

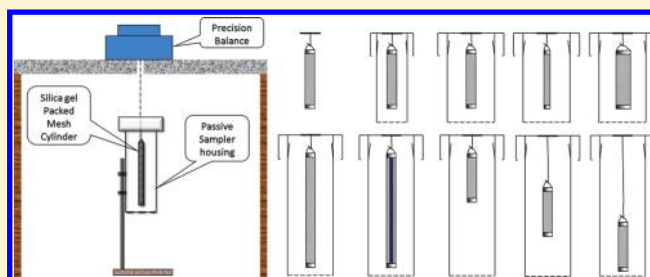
Influence of Sampler Configuration on the Uptake Kinetics of a Passive Air Sampler

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S Supporting Information

ABSTRACT: Passive air samplers (PAS) are simple and cost-effective tools to monitor semivolatile organic compounds in air. Chemical uptake occurs by molecular diffusion from ambient air to a passive sampling medium (PSM). Previous calibration studies indicate that even for the same type of PAS, passive air sampling rates (R , $\text{m}^3_{\text{air}}/\text{d}$) can be highly variable due to the influence of a number of factors. Earlier studies mainly focused on factors (e.g., wind speed and temperature) influencing R via the kinetic resistance posed by the air boundary layer surrounding the PSM because that layer was deemed to be the main factor determining the uptake kinetics. Whereas recent calibration studies suggest that the PAS configuration can influence R , so far few studies have specifically focused on this factor. In this study, with the objective to understand the effect of PAS configurations on R , we applied a gravimetric approach to study the kinetics of water vapor uptake from indoor air by silica gel placed inside cylindrical PAS of various configurations. We also conducted an indoor calibration for polychlorinated biphenyls on the same type of PAS using XAD-resin as the PSM. R was found to be proportional to the interfacial transfer area of the PSM but not the amount of the PSM because chemicals mainly accumulated in the outer layer of the PSM during the deployment time of the PAS. The sampler housing and the PSM can introduce kinetic resistance to chemical uptake as indicated by changes in R caused by positioning the PSM at different distances from the opening of the sampler housing and by using PSM of different diameters. Information gained from this study is useful for optimizing the PAS design with the objective to reduce the material and shipping costs without sacrificing sampling efficiency.



The uptake can be approximated as a linear function of t when surface evaporation of the SVOC from the PSM to the air is negligible during the initial uptake stage, which is referred as the quasi-linear range and operationally defined as the period when the amount of chemical in the PSM is less than 25% of the equilibration amount.^{8,9} During the quasi-linear range, the amount of SVOCs accumulated in the PSM as a function of PAS deployment time can be simplified from eq 1:

$$m_s = k_o \cdot A \cdot C_A \cdot t = R \cdot C_A \cdot t \quad (2)$$

where the passive sampling rate R equals $k_o \cdot A$. In order to derive C_A from m_s and t , using eq 2, PAS for SVOCs should be deployed within the quasi-linear range, during which R does not vary with t . The overall mass transfer coefficient for chemical uptake from ambient air to PSM (k_o) is inversely proportional to the overall kinetic resistance (r_o) which is the sum of the kinetic resistances posed by the sampler housing (r_H), by the air boundary layer surrounding the PSM (r_{BL}), and by the PSM (r_{PSM}).¹⁰ These individual kinetic resistance terms depend on boundary layer

Received: September 19, 2011

Accepted: November 21, 2011

Revised: November 17, 2011

Published: November 21, 2011

INTRODUCTION

Passive air samplers (PAS) are finding widespread and increasing use in monitoring semivolatile organic contaminants (SVOC) in air due to a number of advantages, which include (i) the capability of extended time-integrated sampling; (ii) the independence from power supplies and regular maintenance, and (iii) the relatively low production and operational cost. As a result, PAS have been widely applied in studies on SVOC in both outdoor^{1,2} and indoor^{3,4} environments and proved effective in characterizing concentrations, temporal and spatial trends, and potential human exposure to SVOC in air.^{5–7}

Passive air sampling is based on molecular diffusion of the SVOC from ambient air into the passive sampling medium (PSM). This uptake process has been described with the two-film diffusion model, which assumes uniform chemical distribution within both air and the PSM. Applying a mass balance to the SVOC in the PSM, the amount of SVOC accumulated in the PSM (m_s) can be derived as a function of PAS deployment time (t), SVOC air concentration (C_A), PSM-air equilibrium partition or sorption coefficient (K_{SA}), the volume (V_S) and surface area (A) of the PSM, and the overall mass transfer coefficient (k_o) for the uptake of the SVOC:

$$m_s = C_A \cdot V_S \cdot K_{SA} (1 - e^{-k_o \cdot A / K_{SA} \cdot V_S \cdot t}) \quad (1)$$

thickness and diffusion length, which are difficult to measure directly. Thus, it is not practical to calculate R from the individual kinetic resistance terms. Instead, R is typically acquired from a calibration of the PAS against an active air sampler.

PAS calibrations have been conducted under various environmental conditions using polyurethane foam (PUF) disk or XAD resin as the PSM.^{9,11–14} Even for the same type of PUF-disk PAS, R can vary by as much as an order of magnitude between different studies.¹² Such a large variation in R can introduce uncertainty to PAS-derived air concentrations. Therefore, it is important to understand the factors influencing R . So far, several studies have attempted to understand the effect of temperature and wind speed on R .^{14–16} Besides the temperature and wind effect, there is evidence showing PAS configuration could also affect R . In a previous indoor calibration study, Tao et al.¹³ observed a lower R (and a lower surface area normalized R) for a PAS with the PUF disk positioned in a housing that was more confined than the typically used double-bowl PAS.¹² Abdallah and Harrad¹⁷ noted a decreased rate of chemical uptake by PUF when it was moved further from the opening of the housing compared to the original PUF-PAS design.¹⁸ While these studies clearly indicate that the PAS configurations can affect R , no studies have systematically focused on this effect so far.

With the objective to understand the effect of PAS configurations on R , we applied a gravimetric approach to study the uptake of water vapor from indoor air by silica gel placed inside cylindrical PAS of variable configuration (a schematic of the PAS is shown in Figure S1 of the Supporting Information, SI). These studies were supplemented with an indoor calibration for polychlorinated biphenyl (PCB) uptake in the same type of PAS with XAD-resin as the PSM.

MATERIALS AND METHODS

Setup for Water Uptake Experiments. The experiments were performed using the PAS design by Wania et al.¹⁴ This sampler consists of a stainless steel mesh cylinder (cylinder diameter $d_C = 2$ cm) filled with XAD resin as the PSM, which is hung into an inverted cylindrical steel can (housing diameter $d_H = 10.5$ cm). Both long (cylinder length $l_C = 20$ cm, housing length $l_H = 30$ cm) and short versions ($l_C = 10$ cm, $l_H = 18$ cm) of the sampler have been used. Using water as a surrogate for SVOCs in PAS experiments has proven to be an effective approach to studying the influence of factors that are largely independent of the chemical nature of the sampling medium and the sampled chemicals.^{14,19} An earlier experimental setup¹⁴ required taking the PSM out of the PAS housing to gravimetrically measure the amount of water taken up. In this study, we hung mesh cylinders filled with silica-gel (Aldrich, 35–60 mesh, pore size 150 Å, bulk density 0.33 g/cm³, conditioned overnight at 120 °C before use) from a precision balance (Sartorius ED423S, Readability 0.001 g) placed on a table with a hole (Figure S2 of the SI). The cylinder can still be placed into a housing, if its lid has a small opening. The balance reading (gram of water accumulated, m_S), ambient temperature and relative humidity, measured with a digital psychrometer (Reuter-Stokes RSS230), were recorded at preset time intervals using a data logger. The sensor of the psychrometer was placed outside of the housing with a horizontal distance of 2 cm away from the opening of the housing. From the temperature and relative humidity, the water concentration in air ($C_{A, \text{gwater}}/m^3_{\text{air}}$) could be derived,²⁰ and the equivalent volume (m^3) of air sampled was calculated as $V_{A, \text{eqv}} = m_S / C_{A, \text{gwater}}$.

Characterizing Water Uptake by Silica-Gel. With the experimental setup, we tested the characteristics of silica gel using a long PAS ($l_C=20$ cm, $d_C=2$ cm) placed in a long housing ($l_H=30$ cm, $d_H=10.5$ cm) (Figure S1a of the SI). Duplicate experiments on water uptake for 3 h were conducted and the $V_{A, \text{eqv}}$ was plotted against time and fitted with the following equation:

$$V_{A, \text{eqv}} = a(1 - e^{-b \cdot t}) \quad (3)$$

where $a = K_{SA} \cdot V_S$ and $b = A \cdot k_O / (K_{SA} \cdot V_S)$. K_{SA} [dimension: unitless] is the partition or sorption coefficient between the sorbent (silica-gel) and air; V_S [L³] is the volume of the PSM; A [L²] is the interfacial transfer area between the PSM and air (the lateral area of the mesh cylinder); k_O [L³·T⁻¹] is the overall mass transfer coefficient. In other studies,⁹ k_A (the mass transfer coefficient on the air side) may have been used instead of k_O because the uptake was thought kinetically limited by the air-side boundary layer. However, kinetic resistance could also be introduced from the sampler housing and the PSM.^{10,21} Thus, we use the overall mass transfer coefficient here to represent all possible kinetic resistances. K_{SA} and k_O were derived from the fitting parameters a and b (see SI for details).

Assessment of Different Sampler Configurations. In order to test the hypothesis that during the linear uptake stage, R is governed by the interfacial transfer area rather than the amount of sorbent, we performed a water uptake experiment with short and long cylinders ($l_C = 10$ or 20 cm, $d_C = 2$ cm) filled completely with silica gel (~9.5 and 19 g), and a long mesh cylinder with a metal rod (20 cm long, 0.9 cm in diameter) placed at the center with silica gel (~15 g) surrounding it (Figure S3 of the SI). We further tested whether R is affected by the distance of the PSM cylinder from the opening of the PAS housing. R was measured for a 20 cm cylinder positioned at two different positions and a 10 cm cylinder (both with $d_C = 2$ cm) positioned at three different positions within the long PAS housing ($l_H = 30$ cm, $d_H = 10.5$ cm) (Figure S4 of the SI). In addition, we investigated how the configurations of the PAS housing and PSM affect R . Uptake experiments were performed using the regular PAS housing ($d_H = 10.5$ cm) with thin ($d_C = 1.2$ cm), regular ($d_C = 2$ cm) and thick ($d_C = 3$ cm) mesh cylinders, and using the 2 cm diameter mesh cylinder without PAS housing, with thin ($d_H = 6$ cm) and regular PAS housing (Figure S5 of the SI).

Indoor Calibration of XAD-based Passive Air Samplers Using Sampling Media of Different Diameters. An experiment on the uptake kinetics of PCBs by the XAD-PAS (Figure S1b of the SI) was conducted in an unoccupied office. The office had previously been identified as being heavily contaminated with PCBs (air concentration of $\Sigma\text{PCB} = 200 \pm 40$ ng/m³). Previously extracted XAD-2 resin (20–60 mesh) was cleaned by Soxhlet extraction with acetone for 24 h and hexane for 24 h. PAS with XAD-filled mesh cylinders ($l_C = 10$ cm, $d_C = 1.2$ or 2 cm) were deployed in the office for 0 (as the field blanks), 2, 4, 6, 8, 10, and 12 weeks between July and September, 2010. PCBs in the air of the office had been continuously monitored at monthly resolution since April 2010 using a low volume air sampler (BGI Inc., 2.9 ± 0.2 m³/d) with a PUF-XAD-PUF sandwich (5 g of XAD between two 2 cm i.d. × 3 cm PUF plugs) as the sampling medium.²¹ The passive air sampling rate was calibrated based on the PCB concentrations in the bulk air (gas and particle phase not separated) monitored with the low volume air sampler. The active sampling periods (monthly) were double the interval between PAS retrievals (biweekly), which could potentially

introduce some uncertainty to the calibration. To evaluate this uncertainty, another set of seven PAS with XAD-filled mesh cylinders

($d_C = 2$ cm) were deployed two weeks after the first set and retrieved at the same frequency (sampling scheme illustrated in Figure S6 of the SI). Upon retrieval, the PSM were individually sealed in precleaned aluminum foil and Ziploc bags, and stored at -20 °C (storage time <1 month) until extraction.

Unlike the water uptake experiment, which investigated uptake using mesh cylinders of three diameters (1.2, 2, and 3 cm), we did not include XAD-filled mesh cylinders of $d_C = 3$ cm in the PCB uptake experiment of this study because we had gained such information in a previous study.²¹ In that study, mesh cylinders of $d_C = 3$ cm were concentrically separated into three layers, and PCB uptake by the XAD within each of the three layers was analyzed. Herein, we used the sum of the amount of PCB accumulated in the three concentric layers to represent uptake to mesh cylinders of $d_C = 3$ cm.

Sample Extraction and Preparation. The XAD resin of each sample was extracted using a Dionex ASE-350 system with 33 mL extraction cells. Before use, the extraction cells had been ultrasonically cleaned sequentially with deionized water, acetone, and hexane. Prior to extraction, each sample was spiked with $100 \mu\text{L}$ $0.25 \text{ ng} \cdot \mu\text{L}^{-1}$ of ^{13}C -labeled PCB-77, -101, -141, and -178 as surrogate standards. The ASE conditions followed that by Primbs et al.²² solvent 50:50 hexane:acetone; temperature 75 °C; pressure 1500 psi; static time 5 min; static cycles 3; flush volume 100%; purge time 240 s. Each extract was rotoevaporated to ~ 2 mL and filtered through ~ 1 g of anhydrous sodium sulfate packed in a disposable pasteur pipet to remove moisture. The eluent was solvent exchanged to isooctane, blown down with high purity nitrogen, transferred to a GC vial, and further reduced to 0.5 mL. To the GC vial, $10 \mu\text{L}$ of $10 \text{ ng} \cdot \mu\text{L}^{-1}$ mirex was added as the internal standard for PCB quantification.

PCB Analysis. PCBs in the samples were analyzed using an Agilent 6890 gas chromatograph coupled with an Agilent 7683 autosampler and an Agilent 5973 mass spectrometric detector. $1.0 \mu\text{L}$ of the sample was injected in splitless mode with the injector temperature at 250 °C. PCBs in the sample were separated using a DB5-MS capillary column (60 m length \times 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific) with helium (25 psi, 1.4 mL/min) as the carrier gas. The column temperature program started from 80 °C for 1 min, to 160 at $10 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, to 280 at $3 \text{ }^\circ\text{C} \cdot \text{min}^{-1}$, and held for 6 min. The mass spectrometric detector was operated in electron impact ionization (70 eV) and selective ion monitoring mode. Temperatures for the ion source and quadrupole were 230 and 150 °C. The targeted PCB congeners and the monitored ions analyzed are listed in Table S1 of the SI.

QA/QC. The relative difference of the K_{SA} and k_O derived from the duplicates of 3-h water uptake experiments were $\sim 5\%$ (Figures 1 and S7 of the SI). The coefficients of variation of water uptake rates derived from 6 replicates for each PAS configuration were <10% (Figure S8 of the SI). In the PAS indoor calibration experiment, the differences between the sampling rates (R) derived from the two sets of PAS deployed with two-week lag time were $\sim 30\%$. This represents the uncertainty of the R -values derived from the low volume air sampler with a sampling period double the interval between PAS retrievals. Method recoveries derived from the labeled PCB congeners were 76–120% with an interquartile range of 21% (Figure S9 of the SI). Three solvent blanks and three field blanks were analyzed. No

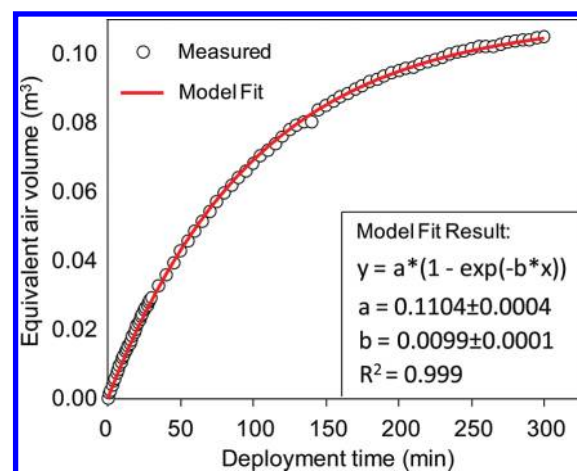


Figure 1. Measured and model-fitted equivalent air volume derived from passive sampling of water vapor from air using silica gel filled mesh cylinder as a sampling medium. Data were recorded every 1 min for the first 30 min and every 5 min afterward.

target compounds were observed in the solvent and field blanks except for PCB-44 in the field blanks. The PCB-44 field blank levels were $\sim 20\%$ of the sample with the lowest concentration. The blanks were considered as time zero levels in the linear fitting to derive R .

RESULTS AND DISCUSSION

Characteristics of Water Uptake by Silica Gel. Water uptake by a silica gel filled mesh cylinder placed in a housing was continuously monitored for 3 h using the gravimetric method (Figure S2 of the SI). The plot between the equivalent volume of air sampled and sampling time (Figure 1) reveals that the sampling rate (slope of the plot) gradually decreased over the 3 h deployment time. This is due to the evaporation of the accumulated water vapor from silica gel to air. Similar to the uptake of SVOC by an XAD-filled mesh cylinder,¹⁴ the initial uptake stage is quasi-linear. The slope of the uptake curve changes little within this quasi-linear range. On the basis of this slope, the air concentration of a chemical can be calculated from the amount accumulated in the PSM.

The quasi-linear range is determined by the kinetic (k_O) and thermodynamic (K_{SA}) properties of the sampled chemicals. Fitting the uptake curve to the theoretical equation (eq 1 and Table S2 of the SI), we derived a k_O for the water uptake by a silica gel filled mesh cylinder of 127 m/d; the equilibrium sorption coefficient of water vapor to silica gel (K_{SA}) was 1.8×10^3 . Applying these two parameters in eq 3, the quasi-linear range for water uptake by silica gel is 27 min. Note this quasi-linear range is based on an experiment using the long mesh cylinder. To ensure uptake is within the quasi-linear range during all experiments, the first 10 min were selected to derive the R .

Effect of Interfacial Transfer Area and Sorbent Amount on Uptake. Water uptake experiments were conducted on the regular short and long PAS (Figure S3 of the SI). The short PAS gave an R of $0.87 \pm 0.02 \text{ m}^3/\text{d}$, which is about half of the R for the long PAS ($1.58 \pm 0.08 \text{ m}^3/\text{d}$). This difference between short and long PAS agrees with the field-calibrated sampling rates of SVOCs using XAD-resin as the PSM.²³ The reduced sampling rate for the short PAS could be due to the reduced interfacial

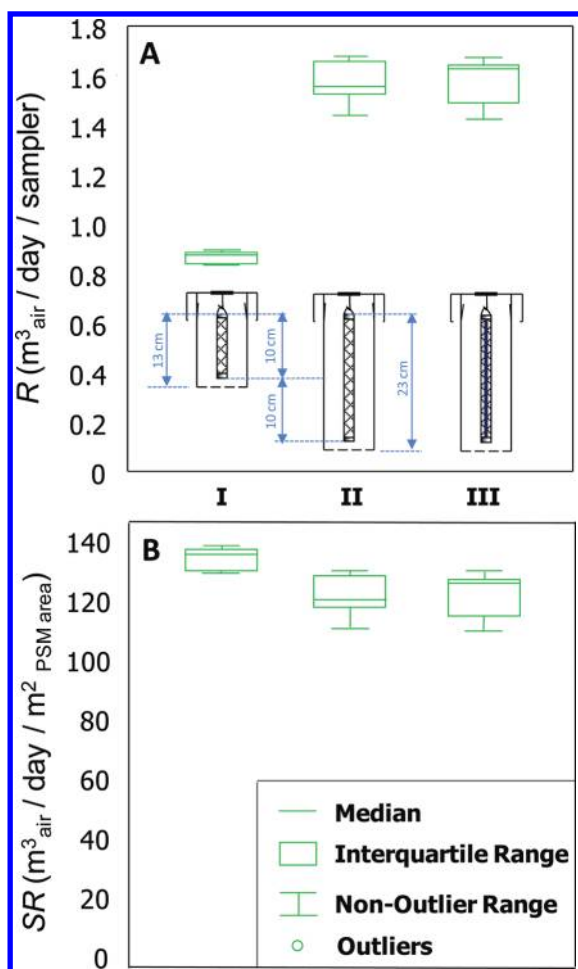


Figure 2. Effect of interfacial transfer area and sorbent amount on the uptake of water vapor from air by silica gel. I and II: short and long silica gel filled mesh cylinder in short and long housing; III: long mesh cylinder with a metal rod positioned at the center with silica gel surrounding it. Ratios of the interfacial transfer area to bulk XAD volume for I, II, and III are 1, 1, and 1.25 cm^{-1} respectively.

transfer area between air and PSM and/or the reduced PSM amount.

Water uptake was also measured in a long PAS with silica gel in the outer part of the mesh cylinder and a metal rod at the center. The interfacial transfer area is the same as for the regular long PAS, while the amount of sorbent is reduced by $\sim 25\%$. Despite the reduced sorbent amount, R was not statistically different (Mann–Whitney U test, $p = 0.8$) from that of the regular long PAS (Figure 2a). This indicates that water vapor penetrates into the inside of the silica gel filled mesh cylinder more slowly than uptake from the air occurs; i.e., most of the water molecules sorb to the outer layer of the silica gel and the inner portion of the silica gel is not participating in the accumulation of water molecules, at least during the initial 1/3 of the quasi-linear uptake range, during which the experiments were conducted. Such nonuniform distribution of the sorbate within the PSM has also been observed for SVOCs in PUF and XAD.²¹ This observation confirms that passive sampling efficiency could be improved by maximizing the surface area/volume ratio A/V_S of the PSM.¹⁰ For example, with the same amount (volume) of sorbent, the normal cylindrical mesh cylinders can be replaced with several

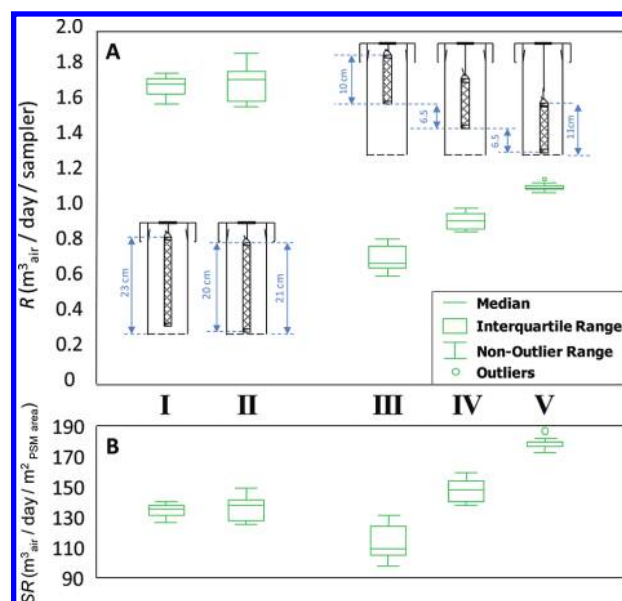


Figure 3. Effect of the distance of the silica gel filled mesh cylinder to the opening of the sampler housing on the uptake of water vapor from air by silica gel. I and II: long mesh cylinder at different positions within long housing; III–V: short mesh cylinder at different positions within long housing.

slim ones, which would yield an increased A/V_S and thus sampling rate.

Because interfacial transfer area is a key factor in determining R , we also compared sampling rates normalized to the interfacial transfer area (SR, $\text{m}^3/\text{d}/\text{m}^2$). SR of the long PAS with the metal rod in the center and of the regular long PAS are not statistically different (Mann–Whitney U test, $p = 0.8$) but are lower (Mann–Whitney U test, $p = 10^{-4}$) than that of the short PAS (Figure 2b).

Effect of the Position of the PSM within the Sampler Housing On Uptake. We hypothesized that the average distance between the PSM and the opening of the sampler housing could affect the uptake rate. To test this hypothesis, water uptake experiments were conducted by positioning the silica gel filled mesh cylinder at different positions within the sampler housing (Figure S4 of the SI). We could vary the distance of the 20-cm mesh cylinder to the opening of the long housing by 2 cm (Figure 3-I and -II). This small difference had no statistically significant effect on R (Mann–Whitney U test, $p = 0.7$). Thus, we set up three configurations (Figure 3-III to V) using the 10-cm mesh cylinder in the long housing. The distance of the mesh cylinder to the opening of the housing varied by 6.5 cm between the three configurations. Statistically significant different R between each of the three configurations were observed (Mann–Whitney U test, $p < 10^{-3}$). The closer the PSM to the opening, the higher was R . This also explained why the short cylindrical PAS (Figure 2-I) had a higher SR than the long one (Figure 2-II). This result is also in line with the studies using PUF-disk PAS to sample SVOCs. When Abdallah and Harrad¹⁷ mounted the PUF-disk further from the opening of the housing than in the regular configuration of the PUF-disk PAS, lower uptake rates were observed.^{17,18}

The different sampling rates for PSM-filled cylinders positioned at different positions of the housing can be explained by a different air boundary layer thickness and/or housing

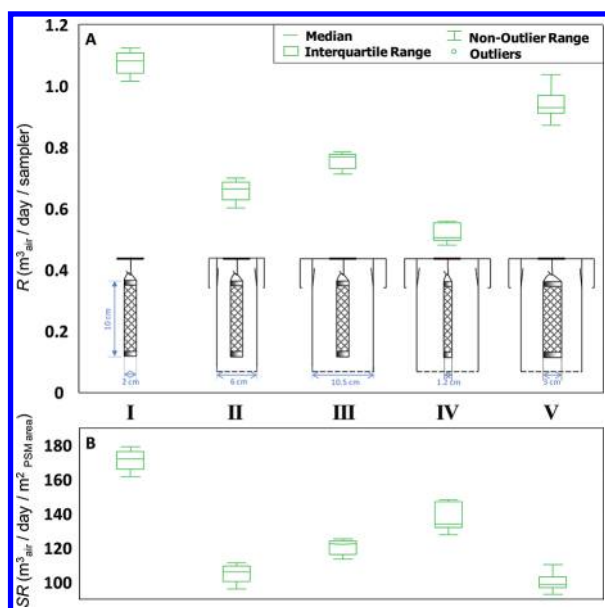


Figure 4. Effect of dimensions of the sampling medium and sampler housing on the uptake of water vapor from air by silica gel. I–III: silica-gel filled mesh cylinder ($l_C = 10 \text{ cm}$, $d_C = 2 \text{ cm}$) without housing, in a housing with $d_H = 6 \text{ cm}$, and in a housing with $d_H = 10.5 \text{ cm}$; IV and V: silica-gel filled mesh cylinder ($l_C = 10 \text{ cm}$, $d_C = 1.2 \text{ cm}$ and 3 cm) in a housing with $d_H = 10.5 \text{ cm}$.

resistance r_H . The thickness of the air boundary layer is negatively correlated with the strength of air turbulence.²⁴ The closer the sampling medium is to the opening of the housing, the more susceptible it is to turbulence in ambient air. Thus, PSM placed closer to the opening will presumably be surrounded by a thinner boundary layer, which leads to a higher uptake rate. Besides the boundary layer thickness, the housing resistance r_H could also contribute to different sampling rates. In a previous definition,¹⁰ r_H is only related to the rate of air entering the PAS housing via advection. When air around the PAS is turbulent, chemical may indeed enter the housing via advection and r_H is unlikely to affect the overall sampling rate. However, under wind still conditions chemical is more likely to enter the housing via diffusion. The diffusion length for molecules transferring from ambient air to the boundary layer is different for PSM mounted at different positions within the housing, which would lead to different r_H . If the overall mass transfer coefficient for this transfer through the housing is lower than that for transfer through the boundary layer, then r_H could also explain different uptake rates. Although both the boundary layer thickness and r_H could play a role, we cannot presently distinguish the two or tell which is more influential.

This study was conducted indoors. In outdoor environments, stronger air turbulence reduces the boundary layer thickness and, in addition to diffusion, advection can contribute to chemical transport from ambient air to the PSM-air boundary layer. This advection could reduce r_H . Thus, whether similar results would be observed for the PAS deployed outdoors merits further study.

Effect of Dimensions of the Sampling Medium and Sampler Housing on Uptake. Water uptake experiments were conducted using the silica gel filled mesh cylinders directly exposed to ambient air, and mounted in a housing with a narrow diameter ($d_H = 6 \text{ cm}$) and in a regular housing (Figure S5 of the SI). When the PSM cylinder was directly exposed to ambient air,

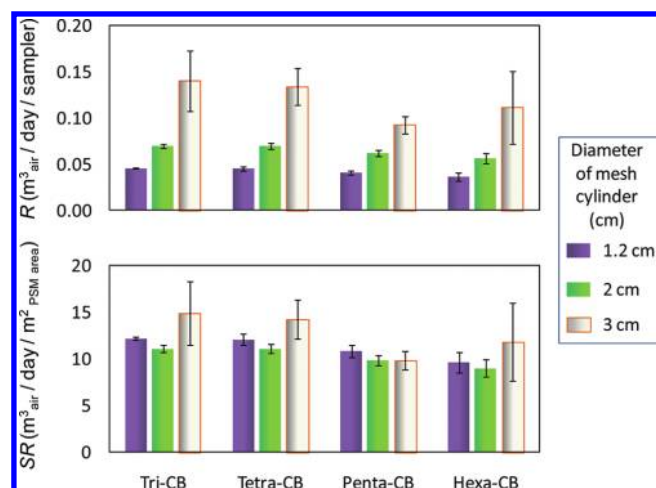


Figure 5. Comparison of passive sampling rates of PCBs between passive sampling medium of different diameters. Data of 1.2-cm and 2-cm mesh cylinder were obtained in this study; data of the 3-cm mesh cylinder were based on the sum of three concentric layers in a previous study.²¹

R was ~ 1.5 times higher than when it was positioned in the housing (Figure 4-I to III). This is expected because there is no housing resistance r_H if the PSM is directly exposed to ambient air. Besides, stronger air turbulence and thus a thinner air boundary layer around a PSM directly exposed to ambient air would also explain an increase in R . This observation is consistent with a study using semipermeable membrane devices as PSM: the sampling rate decreased when the PSM was protected within a shelter.²⁵ The sampling rate for the PSM cylinder positioned in the narrow housing (Figure 4-II) was $\sim 20\%$ lower than that of the regular configuration (Figure 4-III). This agrees with the lower indoor passive air sampling rates of PAHs determined by Tao et al.,¹³ who mounted PUF disks in a more confined housing than the regular double-bowl PAS.⁹ A lower R for a PSM in more confined housing can be explained by the limited air turbulence and thicker boundary layer around the PSM.

Water uptake experiments were also conducted using silica gel filled mesh cylinders of different diameters d_C mounted in regular housings ($d_H = 10.5 \text{ cm}$) (Figure 4-III to V). Since the interfacial transfer area determines the sampling rate, R increased with increasing d_C . When normalizing the sampling rate to the interfacial transfer area, we noted that SR decreased with increasing d_C . One possible cause for the reduced SR with PSM of larger d_C is the reduced space between the PSM and the inner wall of the housing ($(d_H - d_C)/2$), which may increase r_H or the boundary layer thickness and thus r_{BL} . Comparing Figure 4-II and -III, SR decreased $\sim 20\%$ upon a reduction of $(d_H - d_C)/2$ by $\sim 50\%$ (from 4.25 to 2 cm). The SR differences between the set-ups shown in Figure 4-III, -IV, and -V are of the same magnitude ($\sim 20\%$), even though $(d_H - d_C)/2$ changed much less. This indicates that this distance plays a minor role and the different observed SR can be attributed to the PSM of different d_C .

Uptake of PCBs by XAD-filled Mesh Cylinder of Different Diameters. An indoor calibration of PCBs uptake in XAD-PAS was conducted using PSM cylinders with d_C of 1.2 and 2 cm . The sampling rates for XAD-PAS using a PSM with d_C of 3 cm were retrieved from an earlier study²¹ based on the sum of the amount of chemical accumulated in three concentric layers. Similar to the

water uptake by silica gel, the R for PCB uptake by XAD-PAS increases with d_C and thus with the interfacial transfer area (Figure 5). The interfacial transfer area normalized sampling rates SR for the PAS with $d_C = 2$ cm was slight, but significantly lower ($p < 10^{-5}$, Wilcoxon signed-rank test for the PCB congeners in Figure S10 of the SI) than the SR for the PAS with $d_C = 1.2$ cm. This is similar to the water uptake by silica gel-filled mesh cylinder of different d_C . Contrary to expectations based on this trend, SR of the PAS with a d_C of 3 cm was higher than the SR for the PAS with a d_C of 2 and 1.2 cm (Figure 5), except for the penta-CBs. The explanation is likely to be found in the chemical analysis. The SR for the wide cylinders is derived from the sum of the amounts in three layers, which are therefore subject to a higher uncertainty, illustrated by the longer whiskers in Figures 5. Furthermore, the samples for the PAS with a d_C of 3 cm were analyzed at a different laboratory with a different method²¹ and the interlab variation of SVOC analyses (RSD 10–150% with an average of 70% for PCBs in air extract²⁶) could easily be larger than the differences between the SR of a set up with d_C of 1.2 and 3 cm.

Water Uptake by Silica Gel vs SVOC Uptake by XAD. From the above experiments and previous studies on SVOC uptake by XAD-based PAS,^{14,23} we can conclude that water uptake by silica gel (Figure 1) and SVOC uptake by XAD¹⁴ follow the same pattern: an initial quasi-linear uptake phase is followed by a gradually decreasing rate of uptake until eventually equilibrium is reached. Because of such similarity, water uptake and loss kinetics have proven useful in evaluating the kinetics of SVOC uptake in both XAD-based and PUF-based PAS.^{14,19} The time scale of uptake is of course widely different: the quasi-linear range for water uptake by silica gel (<30 min) is much shorter than that of SVOC uptake (a few months²³). This is because of the higher k_O for water uptake by silica gel and the lower holding capacity of silica gel for water (K_{SA}). The short time scale for water uptake makes it feasible to conduct a number of experiments quickly and at low cost to investigate numerous factors. An example of such a factor is the potential resistances posed by housing r_H and boundary layer r_{BL} . These two contributions to the overall kinetic resistance r_O could be further affected by wind conditions¹⁴ and passive sampler configuration. Therefore, uptake of water vapor by silica gel can be used for a preliminary assessment of the influence of various factors on chemical uptake of SVOCs by XAD.

If we assume that only the resistance at the air-boundary layer affects k_O ($k_O = k_A$), k_O would be proportional to the chemical's molecular diffusivity in air (D_A), which can be estimated using the Fuller-Schettler-Giddings equation.²⁷ On the basis of k_O for water uptake (139 m/d based on the configuration of Figure 2-I) and D_A of water (0.0015 m²/min) and SVOCs (Table S3 of the SI), k_O for the SVOCs ($k_{O,SVOC} = k_{O,Water} \cdot D_{A,SVOC}/D_{A,Water}$) are estimated to range from 23 to 29 m/d (Table S3 of the SI). The k_O of tri- to hexa-CBs estimated this way (24–28 m/d) are ~2 times higher than the k_O (9–12 m/d, equivalent to SR in Figure S10 of the SI) calculated from the indoor calibration of the XAD-PAS ($d_C = 2$ cm) for PCBs. Because both experiments were conducted indoors with the same PAS configuration and because the sorbents used as the PSM (silica gel and XAD) have a similar particle size, the thickness of the boundary layer surrounding the PSM is presumably identical in the two experiments. Therefore, if the uptake kinetics were only affected by the resistance from the boundary layer, k_O for SVOC derived from the water uptake experiment should have matched that derived from the

calibration experiment. However, because the observed k_O from the calibration were 2-fold lower, we can infer that the uptake of SVOCs by PSM is kinetically limited not only by the boundary layer, but is also likely affected by a resistance within the PSM. This is in line with our previous study indicating that SVOCs do not uniformly distribute within the PSM.²¹

Implications. Using silica gel as a PSM to sample water vapor from air is an effective approach to study factors that influence uptake in PAS and are independent of the sampling media and target chemicals. The short time scale of the water uptake makes it time-efficient to conduct numerous passive sampling experiments, increasing precision through sufficient replication and allowing for a variety of experimental conditions. Besides the air boundary layer surrounding the sampling medium, the sampler housing and the sampling medium appear to contribute kinetic resistance to chemical uptake, especially in indoor environment where the air turbulence is relatively limited. On the basis of the information gained from this study, a smaller housing with one or multiple cylinders of smaller diameter could be used as an alternative to the current PAS design (Figure S11 of the SI). A smaller housing would reduce the cost of materials and shipping to the sampling sites, although the confined configuration would introduce more kinetic resistance causing the sampling rate to slightly decrease. However, for a given amount of PSM, multiple mesh cylinders with smaller diameter could increase the interfacial transfer area, which would compensate for the increased kinetic resistance introduced by a smaller housing.

■ ASSOCIATED CONTENT

Supporting Information. Further information on experimental setup, QA/QC, data analysis, and results. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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■ ACKNOWLEDGMENT

We acknowledge research funding from the Canadian Foundation for Climate and Atmospheric Sciences and the Natural Sciences and Engineering Research Council of Canada. X.Z. also acknowledges financial support through an Ontario Graduate Scholarship.

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