs concentrations in air. The time-weighted average concentrations of ethylbenzene were 0.016, 0.015, and 0.017 g m^{-3} for 23, 46, and 69 min experimental period, respectively. The average concentration of the real-time analysis was 0.015 g m^{-3} for 69 min. The results show the ePTFE dosimeter can be used to estimate time weighted VOCs concentrations in air.

1. Introduction

One of the most extensively occurring contaminants in the atmosphere and indoors are volatile organic compounds (VOCs) (Edwards et al., 2001; Schlink et al., 2010; Sarkhosh et al., 2012). These compounds pose severe health risks, including carcinogenicity (Agency, U.E.P, 1994; Belpomme et al., 2007; Chang and Chen, 2008; Petry et al., 2014). They accumulate in the environment through improper waste disposal, oil spills, or underground storage tank leaks (Huang et al., 2014) which can invade indoor spaces via soil vapor intrusion (Soucy and Mumford, 2017; Ma et al., 2020). In addition, there are

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numerous indoor VOC sources, including building materials, printers, paints, furnishings, and consumer products; therefore, indoor contamination due to VOCs is continuously increasing (Thevenet et al., 2018; Morin et al., 2019; Cummings and Waring, 2020). Compared to VOC pollution outdoors, higher VOC pollution indoors has been determined in many studies (Geiss et al., 2011; Verriele et al., 2016; Raysoni et al., 2017). As humans generally spend almost 90% of their lifetime indoors, the control of indoor air quality is critical for human health (Robinson and Nelson, 1995; Klepeis et al., 2001). To control indoor VOCs, an effective method for measuring indoor VOCs is needed (Mølhave, 1991; Guo et al., 2004; Weisel et al., 2008; Zhou et al., 2011; McAlary et al., 2015).

Active sampling methods, including active air sampling and purge-and-trap techniques, are commonly used (Amaral et al., 2010; Gallego et al., 2017; Horii et al., 2017), and they have high precision and accuracy over short-term monitoring (Bohlin et al., 2007). However, the major limitations of active sampling are the inability to detect relatively long-term concentrations which are fluctuating and poor practicality in operation due to bulky instrumentations (Seethapathy et al., 2008; Vallecillos et al., 2019; Li et al., 2020; Vallecillos et al., 2020a, 2020b). Compared with the artefacts of active sampling, passive sampling has many benefits, such as simplicity, low cost, and ease of implementation (Bohlin et al., 2007). Although active sampling is more efficient for short time monitoring, passive samplers can determine the time-weighted average concentration over long-term monitoring to capture episodic contaminant fluctuations (Martos and Pawliszyn, 1999; Wennrich et al., 2002; Chen and Pawliszyn, 2003; Namiesnik et al., 2005). Passive sampling is driven solely by changes in chemical potential, which causes contaminants to diffuse into their absorbent phase. Absorbed contaminants can be extracted using simple solid-liquid extraction methods or thermal desorption (Namiesnik et al., 2005). However, there exist several hurdles to overcome. For example, passive sampling is difficult to quantify because of unsettled conditions, air pressure, air turbulence, temperature, and humidity (Lan et al., 2020). In addition, the difference between the concentrations of VOCs in air measured by passive sampling and “true” concentrations could be within a factor of 3(Bohlin et al., 2007; Jones et al., 2007). Hence, the development of a highly precise and accurate passive sampler is required.

The current study investigates the potential use of expanded polytetrafluoroethylene (ePTFE) membrane tube packed with sorbent as a passive sampler for VOCs with dimensionless Henry's constants of 0.052 to 0.682 [−] in gaseous environments. ePTFE is inert, highly hydrophobic, gas-permeating membrane and the retardation effect during the permeation of VOCs through the ePTFE membrane could be negligible. ePTFE has the same structure and properties as normal PTFE and has exceptional inertness, thermal stability, biocompatibility, and hydrophobicity (Ranjbarzadeh-Dibazar et al., 2014; Hao et al., 2005). This provides ePTFE with various desirable properties, such as flexibility and gas permeability (Huang et al., 2004; Huang et al., 2008). For kinetic passive samplers, sampling rates are often important for trace-level contaminant monitoring while capturing concentration fluctuations in the environment. The transport resistances involved in the diffusion of contaminants are important in determining the sampling rates of the passive sampler (Namiesnik and Szefer, 2009). Mass transfer analysis probes the effects of the gaseous phase air boundary layer (ABL) on the sampling rate of the ePTFE dosimeter. The performance of the developed dosimeter was demonstrated by comparing the time-weighted average concentration measured by the ePTFE dosimeter with real-time analysis using a proton transfer reaction quadrupole mass spectrometer.

2. Theory

The dosimeter contains packed adsorbents inside the ePTFE tube; hence, VOC transport can be modeled in cylindrical coordinates with finite length. When the two-film theory in gas transfer is applied to the cylindrical coordinate system, the mass fluxes of VOCs per unit length of the ABL and ePTFE dosimeters at time t are given by

$$M_{\mathrm{ABL}} = \frac{2\pi D_g t\left(C_g - C_{g,i}\right)}{\ln\left(r_2/r_1\right)} L \tag{1}$$

$$M_{\mathrm{ePTFE}} = \frac{2\pi D_{\mathrm{ePTFE}} t\left(C_{g,i}\right)}{\ln\left(r_1/r_0\right)} L \tag{2}$$

where M_{ABL} and M_{ePTFE} are the mass fluxes of VOCs in the ABL and ePTFE tubes, respectively; L is the length of the sampler; r_1 and r_0 are the outer and inner radii of the ePTFE tube, respectively; r_2 is the sum of r_1 and thickness of ABL; D_g and D_{ePTFE} are the diffusion coefficients in the gas and in the membrane of the ePTFE tube, respectively; C_g is the VOC gas phase concentration in air; and $C_{g,i}$ is the VOC concentration at the interface between the ePTFE surface and air. The VOC concentration profiles in different parts of the boundaries are shown in Fig. S1. Based on the conservation of mass at the interface, the mass in the ePTFE dosimeter can be derived as (Supporting information S1 for derivation):

$$M_{ePTFE} = \frac{2\pi C_g L}{\frac{\ln\left(r_1/r_0\right)}{D_{\mathrm{ePTFE}}} + \frac{\ln\left(r_2/r_1\right)}{D_g}} t \tag{3}$$

Assuming that the VOC diffusion in the gas is faster than in the ePTFE tube membrane, the right term in the denominator becomes smaller than the left term in the denominator and can be neglected. Then, the equation can be simplified as follows:

$$M_{ePTFE} = \frac{2\pi C_g t D_{\mathrm{ePTFE}} L}{\ln\left(r_1/r_0\right)} \tag{4}$$

Eq. (3) was used to evaluate the effect of the ABL on the ePTFE sampling rate, and Eq. (4) was used when the ABL effect was negligible.

3. Material and methods

3.1. Chemicals and instruments

High purity, ten gas-chromatography grade VOCs, namely 1,2-dichloroethane (DCA), benzene (BZN), trichloroethene (TCE), 1,1,2-trichloroethane (TCA), tetrachloroethene (PCE), chlorobenzene (CBZ), ethylbenzene (EBZ), p-xylene (PXY), 1,3,5-trimethylbenzene (TMB), and 1,3-dichlorobenzene (DCB), and internal standards (toluene-d_8, chlorobenzene-d_5), were purchased from Sigma-Aldrich (Milwaukee, WI, USA). Dichloromethane (DCM, Sigma Aldrich) spiked with internal standards was used as a solvent to extract VOCs from the resin.

The gas chromatography–mass spectrometry (GC–MS) was conducted using an Agilent 6890A gas chromatograph and Agilent 5973 N mass selective detector with an Agilent 7683 auto-injector and an Agilent DB-5 column (30 m × 0.25 mm × 0.25 μm). Helium, as the carrier gas, flowed constantly at 1.0 mL min^{-1}. Initially, the oven was programmed at 40 °C for 2 min, increased to 100 °C at 10 °C min^{-1}, and then to 270 °C at 10 °C min^{-1}. The injection volume was 2 μL, with a split ratio of 5:1. The MS detector was configured to operate in SIM mode.

A proton transfer reaction quadrupole mass spectrometer (PTR-QMS, Ionicon, Innsbruck, Austria) was used for real-time analysis. When measuring VOCs, H_3O^+ was used as the primary ion. The pressure controller was set to 210 mbar for pressure controller, drift tube pressure was 2.30 mbar, quad was 2.34 E^{-5}, field strength of the drift tube was 115 Td, temperature was 23.3 °C, sanitary remote-controlled valve was 52, H_2O flow rate was 6 $\mathrm{cm}^3\ \mathrm{min}^{-1}$, source-out voltage was 80 V, drift voltage was 600 V, extraction lens voltage was 150 V, and source current was 6 V.

3.2. ePTFE dosimeter

Expanded PTFE tubes (Huizhou Besteflon Industries Co. Ltd.) of 1 mm (ID 2 mm × OD 4 mm) and 2 mm (ID 2 mm × OD 6 mm) tube wall thickness were cut to a 4.5 cm length. The SEM image of the ePTFE in Fig. S2 shows the highly porous structure of the ePTFE tube (porosity = 0.72). These tubes were soaked for 1 d in methanol and rinsed twice with the same solvent. The tubes were Soxhlet extracted for 12 h using 100 mL of a mixture of *n*-hexane and acetone (50:50). Viton rings were placed at both ends of the tubes. The rings constrict both ends of the tube so that the PTFE caps are tightly fitted before sealing with PTFE tape. The PTFE tube was packed with 50 mg of Dowex Optipore-L493 (Sigma Aldrich) as the sorbent, because of high affinity for VOCs (Bonifacio et al., 2017). To extract the VOCs from the dosimeters, the sorbent was transferred into a 2-mL vial with 2 mL of DCM, and the vial was shaken for 1 d. The concentrations of VOCs in the DCM extracts were analyzed using GC–MS. Comparing with a Tenax based passive sampler, which can be thermally desorbed, procedure seem complicated. However, while transporting the Tenax sampler for thermal desorption analysis, desorption by volatilization can occur. ePTFE dosimeter can avoid desorption by field extraction. In addition, mass normalized price of Dowex is over 50 times cheaper.

3.3. Absorption kinetics of the ePTFE dosimeter in the gas phase

The diffusion coefficients of VOCs in the ePTFE tube membrane were derived from the absorption kinetics determined in a 125 L acrylic chamber. A spiking solution composed of 10 VOCs with the same concentration was prepared and injected into the chamber at 2, 4, and 6 μL. The spiking solution was completely vaporized while the mixing fan was on. Five thin and five thick dosimeters were placed in the chamber and removed for extraction 10, 20, 30, 40, and 50 min after deployment. Mass transfer rates were obtained by linear regression of the extracted mass of VOCs and time. Sampling rates were obtained by linear regression of the mass transfer rates and concentration of VOCs in the chamber. The diffusion coefficients of VOCs in the ePTFE tube membrane were derived using Eq. (4). The influence of the fan was observed by comparing the absorbed mass in the chamber (2 μL VOCs in 125 L) with a thin dosimeter for 20 min without mixing.

3.4. Desorption kinetics of the ePTFE dosimeter in the gas phase

To measure the desorption rates, thick ePTFE dosimeters were exposed to a 2 μL/125 L chamber for 20 min. In a ventilated room with an air inhalation rate of 0.25 to 0.33 m s^{-1}, loaded dosimeters were detached. These dosimeters were removed for extraction at 2, 5, 12, 18, and 45 h after deployment. Time-course measurements of the remaining mass in the passive sampler were used to determine the desorption rate constant using the nlsfit function in R software (R Development Core Team, 2020).

3.5. VOC accumulation in the passive sampler under pulsed exposure

The ability to provide time-weighted average VOC concentrations by ePTFE passive samplers was tested and demonstrated under dynamic VOC concentrations in air. Dynamic VOC concentrations in air were simultaneously analyzed in real time to test the accuracy of measurements by passive sampling. Air flowed through the 125 L acrylic chamber at a rate of 10 L min^{-1}, applying negative pressure by a vacuum pump at the outlet. The air inside the chamber was mixed using a fan to satisfy a completely mixed condition. Three thick dosimeters were deployed in the chamber, and 5 μL of DCM solution containing DCA, TCE, and EBZ as surrogates was dropped every 23 min. The concentration in the chamber was monitored in real time using a proton transfer reaction quadrupole mass spectrometer (PTR-QMS) for 70 min. After 23 min, all DCA, TCE, and EBZ exited the chamber. Every 23 min, the dosimeter was removed from the chamber and extracted using DCM.

4. Results and discussion

4.1. VOC accumulation in gas phase

The advantage of kinetic passive samplers, such as the ePTFE dosimeter, is their ability to steadily concentrate VOCs into their absorbents over time to measure the time-weighted average concentration. The mass accumulations of VOCs in the ePTFE dosimeter deployed in the chamber at a constant VOC concentration are shown in Fig. S3. All VOCs accumulated linearly with time. The slopes in Fig. S3 a-f represent the mass accumulation rates (μg h^{-1}). The mass accumulation rates of the thin and thick dosimeters are compared in Fig. 1. The R^2 and slope of the linear regression were 0.99 and 1.44, respectively. However, as can be seen in Eq. (4), the sampling rates of the thin dosimeter were 1.58 times greater than those of the thick dosimeter. The measurement error of the thickness may explain this phenomenon. The thickness of ePTFE could have a 0.1 mm error margin. When the thick and thin ePTFEs are 2.9 and 2.1 mm thick, respectively, the difference is same for 1.44.

From Eq. (4), the diffusion coefficients (m^2 s^{-1}) of VOCs in the thin and thick ePTFE tube membranes were obtained. As shown in Table 1, the calculated values are compared with the diffusion coefficients in air, which were almost one order of magnitude greater than the diffusion coefficients in the ePTFE tube membrane. The lower diffusivity in the ePTFE tube membrane suggests that the mass transfer resistance in the ePTFE wall determines the mass transfer rate. Correlations between the average diffusion coefficients of VOCs in the ePTFE tube membrane and the properties of VOCs, molar volume, Henry's law constants, octanol-water partition coefficient (K_{OW}), molecular weight (MW), vapor pressure, and diffusion coefficients in air were analyzed. The one-to-one relationship between the diffusion coefficients in the ePTFE tube membrane and properties of VOCs was low. For example, all R^2 values of regression were lower than 0.5, except for K_{OW} which was 0.7. However, the R^2 value of regression was 0.86 for multiple

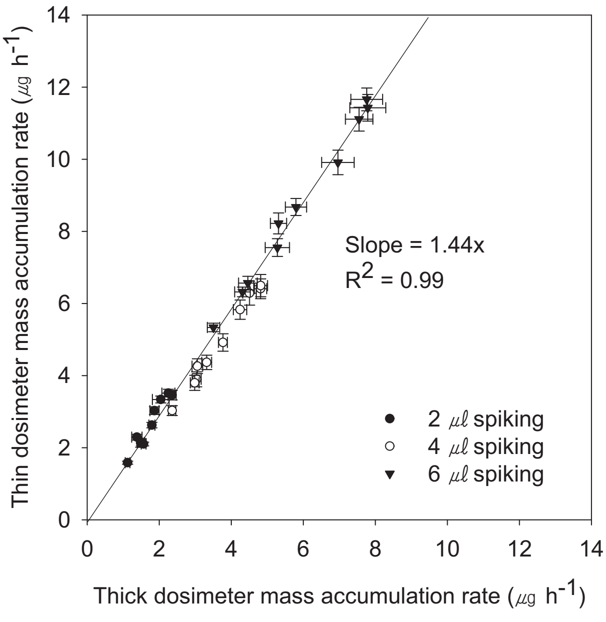

Fig. 1. Comparison of mass accumulation (equivalent to sampling rate, L_{air} h^{-1}, if air concentration is considered) in thin (r_0 = 1 mm, r_1 = 2 mm) and thick (r_0 = 1 mm, r_1 = 3 mm) ePTFE dosimeters.

Table 1
Diffusion coefficients (expressed in $m^2 s^{-1}$) of VOCs in ePTFE dosimeters. Values in the parentheses mean standard deviations.

VOCs	$D_{ePTFE,thick}$ ($\times10^{-6}$)	$D_{ePTFE,thin}$ ($\times10^{-6}$)	$D_{ePTFE,average}$ ($\times10^{-6}$)	D_{air} ($\times10^{-6}$)
DCA	1.14 (0.10)	1.05 (0.06)	1.10 (0.09)	9.15
BZN	1.12 (0.12)	1.12 (0.08)	1.16 (0.11)	8.99
TCE	1.06 (0.11)	1.00 (0.08)	1.03 (0.10)	8.46
TCA	1.14 (0.03)	1.02 (0.06)	1.08 (0.08)	8.34
PCE	1.00 (0.06)	0.93 (0.07)	0.97 (0.07)	7.86
CBZ	1.14 (0.03)	1.02 (0.07)	1.08 (0.08)	8.15
EBZ	1.17 (0.01)	1.03 (0.05)	1.10 (0.08)	7.56
PXY	1.16 (0.02)	1.02 (0.05)	1.10 (0.08)	7.54
TMB	0.90 (0.02)	0.80 (0.06)	0.85 (0.07)	7.08
DCB	0.87 (0.04)	0.77 (0.09)	0.82 (0.09)	7.57
Average	1.08 (0.05)	0.98 (0.01)	1.03 (0.01)	8.10

regression analysis between diffusion coefficients in the ePTFE tube membrane, K_{OW} values, and molecular weight. The p values of K_{OW} and molecular weight were 0.002 and 0.022, respectively. The diffusion coefficients of VOCs in the ePTFE tube membrane can be estimated using:

$$10^{11} \times D_{ePTFE} = 134000 - 7.6K_{OW} - 1.9MW \tag{5}$$

In addition to the tested VOCs, the diffusion coefficient of the target VOC in the ePTFE tube membrane can be predicted using the K_{OW} and MW of VOC using Eq. (5).

Time-dependent VOC sampling volumes were obtained by dividing the mass accumulation rates by the VOC concentrations in the chamber. Fig. 2 shows the time-dependent VOC sampling volumes of the thick and thin ePTFE dosimeters in a 6 μL spiking solution-injected chamber. The sampling volumes increased linearly with time, and those of the thin dosimeter were larger than those of the thick dosimeter. The difference in the dimensions of the thick and thin dosimeters may explain this phenomenon. As can be seen in Eq. (4), the thin dosimeter has a lower r_1, whereas the other factors are the same. A lower r_1 of the thin dosimeter results in a higher mass accumulation. Because VOC gas phase concentrations in air are the same, thin dosimeters have higher sampling volumes. For both thin and thick dosimeters, the sampling volumes were slightly different depending on the VOCs. For example, the sampling volumes of BZN were relatively greater than those of other VOCs for both thin and thick dosimeters, whereas those of TMB were smaller. The properties of VOCs could affect the time-dependent sampling volumes of the ePTFE dosimeters.

Sampling rates ($L\ h^{-1}$) were obtained by linear regression of the mass accumulation rates and VOC concentrations in the chamber. The measured sampling rates, R^2 values, and standard deviations of the linear regression are shown in Table S1. For the 10 VOCs, the sampling rates of the thin dosimeter were 1.42–1.46 times those of the thick dosimeter. Sampling rates were related to the K_{OW} and MW of VOCs. For the thin sampler, the R^2 value was 0.93 for multiple regression analysis between sampling rates, K_{OW}, and MW of VOCs. The p values of K_{OW} and molecular weight were 0.00017 and 0.013, respectively. For the thick sampler, the R^2 value of regression was 0.92 for multiple regression analysis between sampling rates, K_{OW}, and MW of VOCs. The p values of K_{OW} and molecular weight were 0.00026 and 0.0064, respectively. The sampling rate (SR) can be estimated as

$$10^4 \times SR_{thin} = 18603.45 - 1.2K_{OW} - 21.2MW \tag{6}$$

$$10^5 \times SR_{thick} = 134491.5 - 8.2K_{OW} - 189MW \tag{7}$$

In addition to the 10 VOCs, sampling rates for target VOCs can be predicted using the K_{OW} and MW of VOC using Eqs. (6) and (7).

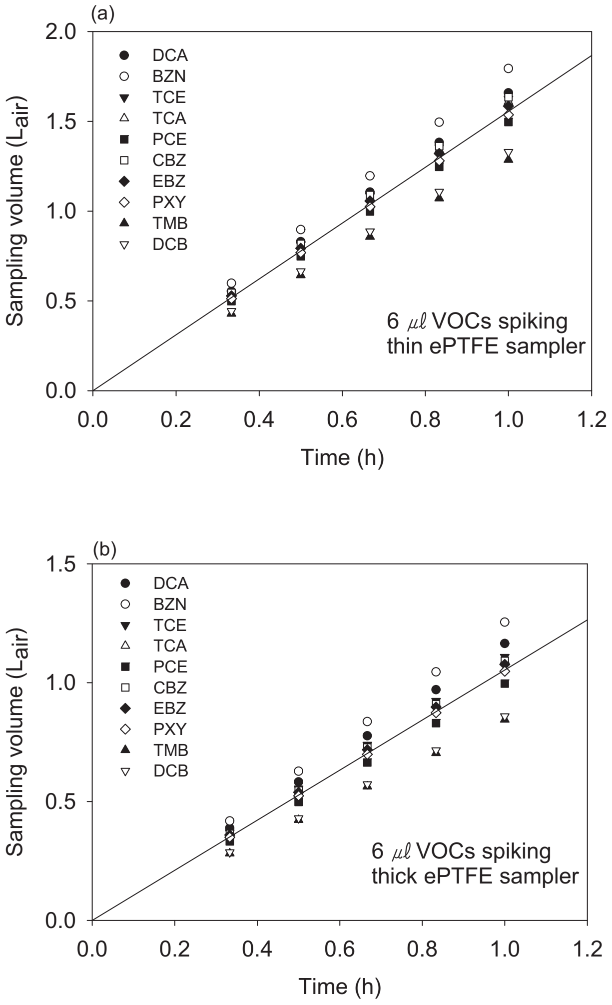

Fig. 2. Time dependent VOCs sampling volume (L_{air}) by (a) thin ($r_0 = 1$ mm, $r_1 = 2$ mm) and (b) thick ($r_0 = 1$ mm, $r_1 = 3$ mm) ePTFE dosimeter for 6 μL of spiking solution injected chamber.

As shown in Table 2, the measured sampling rates were compared with the values obtained in the literature. Compared with the sampling rates of passive samplers in different forms, those of the cylindrical passive samplers were larger. Considering the mass of the absorbents, 50 mg of Dowex in ePTFE dosimeter, the sampling rates of the ePTFE dosimeter were higher than those of the other cylindrical passive samplers. The mass of the inserted absorbents in the ePTFE dosimeters was 6 and 8 times less than those of the Radiello diffusive sampler and Tenax GC, respectively (Lewis and Mulik, 1985; Lewis et al., 1985; Coutant et al., 1986; Pennequin-Cardinal et al., 2005; Król et al., 2012). Although further studies are needed for field applications, ePTFE dosimeters could be an effective alternative to existing passive samplers.

4.2. Effects of air boundary layer

In Fig. 3, the mass accumulations (μg) of individual VOCs with and without mixing were compared. The accumulated masses with and without mixing are shown in Table S2. The mass accumulation of VOCs with mixing was slightly greater than that without mixing. The slope was 0.86 ± 0.10, suggesting that the VOC accumulation decreased by 14%, likely due to the unavoidable air boundary layer outside of the ePTFE tubing.

To investigate the effect of the air boundary layer thickness on limiting the ideal mass transfer behaviors shown in Eq. (4), the contribution

Table 2
Sampling rates measured in this study and sampling rates from the literature (expressed in L h^{-1}).

Reference	Chemicals	Type of passive sampler	Absorbents	Sampling rate (L h^{-1})
McAlary et al., 2015	VOCs	SKC Ultra passive sampler	Tenax® TA, Chromosorb® 106, Anasorb® GCB1, or Carbopack X	~0.28–1.04
Król et al., 2012	Benzene	Radiello diffusive sampler	Graphitized carbon	1.61
Ly-Verdú et al., 2010a, 2010b	VOCs	VERAM samplers (LDPE)	Activated carbon	~0.013–0.10
Pennequin-Cardinal et al., 2005	BTEX	Radiello diffusive sampler	Graphitized carbon	~1.32–1.69
Xian et al., 2011	BTEX	Cylinder	Carbopack B 60/80	0.17
Jia et al., 2007	VOCs	Thermal desorption tube	Tenax GR	~0.021–0.028
Lewis and Mulik, 1985	VOCs	Cylinder	Tenax GC	1.8
Lewis et al., 1985	VOCs	Cylinder	Tenax GC	1.8
Coutant et al., 1986	VOCs	Cylinder	Tenax GC	1.8
Chen and Pawliszyn, 2003	n-Hexane	SPME (PDMS)	Carboxen/poly(dimethylsiloxane)	0.00048
Ly-Verdú et al., 2010a, 2010b	Benzene	SPMD (LDPE)	Low-density polyethylene	0.8
Measured in this study	VOCs	Thin ePTFE dosimeter	Dowex	1.22–1.70

of individual mass transfer resistance, that is, mass transfer controlled by the ePTFE sampler vs. mass transfer controlled by the air boundary layer, was evaluated as follows:

$$fraction\ of\ ePTFE\ mass\ transfer = \frac{\frac{\ln(r_1/r_0)}{D_{\mathrm{ePTFE}}}}{\frac{\ln(r_1/r_0)}{D_{\mathrm{ePTFE}}} + \frac{\ln(r_2/r_1)}{D_g}} \quad (8)$$

$$fraction\ of\ air\ boundary\ layer\ mass\ transfer = \frac{\frac{\ln(r_2/r_1)}{D_g}}{\frac{\ln(r_1/r_0)}{D_{\mathrm{ePTFE}}} + \frac{\ln(r_2/r_1)}{D_g}} \quad (9)$$

The average D_{ePTFE} and D_{air} values of 10 VOCs and thick ePTFE tubing with $r_0 = 1.0$ mm and $r_1 = 3.0$ mm values were used for estimating the contribution of individual mass transfer resistance, as shown in Fig. 4. When the air boundary layer was <1 cm, the overall mass accumulation in the sampler was completely controlled by the ePTFE sampler. As the air boundary layer increased from 1 cm, the contribution of the air boundary layer started to occur. When the air boundary layer was >100 m, the mass transfer resistance of the air boundary layer dominated. Generally, the mass transfer resistance of ePTFE sampler is dominant for air sampling because the air boundary layer is assumed to be much smaller than 100 m. Studies have shown that the air boundary layer could vary between 7.5 and 15 mm for the passive Radiello samplers (Armitage et al., 2013; McLagan et al., 2016; Huang et al., 2018; Jeon et al., 2019). Assuming that the air boundary layer varies between 7.5 and 15 mm, the fraction of ePTFE mass transfer varies between 82 and 87%. This describes the decreased accumulation of VOCs by 14%, as shown in Fig. 3.

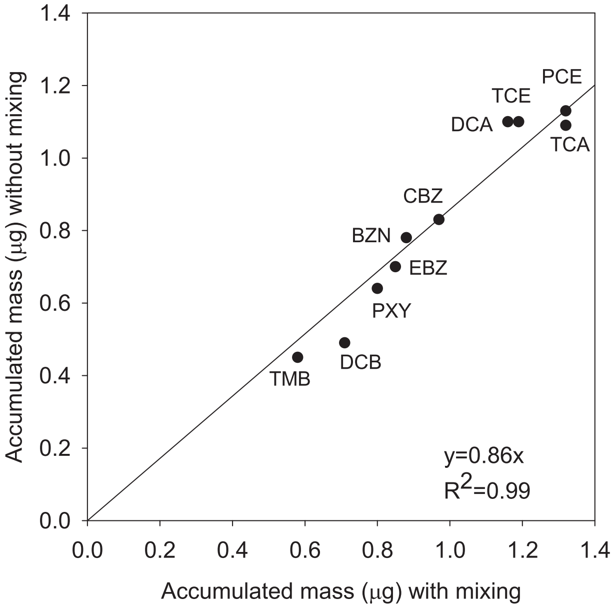

Fig. 3. Mass accumulation of VOCs in chamber mixed by fan plotted against mass accumulation in chamber without mixing for 20 min, with thin ePTFE sampler.

4.3. VOC desorption in the gas phase

Table S3 shows the time-dependent desorption ratios. VOCs desorbed from the ePTFE dosimeter in a first order reaction, and desorption rate constants (h^{-1}) were evaluated as follows:

$$desorption\ rate\ constant = \frac{-\ln\left(\frac{C_t}{C_0}\right)}{t} \quad (10)$$

where C_t is the time-dependent VOC gas phase concentration in air; C_0 is the initial VOC gas phase concentration in air.

As shown in Fig. 5, the desorption rate constants for 10 VOCs linearly increased with the vapor pressure. According to the desorption rate constant values, 10 VOCs can be classified into three groups. The desorption rate constants of DCA, BZN, and TCE were relatively large, ranging from 0.06 to 0.1 h^{-1}. The half-lives of those VOCs were within one day, namely from 7 to 12 h. Desorption rate constants of PCE, TCA, and CBZ varied between 0.01 and 0.02 h^{-1} and the half-lives of those VOCs were 45 to 62 h, respectively. The half-lives of EBZ, PXY, TMB, and DCB were more than 134 h. Considering the desorbed mass from the dosimeters, the absorbed mass can be calculated as follows:

$$absorbed\ mass\ considering\ desorption\ over\ time = \frac{M_{ePTFE}\left(1-e^{-kt}\right)}{k} \quad (11)$$

Fig. 6 shows the ratio of absorbed mass considering desorption to absorbed mass without considering desorption according to vapor pressure over 0.25, 0.5, 1.0, and 2.0 d. VOCs with larger vapor pressure have higher desorption from dosimeters. In such cases, the concentration of VOCs in air can be underestimated. For example, when sampling for 6 h, the absorbed mass of benzene can decrease by 20% because of desorption. When the sampling time increased to 2 d, the decreased mass increased to 70%. In addition to selected VOCs, the desorption constant can be estimated with a vapor pressure of the target VOC. Excluding the 10 VOCs selected in this study, vapor pressure values of 28 VOCs are shown in Table S4 (Heinrich-Ramm et al., 2000). For example, the estimated desorption constant and half-life of styrene were 0.004 h^{-1} and 161 h, respectively. The estimated desorption constant and half-life of phenol, a VOC with larger vapor pressure, were 0.03 h^{-1} and 21 h, respectively. Considering the half-life of target VOCs, the appropriate sampling time for target VOCs can be determined. Additionally, absorbed mass considering desorption can be estimated with the vapor pressure of target VOCs. The decreased mass ratios by desorption when sampling aniline for 6 h was an estimated 10%. When the

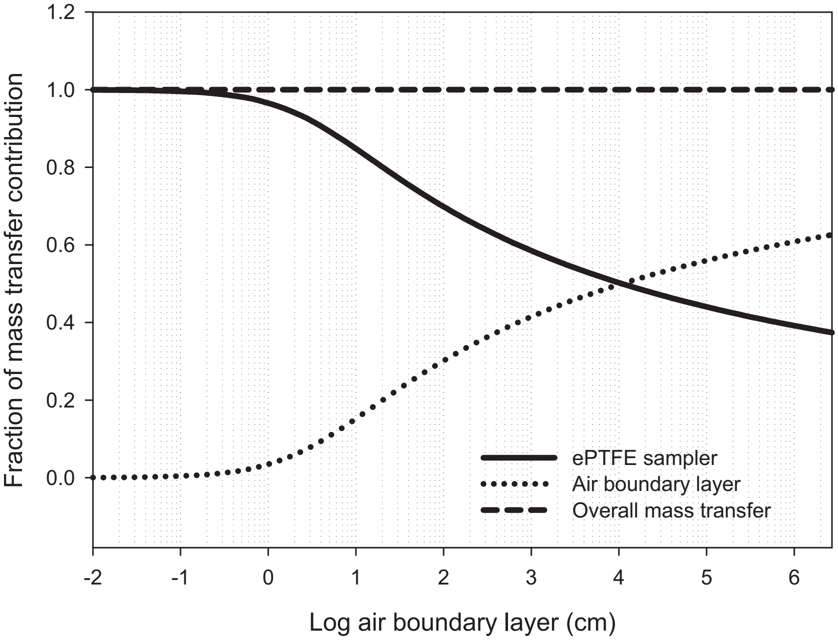

Fig. 4. Mass transfer contribution of ePTFE sampler and air boundary layer to the overall mass accumulation in sampler.

sampling time increased to 2 days, the decreased mass ratios by desorption increased to 60%. Estimating absorbed mass considering desorption can compensate for the underestimation by desorption.

4.4. Dynamic change of VOC concentrations in air and determination of time-weighted average concentration

As shown in Fig. 7, the concentrations of DCA, TCE, and EBZ in the 125 L chamber were measured using a passive sampler and PTR-MS simultaneously. The absorbed mass of each chemical in the passive sampler is shown in Fig. S4. The absorbed mass increases linearly with time. The time-weighted average concentrations measured by the passive sampler are shown in Table S5. The three time-weighted average concentrations of each VOC in the chamber for 0–23, 0–46, and 0–69 min were similar. For example, for DCA, the average concentrations of the chamber were 0.022, 0.023, and 0.024 g m^{-3} at 0–23, 0–46, and 0–69 min, respectively. This suggests that measuring the time-weighted average concentration using a passive sampler is precise and repeatable. Interestingly, differences between time-weighted average concentration measured by the passive sampler and real-time analyzed concentration measured by PTR-MS were small. For example, in the case of EBZ, time-weighted average concentrations were 0.016, 0.015, and 0.017 g m^{-3} for 0–23, 0–46, and 0–69 min, respectively. The average of the real-time analyzed concentrations for 0 to 69 min was 0.015 g m^{-3}. The results showed that the difference in performance between the passive and active sampling methods was almost negligible.

5. Conclusions

In this study, the ePTFE dosimeter exhibited good precision and accuracy. For example, the time-weighted average concentrations of ethylbenzene were 0.016, 0.015, and 0.017 g m^{-3} for 23, 46, and 69 min, respectively. The average concentration of the real-time analysis was 0.015 g m^{-3} for 69 min. In addition, the ePTFE dosimeter has larger

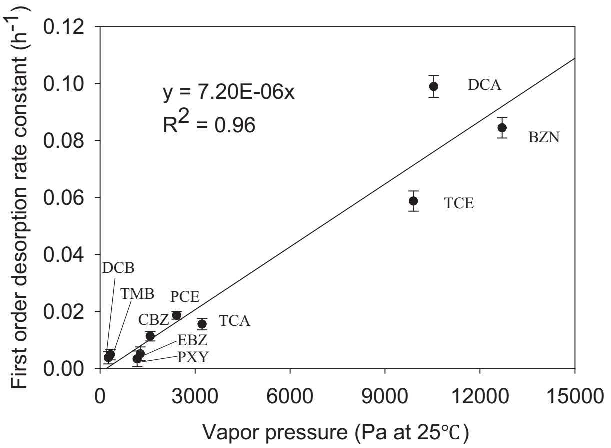

Fig. 5. Measured desorption rate constants for vapor pressures. Error bars represent the standard errors.

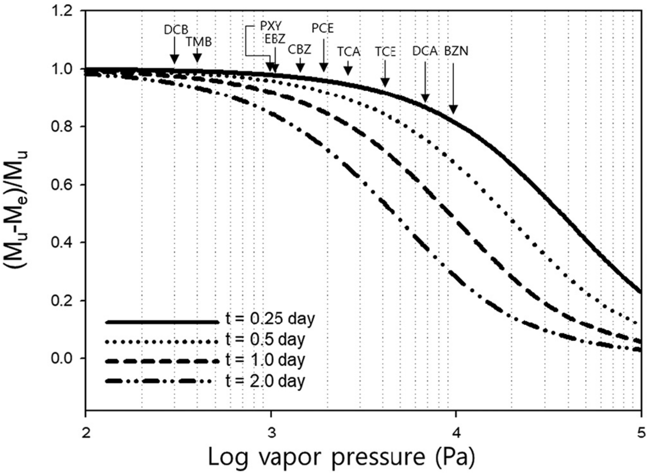

Fig. 6. Time dependent ratio of absorbed mass considering desorption to absorbed mass, without considering desorption according to vapor pressure. M_u is the estimated time-dependent absorbed mass, M_e is the estimated time-dependent desorbed mass.

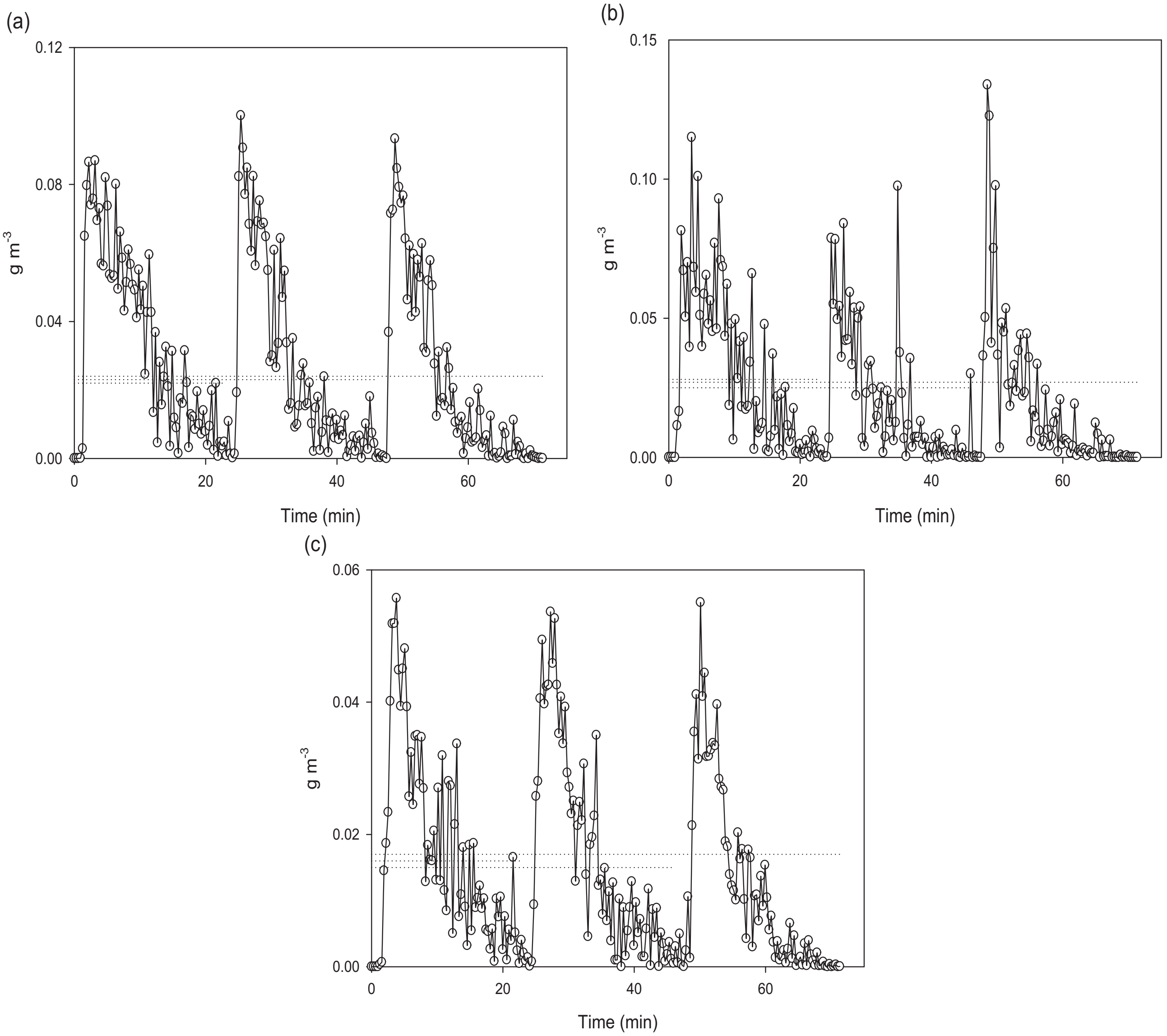

Fig. 7. Measured concentration in 125 L chamber by passive sampler and PTR-MS for (a) DCA, (b) TCE, and (c) EBZ. Dotted line denotes time-weighted average concentrations measured by passive samplers for 23, 46, and 69 min, respectively. Hollow points denote real time analyzed concentration measured by PTR-MS.

sampling rates among passive samplers in the literature, considering the mass of the absorbent. This results in the detection of VOCs in less contaminated air, including indoors. The ePTFE dosimeter has larger sampling rates than those of other passive samplers reported in the literature. Although future work is needed for application in unsettled conditions, ePTFE dosimeters can be deployed without consideration of turbulence in air, because the effect of ABL on passive sampling could be neglected.

CRediT authorship contribution statement

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

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.149026.

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