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## Passive air sampling for semi-volatile organic chemicals

Frank Wania \* and Chubashini Shunthirasingham †

During passive air sampling, the amount of a chemical taken up in a sorbent from the air without the help of a pump is quantified and converted into an air concentration. In an equilibrium sampler, this conversion requires a thermodynamic parameter, the equilibrium sorption coefficient between gas-phase and sorbent. In a kinetic sampler, a time-averaged air concentration is obtained using a sampling rate, which is a kinetic parameter. Design requirements for kinetic and equilibrium sampling conflict with each other. The volatility of semi-volatile organic compounds (SVOCs) varies over five orders of magnitude, which implies that passive air samplers are inevitably kinetic samplers for less volatile SVOCs and equilibrium samplers for more volatile SVOCs. Therefore, most currently used passive sampler designs for SVOCs are a compromise that requires the consideration of both a thermodynamic and a kinetic parameter. Their quantitative interpretation depends on assumptions that are rarely fulfilled, and on input parameters, that are often only known with high uncertainty. Kinetic passive air sampling for SVOCs is also challenging because their typically very low atmospheric concentrations necessitate relatively high sampling rates that can only be achieved without the use of diffusive barriers. This in turn renders sampling rates dependent on wind conditions and therefore highly variable. Despite the overall high uncertainty arising from these challenges, passive air samplers for SVOCs have valuable roles to play in recording (i) spatial concentration variability at scales ranging from a few centimeters to tens of thousands of kilometers, (ii) long-term trends, (iii) air contamination in remote and inaccessible locations and (iv) indoor inhalation exposure. Going forward, thermal desorption of sorbents may lower the detection limits for some SVOCs to an extent that the use of diffusive barriers in the kinetic sampling of SVOCs becomes feasible, which is a prerequisite to decreasing the uncertainty of sampling rates. If the thermally stable sorbent additionally has a high sorptive capacity, it may be possible to design true kinetic samplers for most SVOCs. In the meantime, the passive air sampling community would benefit from being more transparent by rigorously quantifying and explicitly reporting uncertainty.

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### Environmental significance

Over the past 25 years, numerous passive air samplers (PASs) for SVOCs have been introduced, characterised, and tested. More recently, the applications of PASs, initially focused on recording the variability in atmospheric contamination on a wide range of spatial scales, has expanded to include measuring indoor inhalation exposure to SVOCs, probing the exchange of SVOCs between the atmosphere and soil and water, mapping the toxicity of airborne contamination, and monitoring interannual trends in SVOC air concentrations. The simplicity of passive air sampling is deceptive and many users of PASs do not fully appreciate their strength and limitations and may have misconceptions as to their applicability and reliability. This comprehensive and critical review assembles and curates the current knowledge on this topic in order to equip anyone to use PAS appropriately and with confidence and to guide further development of PASs in a direction that will overcome their largest shortcomings.

### A. Introduction

#### A.1 Definition of passive air sampling and semi-volatile organic compounds

Passive air sampling involves the diffusive uptake of a chemical vapour in a sorbent over time. The amount of vapour being sorbed during a sampler's deployment is determined by both kinetic and thermodynamic factors and can be interpreted in terms of volumetric air concentrations based on a quantitative understanding of these factors. In contrast to active air

Department of Physical and Environmental Sciences, University of Toronto Scarborough, 1265 Military Trail, Toronto, Ontario, M1C 1A4, Canada. E-mail: [frank.wania@utoronto.ca](mailto:frank.wania@utoronto.ca); Tel: +1-416-287-7225

† Current affiliation and address: Air Quality Processes Research Section, Environment and Climate Change Canada, 4905 Dufferin St, Ontario, M3H 5T4, Canada.

samplers that rely on a pump to pass a volume of air through or past a sorbent, passive air samplers (PASs) have the advantage of low price, simple operation, and independence of power sources. On the other hand, they typically allow only for coarse temporal resolution. PASs have been developed for a variety of gaseous chemicals, including volatile organic chemicals (VOCs) such as benzene, toluene, ethylbenzene, and xylene, classical air pollutants such as sulfur dioxide, various nitrogen oxides, hydrochloric acid, ozone and ammonia, as well as mercury.<sup>1–5</sup>

A distinct set of PASs has been developed for semi-volatile organic chemicals (SVOCs). The term SVOCs comprises organic molecules that can occur to a significant extent in both the gas-phase and condensed phases, which corresponds to the vapour pressure range of approx.  $10^{-1}$  to  $10^{-6}$  Pa. The group of SVOCs comprises a large number of commercially produced substances, including industrial chemicals, pesticides, and additives to consumer products. Prominent examples are the polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs), and organochlorine pesticides (OCPs). Combustion products such as the polycyclic aromatic hydrocarbons (PAHs) also count among the SVOCs. Many SVOCs are a concern for human and environmental health. The atmosphere often plays an important role in the dispersal of SVOCs and in facilitating organism exposure to SVOCs. PASs for SVOCs thus address a need for information on the concentrations of SVOCs in indoor and outdoor air.

## A.2 Motivation for, and scope of, review

Over the past 20 years, there has been explosive growth in the development, characterization, testing and application of passive air sampling techniques of SVOCs. A literature search suggests that more than 40 papers are published in this area every year, garnering *ca.* 1500 citations annually (Fig. 1).

There have been a number of reviews on the passive sampling of atmospheric SVOCs, but they are either somewhat out-of-date and/or have a wider scope by focusing on passive

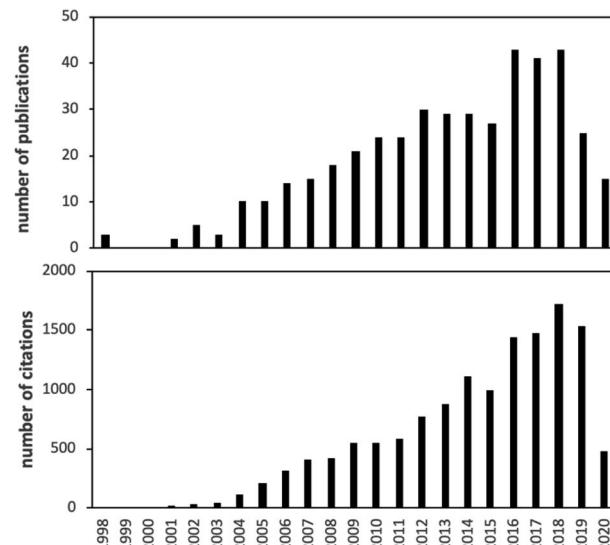


Fig. 1 Number of publications and citations on the topic of passive air sampling for semivolatile organic compounds, based on an analysis using Web of Science using the search string TOPIC: ("passive air sampl\*") and TOPIC: (POPs or SVOCs or PCBs or PAHs or semivolatile or semi-volatile) on April 11, 2020.

(air) sampling in general.<sup>6–11</sup> In other cases, the scope is limited to only one type of PAS.<sup>12,13</sup> Recently, Salim and Górecki<sup>14</sup> thoroughly reviewed the theory and modelling of passive sampling, which complements our current effort well, as we do not delve as thoroughly into this aspect in this review.

While the operation of PASs for SVOCs can be deceptively simple, the kinetic and thermodynamic factors controlling the uptake of SVOCs in PASs can be surprisingly complex and are not always fully understood, even by the community using them. Reasons include the diversity of sampler designs, the large and diverse group of SVOCs being sampled, and the wide range of environments in which PASs are finding use. Here we



Frank Wania studied Environmental Science at the University Bayreuth in Germany and received his Doctorate in Chemical Engineering and Applied Chemistry from the University of Toronto in 1995. After two years as a scientist at the Norwegian Institute for Air Research, and three years as an independent researcher, he joined the University of Toronto Scarborough in 1999, where he is currently a professor of environmental chemistry.

A co-developer of the XAD-PAS, the FTS and a PAS for gaseous elemental mercury, he has been calibrating, characterising, evaluating and applying passive air sampling techniques for the past two decades.



Chubashini Shunthirasingham is a chemist in the Air Quality Research Division at Environment and Climate Change Canada. She obtained her BSc in Chemistry and Biology as well as her MSc and PhD in Environmental Chemistry from the University of Toronto. Her PhD work focused on the measurement of pesticides in the physical environment of developing countries using XAD-resin based passive air samplers and on the measurement of Henry's law constants using the inert gas stripping method. Her research interests are atmospheric chemistry, fate and transport of SVOCs and method development and validation for emerging organic pollutants using gas chromatography mass spectrometry.



aim to summarise comprehensively the current state-of-knowledge on passive sampling of SVOCs and to provide guidance on the use of PASs for SVOCs to existing and prospective users.

Section B provides an introduction into the basic principles of passive air sampling and in doing so identifies the two central characteristics of a PAS. These are the PAS's uptake capacity at equilibrium, *i.e.* the maximum amount of a target chemical that the sorbent will take up given a certain concentration in the gas-phase, and the PAS's inherent sampling rate, *i.e.* the maximum rate at which a target chemical is taken up in the sorbent. Section C then highlights the specific challenges faced when developing a PAS for SVOCs, namely the balancing of conflicting needs (i) for high *vs.* tightly controlled sampling rates and (ii) of SVOCs of variable volatility. Section D introduces, contrasts and critically assesses the approximately 50 PAS designs for SVOCs that have been presented in the peer-reviewed literature over the past 25 years. Section E discusses the empirical and theoretical means by which the uptake capacity of different PAS sorbents has been determined. Section F presents information on how the kinetics of uptake in PASs is approached experimentally and theoretically. Section G reviews the various ways in which PASs for SVOCs have been applied. Finally, Section H will conclude with an overall assessment of the state-of-the-art in passive air sampling of SVOCs and provide an outlook for future activities in this area. Section I provides a glossary for acronyms, abbreviations and variables used in this review.

Not covered in this review are substances other than SVOCs, namely VOCs and inorganic gases or passive samplers for media other than air. We also do not consider biological matrices, such as plants (moss, needles, tree bark, wood, *etc.*), that are often used in a similar way as PASs for SVOCs.<sup>15</sup> Furthermore, we do not count organic "films" forming on glass surfaces among the passive air samplers in this review.<sup>16–19</sup>

## B. Principles of passive air sampling

### B.1 The equation describing diffusive uptake in a PAS

The amount of a target analyte in the passive sampling sorbent,  $m_s$  in mol, changes over time,  $t$  in days, as a chemical is taken up from the atmosphere at a rate proportional to the concentration in the gas-phase,  $C_G$  in mol m<sup>-3</sup>, and is lost from the sorbent at a rate proportional to the concentration in the sorbent,  $C_s$  in mol m<sup>-3</sup> (or mol m<sup>-2</sup> if it is an adsorbent):<sup>20</sup>

$$\frac{dm_s}{dt} = V_s(k_u C_G - k_l C_s) \quad (1)$$

where  $k_u$  and  $k_l$  are rate constants for uptake and loss in per day and  $V_s$  is the volume of the PAS sorbent in m<sup>3</sup>. If chemical uptake and loss in a PAS is controlled by the air-side resistance, *i.e.* transport within the sorbent is not rate-limiting, the rate constants for uptake can be derived by applying Fick's first law to the molecular diffusion of the target analyte through a stagnant air boundary layer surrounding the sorbent of thickness  $\Delta z$  in m:<sup>20</sup>

$$k_u = \frac{DA}{\Delta z V_s} \quad (2)$$

where  $D$  is the molecular diffusivity of the target analyte in the gas-phase  $D$  in m<sup>2</sup> per day and  $A$  is the geometric surface area of the PAS sorbent in m<sup>2</sup>. The rate constant for loss is additionally proportional to the reciprocal of the equilibrium sorption coefficients between the gas-phase and the PAS sorbent  $K_{SG}$  in units of m<sup>3</sup> gas per m<sup>3</sup> absorbent (or m<sup>3</sup> gas per m<sup>2</sup> adsorbent):

$$k_l = \frac{DA}{\Delta z V_s K_{SG}} \quad (3)$$

The amount of analyte in the PAS sorbent,  $\Delta m_s$  in mol, taken up during its deployment time,  $\Delta t$  in days, then becomes:<sup>20</sup>

$$\frac{\Delta m_s}{\Delta t} = \frac{DA}{\Delta z} \left( C_G - \frac{C_s}{K_{SG}} \right) = SR \left( C_G - \frac{C_s}{K_{SG}} \right) \quad (4)$$

In eqn (4), the ratio  $C_s/K_{SG}$  designates the gas-phase concentration in equilibrium with the concentration in the PAS sorbent. The term  $(C_G - C_s/K_{SG})$  is the concentration difference that provides the driving force for the diffusive transport from bulk air to PAS sorbent. The term  $DA/\Delta z$  designates how fast this diffusive transport can take place and is often called a sampling rate  $SR$  in m<sup>3</sup> per day. The ratio  $D/\Delta z$  is sometimes termed a diffusive mass transfer coefficient in units of m per day. A PAS's foremost characteristics are thus described in one kinetic parameter ( $SR$ ) and one thermodynamic parameter ( $K_{SG}$ ) describing the rate of uptake and the maximum uptake capacity of the PAS, respectively.

### B.2 The uptake curve: kinetic *vs.* equilibrium sampling

A plot of the change in the amount of a chemical sorbed to a PAS with increasing length of deployment is called an *uptake curve*. A generic example of such a curve is shown in Fig. 2. In this curve, the sorbed amount is divided by  $C_G$  in order to eliminate the variability caused by changing analyte concentrations in the atmosphere. The ratio  $m_s/C_G$ , which has units of m<sup>3</sup>, is sometimes referred to as the equivalent sampling volume. The uptake curve goes through three distinct phases. The so-called *linear uptake phase*, when the rate of uptake is kinetically controlled, a transitional *curvi-linear uptake phase*, and the *equilibrium phase* when the gas-phase and the PAS sorbent have reached a state of chemical equilibrium and therefore the sorbed amount is thermodynamically controlled. The initial slope of the uptake curve in Fig. 2 corresponds to the sampling rate  $SR$ , whereas the maximum amount taken up depends on the uptake capacity, which is the product of the equilibrium sorption coefficient between sorbent and gas-phase  $K_{SG}$  and the size of the passive sampling sorbent ( $V_s$  or  $A_s$ ).

**B.2.1 Kinetically controlled uptake.** Initially, the sorbent is clean, *i.e.*  $C_s$  is very small. If the sorbent has a high uptake capacity,  $K_{SG}$  is large. Then,  $C_s/K_{SG} \ll C_G$  and  $(C_G - C_s/K_{SG}) \sim C_G$  and eqn (4) simplifies to:

$$\frac{\Delta m_s}{\Delta t} = \frac{DA}{\Delta z} C_G = SR \times C_G \quad (5)$$

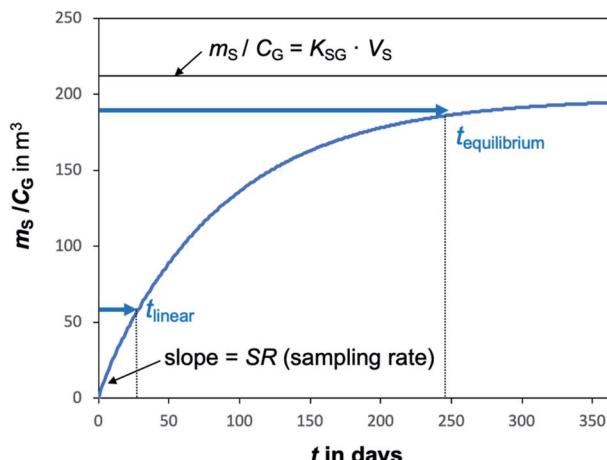


Fig. 2 Generic illustration of the uptake of an SVOC in a passive air sampler, showing the increase in the sorbed amount  $m_s$  divided by the atmospheric concentration  $C_G$  as a function of deployment time  $t$ . The time period of linear uptake  $t_{\text{linear}}$  and the time to equilibrium  $t_{\text{equilibrium}}$  are important characteristics of a passive sampler. The displayed curve was calculated with PAS-SIM<sup>21</sup> for a compound with  $\log K_{\text{SG}}$  of 6 in a PUF-PAS and an SR of  $3.2 \text{ m}^3$  per day. A  $t_{\text{equilibrium}}$  of 246 days is based on  $C_s/K_{\text{SG}} > 0.90C_G$  and a  $t_{\text{linear}}$  of 24 days is based on  $C_s/K_{\text{SG}} < 0.25C_G$ . See Section F.5 for more information on the PAS-SIM model.

The amount taken up in the sampler  $\Delta m_s$  is then simply the product of the sampling rate SR, the gas-phase concentration  $C_G$  and the deployment length  $\Delta t$ .

**B.2.2 Thermodynamically controlled uptake.** Once equilibrium is established between sorbent and gas-phase,  $C_s/K_{\text{SG}} = C_G$  and  $(C_G - C_s/K_{\text{SG}}) = 0$ . If that is the case, eqn (4) yields  $\Delta m/\Delta t = 0$ , *i.e.* there is no more net uptake of chemical on the PAS sorbent. The amount of chemical in the sorbent then is:

$$m_s = K_{\text{SG}} V_s C_G \quad (6A)$$

if the sorbent is an absorbent, *i.e.*  $C_s = \Delta m/V_s$ , or

$$m_s = K_{\text{SG}} A_s C_G \quad (6B)$$

if the sorbent is an adsorbent, *i.e.*  $C_s = \Delta m/A_s$ . It is important to stress that  $A_s$  here refers to the total surface area of the adsorbent and not the geometric surface area of the sorbent or of the container holding the sorbent, *i.e.* one should not confuse  $A$  with  $A_s$ . The terms  $K_{\text{SG}} V_s$  and  $K_{\text{SG}} A_s$  are expressions of the maximum uptake capacity of a PAS, both with units of  $\text{m}^3$  of air. The use of an air volume to describe the capacity of a sorbent for a chemical can be understood if we imagine this to be the volume of air that contains the same amount of a chemical at equilibrium as the sorbent within the PAS.

After  $C_s/K_{\text{SG}}$  is no longer negligibly small relative to  $C_G$  and equilibrium is not yet reached, uptake in the PAS is in the curvilinear transition region when both kinetic and thermodynamic factors govern the rate of uptake.

Two characteristic times can be used to describe a particular sampler-analyte combination, namely the length of linear uptake ( $t_{\text{linear}}$ ) and the time to equilibrium ( $t_{\text{equilibrium}}$ ). The

precise value of these times depends on the acceptable deviations from linearity and equilibrium. For example, uptake may be considered linear as long as  $C_s/K_{\text{SG}}$  is smaller than 25% of  $C_G$  and equilibrium may be considered reached when  $C_s/K_{\text{SG}}$  exceeds 90% of  $C_G$  (Fig. 2 and 3).

There are two types of PASs. A kinetic sampler seeks to remain in the kinetically controlled uptake phase during the entire length of deployment, *i.e.*  $t_{\text{linear}}$  is the maximum deployment length of a kinetic sampler. A kinetic sampler yields a gas-phase concentration averaged over the time of deployment by using a rearrangement of eqn (5):

$$C_G = \frac{\Delta m_s}{\text{SR} \times \Delta t} \quad (7)$$

An equilibrium sampler, on the other hand, seeks to reach equilibrium, whereupon the gas-phase concentration at the time of retrieval is obtained using a version of eqn (6):

$$C_G = \frac{m_s}{V_s K_{\text{SG}}} \quad (8A)$$

$$C_G = \frac{m_s}{A_s K_{\text{SG}}} \quad (8B)$$

The  $t_{\text{equilibrium}}$  is the minimum deployment length of an equilibrium sampler.

Samplers that are neither kinetic nor equilibrium samplers, need to derive  $C_G$  from eqn (4), which is challenging as  $C_G$  and  $K_{\text{SG}}$  generally vary with time (see Section F.3).

### B.3 Design considerations for an equilibrium sampler

Because the establishment of equilibrium is essential to the functioning of an equilibrium PAS, optimizing the design of such a PAS involves minimizing the time to equilibrium. There are two means to shorten  $t_{\text{equilibrium}}$ , namely maximizing the sampling rate SR and minimizing the uptake capacity  $K_{\text{SG}} V_s$  (or  $K_{\text{SG}} A_s$ ) (Fig. 3).

A large SR can be achieved by a large  $A$  and a small  $\Delta z$ , whereas a small sorption coefficient  $K_{\text{SG}}$  and a small size of the sorbent  $V_s$  (or  $A_s$ ) contribute to a small uptake capacity. A small  $\Delta z$  is achieved by not sheltering the sorbent from wind or other air turbulence. If an absorbent is used, it should have a large  $A$  and a small  $V_s$ , *i.e.* one should seek to maximise its surface area to volume ratio, *e.g.* by using very thin sheets or films of the absorbent. If an adsorbent is used, it should have a large geometric surface area  $A$ , but a small total surface area available for adsorption  $A_s$ .

There are, however, important limitations to how small the uptake capacity of an equilibrium sampler could be. The first is that the sorbent needs to take up an amount of the target analyte that is sufficient for reliable quantification. If the  $K_{\text{SG}} V_s$  is too small, the amount  $m_s$  may be below the limit of detection (LOD) of the chosen quantification technique. The second is that the target chemical may be lost too easily by volatilization from a PAS with too small an uptake capacity, because then the chemicals can be lost during retrieval, transport, storage and the processing of the sorbent prior to analysis.



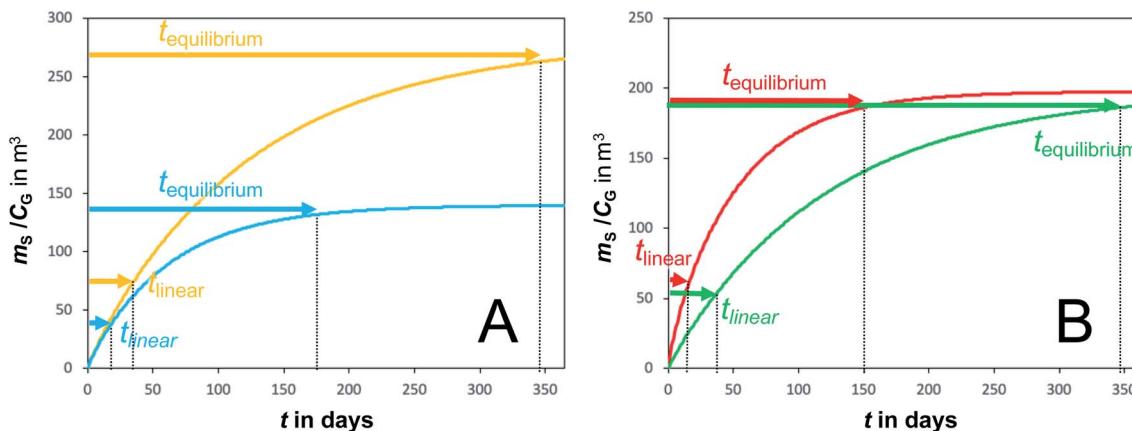


Fig. 3 The length of the linear uptake phase,  $t_{\text{linear}}$ , and the time to equilibrium,  $t_{\text{equilibrium}}$ , depend both on kinetic and thermodynamic factors. Uptake curves for two PASs with equal sampling rate (SR of  $3.2 \text{ m}^3$  per day), but divergent uptake capacity ( $\log K_{\text{SG}}$  of 5.85 (blue) vs. 6.15 (yellow)) (A) and two PASs with equal uptake capacity ( $\log K_{\text{SG}}$  of 6), yet different uptake kinetics (SR of 2.0 (green) vs.  $7.6 \text{ m}^3$  per day (red)) (B).  $t_{\text{linear}}$  and  $t_{\text{equilibrium}}$  increase with increasing uptake capacity (17 to 34 days, 175 to 347 days) and decreasing uptake rate (13 to 36 days, 150 to 345 days). The displayed curves were calculated with PAS-SIM<sup>21</sup> using the parameterization for the PUF-PAS. See Section F.5 for more information on the PAS-SIM model.

The accuracy of the  $C_{\text{G}}$  derived from an equilibrium sampler depends on the accuracy of the knowledge of the uptake capacity, in particular the  $K_{\text{SG}}$ . The sampling rate SR does not need to be known, except that it should be known to be large. The strong dependence of  $K_{\text{SG}}$  on temperature is one of the challenges of using equilibrium samplers for ambient applications, because the uptake capacity of the PAS is changing substantively with changes in ambient temperature. It is necessary to know the temperature dependence of  $K_{\text{SG}}$  quantitatively and the temperature of equilibration in order to obtain reliable  $C_{\text{G}}$  values from an equilibrium PAS.

Temperatures and SVOC air concentrations in the atmosphere are highly variable on a number of time scales. As a consequence, the amount of an SVOC on a sampler that is in equilibrium with the atmosphere is changing rapidly. In other words, chemical equilibrium is a constantly moving target, *e.g.* being different in a cold night than during a warmer day. To illustrate this effect, Fig. 4 shows simulated uptake curves in a PAS under the hypothetical assumption that air concentrations alternate from high to low every other week. It demonstrates that the more volatile chemicals (low  $\log K_{\text{SG}}$ ), which are suited for equilibrium sampling because of their short  $t_{\text{equilibrium}}$ , are the ones that experience the most pronounced fluctuations in the amount sequestered in the PAS. For such chemicals, the amount sorbed in the PAS at any moment in time is reflective of the conditions immediately prior to a sampler's retrieval, but also influenced to some extent by the exposure history. This suggests that equilibrium sampling for SVOCs is likely only suitable for situations when both  $T$  and  $C_{\text{G}}$  are reasonably constant, which may apply for certain compounds in indoor environments.

#### B.4 Design considerations for a kinetic sampler

Because the condition  $C_{\text{S}}/K_{\text{SG}} \ll C_{\text{G}}$  is essential to the functioning of a kinetic sampler, optimizing the design of a kinetic PAS involves choosing a sorbent with a very high sorptive

capacity, *i.e.* a large  $K_{\text{SG}}$ . The actual size of the  $K_{\text{SG}}$  does not need to be known, as long as it is known to be large enough to assure negligible loss of target analyte from the sorbent during deployment.

The accuracy of the  $C_{\text{G}}$  derived from a kinetic sampler depends on the accuracy of the knowledge of SR, which is  $DA/\Delta z$ . The molecular diffusion coefficient  $D$  of the target analytes in the gas-phase is typically well established or can be easily estimated through relationships between  $D$  and molecular size. Also, the dependence of  $D$  on atmospheric pressure and temperature can be estimated with good accuracy. The diffusive area  $A$  can generally also be derived easily from the geometric dimensions of the sampler.

The most challenging aspect of characterizing the SR of a kinetic sampler is therefore the quantification of the diffusive distance  $\Delta z$ , because  $\Delta z$  depends on the thickness of the stagnant boundary layer surrounding the PAS sorbent and this

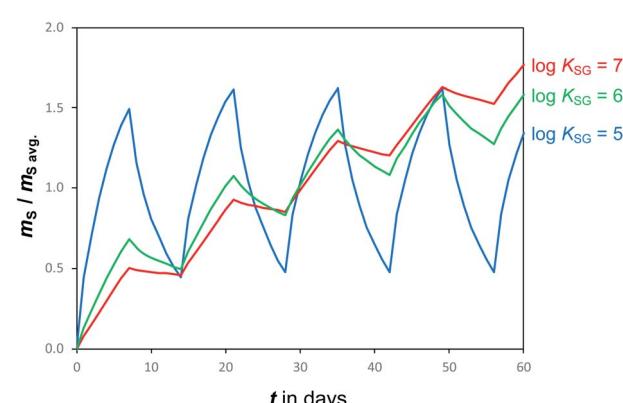


Fig. 4 Illustrative simulations of uptake curves of three hypothetical chemicals in response to fluctuating air concentrations  $C_{\text{G}}$ . Fluctuations in the amount of a chemical sequestered in a PAS increase with increasing volatility, *i.e.* decreasing  $\log K_{\text{SG}}$ .



thickness is (i) difficult to estimate theoretically and (ii) is strongly influenced by atmospheric turbulence, *i.e.* is susceptible to being dependent on wind speed. As will be discussed next, there are strategies that seek to reduce this dependence of  $\Delta z$  on wind speed, but they tend to lower the SR. This needs to be balanced with the need to sample an amount of chemical during the deployment period that is sufficient for reliable quantification.

**B.4.1 Strategies to reduce the wind speed dependence of the sampling rate.** The SR of PASs is dependent on wind speed, which can introduce considerable uncertainty in the derived air concentrations. Mechanistically, we can conceptualise this wind speed dependence as the effect of atmospheric turbulence on the thickness of the stagnant boundary layer surrounding the sampler sorbent (panel A in Fig. 5). Under low wind conditions, this layer is thicker and therefore the diffusive pathlength that the analyte has to travel to reach the sorbent is longer than under high wind conditions. As shown above, in PASs, where the SR is controlled by the air-side resistance, the SR is inversely proportional to the diffusive pathlength  $\Delta z$ . In the design of PASs, two strategies are employed to reduce the wind speed dependence of SR.

The first strategy is wind sheltering that is accomplished by placing the sorbent in some sort of housing that prevents the wind from directly blowing onto the sorbent (panel B in Fig. 5). At low wind conditions this shelter will have little effect on the diffusive pathlength, but at high wind speeds the calming effect of the shelter will result in a thicker stagnant layer, a longer diffusive distance and thus a lower SR. More importantly, the

difference in the diffusive pathlengths under different wind conditions will be reduced, or – in other words – the wind speed dependence of the SR will be smaller.

The second strategy involves the addition of a diffusive barrier that forces the analyte to diffuse a longer distance to reach the sorbent (panel C in Fig. 5). The stagnant boundary layer now is no longer adjacent to the sorbent, but next to the diffusive barrier. The thickness of that boundary layer continues to be variable with wind speed, but the relative difference in the total diffusion pathlength, which is the sum of the thickness of the stagnant layer and the effective diffusion distance through the barrier, become much less variable between high and low wind speed conditions. Again, the effect is a reduced wind speed dependence of the SR. Obviously, the thicker the diffusive barrier, the smaller the difference in the relative diffusion pathlengths and therefore the smaller the wind speed dependence of the SR (compare panels C and E in Fig. 5).

It is of course possible to deploy both strategies at the same time, *i.e.* place a sampler with a diffusive barrier within a wind shelter. However, depending on the thickness of the boundary layer relative to the effective diffusion distance within the barrier, the further reduction in the wind speed dependence afforded by a wind shelter may be marginal and is generally much smaller than the effect of sheltering a sampler without a diffusive barrier (compare panels C and D and E and F in Fig. 5).

Fig. 5 seeks to illustrate the effect of these two strategies by depicting the diffusion distance of an analyte from the bulk

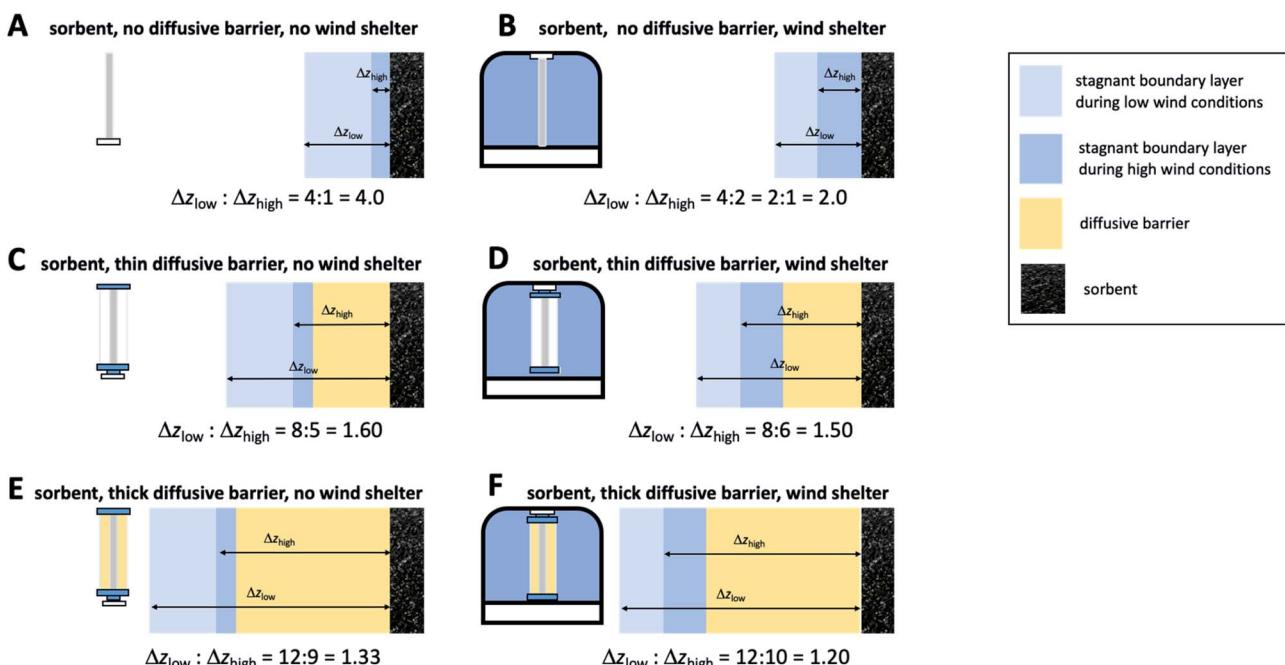


Fig. 5 Illustration of the effect of different sampler configurations on the diffusion distance of an analyte from the ambient atmosphere to the passive sampling sorbent under high ( $\Delta z_{high}$ ) and low wind conditions ( $\Delta z_{low}$ ). In particular, the effect of a wind shelter (A vs. B, C vs. D, E vs. F) and the effect of a thin or a thick diffusive barrier (A and B vs. C and D vs., E and F) is shown. The ratio  $\Delta z_{low} : \Delta z_{high}$  indicates the extent to which the SR is influenced by wind speed.



atmosphere to the PAS sorbent both at high ( $\Delta z_{\text{high}}$ ) and low wind speed ( $\Delta z_{\text{low}}$ ) conditions. The quotient  $\Delta z_{\text{low}}/\Delta z_{\text{high}}$  expresses by how much the diffusion distance and therefore the SR is dependent on wind. The numbers for  $\Delta z$  assigned to different PAS configurations in Fig. 5 are hypothetical, but plausible. The schematic of different sampler configuration is based on a sampler design using a sorbent in cylindrical form, a radial diffusion barrier (such as the Radiello), and a jar as a wind shelter, and is inspired by two passive samplers for gaseous mercury<sup>22,23</sup> (panels D and E, respectively).

Reducing the wind speed dependence of the SR of a PAS comes at a price, namely the reduction of the SR. This is less pronounced in the wind shelter strategy, as it mostly reduces the SR at high wind speeds, but barely affects the SR under low wind conditions. It is more notable with the application of diffusive barriers, as they increase the diffusion distance under any wind speed regime. Also, the thicker the barrier and therefore the more effective the reduction in wind speed dependence, the lower the SR becomes. Therefore, eliminating the effect of wind speed always needs to be balanced with the desire to sample sufficient amounts of an analyte for reliable quantification.

## C. The major challenges of passive air sampling for SVOCs

There are a number of reasons why passive air sampling for SVOCs is uniquely challenging.

### C.1 Opposing demands for high vs. tightly controlled uptake rates

Concentrations of individual SVOCs in the atmosphere tend to be very low, often in the range of  $10^{-12} \text{ g m}^{-3}$  (*i.e.* picograms per  $\text{m}^3$ ) or even less. Even though the detection limits of modern analytical methods for SVOCs are extremely low, during active air sampling for SVOCs, sampling volumes of several hundred  $\text{m}^3$  or even several thousand  $\text{m}^3$  are commonly used to allow for reliable detection and quantification, especially in remote regions with background concentrations. Such high sampling volumes are not attainable with classical PASs with typical SRs on the order of  $0.1 \text{ m}^3$  per day or less. In most cases, SRs on the order of  $1 \text{ m}^3$  per day or higher are required to collect sufficient chemical for quantification during reasonable deployment periods (months).

Kinetic PASs for substances other than SVOCs, whether batch, tube or radial diffusion samplers, have largely relied on diffusive barriers to standardise diffusion distances, and thus control SRs (see Section B.4). PASs for SVOCs, on the other hand, tend not to include diffusion barriers in their design. The main reason is that the uptake rates of PAS designs that incorporate diffusion barriers are too low to be compatible with the very low trace concentrations of SVOCs and the detection limits that can be achieved. Another reason is that the diffusive barrier itself may act as sorbents for SVOCs and thus interfere with sampling.

A fundamental challenge of a PAS for SVOCs is therefore to find the appropriate balance between an SR that is sufficiently high to sample chemical amounts that can be reliably quantified, yet is also reasonably stable and well defined to allow for a quantitative interpretation of the sampled amounts.

Whether a PAS should have a high, but variable SR or a low, tightly controlled SR depends to some extent on the magnitude and the spatial variability of the air concentrations of the target chemical. A compound with low, but spatially highly variable air concentrations is better sampled with a PAS that samples a lot of air (has a high SR), even if the volume sampled is quite uncertain. This makes sure that the sampled amounts are above LOD, yet it is still possible to compare PAS-derived concentrations at different locations. On the other hand, a compound with spatially fairly uniform air concentrations demands a PAS with a well-controlled SR, because only then can differences in the sampled amounts be interpreted as differences in volumetric air concentrations.

The concentrations of most SVOCs in the atmosphere are low and declining. Also, concentration differences of most SVOCs in the atmosphere are quite large, often ranging over many orders of magnitude. As a result, most PASs for SVOCs were designed to have high SRs, even if it meant that the SRs are quite variable and therefore uncertain. For example, the widely used PAS based on polyurethane foam (PUF) disks has an SR around  $4 \text{ m}^3$  per day (range:  $0.5$  to  $15 \text{ m}^3$  per day),<sup>24,25</sup> whereas the PAS using XAD-resin as a sorbent has an SR around  $0.5$  to  $1 \text{ m}^3$  per day (range  $0.4$  to  $5.5 \text{ m}^3$  per day).<sup>26-28</sup>

On the other hand, some SVOCs, such as hexachlorobenzene (HCB) and hexachlorobutadiene (HCBD), have very long atmospheric residence times and therefore fairly uniform concentrations in the atmosphere.<sup>29-31</sup> Unless a sampling site is in the immediate vicinity of a strong source, concentrations in the global atmosphere may only vary within less than an order of magnitude. A PAS would need a tightly controlled SR to distinguish such small concentration differences with confidence. While a PAS for SVOCs with a sufficiently precise SR may not presently exist, an existing PAS for gaseous elemental mercury<sup>22</sup> demonstrates that it is feasible in principle for a PAS to elucidate small concentration differences. Its SR is low relative to those of commonly used PAS for SVOCs ( $0.135 \text{ m}^3$  per day), but this is of little concern as the analytical technique for quantification is powerful enough to detect the analyte even after sampling over as little as a week at global background concentrations. One of the main reasons for this is that the entire sampled amount is analyzed (by combustion of the entire sorbent present in the PAS). In the typical PAS for SVOCs, the sorbent is solvent extracted and only a small amount of the sampled compound is injected onto the chromatographic column. Interestingly, SVOCs such as HCB and HCBD, also tend to have relatively high ambient gas-phase concentrations, precisely because of their long atmospheric residence time. If an analytical method were to be used that delivers all of the sorbed amount onto the analytical column (*e.g.* thermal desorption), even PASs with diffusive barrier may be able to take up amounts of HCB and HCBD above the LOD.



## C.2 Large diversity of SVOCs vs. limited applicability range of PASs in terms of volatility

The term SVOCs comprises a wide variety of compounds whose volatility spans several orders of magnitude. For example, the vapour pressure of a 3-ring PAH is approx. 4 orders of magnitude higher than that of a 5-ring PAH.<sup>32</sup> PCB congeners of different degree of chlorination cover a similar volatility range.<sup>33</sup> Volatility is, of course, also strongly governed by the temperature of deployment. Because the uptake capacity of a sampler is governed to a large extent by compound volatility, this means that a sampler will have widely divergent uptake capacities for different SVOCs and even the uptake capacity for the same compound will be different at different deployment temperatures. One consequence is that the characteristic times,  $t_{\text{linear}}$  and  $t_{\text{equilibrium}}$ , can range over several orders of magnitude for different SVOCs and for the same SVOC at different ambient temperatures.

For example, for the PUF-PAS, the simulation model PAS-SIM<sup>21</sup> estimates  $t_{\text{linear}}$  to decrease from ~8 months to ~8 days, when the  $\log K_{\text{PUF-G}}$  is decreased from 7 to 5.5.  $K_{\text{PUF-G}}$  changes by approximately 1.5 log units between a two-ring and a three-ring PAHs or for one compound if temperature is changed by 30 K. It is obvious that (i) equilibrium sampling for less volatile SVOCs is not feasible because of excessively long times to equilibrium, and (ii) it would be difficult to find a deployment period suitable for a range of SVOCs with divergent volatility, because even within the group of relatively volatile SVOCs,  $t_{\text{equilibrium}}$  will range over orders of magnitude.

However, also kinetic passive sampling is only applicable to substances within a certain range of volatility. A chemical that is too volatile will approach equilibrium too quickly and therefore have a very short  $t_{\text{linear}}$  and thus maximum deployment time. A chemical that is too involatile will be sorbed to particles in the atmosphere and therefore not be available for uptake in the PAS in gaseous form (Section F.6 will discuss the uptake of particle-sorbed SVOCs in PAS.). The range of applicability is dependent on the sampler design (uptake capacity and kinetics) and also environmental conditions (e.g. atmospheric particle concentrations), but spans approx. 4 orders of magnitude in volatility. Consequently, it will be impossible to design a kinetic PAS and to use a common set of deployment characteristics (e.g. deployment length) that is applicable to all SVOCs all the time. Unless one is willing to deploy a range of PASs tailored to different volatility ranges, the ambition therefore should be to design a sampler that is applicable to as many SVOCs as possible and under as many different environmental conditions as possible.

## D. Description of different types of passive air samplers for SVOCs

A number of different PASs have been proposed for SVOC sampling (Tables 1, 2, 4, and 5). There have been principally two commonly employed strategies for the development of PASs for SVOCs. One involves the use of materials originally developed for water passive sampling, the other the use of sorbents that

had found common use in active air sampling for SVOCs. One attractive feature of adopting a passive water sampler design for passive air sampling is the possibility of sampling air and water with the same device and the prospect of recording the air-water equilibrium status. However, caution is necessary to appreciate the different requirements for air and water sampling; for example, while a water sampler can be expected to be exposed to a relatively small range of temperatures during a deployment period, PASs may be deployed at sites with hugely different ambient temperatures that can change rapidly on the time scale of deployment. Also, because the diffusivity of SVOCs in water is so much slower than in the gas-phase and the thickness of boundary layers in air and water varies considerably, different factors may be controlling uptake from water than from air. Most of the PASs that are adopting sorbents from water sampling rely on non-porous materials such as polymeric sheets and films, whereas PASs using sorbents adopted from active sampling tend to rely on porous materials such as polymer foam and resins.

### D.1 Samplers involving sorbents enclosed within low-density polyethylene

**D.1.1 Semipermeable membrane devices (SPMDs).** The first PAS for SVOCs that adopted a passive sampler for water relied on semipermeable membrane devices (SPMDs), which consist of thin-walled low-density polyethylene (LDPE) lay-flat tubing containing a thin film of the neutral synthetic lipid triolein.<sup>34</sup> Most of the early studies using SPMDs as PASs were interested in sampling both air and water.<sup>35–37</sup> Ockenden *et al.* calibrated SPMDs as PASs for PCBs<sup>38,39</sup> and then applied them to repeatedly record a latitudinal gradient in atmospheric contamination in Western Europe.<sup>40–45</sup> Söderström *et al.*<sup>46,47</sup> were other early adopters and explored the wind speed dependence of uptake in SPMD-based PASs<sup>47,48</sup> and were the first to use SPMDs for indoor deployments.<sup>49</sup>

Cranor *et al.*<sup>50</sup> used a laboratory set-up to determine both the uptake kinetics and the uptake capacity of SPMDs for 48 compounds including several PAHs, PBDEs, OCPs, and current-use pesticides (CUPs). Cicinatti *et al.*<sup>51</sup> also used laboratory experiments to determine these parameters for three compounds (naphthalene, 2-chlorophenol, 1,4-dichlorobenzene) as a function of temperature in the range from –16 to +40 °C.

**D.1.2 PASs with other sorbents enclosed in PE membranes.** Several modifications of SPMDs have been proposed for air sampling, which substituted triolein with other sorbents (Table 1). The rationales for this substitution included a simplified preparation and clean-up procedure in samplers not containing triolein<sup>52,53</sup> and the high cost of triolein.<sup>54</sup> Also, SPMDs are a patented product which can impede its widespread adoption. In principle, a different sorbent may also increase the uptake capacity of a PAS relative to an SPMD.

Wennrich *et al.*<sup>52</sup> and Paschke and Popp<sup>55</sup> proposed to substitute triolein with polydimethyl siloxane (PDMS or “silicone”) as a sorbent in different configurations (silicone tubing, silicone spiral rods, PDMS-coated stir-bar), either enclosed in



Table 1 Passive air samplers for SVOCs involving sorbents enclosed within low-density polyethylene (LDPE)

Name	Passive sampling material	Housing	Ref.
Semipermeable membrane devices (SPMDs)	Thin-walled LDPE lay flat tubing containing a thin film of synthetic lipid triolein (1,2,3-tri[cis-9-octadecenoyl]glycerol)	White wooden box with louvred sides (Stevenson screen)	34
Poly(dimethylsiloxane) (PDMS)	Thin-walled LDPE lay flat tubing containing either PDMS-coated stir bar ( $V_s = 24 \text{ ml}$ , $A = 2.8 \text{ cm}^2$ ) or silicone tubing ( $V_s = 250 \text{ ml}$ , $A = 12 \text{ cm}^2$ )	Stainless steel box (20 cm diameter, 20 cm high), open at the bottom with perforated sides	52
Poly(dimethylsiloxane) (PDMS)	LDPE cylinder containing either PDMS-coated stir bar ( $A = 1.67 \text{ cm}^2$ ) or spiral silicone rod ( $A = 5 \text{ cm}^2$ )	Cylindrical stainless-steel shelter with an opening at the bottom	55
Membrane-enclosed copolymer (MECOP) samplers	Thin-walled LDPE lay flat tubing containing crystalline ethylvinyl-benzene-divinyl-benzene copolymer	Perforated steel box	53
Versatile, easy and rapid atmospheric monitor (VERAM)	Various sorbent materials enclosed in thin-walled LDPE lay flat tubing (a mixture of florisil and activated carbon recommended for VOCs sampling)	Unknown	54

a PE membrane similar to an SPMD<sup>52</sup> or in a cylindrical PE tube.<sup>55</sup> The fairly low SRs of these PAS designs (on the order of  $0.01 \text{ m}^3$  per day) are at least partly overcome by an analytical technique that relies on thermal desorption of the PDMS. This not only delivers the entire sampled amount onto a gas chromatographic column, but the lack of sample extraction procedures may allow for lower blank levels and thus detection limits. Unfortunately, very large differences in uptake rates observed between compounds, between indoor and outdoor deployments, and between different sampler configurations remained unexplained<sup>52,55</sup> and no follow-up studies based on these approaches appear to exist.

Choi *et al.*<sup>53</sup> enclosed a crystalline ethylvinylbenzene-divinylbenzene copolymer in a PE membrane, calling it membrane-enclosed copolymer (MECOP) samplers. No SRs had been determined, so rates for SPMDs were applied after adjusting for the much smaller surface area of the PE membrane in the MECOP relative to an SPMD. Esteve-Turrillas *et al.*<sup>54</sup> experimented with a number of different sorbents in SPMD-type lay flat PE tubing, and recommended a mixture of florisil and activated carbon.

**D.1.3 Limitations of samplers involving sorbents enclosed within LDPE.** The justification for enclosing a sorbent within a PE membrane is the desire to control the diffusion distance through the use of a permeable barrier. As discussed in Section B.4 above, a tightly controlled diffusion distance is a key requirement for a PAS that is not susceptible to large variations in the SR as a result of different wind exposure. A problem with this approach is that a PE membrane itself is a sorbent for SVOCs. Furthermore, capacity and permeability of PE are functions of temperature.<sup>41,56,57</sup> Collectively, this leads to highly complex uptake characteristics of PASs using PE-enclosed sorbents that make a reliable, quantitative interpretation of

results highly challenging. Some studies essentially concluded that an incomplete understanding of the effect of temperature on the uptake characteristics of those types of samplers precluded a quantitative interpretation.<sup>58,59</sup> Whereas SPMDs continue to be used occasionally as PASs,<sup>61–65</sup> the PAS designs in Table 1 can no longer be regarded as representing the state-of-the-art in passive air sampling for SVOCs.

## D.2 Samplers based on non-porous sorbent materials

The samplers described in Section D.1 consist of two sorbing phases, namely the enclosed sorbent and the polyethylene. This appears redundant, because even with two sorbents present, these PASs often do not have sufficient uptake capacity for more volatile SVOCs to remain in the linear uptake phase during typical lengths of deployment (e.g. ref. 41). Also, the presence of two sorbents makes the understanding and quantification of uptake kinetics and uptake capacity unnecessarily complicated. Accordingly, most PASs rely on a single material able to act as a sorbent. In particular, a fairly large number of PASs relies on a non-porous sorbent material, such as a non-porous polymer or a solid lipid as a sorbent (Table 2).

### D.2.1 Samplers based on low-density polyethylene (LDPE).

Müller *et al.*<sup>66</sup> realised that the sorbent enclosed in the PE of the SPMDs may be redundant, as the PE itself can act as a sorbent. Bartkow *et al.*<sup>67</sup> showed that simple PE sheets of different size and thickness suspended in air can constitute a PAS. In particular, they showed that the simultaneous deployment of PE sheets of different thickness can be used to determine whether a chemical is in the linear uptake phase or approaches equilibrium. The amount of substances with kinetically controlled uptake is independent of the volume of the PE sheet  $V_s$  and related to its surface area  $A$ , whereas the amount of substances



Table 2 Passive air samplers for SVOCs based on non-porous sorbent materials

Name	Passive sampling material	Housing	Ref.
Solid phase micro-extraction (SPME) "Synthetic leaf"	SPME fibre made from PDMS Fibreglass cloth (250 mm × 500 mm) coated with 0.3, 1.5 or 3 g of tristearin (2,3-di(octadecanoyloxy) propyl octadecanoate)	Needle housing Stainless-steel frames (0.5 m × 0.5 m) in open-sided container	104 120
Polymer-coated glass (POG)	Hollow glass cylinder (68 mm o.d., 64 mm i.d. and 70 mm tall) coated inside and outside surfaces with thin film (0.5 µm thickness) of ethylene vinyl acetate	Double bowls made of stainless steel	92
Low-density polyethylene (LDPE) films	Low-density polyethylene film (30 cm by 30 cm)	Galvanised iron chambers with an open bottom and louvers on all sides	67
Artificial leaf (AL)-PAS Ethylene vinyl acetate (EVA)	Paraffin oil on cellulose paper Glass fibre filter (GFF) or thick aluminum foil coated with ethylene vinyl acetate	Petri dish None	121 98
PDMS-based PAS	Silicone disk of 0.5 mm thickness in a 15 cm Petri dish or a baking paper sheet (40 cm × 60 cm) coated on both sides with a thin film (0.001 mm) of silicone (0.5 g Si per m <sup>2</sup> )	None	114
PDMS sheet	PDMS sheets of 0.1 cm thickness (11 cm long × 9 cm wide × 0.1 cm thick with total surface area 202 cm <sup>2</sup> )	None	111
PDMS brooch	PDMS strip (9 cm long × 5.5 cm wide × 0.1 cm thick, surface area was 50 cm <sup>2</sup> )	Personal sampler (aluminum plate to prevent contact with clothing)	113
PDMS-coated stir bar	Stir bar, 2 cm long coated with 1 mm thick PDMS film	Double stainless-steel domes	110

achieving equilibrium is proportional to  $V_s$ .<sup>67</sup> Bartkow *et al.*<sup>68</sup> demonstrated the viability of using depuration compounds (DCs) spiked into the PE prior to deployment to account for differences in wind exposure of PASs based on PE-sheets (see also Section F.4 below). PE-based PASs have since been used extensively by US-based researchers.

Somewhat surprisingly, there appears little attempt to standardise the deployment of PE-based PAS. A variety of different sizes of PE sheets, strips, and lay-flat tubing appear to be in use, but dimensions and sheet thickness are not always provided. Furthermore, different housings are being used to shelter the PE sorbent. Some use a metal box with louvred sides and an open bottom,<sup>67</sup> whereas others use a metal cage that is not further described, but appears to be long and upright.<sup>69–71</sup> Lohmann *et al.*<sup>72–75</sup> either use the double bowl shelter of Shoeib and Harner<sup>24</sup> or a version where the bottom bowl is eliminated. It is also often not clear how the PE sheets are being placed in these shelters and photographs suggest that little attention is paid to the precise arrangement (see *e.g.* photograph in ESI in ref. 76). Overall, this suggests that even during outdoor deployments little effort is made to limit or standardise the wind exposure of the PE and a lot of trust is therefore placed in the capability of DCs to correct for variable wind exposure (Section F.4).

Because PE-based samplers are commonly employed in water passive sampling, PE-based PASs offer, similar to SPMDs, the possibility of using the same sampler material in air and water and therefore the possibility to derive the equilibrium status between them.<sup>77–90</sup> This is further discussed in Section G.8.1.

**D.2.2 Samplers based on ethylene vinyl acetate (EVA).** A thin film of ethylene vinyl acetate (EVA) coated on glass was introduced as a means to sample SVOCs from the headspace of a sample vial.<sup>91</sup> Large surface area to volume ratios of the EVA film were meant to assure quick equilibration with the gas-phase. Harner *et al.*<sup>92</sup> proposed to use EVA coated onto glass and placed in a wind-shelter as PAS. Farrar *et al.*<sup>93</sup> determined the uptake and loss kinetics of these so-called Polymer-coated Glass samplers (POGs) and used them to measure concentration variability along a vertical gradient in the urban boundary layer<sup>94</sup> and within a European-scale network.<sup>95</sup> POGs have also been used for sampling in water.<sup>96</sup> Uptake in EVA-films was observed to be somewhat faster than in PE sheets, but equilibration times were longer because the uptake capacity of EVA was larger than that of PE.<sup>97</sup> Instead of glass as a base onto which the EVA is applied, it is also possible to use glass fibre filters (GFFs) or aluminum foil.<sup>98</sup> While explicitly designed to equilibrate fast (within a number of days of deployment), for



less volatile chemicals the time to equilibrium can be quite long. As a result, the interpretation in terms of volumetric air concentrations has to be different for different SVOCs.

**D.2.3 Samplers based on polydimethyl siloxane (PDMS).** A possible drawback of PE-based samplers is the relatively low diffusivity of SVOCs in PE,<sup>99,100</sup> which may compromise the commonly made assumption that resistance to uptake in a sampler material is dominated by diffusion through the air boundary layer. Other polymers, in particular PDMSs, tend to allow for faster diffusion and thus pose lower resistance than PE<sup>99,100</sup> and one can therefore be more confident that uptake is controlled by the air-side resistance. In Section D.1.1, we already learnt that PDMS had been proposed as the main sorbent in a PAS for SVOC,<sup>52,55</sup> but the enclosure of that PDMS in PE compromises the advantage of the higher permeability of the PDMS. Just like SPMDs and LDPE, PDMS is now routinely used for passive water sampling<sup>101–103</sup> and thus could be used for sampling in multiple environmental media.

One of the first kinetic PASs based on PDMS was a solid phase micro-extraction (SPME) fibre which is retracted into its needle housing. Changing the distance by which the fibre is retracted within the needle housing results in a change in the diffusion distance and therefore in the SR.<sup>104</sup> While the SRs are exceptionally small, around  $10^{-5} \text{ m}^3 \text{ per day}$ , all of the chemical sorbed to the PDMS is delivered by thermal desorption onto the analytical column without any sample preparation steps. If a chemical is too volatile, it will be lost from the fibre prior to desorption; if it is too involatile, it will sorb to the inside surface of the needle housing.<sup>105</sup> Despite the low SR, the  $t_{\text{linear}}$  is quite short (less than a day), because the uptake capacity is also small (the PDMS volume  $V_s$  is small). In its non-retracted mode, an exposed SPME fibre could also function as an equilibrium passive air sampler.<sup>106</sup> This approach was applied to the measurements of pesticide concentration in a greenhouse.<sup>107</sup>

The amount of target chemical sorbed to the small volume of PDMS in an SPME fibre may often be too low for reliable quantification. PDMS-coated stir-bars have a higher sorptive capacity because of a larger sorbent volume  $V_s$ , yet can still be analyzed with thermal desorption. Stir bar sorptive extraction (SBSE) combined with thermal desorption gas chromatography-mass spectrometry (GC-MS) has been proposed as a passive air sampling technique and applied to record the concentration variability of an insecticide<sup>108</sup> and PAHs<sup>109</sup> in indoor environments. Matsiko *et al.* showed that the technique is suitable for measuring organophosphate flame retardants (OPFRs) at ambient atmospheric concentrations and reported initial SRs on the order of 2 to  $7 \text{ m}^3 \text{ per day}$ .<sup>110</sup> These SRs appear abnormally high, when considering that other PDMS-based samplers with much larger surface area than a 2 cm-long stir bar have much lower SRs (see next paragraph<sup>111–114</sup>). When SBSE is used to extract an analyte from a liquid, the stir bar can be spun magnetically to lower the boundary layer thickness and thus speed up the uptake kinetics. During its use in air sampling, the stir bar is not actually spun, *i.e.* the fact that the PDMS is coated on a magnetic stir bar is incidental. Unfortunately, it also means that uptake in the stir bar from the air will be dependent on atmospheric turbulence.

In 2016, two research groups<sup>111,114</sup> independently proposed samplers made from PDMS for sampling of SVOCs from indoor air. Okeme *et al.* cut rectangular PDMS sheets of 0.1 cm thickness ( $A = 202 \text{ cm}^2$ ) and suspended them in air.<sup>111</sup> Two 50 day calibrations for this sampler have been reported. The first calibration involving 5 phthalates, 3 brominated monoaromatics and 9 PBDE congeners yielded an average SR of  $1.7 \text{ m}^3 \text{ per day}$ ,<sup>111</sup> whereas a second using more or less the same set of compounds (3 PBDEs less, two OPFRs more) gave an average value of  $6.1 \text{ m}^3 \text{ per day}$ .<sup>112</sup> Going forward Okeme *et al.* recommend the average of all of these values, which translates to a surface area-normalised SR of  $1.5 \pm 1.1 \text{ m}^3 \text{ per day per dm}^2$ .<sup>112</sup>

Vorkamp *et al.* suggested either a silicone disk of 0.5 mm thickness in a 15 cm Petri dish ( $A = 177 \text{ cm}^2$ ) or a baking sheet coated on both sides with a thin film (0.001 mm) of silicone ( $A = 4800 \text{ cm}^2$ ).<sup>114</sup> The latter was specifically designed with an extremely high surface area to volume ratio ( $A/V_s$ ), thus aiming for a low  $t_{\text{equilibrium}}$ . Experiments confirmed that time to equilibrium decreased with  $A/V_s$  ratio and the baking sheets reached equilibrium within two weeks, even for PCB congeners with an intermediate degree of chlorination.<sup>114</sup> SRs increased with surface area, but less than might be expected – while surface area  $A$  for the sheet was 27 times larger than for the disk, the SRs for PCB-101 were only higher by an order of magnitude ( $0.2 \text{ m}^3 \text{ per day vs. } 1.8 \text{ m}^3 \text{ per day}$ ), even though the sheet may be expected to have a smaller air side resistance.

Okeme *et al.* presented another PDMS-based PAS design to be worn as a personal sampler. A 0.1 cm thick sheet of PDMS ( $50 \text{ cm}^2$ ) is attached to an aluminum plate that serves to prevent contact of the sorbent with clothing when worn as a “brooch”.<sup>113</sup> Being calibrated for a number of phthalates against pumped personal samplers, they estimated an SR of around  $0.4 \text{ m}^3 \text{ per day}$  or  $0.86 \pm 0.29 \text{ m}^3 \text{ per day per dm}^2$ , when normalised to surface area. The variability in the SR between individuals and between different SVOCs was large.

Table 3 compares the SRs for the various PDMS-based PASS that have been proposed in the last few years for indoor deployments. The table lists the ranges of the reported SRs for different SVOCs. Unfortunately, the variability in the SRs between different SVOCs for the same sampler and even between different calibration experiments for the same sampler is large. For example, the highest SR for a chemical in a PAS is often a factor of 2 to 4 times higher than the lowest SR, although the theory of PAS uptake predicts that SR for different chemicals should be similar when the resistance to uptake lies on the air side. Even two very similar calibrations for the same sampler yielded SRs that deviate by more than a factor of 3.<sup>111,112</sup> More disconcerting is that surface area-normalised SRs of different PDMS samplers deviate by orders of magnitude. They range from a low of less than  $0.1 \text{ m}^3 \text{ per day per dm}^2$  in the baking sheet<sup>114</sup> to more than  $100 \text{ m}^3 \text{ per day per dm}^2$  for the PDMS-coated stir bar.<sup>110</sup>

The SR is dependent on the extent of air turbulence and therefore the thickness of the stagnant air layer surrounding the PDMS. Exposure to air turbulence could differ between different deployments, different calibration studies and for the various sampler designs, especially because none of the designs



Table 3 Sampling rate, surface area and area-normalised sampling rate for various PDMS-based PAS

Sampler	SR in $\text{m}^3$ per day	Exposed surface area in $\text{cm}^2$	Area-normalised SR in $\text{m}^3$ per day per $\text{dm}^2$	Ref.
Suspended sheet	0.9 to 4.1	202	0.45 to 2.0	111
Suspended sheet	3.5 to 10	202	1.7 to 5	112
Suspended XAD-coated sheet	1.9 to 4.3	102	1.9 to 4.2	112
Sheet attached to aluminum plate	0.2 to 0.66	50	0.4 to 1.32	113
Disk in Petri dish	0.2 to 0.3	177	0.11 to 0.17	114
Coated baking sheet	1.3 to 3	4800	0.03 to 0.06	114
Coated stir bar	1.8 to 6.7	5 <sup>a</sup>	40 to 140	110

<sup>a</sup> Assuming a diameter and length of the stir bar of 0.8 cm and 2 cm, respectively.

discussed here relies on a housing to reduce these effects (see Section B.4) and because indoor environments can be quite inhomogeneous in terms of the air turbulence they experience. However, taken collectively, it suggests that the experimental evidence presented so far is difficult to reconcile with the theoretical expectations on how PDMS-based samplers should behave, in particular with respect to an SR that is proportional to surface area  $A$  and largely invariant for different substances of similar molecular size. Interestingly, the inconsistency in SRs mirrors somewhat the experience with PDMS-based samplers that include a diffusive barrier<sup>52,55</sup> that were discussed in Section D.1.2.

**D.2.4 Samplers based on lipid-coated fibres.** SPMDS had been conceived as mimicking an aquatic organism consisting of a lipid reservoir and a membrane that controls uptake from the aqueous phase.<sup>115</sup> In an analogous way, others have sought to design PASs that are inspired by plant foliage. Leaves and needles have been used for monitoring air concentrations of SVOCs based on diffusive uptake in the waxy plant cuticle<sup>116</sup> and the idea of a “synthetic or artificial leaf” is to standardise this sampling medium and eliminate variations between species and individual plants<sup>117,118</sup> or even within the same plant over time.<sup>119</sup> The approach essentially seeks to represent the plant cuticle with a layer of wax having a large surface area. Proposed designs include stearin-coated fibreglass sheet<sup>120</sup> and cellulose paper coated with paraffin oil and placed in a Petri dish.<sup>121</sup> Müller *et al.* determined both stearin-gas-phase partition coefficients ( $K_{SG}$ ) for PAHs and the mass transfer coefficients controlling uptake in and loss from the synthetic leaf.<sup>120</sup> Field evaluations gave mixed results with agreement within a factor of 2 in one location and poorer agreement in another. Stracquadanio *et al.* exposed their artificial leaf for only a few hours during which PAHs were expected to have achieved equilibrium between paraffin oil and gas-phase.<sup>121</sup>

**D.2.5 Advantages and limitations of samplers based on non-porous sorbent materials.** One advantage of the PASs that rely on a sheet or film of a non-porous polymer, such as PE, PDMS and EVA, is the possibility to custom-design PASs with specific uptake capacities and SRs through the modification of the polymer's surface area-to-volume ratio  $A/V_S$ . Even if the experimental evidence so far does not support a direct proportionality between surface area  $A$  and SR (Table 3), as one should expect if the uptake is limited by the air-side boundary

layer, it should eventually be feasible to design a PAS with the desired  $t_{\text{linear}}$  and  $t_{\text{equilibrium}}$  for a particular target compound. In particular, it should be possible to design a PAS that will reach equilibrium for most SVOCs in a reasonable amount of time. The PDMS-coated baking sheet<sup>114</sup> had some of the highest achievable  $A/V_S$  and therefore is the closest of any design to a true equilibrium PAS for SVOCs. Unfortunately, the sheet has to be quite large for quantifiable amounts to accumulate in the PDMS film, which may make it too obtrusive for some indoor applications.

When comparing the relative merits of PE, PDMS and EVA, we can observe that PE has the lowest  $K_{SG}$  among the three polymers used in these types of PASs.<sup>97,122</sup> However, it is quite simple to increase a sampler's uptake capacity by increasing its  $V_S$ , *e.g.* by using thicker sheets. While PDMS and PE are non-polar polymers, EVA also has polar functional groups, which may increase the  $K_{SG}$  for polar target analytes. The  $K_{SG}$  of PDMS is very well studied and good predictive techniques are available (see Section E.2 below), while the experimental data set for EVA and PE is much thinner and, in the case of PE, relies largely on values derived indirectly from partitioning data between PE and water.

PDMS, and likely also EVA, have the advantage of higher permeability relative to PE,<sup>100,123</sup> which in principle should facilitate validity of the assumption of air-side controlled kinetics, which is important when using commonly applied equations for the interpretation of results in the curvi-linear uptake region. On the other hand, PE appears to be a more robust polymer material, which can withstand the rigors of field deployment better than EVA and possibly also PDMS. Interestingly, PDMS-based PASs have mostly been proposed for indoor use, where the demands on the robustness of a polymer are reduced.

The main limitation of PASs using non-porous polymeric sorbents is their relatively low uptake capacity. When an application of these PASs targets multiple analytes that vary in terms of their  $K_{SG}$ , some target analytes will be in the linear uptake phase, while others will be in the equilibrium or in the transitional phase. They are therefore neither kinetic nor equilibrium samplers. Deciding whether kinetic or thermodynamic factors or both dominate is not straightforward, as it depends on the complex interplay between chemical properties ( $K_{SG}$ , diffusivity in air and polymer), meteorological factors



(temperature, wind), sampler characteristics (thickness of polymer) and deployment parameters (deployment length). Quantitative knowledge of how these factors interact is often lacking. For example, in his critical review of LDPE as a passive sampling material, Lohmann admits that “no data were found on the temperature effect” on the partitioning of SVOCs between LDPE and the gas-phase, and that the strong temperature dependence of the diffusivity of compounds in LDPE “has not been addressed in greater detail”.<sup>124</sup>

Nevertheless, various authors have proposed fitting methods for deriving air concentrations from measurements of SVOCs in the curvi-linear uptake phase of PASs and these are now routinely applied. One should, however, be conscious of the fact that if information required in the quantitative interpretation of relatively low capacity PASs is lacking, incomplete or highly uncertain, this quantitative interpretation will suffer from very considerable uncertainties (see Section F.3 below).

Generally, it appears that PASs based on non-porous polymers have no standardised wind shelter or housing (except possibly the original POGs<sup>92</sup>). In many cases, no housings are used at all. This is somewhat surprising, since in all of those PASs, it is assumed that the air-side resistance is rate-limiting SVOC uptake and therefore the SRs can be expected to be strongly dependent on the air turbulence surrounding the polymer. While this may be acceptable for true equilibrium samplers or for indoor deployments in places with limited turbulence, it makes the SR of such samplers in outdoor field deployments highly variable and wind exposure the main source of uncertainty. One attempt to reduce these uncertainties is the use of DCs. This is discussed in greater detail in Section F.4 below. It is noteworthy that many authors propose non-porous polymer PASs mostly for use indoors,<sup>111–114</sup> where wind exposure is generally limited and where temperatures and concentrations of many SVOCs tend to be reasonably constant, avoiding the challenges described in Section C.

### D.3 Samplers based on porous sorbent materials

#### D.3.1 Samplers based on polyurethane foam (PUF)

**D.3.1.1 The PUF-PAS by Shoeib and Harner.** Polyurethane foam (PUF) has been used as a sorbent for SVOCs in active air sampling for a long time.<sup>125</sup> Shoeib and Harner<sup>24</sup> first introduced this sorbent to PASs for SVOCs, by placing a foam disk in the space between two metal bowls (Fig. 6A). This sampler design has become the most popular PAS for SVOCs because PUF is inexpensive, easy to handle, and has a reasonably high capacity. While the SR for this sampler is often reported to be around 3 to 4 m<sup>3</sup> per day, the variability in SRs between different studies and for different compounds in the same study is quite high. Reported SRs range from less than 1 to 30 m<sup>3</sup> per day.<sup>126,127</sup> Melymuk *et al.* have discussed at length the factors that contribute to this variability.<sup>25</sup> Even under indoor deployment conditions, the variability in SR of the PUF-PAS for different SVOCs and in different calibration studies is large; for example, a range 0.41–11 m<sup>3</sup> per day has been reported for single-sheltered PUF-PAS.<sup>112</sup> Section F.2 below addresses the issue of SR variability in detail.

One factor contributing to this variability is wind. Laboratory experiments<sup>128</sup> and field studies<sup>129,130</sup> have shown that the SR of the PUF-PAS is quite strongly dependent on wind speed. This is because the double bowl is not entirely effective in preventing winds from impacting on the PUF disk. Chaemfa *et al.* measured the wind speed within a double bowl housing exposed to different wind speeds in a wind tunnel.<sup>131</sup> The wind speed above the PUF disk was roughly proportional to the outside wind speed and less than a factor of three smaller. The wind speed below the PUF disk was somewhat lower and increased linearly with outside wind speed at outside wind speeds less than 4 m s<sup>-1</sup>.<sup>131</sup> This is also consistent with computational fluid dynamics simulations of housings involving either one or two bowls,<sup>132</sup> which indicate the dependence of the SR on wind speed and wind angle of incidence.<sup>133</sup> DCs can be used to account for differences in wind exposure between deployments (see also Section F.4 below).<sup>130</sup> Because of the double bowl shelter's inefficiency in blocking wind from impacting on the sorbent, PASs using this design tend to also accumulate particle-bound substances (see Section F.6).

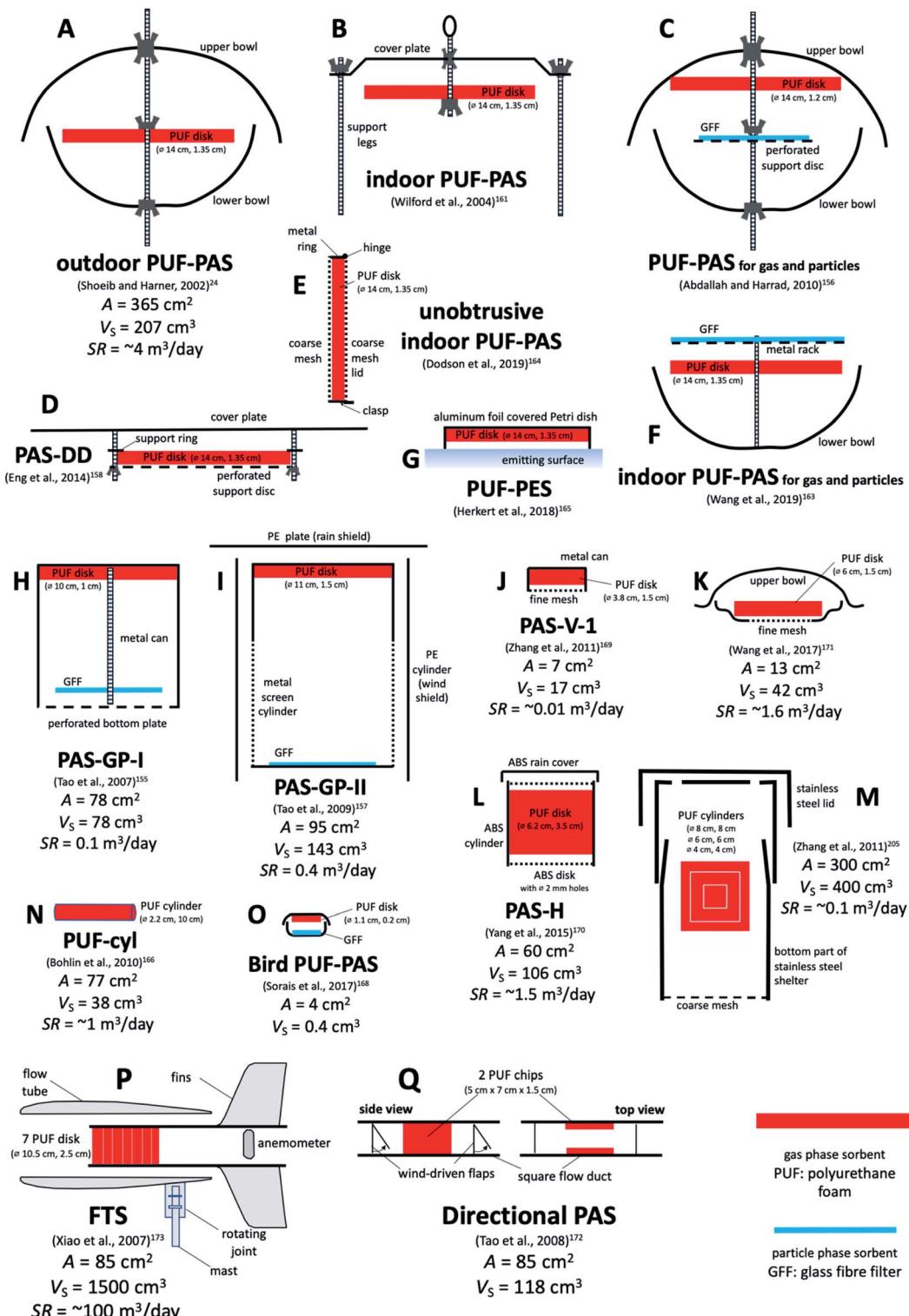
Differences in SR can also be expected between indoor and outdoor deployments. Lower SRs indoors than outdoors are explained by the lower exposure to atmospheric turbulence.<sup>134</sup> Small differences in the dimensions of the double bowl shelter do not contribute to statistically significant differences in the SR.<sup>135</sup>

**D.3.1.2 The sorbent impregnated PUF disks (SIPs) samplers.** Because the PUF has too limited an uptake capacity to sample relatively volatile SVOCs kinetically (see Section E.1.3), Shoeib *et al.* coated polyurethane foam with ground-up XAD-4 (divinylbenzene-styrene copolymer) powder to obtain so-called sorbent impregnated PUF (SIP).<sup>136</sup> Direct side-by-side comparisons showed that this indeed increased the uptake capacity of the sampler and increased  $t_{\text{linear}}$ .<sup>137,138</sup> Use of SIPs since has focused on neutral perfluoroalkyl substances<sup>139–146</sup> and organosiloxanes,<sup>147–149</sup> because these groups of SVOCs comprise some relatively volatile substances. However, SIPs are also being used for SVOCs that had previously been sampled with PUF-PASs<sup>150–152</sup> as well as organophosphate esters<sup>138</sup> and ionic perfluoroalkyl substances.<sup>153</sup>

The idea of adding XAD to a sorbent to increase its uptake capacity has since been used also for filter paper<sup>154</sup> and PDMS sheets.<sup>112</sup> XAD-coated and uncoated PDMS sheets were found to have similar area-normalised SRs, but the SR of the XAD-coated sheet showed less variability for different compounds (RSD reduced almost in half from 31 to 17%).<sup>112</sup> The calibration experiment was too short to confirm that the XAD-coated sheet had a longer  $t_{\text{linear}}$ .<sup>112</sup>

The rationale for increasing the sampling capacity of one sorbent by combining it with a high capacity sorbent is not always apparent, considering that one simply could use a sampler based on a high capacity sorbent in the first place. Drawbacks of using combined sorbents include (1) the need for additional preparation steps that require time and introduce the possibility of sorbent contamination, (2) the challenge of reproducing, and maintaining during deployment and





**Fig. 6** Various PASs based on polyurethane foam (PUF) as sorbent. Designs (A) to (F) are based on a PUF disk of the same size. Designs (B), (E) and (F) are for indoor deployments. Design (C), (F), (H) and (I) are aiming to sample gaseous and particle-bound SVOCs separately with PUF and GFF. Design (G) measures emissions from a surface. Designs (J), (K) and (L) are used to measure small scale elevation gradients above soil. Design (M) was used to probe the existence of a sampler side resistance to uptake in PUF. Designs (N) and (O) are miniaturised samplers to be worn by people or birds. Designs (P) and (Q) rely on the wind to blow through or past the PUF. A is the PUF surface area exposed to the air and  $V_S$  is the PUF volume. Sampling rates SR range from  $0.01 \text{ m}^3/\text{day}$  (design (J)) to  $100 \text{ m}^3/\text{day}$  (design (P)). See Table 4 for more detail.

handling, the exact composition of the mixed sorbents and therefore the uptake capacity of a PAS, and (3) the likelihood of introducing additional complexity to the uptake kinetics, for example with respect to a sampler side resistance.

**D.3.1.3 Other PASs based on PUF.** The design by Shoeib and Harner<sup>24</sup> is not the only PAS that is using PUF as a sorbent (Table 4). In particular, several attempts have been made to complement the PUF with a GFF meant to collect particle-bound SVOCs. Tao *et al.* presented a design, called PAS-GP-I, involving a cylindrical metal can, that has a PUF disk at the closed top and a GFF suspended close to the perforated bottom (Fig. 6H).<sup>155</sup> Abdallah and Harrad adopted essentially the same idea, except that they placed the PUF at the top and the GFF in the middle of the double bowl housing of the

original PUF-PAS (Fig. 6C).<sup>156</sup> During indoor deployments, the PAS-GP-I had very low SR of around 0.1 and 0.01 m<sup>3</sup> per day for gaseous and particle-bound PAHs, respectively,<sup>155</sup> whereas the modified PUF-PAS had a SR of around 1 and 0.5 m<sup>3</sup> per day for gaseous and particulate brominated flame retardants, respectively.<sup>156</sup> In 2009, Tao *et al.* introduced a modified design, called PAS-GP-II, in which the can holding PUF and GFF was made of an open mesh, which in turn was placed in a cylindrical wind shelter made of PE (Fig. 6I).<sup>157</sup> The motivation for the re-design was the need to increase the SR, if the sampler is to be useful in locations where SVOCs are not greatly elevated. Indeed, the SRs of PAS-GP-II were determined to be 0.4 and 0.6 m<sup>3</sup> per day for gaseous and particulate PAHs, respectively.

**Table 4** Passive air samplers for SVOCs based on polyurethane foam described in the literature. The letters in brackets behind the name refer to Fig. 6

Name	Passive sampling material	Housing	Ref.
PUF-PAS (A)	PUF disk (14 cm diameter, 1.35 cm thick, A: 365 cm <sup>2</sup> , V <sub>S</sub> : 207 cm <sup>3</sup> , density 0.0213 g cm <sup>-3</sup> , 4.40 g mass, 0.567 cm effective thickness)	Stainless steel double bowls (diameter: top 30 cm, bottom 24 cm) or single cover plate (indoors)	24 and 161
Modified PUF-PAS (C)	PUF disk (14 cm diameter, 1.2 cm thick, A: 360.6 cm <sup>2</sup> , density 0.02 g cm <sup>-3</sup> ) and GFF (12.5 cm diameter)	Stainless steel double bowls (top 23 cm, 2 L, bottom: 18 cm, 1 L)	156
PAS-GP-I (H)	PUF disk (10 cm diameter × 1 cm thick, density 0.024 g cm <sup>-3</sup> ) and GFF (8 cm diameter)	Stainless steel can (10 cm diameter × 10 cm high) with perforated bottom	155
PAS-GP-II (I)	PUF disk (11 cm diameter × 1.5 cm thick, density 0.024 g cm <sup>-3</sup> ) and GFF (11 cm diameter)	Mesh cylinder (11 cm diameter, 23 cm high) inside a PE cylinder	157
Directional PAS (Q)	2 PUF chips (5 × 7 × 1 cm <sup>3</sup> each, 0.024 g cm <sup>-3</sup> )	Flow duct (20 cm long, 5 cm high, 5 cm wide) with 2 one-way valves	172
PAS-V-I (J)	PUF disk (3.8 cm diameter, 1.5 cm thick, density 0.024 g cm <sup>-3</sup> )	Stainless steel cylinder (3.8 cm diameter, 2 cm high) with mesh-covered bottom (400 mesh, 3 cm diameter)	169
PAS for vertical gradients (K)	PUF disk (6 cm diameter, 1.5 cm thick, density 0.024 g cm <sup>-3</sup> )	Top bowl, bottom ring and fine mesh (4 cm diameter)	171
PAS-DD (D)	PUF disk (14 cm diameter, 1.35 cm thick, A: 365 cm <sup>2</sup> 36% covered)	Circular flat metal plate placed 2 cm above the disk	158
PAS-H (L)	PUF disk (3.5 cm thick, 6.2 mm diameter, density 0.024 g cm <sup>-3</sup> , A: 128 cm <sup>2</sup> , V <sub>S</sub> : 106 cm <sup>3</sup> )	ABS cylinder (5.5 cm high, 6.2 cm inner diameter), 18 2 mm holes in top and bottom, rain shield	170
Miniature bird-borne PAS (O)	PUF (0.2 cm-thick, 0.023 g cm <sup>-3</sup> density, A: 4 cm <sup>2</sup> ) and GFF (0.045 cm thick, 0.19 g cm <sup>-3</sup> , A: 3.45 cm <sup>2</sup> ) Alternatively: PDMS (0.1 cm thick, 1.14 g cm <sup>-3</sup> density, A: 4 cm <sup>2</sup> )	3D-printed elliptical double bowl	168
Mini-PUF or PUF-cyl (N)	PUF cylinder (10 cm long, diameter 2.2 cm, A: 77 cm <sup>2</sup> , density 0.030 g cm <sup>-3</sup> )	Protective cover net mesh size 1.0 mm, placed on helmet or lapel	166
Indoor PUF-PAS (E)	PUF disk (14 cm diameter, 1.35 cm thick)	Aluminum rigid mesh holder big enough to just hold the PUF disk	164
Indoor PUF-PAS (F)	PUF disk (14 cm diameter, 1.35 cm thick) and GFF	Stack of GFF (top), PUF disk (middle) and bowl (bottom)	163
PUF-PES (G)	PUF disk (14 cm diameter, 1.35 cm thick)	Inverted glass Petri dish, covered with aluminium	165
Flow-through sampler (P)	Seven P10z PUF disk (10.5 cm diameter, 2.54 cm thickness and large porosity, 10 pores per inch)	Horizontally oriented, aerodynamically shaped, stainless steel flow tube	173



Eng *et al.* presented a PUF-based PAS specifically designed to quantify the dry deposition of SVOCs.<sup>158</sup> A PUF disk of the same dimensions as is used in the regular PUF-PAS is placed 2 cm beneath a circular flat cover plate, which serves as a sun- and rain shelter (Fig. 6D). The more open shelter design of this so-called passive dry deposition (PAS-DD) sampler allows for more efficient sampling of particles, particularly large particles. However, this open design also results in less wind sheltering than in the double bowl housing, which should make the SR of the PAS-DD even more dependent on variations in wind speed than those of the PUF-PAS. The PAS-DD has been used in combination with the PUF-PAS to determine dry deposition fluxes and velocities of PAHs in two Nepalese cities<sup>159</sup> and to study the dry deposition of pesticides.<sup>160</sup>

A number of modified versions of the original PUF-PAS<sup>24</sup> have been presented specifically for use indoors. In order to speed up uptake indoors, Shoeib *et al.*<sup>161,162</sup> proposed to eliminate the double bowl housing for indoor deployments and only use a plate to prevent gravitational settling of coarse particles (Fig. 6B). Eliminating the bottom bowl, as done by Harrad and Abdallah,<sup>256</sup> amounts to essentially the same thing. The SR of an unsheltered sampler indoors was either  $\sim 2.5 \text{ m}^3 \text{ per day}$ <sup>161,162</sup> or  $1.5 \text{ m}^3 \text{ per day}$ .<sup>256</sup> In order to separate particle-bound and gaseous SVOCs, Wang *et al.* placed a GFF for sampling of particles slightly above the standard PUF disk, which itself was placed at the top of a stainless-steel bowl (Fig. 6F).<sup>163</sup> This resembles the set-up by Abdallah and Harrad,<sup>156</sup> but by not having a cover at the top, the filter will also be sampling larger particles subject to gravitational settling.

Dodson *et al.* designed a small aluminium housing for a PUF-disk of the size used in the PUF-PAS, specifically for

indoor deployments (Fig. 6E).<sup>164</sup> The motivation was to take advantage of a well-characterised PAS sorbent, but have a minimally intrusive and easy-to-set-up housing that still allows for efficient airflow past the PUF and prevents gravitational particle deposition. Side-by-side sampling with an active sampler allowed for the estimation of SRs and to confirm that the PAS derived air concentrations of gas-phase SVOCs were accurately ranked when judged by the results of the active sampler.<sup>164</sup>

Herkert *et al.* placed a PUF-disk in an inverted Petri dish to record the release of SVOC vapours from indoor surfaces and called the device a passive emission sampler (PES) (Fig. 6G).<sup>165</sup> Bohlin *et al.* used a small PUF cylinder (10 cm long, 2.2 cm diameter) in a small mesh net, attached to a helmet or to a person's clothing, as a personal sampler for SVOCs (Fig. 6N).<sup>166</sup> This sampler design could also be used for stationary sampling indoors. SRs for that sampler based on comparisons with concentrations obtained with personal active sampling have been reported.<sup>166,167</sup>

Sorais *et al.*<sup>168</sup> presented a miniaturised version of the sampler of Abdallah and Harrad<sup>156</sup> that could be attached to free-ranging birds, *i.e.* a personal sampler for birds. It combined a small PUF disk and GFF in an elliptical double polyamide bowl manufactured with a 3D printer (Fig. 6O).

Three PUF-based PASs have been presented that sought to determine vertical concentration gradients above the ground.<sup>169–171</sup> In all three cases, a PUF disk was placed in a cylindrical housing, made either of stainless steel<sup>169,171</sup> or acrylonitrile butadiene styrene (ABS)<sup>170</sup> that was just big enough to accommodate the disk. The housing either had an opening at the bottom covered with a stainless-steel screen mesh

**Table 5** Passive air samplers for SVOCs based on granular sorbent material described in the literature. The letters in brackets behind the name refer to Fig. 7

Name	Passive sampling material	Housing	Ref.
XAD-PAS (A)	Stainless steel mesh cylinder (10 cm or 20 cm long, 2 cm diameter) filled with styrene–divinylbenzene copolymer	Inverted cylindrical steel cans	26
High wind version of the XAD-PAS (B)	Same as the XAD-PAS	Inverted cylindrical steel cans with wind-buffering baffles at the bottom	196
Activated carbon felt (ACF PAS) (D)	Activated carbon felt	Double bowls	185
Polyurethane foam disks impregnated with ground XAD resin (SIP-disk PAS) (C)	PUF disk (14 cm diameter, 1.35 cm thick) impregnated with styrene–divinylbenzene copolymer powder (0.4 g of XAD-4 resin)	Double bowls (upper 30 cm diameter and lower 24 cm diameter)	136
Axial PAS (E)	GFF (2.5 cm diameter) coated with 2.3 mg of Tenax TA	Puck holder with spacer ring and mesh cover, placed under plastic rain shelter	200
Tenax TA PAS (H)	Stainless steel mesh cartridge filled with Tenax TA	Custom made PVC shelter	201
XAD-pocket (F)	Stainless steel mesh pocket (9 cm long $\times$ 5.5 cm wide $\times$ 0.2 cm thick; $A = 105 \text{ cm}^2$ ; volume = $9.9 \text{ cm}^3$ ) filled with 7 g of XAD-4 ( $A_s = 750 \text{ m}^2 \text{ g}^{-1}$ )	None	111
XAD-PDMS (G)	PDMS sheet coated with XAD-4 resin	None	112



(Fig. 6J),<sup>169</sup> or had eighteen 2 mm holes drilled into both the top and the bottom of the housing, whereby the top was protected by a rain shield (Fig. 6L).<sup>170</sup> SRs, in both cases obtained by calibration against another PUF-based PAS, were 0.01 to 0.03 m<sup>3</sup> per day,<sup>169</sup> and ~1.5 m<sup>3</sup> per day,<sup>170</sup> respectively. In the design by Wang *et al.* the top of the PUF disk is covered by a small inverted bowl, which allows for a larger area to be exposed to air and therefore an increased SR (~1.5 m<sup>3</sup> per day) (Fig. 6K).<sup>171</sup>

Whereas most PASs seek to prevent the wind from impacting on the sorbent, two PUF-based samplers were explicitly designed to take advantage of the wind in the sampling process. The "directional" PAS seeks to sample only when the wind blows from a particular direction.<sup>172</sup> The air is guided to pass by two small PUF chips within a small wind duct aligned with the desired wind direction. Hinged polypropylene flaps act as one-way valves that shut down the airflow when there is no wind from that direction (Fig. 6Q). Calibrated and field-tested for PAHs,<sup>172</sup> this sampler does not seem to have found use since.

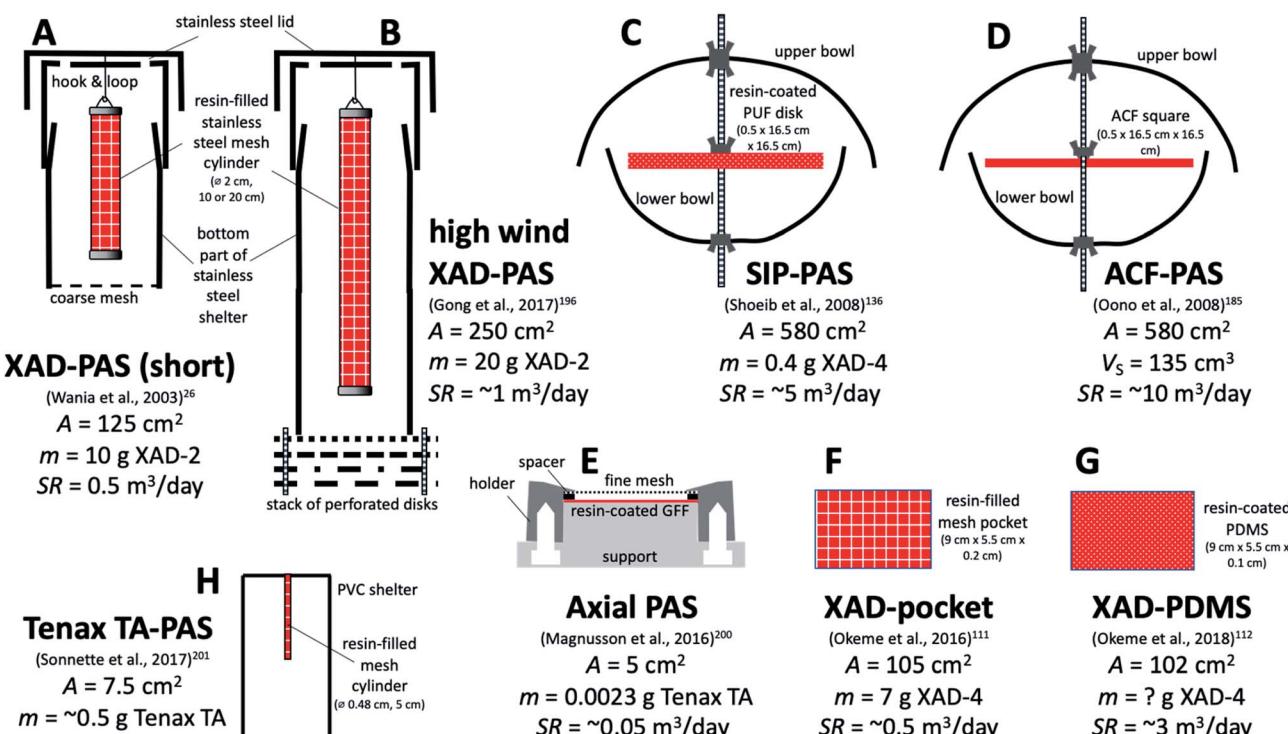
Xiao *et al.* designed a horizontal cylindrical flow tube that turns into the wind with the help of ball bearings and wind baffles.<sup>173–175</sup> The wind is blowing the air through a series of PUF disks placed in the flow tube and is then recorded with a battery-operated anemometer at the outflow of the tube (Fig. 6P). The PUF used in this sampler (P10z) is more porous than that used in other PUF-based PAS. The motivation for this design was to achieve SRs that greatly exceed those of other PAS. The sampling principle of this so-called "Flow-Through

Sampler" (FTS) resembles more that of a pumped active sampler, because it does not rely on the diffusion of the target analytes to the sorbent. The sampled air volume is derived from a calibration involving the measured wind speed. The FTS is particularly useful when trying to measure very low air concentrations in locations where reliable power is difficult to obtain. Examples are the Arctic,<sup>176–178</sup> sub-Arctic,<sup>179</sup> the Tibetan plateau,<sup>176,180</sup> and Antarctica.<sup>181</sup> However, the sampler has also been used closer to sources, for example to measure pesticide spray drift.<sup>182</sup>

Esen introduced a housing for a PUF-based PAS that seeks to minimise the influence of wind.<sup>183</sup> A side-by-side comparison with the double-bowl PUF-PAS indicated lower SRs.<sup>184</sup>

**D.3.2 Activated carbon fibre felt sampler.** Another approach to increase the limited uptake capacity of polyurethane foam is to retain the double bowl housing of the PUF-PAS, but use a different sorbent (Table 5). Oono *et al.* experimented with activated carbon fibre felt to sample fluorotelomer alcohols from the atmosphere (Fig. 7D).<sup>185</sup> During a month-long deployment, uptake remained linear and an equivalent air volume of 300 m<sup>3</sup> during that period suggest a high SR of ~10 m<sup>3</sup> per day.<sup>185</sup> Despite such promising results, no follow-up studies have appeared to be undertaken with this sorbent.

**D.3.3 Samplers based on XAD-resin.** The SIP-PAS described in Section D.3.1.2 sought to increase the uptake capacity of the PUF-PAS by impregnating it with XAD-resin (Fig. 7C). Like PUF, XAD, which is a divinylbenzene-styrene copolymer, also has



**Fig. 7** Various PASs based on porous sorbents other than PUF. Designs (A), (B), and (F) are based on XAD-resin, design (D) on activated carbon felt, and design (H) on Tenax TA. Other designs use resin to enhance the sorptive capacity of other sorbent materials, namely PUF (C), GFF (E) and PDMS (G).  $A$  is the sorbent surface area exposed to the air and  $m$  is the resin mass. Sampling rates SR range from ~0.05 m<sup>3</sup> per day (design (E)) to 10 m<sup>3</sup> per day (design (D)). See Table 5 for more detail.



a long history of use as a sorbent in the air sampling of organic compounds.<sup>186,187</sup> XAD has a higher uptake capacity for SVOCs than PUF<sup>188,189</sup> and also the stability of sorbed compounds during storage of XAD is higher than on PUF.<sup>188</sup> In contrast to the non-porous polymers and polyurethane, XAD is an adsorbent and its large uptake capacity is a result of a very high specific surface area (XAD-2: 350 m<sup>2</sup> g<sup>-1</sup>, XAD-4: 750 m<sup>2</sup> g<sup>-1</sup>). Because it is a powder, a container is required that holds the XAD-resin but does not obstruct the diffusion of the target analytes to the sorbent.

Wania *et al.* introduced a PAS which consists of a XAD-2 resin-filled stainless-steel mesh cylinder, which is suspended in a cylindrical stainless-steel housing (Fig. 7A).<sup>26</sup> This sampler has been extensively characterised in terms of the SR of different SVOCs in different climates<sup>21,27,28,190</sup> and with respect to the influence of wind on the SR.<sup>191</sup> Experiments with different sampler configurations confirmed that the uptake rate is proportional to the surface area of the mesh cylinder<sup>192</sup> and both a short (10 cm) and long (20 cm) version of the sampler have been used. The deployment of multiple mesh cylinders in the same housing does not affect the SR, *i.e.* there is no evidence of a so-called starvation effect.<sup>193</sup> Because very high winds have been shown to increase the SR,<sup>194,195</sup> Gong *et al.* introduced a modified housing with wind baffles that reduce the wind speed dependence of the XAD-PAS's SR (Fig. 7B).<sup>196</sup>

Because of its high uptake capacity (see also section E below), the XAD-PAS is probably the only PAS for SVOCs that can be regarded as a true kinetic sampler. Even for more volatile SVOCs such as the volatile methyl siloxanes (VMS) and the fluorotelomer alcohols (FTOHs), linear uptake was observed for periods as long as three months<sup>28</sup> and one year.<sup>197</sup> The high uptake capacity also explains, why the XAD-based PAS frequently finds use in extremely remote environments, where limited site accessibility may demand very long deployment periods. Examples are the Tibetan plateau, mountains and polar field camps (for details see Section G.6).

The XAD-PAS is suited for outdoor deployments, whereas its housing may be too bulky for indoor deployments and in fact not necessary. XAD-filled stainless steel mesh bags<sup>111</sup> suspended in air have therefore been explored as potential high capacity indoor-PAS (Fig. 7F). Okeme *et al.* used XAD-4, because of a higher specific surface area (750 m<sup>2</sup> g<sup>-1</sup>).<sup>111</sup> Because the XAD-filled mesh bag had a lower SR than a PDMS-based PAS explored at the same time (see Section D.2.3), the authors seemed to favour the PDMS-PAS.<sup>111</sup> Later, they also explored the possibility of enhancing the uptake capacity of PDMS by adding XAD-4 powder (Fig. 7G).<sup>112</sup>

**D.3.4 Samplers based on TENAX.** Building on the passive particle sampler by Wagner and Leith,<sup>198</sup> Arnoldsson *et al.* presented an axial diffusion sampler with a GFF (2.5 cm diameter), either bare or coated with 2.3 mg of Tenax TA, as the sorbent (Fig. 7E).<sup>199</sup> For analysis, the GFF is folded and placed into a tube, from which the target compounds are thermally desorbed and transferred to a GC-MS. The working hypothesis is that the PAS outfitted with an uncoated GFF takes up particle-sorbed compounds, whereas the Tenax-coated GFF additionally takes up gas-phase substances. By having the GFF facing

either up or down, the PAS is expected to distinguish particle-bound substances settling gravitationally or by other means.<sup>200</sup> SRs for PAHs and oxygenated PAHs in this sampler have been determined in an exposure chamber receiving diesel exhaust<sup>199</sup> and in a field study above an urban roadway.<sup>200</sup> While the variability in those SRs was large during the first test,<sup>199</sup> the field study yielded more consistent SRs on the order of 0.05 to 0.1 m<sup>3</sup> per day.<sup>200</sup> The small SR relative to other PAs for SVOCs is mostly due to the small size of the sampler and is compensated for by the quantification technique that delivers the entirety of the sequestered amount onto the gas chromatographic column.<sup>200</sup>

Sonnette *et al.* used a Radiello stainless steel mesh cartridge filled with Tenax TA as a PAS sorbent.<sup>201</sup> During sampling, they placed the cartridge into a PVC shelter but did not use a Radiello diffusive body to control the diffusion distance (Fig. 7H). They also used thermal desorption onto GC/MS for quantification. While some initial indoor and outdoor deployments are described, no attempts to characterise the samplers have been reported.

**D.3.5 Extraction of porous sorbent materials.** Porous sampling sorbents, such as PUF and XAD-resin are typically solvent-extracted using either a Soxhlet-apparatus or pressurised liquid extraction.<sup>202</sup> Alternatively, microwave- or ultrasound-assisted techniques have been proposed for extracting organic trace compounds from PUF with the aim to reduce solvent volumes and extraction time. A recently presented micro-scale version of an ultrasound-assisted extraction technique was judged simpler, faster, cheaper and more environmentally friendly than other methods.<sup>203</sup>

**D.3.6 Advantages and limitations of samplers based on porous sorbent materials.** The PASs based on PUF share with the non-porous polymer samplers described in Section D.2, a quite limited uptake capacity and therefore cannot be considered linear samplers for more volatile SVOCs (*e.g.* lighter PCB congeners during warm deployments<sup>204</sup>). The same issues related to the uncertainty of the quantitative interpretation (Section D.2.5) apply therefore also to the PUF-PAS. This is discussed in more depth in Section F.3 below.

The kinetic samplers (XAD-PAS, SIP-PAS), on the other hand, have the advantage that no knowledge of  $K_{SG}$  is required, and that long deployment times or sampling of relatively volatile SVOCs are possible without worrying about approaching equilibrium. They are also the only samplers that give air concentrations that are truly the average over the entire length of deployment. This is not the case when sampling in the curvilinear uptake range while the air concentrations vary with time.

A disadvantage of the PASs with porous sorbents is that the assumption of air-side resistance is not valid. This has been shown for both the XAD-PAS and the PUF-PAS, by demonstrating a concentration gradient within the sorbent<sup>205</sup> and through a critical evaluation of reported  $K_{PUF-G}$  values.<sup>206</sup> This also implies that the equations in Section B for interpreting the uptake of SVOCs in the sorbent cannot be applied uncritically. Instead, more complex uptake models are required for a quantitative interpretation of SRs (see Section F.5 below).<sup>21,207</sup>



Despite the use of wind-sheltering housings, the SRs of PASs using the double bowl design (PUF-PAS, SIP-PAS, carbon felt fibre-PAS and others) are quite substantially impacted by wind, especially, but not only, at high wind speeds.<sup>128</sup> The wind effect on the shelter used for the XAD-PAS is much smaller,<sup>26,191</sup> especially in the version by Gong *et al.*<sup>196</sup> In the balancing of the conflicting needs for a large *vs.* a tightly controlled SR (Section C.1), the double bowl design samplers lean towards higher, yet more variable SRs and the XAD-PAS leans towards lower, but less wind-dependent SRs.

Among the strategies to account for the effect of wind on SR is the use of DCs. It is important to realise that the use of DCs requires the assumption of air-side resistance to be valid (see Section F.4 below). DCs therefore have not been used in the XAD-PAS. Even though there is also evidence that this assumption is violated in the PUF-PAS,<sup>205</sup> DCs are routinely employed in the PUF-PAS.<sup>127,208,209</sup>

By normalizing the SR to the sequestered amount of a compound whose concentration can be assumed to be uniform in space,<sup>194</sup> it is possible to account for differences in the wind exposure of the XAD-PAS. HCB can often be used if it can be assured that there are no HCB sources in the vicinity of a sampling site.<sup>195,210</sup>

XAD-resin is quite expensive and it can be difficult to handle, especially when electrostatic effects occur. Coating XAD-resin onto PUF disks when making SIPs in particular, can be laborious and difficult and can easily lead to sorbent contamination. On the other hand, high capacity samplers do not require DCs, which is a considerable expense associated when seeking to quantitatively interpret results of PASs with limited uptake capacity in the curvi-linear uptake regions.

While a surprisingly large number of PASs for SVOCs have been introduced, they are for the most part described in a stand-alone paper with no follow-up studies seeking to characterise, test or apply the sampler. Among the PASs discussed in section D, only the PUF-PAS and XAD-PAS, and to a smaller extent also the SIP-PAS and PE-based samplers have been thoroughly characterised and are used most extensively. Therefore, the remainder of the review will largely focus on those PAS designs.

## E. The capacity of different PAS sorbents for SVOCs

As discussed in Section B above, knowledge of the  $K_{SG}$  at the temperature of deployment is essential for using equilibrium PASs as well as for interpreting measurements in the curvi-linear part of a PAS's uptake curve. Even if a sampler is operated in the kinetic range, knowledge of the  $K_{SG}$  is useful to estimate  $t_{\text{linear}}$ .

We defined  $K_{SG}$  in Section B.1 as the equilibrium sorption coefficients between the gas-phase and the PAS sorbent, which is the ratio of the concentration of a chemical in the sorbent  $C_S$  (in units of mol m<sup>-3</sup> sorbent or mol m<sup>-2</sup> adsorbent) and in the gas-phase  $C_G$  (in units of mol m<sup>-3</sup> gas) if the chemical has reached equilibrium between the two phases:

$$K_{SG} = \frac{C_S}{C_G} \quad (9)$$

$K_{SG}$  thus has units of m<sup>3</sup> gas per m<sup>3</sup> adsorbent (or m<sup>3</sup> gas per m<sup>2</sup> adsorbent). As  $K_{SG}$  is an equilibrium constant, we can use a van't Hoff type equation to relate it to temperature:

$$\frac{d\ln K_{SG}}{dT} = \frac{\Delta U_{SG}}{RT^2} \quad (10)$$

where  $T$  is absolute temperature in K,  $R$  is the ideal gas constant, and  $\Delta U_{SG}$  is the internal energy of transfer between sorbent and gas-phase in J mol<sup>-1</sup>. Note that we use the internal energy  $\Delta U_{SG}$  instead of the enthalpy of phase transfer  $\Delta H_{SG}$ , because in the PAS community the abundance of chemical in the gas-phase is typically expressed in volumetric air concentrations and not in partial pressure. If  $K_{SG}$  is expressed in units of mol per m<sup>3</sup> sorbent per Pa or mol per m<sup>2</sup> adsorbent per Pa, the use of  $\Delta H_{SG}$  would be appropriate. The two are easily derived from each other:

$$\Delta U_{SG} = \Delta H_{SG} - RT \quad (11)$$

If  $\Delta U_{SG}$  is assumed to be a constant, the integration of eqn (10) yields:

$$\ln \frac{K_{SG}(T)}{K_{SG}(T_{\text{ref}})} = \frac{-\Delta U_{SG}}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \quad (12)$$

With eqn (12) it is possible to calculate  $K_{SG}$  at a temperature  $T$ , if  $\Delta U_{SG}$  and  $K_{SG}$  at a reference temperature are known.

This section reviews both the experimental and theoretical studies that have been conducted to determine  $K_{SG}$  and  $\Delta U_{SG}$  for different types of sorbents used in passive air sampling. When referring to the  $K_{SG}$  and  $\Delta U_{SG}$  for a specific sorbent, we substitute S with the sorbent acronym. For example,  $K_{\text{PUF-G}}$  and  $\Delta U_{\text{PUF-G}}$  refer to the sorption coefficients and internal energy of phase transfer between PUF and the gas phase, respectively.

### E.1 Experimentally determined uptake capacities of PAS

**E.1.1 Studies reporting on  $K_{\text{PE-G}}$ .** While there appear to have been no experiments yet that sought to measure the equilibrium sorption coefficient between LDPE and the gas-phase ( $K_{\text{PE-G}}$ ) and its temperature dependence under controlled conditions,<sup>124</sup> such data have been repeatedly obtained from field data. In early work, Bartkow *et al.*<sup>67</sup> and Kennedy *et al.*<sup>97</sup> derived such sorption coefficients for PAHs from field data. Khairy and Lohmann<sup>73-75</sup> derived  $K_{\text{PE-G}}$  for PAHs, OCPs, PCBs and PBDEs from deployments in Alexandria, Egypt, and Providence, RI, USA, using concentrations measured in the atmosphere and concentrations in the LDPE-PAS, mathematically adjusted for equilibrium. However, partitioning data derived from field data inevitably apply to the temperature conditions during deployment and need to be adjusted. It should be possible to derive values of  $K_{\text{PE-G}}$  through a thermodynamic triangle with water-PE equilibrium partition coefficients  $K_{\text{PE-W}}$  and Henry's law constants  $K_{\text{G-W}}$ , because uptake in



PE is a bulk phase sorption process and is not influenced by the presence of water.<sup>124</sup> Measured values of  $K_{PE-W}$  are much more common, due to the wide-spread use of PE in passive water sampling.

**E.1.2 Studies reporting on  $K_{PDMS-G}$ .** Equilibrium sorption coefficients between PDMS and the gas-phase  $K_{PDMS-G}$  have been measured for a fairly large number of organic compounds, because of the use of PDMS in SPME fibres. Sprunger *et al.* have compiled  $K_{PDMS-G}$  values measured for 64 solutes at room temperature by a number of research groups.<sup>211</sup> Gilbert *et al.* showed that polymer–polymer partition coefficients can be used to derive  $K_{SG}$  values, *e.g.* by combining  $K_{PE-G}$  with  $K_{PDMS-PE}$  partition coefficients in a thermodynamic triangle to calculate  $K_{PDMS-G}$  values for PCB congeners.<sup>122</sup> Recently, Okeme *et al.*<sup>212</sup> and Tromp *et al.*<sup>213</sup> have greatly expanded the set of measured  $K_{PDMS-G}$  values, either from isothermal retention volumes on a DB-1 column that has PDMS as a stationary phase<sup>212</sup> or by using a calibration involving an exposure vessel with controlled temperature and wind speed.<sup>213</sup>

**E.1.3 Studies reporting on  $K_{PUF-G}$ .** Shoeib and Harner derived  $K_{PUF-G}$  for several lighter PCB congeners by assuming that they had reached equilibrium with laboratory air after extended exposure, and solving eqn (6A) for  $K_{SG}$  and using measured concentrations in air and PUF.<sup>24</sup> Zhao *et al.* reported  $K_{PUF-G}$  for eight aromatic VOCs at 21 °C.<sup>214</sup> Kamprad and Goss determined  $K_{PUF-G}$  for 103 relatively volatile organic compounds with diverse functionalities by measuring the chromatographic retention volume of analytes on a column filled with PUF.<sup>215</sup> Bidleman *et al.* determined  $K_{PUF-G}$  by equilibrating PUF with ambient air at different temperatures in the field for HCB,  $\alpha$ -hexachlorocyclohexane ( $\alpha$ -HCH) and two brominated anisoles.<sup>216</sup> More recently, Harner and co-workers have used dedicated laboratory experiments using a generator column approach to determine  $K_{PUF-G}$  as a function of temperature for parent PAHs and alkylated PAHs,<sup>217–219</sup> pentachlorobenzene (PeCBz), HCB,  $\alpha$ - and  $\gamma$ -HCH,<sup>219</sup> four OPFRs, six novel brominated flame retardants (BFRs), HCBD and pentachloroanisole (PCA).<sup>220</sup> Tromp *et al.*<sup>213</sup> measured  $K_{PUF-G}$  for 98 SVOCs at 20.7 °C during a 160 day-long calibration study in an exposure chamber.

We should note that for a porous sorbent such as PUF, the  $K_{PUF-G}$  with units of  $\text{m}^3$  gas per  $\text{m}^3$  absorbent, as it is reported in many of the studies mentioned here,<sup>213,217–220</sup> can be confusing as the volume of the absorbent could refer to solid polyurethane or to foam. To avoid misunderstandings, it would be preferable to report the  $K_{PUF-G}$  with units of  $\text{m}^3$  gas per g absorbent<sup>215</sup> or to include information on whether the volume of the foam or the polymer was used.<sup>214</sup> No work has been reported that explored whether  $K_{PUF-G}$  varies with the type or the density of the PUF, or whether variables such as relative humidity have an influence on the sorptive capacity of PUF.

Comparing different prediction methods for  $K_{PUF-G}$ , Okeme *et al.*<sup>206</sup> noted that some experimental  $K_{PUF-G}$  are likely erroneous, because the compounds did not achieve equilibrium between all of the exposed PUF and the gas-phase.

**E.1.4 Studies reporting on  $K_{XAD-G}$ .** Pankow *et al.* measured and compiled gas chromatographic retention volumes of

a whole range of VOCs, including aliphatics, chlorinated aliphatics, monoaromatic (BTEX, halogenated benzenes, phenols), ketones, amines, alcohols, and carboxylic acids at 20 °C using XAD as a stationary phase.<sup>221</sup> For a subset of these substances, they also reported retention volumes at temperatures between 40 °C and 90 °C. These retention volumes allow for the calculation of equilibrium sorption coefficients between XAD and the gas-phase  $K_{XAD-G}$ . Shen *et al.* used a headspace technique to directly measure the sorption of 1,2-dichlorobenzene, 1,2,4,5-tetrachlorobenzene and HCB onto XAD-2 resin,<sup>222</sup> whereas Hayward *et al.* applied inverse GC involving a column filled with XAD-resin to determine  $K_{XAD-G}$  for a selection of 52 diverse organic compounds as a function of temperature.<sup>223</sup> A limitation of these studies is that they often focus on VOCs and not on the SVOCs that are typically sampled with the XAD-PAS. This is because the  $K_{XAD-G}$  for SVOCs are typically too large to be amenable to reliable measurements. Sometimes, it is possible to infer minimum values of  $K_{XAD-G}$  from a field calibration experiment, even if equilibrium was not reached during the longest deployment. Krogseth *et al.*, for example estimated a lower limit of 6.5 for the  $\log K_{XAD-G}$  of a number of cyclical and linear VMS.<sup>28</sup>

## E.2 Prediction techniques for the uptake capacity of different PAS sorbents

**E.2.1 Single-parameter linear free energy relationships.** Because measurements of  $K_{SG}$  are generally only available for a few substances and at a limited number of temperatures, there has been interest in deriving techniques for predicting  $K_{SG}$ . Most often they take the form of single parameter linear free energy relationships that seek to linearly regress  $\log K_{SG}$  with the logarithm of either liquid-state vapour pressure or the octanol-air equilibrium partition coefficient ( $K_{OA}$ ) of a compound. For example, Pankow *et al.* regressed the retention volumes on XAD resin against vapour pressure.<sup>221</sup> Shoeib and Harner regressed the measured  $\log K_{PUF-G}$  for eight PCB congeners against  $\log K_{OA}$ ,<sup>24</sup> and Bartkow *et al.* regressed the  $K_{PE-G}$  of several PAHs against  $\log K_{OA}$ .<sup>67,97</sup> There are many more equations of this type reported in the literature (*e.g.* see compilation for  $K_{PUF-G}$  in Okeme *et al.*<sup>206</sup>). However, it is now well established that such relationships tend to be only valid for groups of closely related substances that interact with the sorbent with the same type of intermolecular interactions.<sup>224</sup> As such, their use might be defensible for a group of non-polar organic compounds, but they clearly cannot be expected to provide reliable estimates for substances that engage in polar interactions.<sup>220</sup>

**E.2.2 Poly-parameter linear free energy relationships.** More widely applicable are so-called poly-parameter linear free energy relationships (ppLFER), which are multi-variate linear regressions of measured sorption constants against a series of solute descriptors that quantify a compound's ability to undergo various types of intermolecular interactions such as hydrogen bonding.<sup>225</sup> Kamprad and Goss,<sup>215</sup> Sprunger *et al.*<sup>211</sup> and Hayward *et al.*<sup>223</sup> used their respective data sets to derive such relationships for  $K_{PUF-G}$ ,  $K_{PDMS-G}$  and  $K_{XAD-G}$ , respectively.



Whereas Hayward *et al.* presented such equations for  $K_{\text{XAD-G}}$  at different temperatures,<sup>223</sup> Kamprad and Goss derived a separate equation for the enthalpy of PUF-gas-phase transfer  $\Delta H_{\text{PUF-G}}$ .<sup>215</sup> Uber *et al.* presented ppLFERs for  $K_{\text{PE-W}}$ ,<sup>226</sup> including one for LDPE based on the experimental data by Choi *et al.*<sup>227</sup> If combined with a ppLFER for air-water partitioning, this should allow for the derivation of a predictive equation for  $K_{\text{PE-G}}$ . Finally, there are such relationships for solute uptake in other sorbents from the gas-phase. These sorbents have found or could conceivably find use in PAS, such as Chromosorb, Tenax and Porapak.<sup>228</sup>

While experimental solute descriptors for frequently measured SVOCs, such as the PCBs and PAHs are readily available, there has in recent years also been a concerted effort to determine experimental solute descriptors for other environmentally relevant SVOCs.<sup>229–231</sup> Even if no solute descriptors are available, they can now be predicted quite well for many SVOCs using the quantitative structure property relationships implemented in the UFZ LSER website.<sup>232</sup> The ppLFER-based prediction of  $K_{\text{PUF-G}}$ ,  $K_{\text{PDMS-G}}$ ,  $K_{\text{XAD-G}}$  and  $K_{\text{PE-G}}$  values is now feasible for a wide range of substances.<sup>206</sup>

**E.2.3 Predictions based on quantum-chemical calculations and statistical thermodynamics.** Whereas the single- and poly-parameter linear free energy relationships require experimental data for calibration, prediction techniques based on quantum-chemical calculations and statistical thermodynamics can predict equilibrium sorption properties directly from molecular structure. In particular, Goss demonstrated that the commercial software COSMOtherm can be used to predict partitioning into various polymer matrices by treating the polymer as a “liquid of monomer repeat units that can move independently from each other.”<sup>233</sup> The method was successful in predicting the  $K_{\text{PDMS-G}}$  at 25 °C and the  $K_{\text{PUF-G}}$  at 15 °C and 95 °C.<sup>233</sup> Loschen and Klamt later improved the approach “by incorporation of polymer-specific entropic contributions due to free volume effects”.<sup>234</sup> PDMS can be represented as liquid oligomer (hexamethyldisiloxane) when using COSMOtherm to predict  $K_{\text{PDMS-G}}$ ,<sup>212</sup> but this approach greatly overpredicts the measured  $K_{\text{PDMS-G}}$ , with an average difference in excess of 2 orders of magnitude. Smaller overpredictions, generally less than an order of magnitude, were achieved when predicting  $K_{\text{PUF-G}}$  for various compounds at different temperature, representing polyurethane as “a simple oligomeric 1:1 condensed pair of 2,4-toluene-diisocyanide and glycerol with ethyl and acetate end-caps”. Parnis *et al.*<sup>217,218</sup> used COSMOtherm to predict  $K_{\text{PUF-G}}$  and its temperature dependence for substituted PAHs. Chen *et al.* noted that COSMOtherm was able to predict the  $K_{\text{XAD-G}}$  at different temperatures with a root mean square error of 0.35,<sup>235</sup> when compared with the experimental values by Hayward *et al.*<sup>223</sup>

### E.3 Comparison of uptake capacity of different PASs for HCB

The overall uptake capacity of a PAS is not only dependent on the sorption coefficient between the PAS sorbent and the gas-phase, but also on the amount of the sorbent in the PAS, namely by the products  $K_{\text{SG}}V_{\text{S}}$  and  $K_{\text{SG}}A_{\text{S}}$  for PASs based on

absorbents and adsorbents, respectively. In order to compare the uptake capacity of different commonly used PAS, we estimated their  $K_{\text{SG}}V_{\text{S}}$  or  $K_{\text{SG}}A_{\text{S}}$  values for HCB at approximately 20 °C (Table 6). Not only is HCB a relatively volatile SVOC, for which  $t_{\text{linear}}$  could be quite short, but experimental  $K_{\text{SG}}$  values exist for most sorbents relevant for PAS.

The calculation confirms that in the SIP, the addition of 10% by mass of XAD-4 resin results in a more than 100-fold increase in the overall sorption capacity of the PUF disk for HCB. Overall, this calculation reveals that the sorption capacity of different PAS for one compound can vary by five orders of magnitude. This difference would be even larger if the SPME-PAS<sup>104</sup> were to be included in the comparison, as its  $V_{\text{S}}$  is tiny.

The estimation suggests that the XAD-PAS has a theoretical uptake capacity that is four orders of magnitudes higher than that of most other PASs for SVOCs. The comparison is somewhat misleading, as not all of the sorbent in a PAS necessarily participates in the uptake. For example, most of the XAD in the XAD-PAS is not accessible to the compounds from the atmosphere because of a notable transport resistance within the passive sampling medium.<sup>205,207</sup> However, this is partly also true for the other sorbents.<sup>205,206</sup> Nevertheless, the comparison illustrates why the XAD-PAS is the closest to a kinetic PAS for SVOCs. It also explains why the XAD-PAS generally does not require the consideration of curvi-linear uptake, even for more volatile SVOCs, and is more suited for long deployment periods than other PAS.

## F. The sampling rates of different types of PASs

### F.1 Empirical determinations of sampling rates

**F.1.1 Deriving a sampling rate from a calibration experiment.** Rearranging eqn (5) we obtain:

$$\text{SR} = \frac{\Delta m_{\text{S}}}{C_{\text{G}} \times \Delta t} \quad (13)$$

which implies that we can derive the SR of chemical in a PAS by dividing the amount of the chemical  $\Delta m_{\text{S}}$  taken up during the time period  $\Delta t$  by the product of the gas-phase concentration  $C_{\text{G}}$  and this time period. It thus requires  $C_{\text{G}}$  during the time of PAS deployment to be determined by another method, most commonly an active sampling method. This empirically derived  $\text{SR}_{\text{e}}$  only corresponds to the inherent SR, if the PAS is operating in the linear uptake period. Quite frequently,  $\text{SR}_{\text{e}}$ s are indeed determined with eqn (13) and a single PAS deployment.<sup>210,236,237</sup> More commonly, however, SRs of SVOCs in PAS are determined from the slope of an uptake curve.<sup>26–28</sup> Assembling such a curve requires the deployment of multiple samplers at the same time and their staggered retrieval after different lengths of time  $\Delta t$ . Being based on multiple PASs deployed for variable lengths of time, such calibrations tend to give more reliable SRs and allow for a recording of the uptake curve, which in turn can provide information on the approach to equilibrium.

In order to linearise an uptake curve during a calibration that experiences variations in  $C_{\text{G}}$ , one either plots the amount found in the PASs,  $m_{\text{S}}$ , against the product of  $C_{\text{G}}$  and  $\Delta t$  (see Fig. 8) or,



Table 6 Estimation of the total uptake capacity of different PASs for hexachlorobenzene at 20 °C

Name	$K_{SG}$	Mass of sorbent	$A_S$ or $V_S$	Uptake capacity
PDMS-PAS <sup>111</sup>	$K_{PDMS-G} = 10^{5.9}$ (ref. 212)		$\sim 10^{-5} \text{ m}^3$	$8 \text{ m}^3$
LDPE-PAS <sup>67</sup>	$K_{PE-G} = 10^{6.8}$ (ref. 74)		$\sim 10^{-6} \text{ m}^3$	$6 \text{ m}^3$
PUF-PAS <sup>24</sup>	$K_{PUF-G} = 10^{7.1}$ (ref. 213, 216 and 219)	4.4 g of PUF ( $10^{-6} \text{ m}^3 \text{ g}^{-1}$ )	$4.4 \times 10^{-6} \text{ m}^3$	$55 \text{ m}^3$
SIP-PAS <sup>136</sup>	$K_{XAD-G} = \sim 30 \text{ m}$ (ref. 222) <sup>a</sup>	0.435 g of XAD-4 ( $750 \text{ m}^2 \text{ g}^{-1}$ )	$315 \text{ m}^2$	$9000 \text{ m}^3$
XAD-PAS <sup>26</sup>	$K_{XAD-G} = \sim 30 \text{ m}$ (ref. 222) <sup>a</sup>	Long: 20 g of XAD-2 Short: 10 g of XAD-2 ( $350 \text{ m}^2 \text{ g}^{-1}$ )	$7000 \text{ m}^2$ $3500 \text{ m}^2$	$200\,000 \text{ m}^3$ $100\,000 \text{ m}^3$

<sup>a</sup> Adsorption coefficient has units of length (m is metre).

equivalently plots  $m_S/C_G$ , *i.e.* the “equivalent sampling volume”, against the time of deployment. In either case, the slope of the resulting curve corresponds to the SR.

Different methods can be applied to derive a SR from such a plot (Fig. 8).<sup>190</sup> Each PAS can be treated as a single calibration experiment yielding an empirical  $SR_e$  according to eqn (13). The overall  $SR_e$  is then the average of the  $SR_e$  obtained for each PAS. Alternatively, one performs a least square regression on the linearised uptake curve and derives the  $SR_e$  from its slope. Finally, it is also possible to derive an  $SR_e$  for each time period between subsequent PAS retrievals, by using the increase in the  $m_S$  in PASs from one retrieval to the next. The latter approach is advisable if the SR can be expected to vary during the deployment periods, *e.g.* if different deployment periods experienced different temperatures or wind speeds. Generally, a linear regression gives the most reliable  $SR_e$ . Longer deployments tend to have a stronger impact on the slope of the regression than short deployments, which is often desirable as the larger  $m_S$  in PASs deployed for a longer length of time can often be quantified more confidently.

For PASs that also take up particles,  $C_G$  in eqn (13) can be replaced with the concentration of both gaseous and particle-bound SVOCs or of only the particle-bound substance, and a calibration then will yield SRs for the total SVOCs in the

atmosphere or for the particle-bound substance. See Section F.6 for in-depth discussion of particle uptake in PAS.

#### F.1.2 Outdoor calibration experiments for PAS.

Tables are used to summarise outdoor calibrations studies that have been conducted for the PUF-PAS (Table 7), XAD-PAS (Table 8), LDPE-PAS (Table 9), SIP-PAS (Table 10) and SPMD (Table 11). The PUF-PAS has been calibrated for more different SVOCs than any other PAS. This includes OCPs, CUPs, PCBs, parent PAHs, alkylated PAHs, PBDEs, polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), polychlorinated naphthalenes (PCNs), polycyclic musk compounds, BFRs and a number of perfluorinated alkyl substances (PFAS) (Table 7). The XAD-PAS has been calibrated for OCPs, CUPs, PCBs, PAHs, neutral PFAS and VMS (Table 8). The number of analytes for which empirical SRs have been determined in other PASs is much smaller (Tables 9–11).

Air concentrations during the calibrations were determined either with sporadic high volume (HiVol) or more continuous low volume (LoVol) samplers. The fraction of time that is covered by the active sampling ranges from a few percent to 100%.

Despite a large number of studies, the PUF-PAS has been calibrated mostly in temperate climates, with one calibration study in tropical Singapore.<sup>238</sup> The outdoor calibration studies for the XAD-PAS also extend to locations in tropical,<sup>27,197</sup>

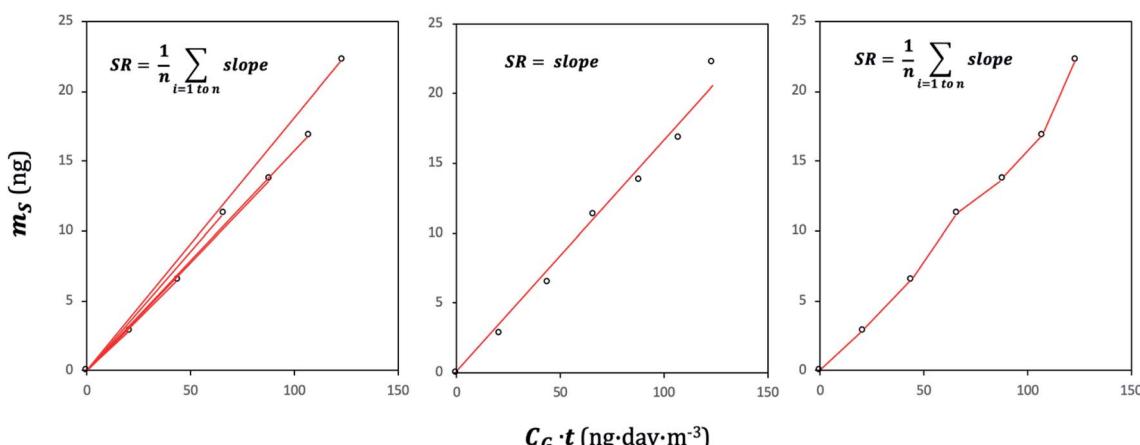


Fig. 8 Illustration of the three different methods of deriving a sampling rate SR from a calibration experiment involving  $n$  PASs deployed at the same time and retrieved after variable deployment periods ( $n = 6$  in the displayed example) as discussed in ref. 190. In each case, the amount taken up in a PAS  $m_S$  is plotted against the product of the length of deployment  $t$  and the gas-phase concentration during the time of deployment  $C_G$ . The SR is derived either (i) as the average of the SRs calculated for each of the  $n$  samplers, (ii) from a linear regression involving all  $n$  samplers, or (iii) from the increase in  $m_S$  between subsequently retrieved samplers. Only the last method allows for SR to be time-variant.



Table 7 Outdoor studies calibrating the PUF-PAS for semi-volatile organic compounds

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
PUF-PAS	Regina, Saskatchewan Canada, rural, temperate	Jun. to Jul. and Jul. to Aug. 2003	Dicamba, $\gamma$ -HCH, 2,4-D, triallate, bromoxynil, MCPA	Eight 168 hour HiVol samples, borosilicate microfibre filter and PUF-XAD-PUF sandwich	8 samples (duplicates at 10 m and 30 m during two periods of 28 days)	241
PUF-PAS	Lancaster, UK, semi-rural temperate	Apr. to Jun. 2006	HCB, HCHs, DDTs, chlordanes, PCBs PBDE	Eight 168 hour HiVol samples using GFF/PUF-PUF	23 samples (1, 2, 3, 4, 6, 8 weeks) (triplicates during first six weeks, 8 samples at week 8)	135
PUF-PAS (low & high density)	Košetice, Czech Republic, sub-urban, temperate	Oct. to Dec. 2007	PCBs, PBDEs	Thirteen 168 hour samples using GFF/PUF-PUF	8 triplicated samples (0.5, 1, 2, 3, 4, 6, 8, 12 weeks)	243
PUF-PAS	Barcelona, Spain, 3 urban/industrial sites, 1 semi-rural site, Mediterranean	Oct. 2003 to Jan. 2007 (3 year period)	PeOB, HCB, HCHs, DDTs, PCBs, PAHs	Hundred-sixty-eight 24 hour HiVol samples using GFF/PUF-PUF	42 samples (consecutive periods of 28 days each)	129
PUF-PAS	Iowa, United States, semi-urban, temperate Singapore, urban/industrial, tropical	Mar. to Jun. 2005	PCDD/Fs, PCBs, PCNs	HiVol samples using quartz fibre filter/PUF	4 samples, 3 months	236
PUF-PAS		Aug. 2006 to Oct. 2006	PCBs	Three 8 hour HiVol samples using GFF/XAD-2	3 quadruplicated samples (21, 28, 46 days)	209
PUF-PAS		Apr. to Jun. 2008	PAHs, OCPS	Twelve 48 hour HiVol samples using quartz fibre filter/PUF	6 duplicated samples (10, 21, 32, 43, 60, 68 days)	238
PUF-PAS	Toronto, Ontario Canada, semi-urban, temperate	Feb. to Jun., 2008	PAHs, PCBs, PBDEs, musks (ADBI, ATII, HHCB, AHTN)	Five 600 hour LoVol samples using GFF/PUF-PUF	10 samples (0, 25, 50, 75, 90, 100, 125 days), 3 duplicates	25
PUF-PAS	Toronto, Ontario Canada, semi-urban, temperate	Mar. to Oct. 2010	PFAS (PFBS, PFOS, PFDS) VMS not detected	Thirty-eight 24 hour HiVol samples using GFF/PUF-XAD-2-PUF	13 samples (7, 21, 28, 42, 56, 84, 112, 140, 168, 197 days), 3 duplicates	137
PUF-PAS modified PUF-PAS	Bursa, Turkey, urban, Mediterranean	Jun. 2008 to Jun. 2009	PCBs, OCPS	Thirty 24 hour samples using GFF/PUF-PUF	3 samples (10 days each)	149
PUF-PAS modified PUF-PAS	Yakima Valley, Washington USA, rural/agricultural, temperate	Mar. to Apr. and Jun. to Aug. 2011	Chlorpyrifos, azinphos-methyl, chlorpyrifos-oxon, azinphos methyl-oxon PCBs, PeCB, HCB, DDTs, PBDEs, PAHs, PCDD/Fs, BFRs (ATE, TBECH, TBCO, <i>p</i> -TBX, PBEB, PBT, DPTE, HBB, EHTBB, BTBPE, DBDPE)	Five 24 hour active air samples using PUF	30 days	183
PUF-PAS	Brno, Czech Republic, urban-background, temperate	Sep. 2010	PCDD/Fs, PCBs, PCBs	Twelve 168 hour LoVol samples using GFF/PUF-PUF	12 triplicated samples (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12 weeks)	244
PUF-PAS	Suwon, and Ansan, Gyeonggi-do, South Korea, urban and industrial areas, temperate	Feb. 2010 to Feb. 2011	PCDD/Fs, PCBs	Suwon: six 168 hour HiVol samples using GFF/PUF-PUF (28%)	Suwon: 8 samples; (63, 37, 73, 79, 56, 62 days)	246
PUF-PAS				Anasan: twenty four 168 hours HiVol samples using GFF/PUF-PUF	Anasan: 3 samples (51, 56, 66 days)	



Table 7 (Contd.)

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
PUF-PAS	3 locations in the Alberta Oilsands region, boreal, industrial	Dec. 2010 to Jan 2011	PAHs, alkylated PAHs, parent and alkylated dibenzo-thiophenes	21 HiVol samples	1 sample of 60 days at 3 sites	247
PUF-PAS	Bursa, Turkey	Feb. 2013 to Feb. 2014	PAHs PCBs	Active sampling (2 days), unknown number of samples	4 seasonal calibrations, each with 3 to 5 samples (10, 20, 30, 40, 60 days), replication of 10 day samples	248 249
PUF-PAS	Toronto, Ontario, suburban, temperate	Mar. to Oct. 2010	OPFRs	Twenty-one 24 hour HiVol samples using GF/F/PUF-XAD	7, 21, 28, 42, 56, 84, 112, 140, 168, 197 days, duplication of 3 samples	250
PUF-PAS	Guangzhou, China, urban, subtropical	Jul. to Oct. 2016	Levoglucosan, galactosan, mannosan	Sixteen active air samples	5 triplicated samples (16, 30, 50, 73, 92 days)	251
PUF-PAS modified	Dalian, China, urban, temperate	Sep. 2016 to May 2017	SCCPs	Sixteen active air samples	6 duplicated samples (1, 2, 3, 4, 6, 8 months)	252

subtropical<sup>210</sup> and polar<sup>26</sup> locations. The longest deployment period in most of the PUF-PAS calibrations was three months. Reflecting the higher uptake capacity of the XAD-PAS and therefore longer  $t_{\text{linear}}$ , most of the calibrations involving the XAD-PAS lasted one year, except for the one for VMS, which lasted three months.<sup>28</sup>

**F.1.3 Indoor calibration experiments for PASSs.** Table 12 summarises the indoor calibrations studies that have been conducted for PUF-PAS. The PUF-PAS has been calibrated for PCBs, PAHs, PBDEs and a number of PFAS. Indoor calibrations have also been performed for the uptake of PCBs in the XAD-PAS<sup>191,192,205</sup> and neutral PFAS<sup>239</sup> and phthalates and PBDEs<sup>240</sup> in the SIP-PAS.

## F.2 Explanations of the variability in empirically determined sampling rates

The calibrations studies detailed in Sections F.1.2 and F.1.3 revealed that  $SR_e$  vary considerably between chemicals and between sampling sites and even between different deployment periods at the same site. This has been well documented for the  $SR_e$  values of PCBs, PBDEs and PAHs in the PUF-PAS.<sup>25</sup> Herkert *et al.*<sup>126</sup> also compiled the ranges of the  $SR_e$ s reported for PCBs in the PUF-PAS, noting large differences within and between studies. For a long time, the prevailing assumption in the SVOC-PAS community was that uptake in PASSs is air-side controlled, *i.e.* the diffusion through air to the sampling sorbent is the rate-limiting step to the uptake of chemical in the sampler. If this were true, we would expect only minor differences in the SR between different chemicals at the same place and during the same deployment, as long as the sampler is operating in the linear uptake phase. The reason is that the effective thickness of the air boundary layer surrounding the PAS sorbent (and therefore the diffusion path length) is the same for all chemicals and differences in the SR would only arise from differences in the diffusion coefficients. Diffusivities in air are related to molecular size, but the dependence is relatively weak and the range of molecular size of SVOCs is limited, so we would expect only slightly faster SRs for smaller SVOCs than larger ones. Similarly, diffusivity in air is dependent on temperature and we might expect slightly faster SRs at higher deployment temperatures than during deployments at low temperatures.

Larger differences in SRs between different sites are easier to reconcile with air-side controlled uptake, as the boundary layer thickness can be expected to vary strongly with air turbulence, and windy sites should have higher SRs for all chemicals than those experiencing less turbulence. This has indeed been observed, both in the field<sup>126,129,194,195</sup> and during controlled experiments in the laboratory.<sup>26,48,128,191</sup> This is also the reason for the generally much lower SRs observed during indoor compared to outdoor deployments. Other factors also affect the diffusion distance in air, namely the sampler configuration<sup>192</sup> and the presence and design of a housing,<sup>193</sup> and thereby contribute to variability in SR between different samplers and sampler configurations.

There are a number of reasons, why  $SR_e$ s can differ (i) between different chemicals during the same deployment and



Table 8 Outdoor studies calibrating the XAD-PAS for semi-volatile organic compounds

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
XAD-PAS (20 cm sampler)	Point Petre, Ontario, Canada, background, temperate	May 2000 to May 2001	HCB, $\alpha$ -HCH	Data taken from ongoing active monitoring	7 duplicated samples (1, 2, 4, 6, 8, 10, 12 months)	26
	Burnt Island, Ontario, Canada, background, temperate	Jun. 2000 to Jun. 2001	HCB, $\alpha$ -HCH, $\gamma$ -HCH, dieldrin, <i>trans</i> -nonachlor			
	Alert, Nunavut, Canada background, polar	Aug. 2000 to Aug. 2001	HCB, $\alpha$ -HCH, $\gamma$ -HCH, endosulfan I			
	San Antonio de Belen, Costa Rica, suburban, tropics	Oct. 2005 to Oct. 2006	HCB, chlorothalonil, chlorpyrifos, dieldrin, pendimethalin, endosulfans, chlordanes	Nine 24 hour HiVol samples using GFF/PUF-XAD-2-PUF	5 duplicate samples (4, 6, 8, 10 12 months)	27
XAD-PAS (20 cm sampler)	Maun, Botswana, semi-urban, semi-arid	Passive: May 2006 to May 2007, active: Jul. 2006 to Aug. 2007	8:2 FTOH, 10:2 FTOH, MeFOSA, EfFOSA, MeFOSE HCHs, HCB, chlorothalonil, chlordanes, endosulfan I, endosulfan II, endosulfan sulfate PAHs, PCBs PFAS (8:2 FTOH, 10:2 FTOH, MeFOSA, EfFOSA, MeFOSE)	Twenty-seven 24 hour HiVol samples using GFF/PUF-XAD-2-PUF	1 duplicated sample (1 year)	197
XAD-PAS (10 cm sampler)	Egbert, Ontario Canada, rural, temperate	Mar. 2006 to Feb. 2007	Chlorothalonil, endosulfan I, endosulfan II, endosulfan sulfate, dacthal, disulfoton, atrazine, alachlor, metolachlor, HCB, HCHs, chlordanes VMS (D4, D5, MDM, MD2M, MD3M)	Twenty-one 336 hour LoVol samples using PUF-XAD-2-PUF	5 duplicate samples (56, 122, 185, 241, 365 days)	21
XAD-PAS (10 cm sampler)	Toronto, Ontario Canada, suburban, temperate	Mar. to Jun. 2012	45 PAHs	Forty-two 57 hour LoVol samples using SPE (PE cartridge with 120 mg of ENV + resin)	8 duplicate samples (7, 14, 21, 28, 42, 60, 77, 98 days)	28
XAD-PAS (XAD-4 resin)	1 urban site and 1 rural site in Minnesota, USA, temperate	Jun. 2013 to Jun. 2015		72 hour HiVol samples once every 12 days	Consecutive 3 months samples	253

Table 9 Outdoor studies calibrating the LDPE-PAS for semi-volatile organic compounds

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
LDPE (film thickness 200 to 100 $\mu\text{m}$ )	Brisbane, Queensland, Australia, semi-urban, tropics	Apr. 2002 to Jun. 2003	PAHs	One 720 hour, one 1440 hour and one 2160 hour HiVol sample using GFF/two XAD-2 cartridges	3 duplicated samples (30, 50, 90 days)	67
LDPE sampler	Providence, Rhode Island USA, semi-urban, temperate	Nov. to Dec. 2012	HCHs, HCB, heptachlors, chlordanes, endosulfans, DDTs, PCBs, PBDEs	72 and 96 hour samples using GFF/PUF-PUF	6 duplicated samples (3, 7, 10, 14, 17, 21 days)	75

Table 10 Outdoor studies calibrating the SIP-PAS for semi-volatile organic compounds

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
SIP-PAS	Lancaster, UK, semi-rural, temperate	May 2009 to Apr. 2010	PCBs, PBDEs	Twenty-five 336 hour HiVol samples using GFF/PUF-PUF	22 and more (duplicate or triplicate); 4, 7, 14, 21, 28, 35, 42, 112, 182, 266, 350 days	150
SIP-PAS	Toronto, Ontario, Canada, semi-urban, temperate	Mar. to Oct. 2010	PFAS (neutral & ionic) VMS (D3, D4, D5, D6, MDM, MD2M, MD3M)	Thirty-eight 24 hour HiVol samples using GFF/PUF-XAD-2-PUF	13 samples (7, 21, 28, 42, 56, 84, 112, 140, 168, 197 days), 149 3 duplicates	137
SIP-PAS	Toronto, Ontario, Canada, suburban, temperate	Mar. to Oct. 2010	OPFRs	Twenty-one 24 hour HiVol samples using GFF/PUF-XAD	7, 21, 28, 42, 56, 84, 112, 140, 168, 197 days, duplication of 3 samples	250

Table 11 Outdoor studies calibrating SPMD-PAS for semi-volatile organic compounds

Sampler	Site/type/climate	Period	SVOCs	Active sampling	Passive sampling	Ref.
SPMD	Lancaster, UK, semi-urban, temperate	Summer, 1995	PCBs	Thirteen 168 hour HiVol samples using GFF/PUF-PUF	Six duplicated samples (15, 29, 45, 59, 71, 88 days)	38
		Winter, 1995/1996		Twelve 168 hour HiVol samples using GFF/PUF-PUF	Five duplicated samples (14, 26, 39, 61, 84 days)	
SPMD	Lancaster region, UK, urban/industrial/coastal, temperate	Passive: Nov. to Dec. 1999 Active: Jan. to Feb. 1998	PCDD/Fs	Fifteen 72 to 96 hours HiVol samples using GFF/PUF	Two samples (42 to 45 days)	39
SPMD	Brisbane, Queensland, Australia, urban, tropics	Apr. 2002	PAHs	One 32 day HiVol samples using GFF/XAD cartridge	One quadruplicated sample (32 days)	254
SPMD	Guangzhou, Guangdong, China, urban, subtropics	Apr. 2001 to Mar. 2002	PAHs	Fifty-two 24-hour HiVol samples using GFF/PUF-PUF	Four consecutive 3 month periods	255
SPMD	Weissfluhjoch, Switzerland Zugspitze, Germany Sonnbliek, Austria, background, alpine	May 2005 to Nov. 2006	HCHs, chlordanes, endosulfan, dieldrin	Three 4 months LoVol samples using XAD cartridge	Three consecutive sampling periods (190, 210, 400 days)	60

(ii) for the same chemical between deployments at different temperature. One reason is that air-side resistance may not be controlling (solely) the diffusive exchange between the ambient atmospheric gas-phase and the PAS sorbent. Zhang *et al.*<sup>205</sup> have demonstrated the existence of a sampler-side resistance in a number of uptake experiments, which revealed a strong gradient of SVOC concentrations within PUF disks and XAD-resin filled cylinders. If the sampler side resistance is rate-controlling,

the uptake rate is expected to be proportional to the  $K_{SG}$  of the compound being sampled,<sup>20</sup> *i.e.* less volatile compounds would have a higher SR than more volatile compounds and the same compound would be taken up faster at low temperatures than at high temperatures. Higher SR<sub>s</sub> for less volatile PCBs have for example been observed for SPMDs.<sup>38,135,209</sup>

However, the situation can be even more complex when the kinetics of the sorption is being taken into account.<sup>207</sup> Model

Table 12 Indoor studies calibrating the PUF-PAS for semi-volatile organic compounds

Sampler	Site	SVOCs	Active sampling	Passive sampling	Ref.
PUF-PAS	8 offices and laboratories, Ontario, Canada	PBDEs MeFOSE, EtFOSE, EtFOSA, MeFOSEA	LoVol samples using PUF-PUF	17–20 days	161 162
PUF-PAS	Office, Birmingham, United Kingdom	PCBs	Five 240 hours LoVol samples using GFF/PUF-PUF	Eight samples (10, 20, 30, 40, 50 days), 2 replicates	134
PUF-PAS	2 laboratories, Iowa, United States	PCBs	Three 8 hours HiVol samples using GFF/XAD-2	Three quadruplicated samples (21, 28, 46 days)	209
PUF-PAS (with GFF for particles)	Office, United Kingdom	TBBP-A, $\alpha$ -HBCD, $\beta$ -HBCD, $\gamma$ -HBCD, PBDEs	Five 240 hours LoVol samples (triplicate) using GFF/PUF-PUF	Eight samples (10, 20, 30, 40, 50 days), 2 replicates	156 and 256
PUF-PAS (low protection chamber)	Alloy factory (4 sampling points), Sweden	PAHs	Two 168 hour LoVol samples using GFF/PUF-PUF at each sampling point	4 triplicated samples, 2 weeks	257
PUF-PAS	2 homes in each of Seoul, Ansan/Shiheung, Daegu, Korea	PFAS (1MeFOSE, EtFOSE)	One 480 hours LoVol sample using PUF-XAD-PUF at each site	7 samples (20 days)	239
PUF-PAS	5 living room, Korea	8:2 FTOH, 10:2 FTOH, EtFOSA, MeFOSE, EtFOSE, MeFOSEA	504 hour LoVol samples using GFF/PUF-XAD-PUF sandwich (unknown sample number)	21 days (unknown sample number)	258
PUF-PAS (plug in cylindrical housing)	University office, Toronto, Canada	PCBs	Six 720 hour LoVol samples using PUF-XAD-PUF	6 duplicated samples (0.5, 1, 2, 4, 6, 12 weeks)	205
PUF-PAS	Lecture room, Brno, Czech Republic	PCBs, OCPs, PBDEs, novel BFRs, PAHs, PCDD/Fs	Twelve consecutive LoVol, QFF and PUF-PUF	12 triplicated samples (1 to 12 weeks)	259
PUF-PAS	2 university rooms, Toronto, Canada	Pentabromobenzene, Pentabromotoluene, Phthalates, PBDEs	Continuous LoVol samples, collected at weekly intervals	1 <sup>st</sup> exp.: 0, 7, 14, 21, 28, 35 days, 2 <sup>nd</sup> exp.: 7, 28, 49 days, duplicate	240
PUF-PAS (open bottom)	Computer laboratory, Toronto, Canada	Phthalates, PBDEs, OPFRs	Continuous LoVol samples collected at 10 day intervals	0, 10, 20, 30, 40, 50 days, triplicate	112

simulations indicated that both an increase and decrease in the SR with  $K_{SG}$  and with temperature can occur. The SR of chemicals that sorb strongly (high  $K_{SG}$ ) and slowly is predicted to increase with molecular size and temperature, whereas the SR of chemicals that sorb quickly and less strongly (low  $K_{SG}$ ) show the opposite behaviour.<sup>207</sup>

Finally, there are reasons why empirically determined  $SR_e$  can be compound and temperature-dependent, even if the assumption of air-side control is valid:

(1) Because of large differences in sampling capacity for different SVOCs, more volatile chemicals will enter the curvilinear region of uptake earlier and therefore have lower apparent SRs than less volatile SVOCs, which maintain strictly linear uptake for a longer period of time, *i.e.*  $SR_e < SR$ . For the same reason, we might anticipate lower  $SR_e$ s at higher temperatures than at lower temperatures, because the latter increases sampler capacity and lengthens the linear uptake period.

(2) If an SVOC is partially particle-bound and the SR for particles is lower than for vapours, we would expect lower empirical  $SR_e$ s both for the less volatile SVOCs and at lower temperatures.

The trend in (2) is opposite to the effect in (1), but applies to SVOCs at the lower volatility spectrum, whereas the effect in (1) applies to the more volatile SVOCs.

(3) Finally, if a chemical sorbed to the PAS sorbent is undergoing degradation, it could appear as if the  $SR_e$  is reduced. Evidence for this has been observed for selected pesticide (chlorpyrifos, trifluralin, pendimethalin) in XAD-PASs deployed for long time periods.<sup>27,190</sup> There is indeed evidence that transformation of chlorpyrifos into its oxon-analog can occur when air is pulled through XAD-2 resin.<sup>260</sup> When exposing parent PAHs and alkylated PAHs spiked onto PUF-disks to ozone levels equivalent to two months of deployment in a flow tube, many compounds showed significant reactive loss, especially at low relative humidity.<sup>261</sup> When comparing the amounts of SVOCs sequestered in four PUF-PASs deployed for four consecutive weekly periods with those in a PUF-PAS deployed simultaneously for one full month, much higher levels of several PAHs, PBDEs and other BFRs in the PASs deployed for shorter periods were taken as an indication that those substances were degraded during the longer sampling period.<sup>262</sup> This implies that  $SR_e$ s for such degradable compounds would depend on the length of the deployments used during a calibration study.



### F.3 Accounting for deviations from non-linear uptake

For the PASs with relatively small uptake capacity for the more volatile SVOCs (e.g. those based on PE and PUF), some researchers try to account for the non-linearity of uptake. If  $C_G$  is assumed to be constant, the integrated form of eqn (1) is:<sup>20</sup>

$$m_S = V_S \frac{k_u}{k_l} C_G (1 - e^{-k_l t}) \quad (14)$$

In the specific case, that the air boundary layer is controlling the diffusive exchange between atmospheric gas-phase and PAS sorbent:

$$m_S = V_S K_{SG} C_G \left(1 - e^{-\frac{SR}{K_{SG} V_S} t}\right) \quad (15)$$

This equation essentially describes the entire uptake curve in a PAS. Harner and colleagues<sup>139</sup> routinely use a version of this equation to estimate the effective sampling volume  $V_{air}$  of chemicals in the PUF-PAS and SIP-PAS in the curvi-linear uptake phase:

$$V_{air} = \frac{m_S}{C_G} = K_{SG} V_S \left(1 - e^{-\frac{SR}{K_{SG} V_S} t}\right) \quad (16)$$

Importantly, this equation for estimating  $V_{air}$  is implemented in the widely used “Template for calculating PUF and SIP disk sample air volumes”<sup>263</sup> and also in the model by Herkert *et al.*,<sup>126</sup> which is discussed in detail in Section F.5 below. Lohmann and colleagues take the same approach with the PE-based PAS, when calculating the % of equilibrium that is achieved after a deployment time  $t$  using (e.g. ref. 87):

$$\begin{aligned} \text{% of equilibrium} &= \frac{m_S}{V_S K_{SG} C_G} \times 100\% \\ &= \left(1 - e^{-\frac{SR}{K_{SG} V_S} t}\right) \times 100\% \end{aligned} \quad (17)$$

While the use of eqn (14) through (17) may be considered the state-of-the-art for calculating the effective sampling volume for situations where linear uptake for a compound during deployment cannot be assumed, it is important to be aware of the underlying assumptions. These equations are based on the assumption that the air-side is controlling the kinetics of uptake. While this is likely the case for some passive sampling material, especially those with high permeability, this has already been shown to not always be the case for the PUF-PAS.<sup>205</sup>

When applying these equations, one also makes the assumption that  $C_G$  stays constant during the deployment period of the PAS. If sampling is conducted during the curvi-linear uptake phase, it means that the rate of uptake is gradually decreasing during the sampling period, or in other words, air concentrations at the beginning of the sampling period have more impact on the amount of chemical accumulated in the sorbent than those at the end of the sampling period. This implies that the results will only give an unbiased account of  $C_G$  if  $C_G$  is constant. If  $C_G$  is increasing during deployment, the PAS

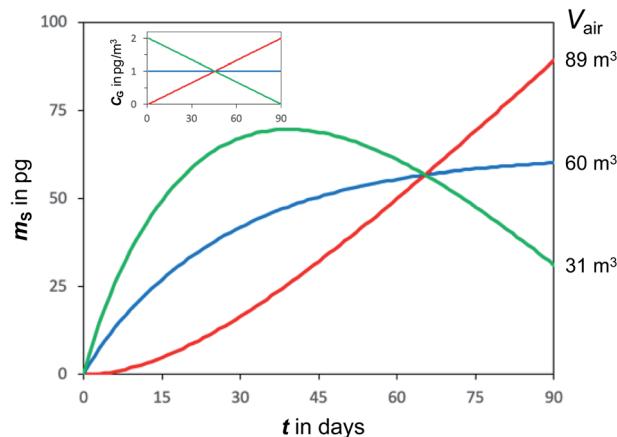


Fig. 9 Simulated uptake curve for a compound with  $\log K_{\text{PUF}-\text{G}}$  of 5.5 in a PUF-PAS during 90 days of constant (blue), increasing (red) and decreasing (green) air concentrations.

will underestimate  $C_G$  and *vice versa*. Or, stated differently, a PAS does not provide a true time-averaged concentration, if it operates in the curvi-linear uptake region.

We illustrate the magnitude of these effects with PAS-SIM<sup>21</sup> calculations of a 90 day deployment of a PUF-PAS for a hypothetical SVOC with a  $\log K_{\text{PUF}-\text{G}}$  of 5.5, *i.e.* a compound whose uptake is curvi-linear within the deployment period. Three simulations have the same conditions including the same time-averaged concentration  $C_G$  during the 90 days. The only difference is that  $C_G$  is either constant, increases from 0 on day 1 to 2 times the average  $C_G$  on day 90, or decreases from twice the average  $C_G$  on day 1 to 0 on day 90. The uptake curves are very different (Fig. 9) and importantly the amount taken up after 90 days diverges substantially, which can be expressed by effective sampling volumes  $V_{air}$  of 60  $\text{m}^3$  (constant  $C_G$ ), 89  $\text{m}^3$  (increasing  $C_G$ ) or 31  $\text{m}^3$  (decreasing  $C_G$ ). Eqn (16) yields a  $V_{air}$  of 65  $\text{m}^3$ . This implies that the assumption of no sampler side resistance implicit in eqn (16) in this case only leads to a minor error (5  $\text{m}^3$ ), largely because of the relatively high volatility of a compound with a  $\log K_{\text{PUF}-\text{G}}$  of 5.5. On the other hand, the assumption of constant  $C_G$ , also implicit in eqn (16), gives a large error (29  $\text{m}^3$ ).

Increasing or decreasing trends of  $C_G$  during a PAS deployment period are common, considering the pronounced seasonal variability of the air concentrations of many SVOCs, which is due either to seasonal source strength (e.g. pesticides elevated during application season,<sup>264</sup> PAHs elevated during heating season<sup>265</sup>), temperature effects<sup>266</sup> or oxidation by photooxidants.<sup>267</sup> This issue is not restricted to the PUF-PAS, but applies to all PAS operating in the curvi-linear uptake phase. While the precise size of the error depends on the particular combination of  $K_{SG} V_S$ , deployment time and temporal concentration trend, and will often be smaller than in the illustrative example of Fig. 9, it is reasonable to assume that in many instances applying eqn (16) and (17) will incur very substantial errors.

It is further important to be aware that these equations require quantitative knowledge of both the PAS's uptake



capacity  $K_{SG}V_S$  and inherent SR, which can be challenging to obtain as both are strongly dependent on meteorological conditions that also can be variable during the time of deployment:

– The SVOC's equilibrium partitioning coefficient  $K_{SG}$  between sampler sorbent and the gas-phase is a strong function of the temperature of deployment  $T_d$ . It is customary to correct  $K_{SG}$  to the average temperature of deployment using the van't Hoff equation and the internal energy of phase transfer between sampling sorbent and the gas-phase  $\Delta U_{SG}$ . If  $\Delta U_{SG}$  is unknown, the enthalpy of vaporization  $\Delta H_{vap}$  is often used to approximate  $\Delta U_{SG}$  (e.g. ref. 87). The relationship between  $K_{SG}$  and  $T$  is not a linear one, so the use of an average  $T_d$  is problematic if  $T$  is increasing or decreasing during the deployment period (see also ref. 204). A further complication arises if the temperature of the PAS sorbent deviates from ambient temperature, because of radiative effects associated with the sampler housing.<sup>193,268,269</sup>

– The inherent sampling rate SR ( $\text{m}^3$  per day), *i.e.* the SR during the linear uptake phase, is dependent on wind speed (because of the effect on the thickness of the boundary layer) and also somewhat on temperature (because of its effect on the diffusivity). Because SR is most often deployment-specific, it is usually determined from the loss of depuration compounds spiked onto the sampler prior to deployment, which implies that a further set of assumptions needs to be met (see Section F.4 below).

In summary, it is important to keep in mind that even if the assumptions underlying the use of eqn (14) through (17) were correct, the interpretation of PAS results within the curvi-linear region incurs very significant uncertainties. As such, it is generally preferable to use a sampler that remains in the linear uptake region. The XAD-PAS has not been used in the curvi-linear uptake region, because it is generally acknowledged that the sampler-side resistance is not negligible and the assumptions underlying the use of depuration compounds are violated.

#### F.4 The use of depuration compounds in PAS

As was discussed in Section C.1, PASs for SVOC tend not to have a diffusive barrier in order to allow for SRs that are sufficiently high for reliable quantification. One of the consequences is that the SR of the PASs tends to be quite dependent on wind exposure, especially if the sampling sorbent is not protected by a wind shelter or if the shelter is ineffective in preventing the wind from impacting the sorbent. Adopting an approach pioneered within the passive water sampling community, some PAS users spike the passive sampling sorbent with compounds prior to exposure and derive information on the kinetics of uptake from the extent of loss of those spiked compounds during the deployment. These compounds are referred to as either depuration compounds (DCs) or performance reference compounds. Because it is necessary to distinguish the spiked compounds from those taken up in the PAS sorbent during exposure, DCs are often isotopically labelled SVOCs. Alternatively, compounds are selected that are known to not be present in the sampled atmosphere. The idea underlying the use of DCs

is that wind exposure affects the kinetics of loss of DCs to the same extent as it affects the kinetics of uptake of the target compounds.

Müller *et al.*<sup>120</sup> were the first to investigate the rate of loss of compounds spiked onto the sorbent of a PAS, specifically the stearin-coated fibre cloth. A log–log linear relationship between the rate of loss and a compound's  $K_{SG}$  was interpreted as indicating an air-side control on the rate of mass transfer between atmospheric gas-phase and the sorbent. Ockenden *et al.*<sup>41</sup> and Booij and van Drooge<sup>37</sup> introduced DCs to the use of SPMDs as PAS, arguing that they can be used to account for differences in exposure conditions. Söderström and Bergqvist<sup>48</sup> confirmed that the extent of loss of deuterated PAHs and <sup>13</sup>C-labelled PCBs from SPMDs was related to their exposure to different wind speeds in a wind tunnel experiment. Farrar *et al.*<sup>93</sup> observed that the loss of different PCB congeners spiked into EVA-coated glass-PASs (POGS) increased with compound volatility, wind speed, temperature and deployment time. Bartkow *et al.*<sup>68</sup> and Moeckel *et al.*<sup>130</sup> showed that this was also the case with LDPE-PASs and PUF-PASs. PUF-PASs and PE-based PASs are frequently used with DCs, largely owing to the short  $t_{\text{linear}}$  for many SVOCs in these sorbents.

The concentration of DCs in the ambient gas-phase  $C_G$  is zero. Therefore, eqn (1) simplifies to:

$$\frac{dm_S}{dt} = -k_l m_S \quad (18)$$

In integrated form:

$$m_S = m_{S0} e^{-k_l t} \quad (19)$$

Therefore, from the amount of the DC in the PAS at the beginning of deployment  $m_{S0}$  and at the time of retrieval  $m_S$ , the loss rate constant  $k_l$  can be derived:

$$k_l = \frac{-\ln\left(\frac{m_S}{m_{S0}}\right)}{t} \quad (20)$$

Under air-side controlled kinetics, eqn (3) relates  $k_l$  with the inherent SR:<sup>20</sup>

$$\text{SR} = \frac{DA}{\Delta z} = k_l K_{SG} V_S \quad (21)$$

Therefore, the SR for the conditions of the deployment can be calculated from the empirical  $k_l$  of a DC using:

$$\text{SR} = \frac{-\ln\left(\frac{m_S}{m_{S0}}\right)}{t} K_{SG} V_S \quad (22)$$

This implies that the  $K_{SG}$  of the DC at the temperature of deployment needs to be known. SRs estimated with eqn (22) can be seriously flawed if the actual temperature in the sampler housing deviates from ambient temperature and the latter is used to estimate  $K_{SG}$ .<sup>268</sup>



A special case occurs if target chemical and depuration compound are the same, except that the latter is isotopically labelled. In this case, the  $K_{SG}$  in eqn (16) and (22) applies to the same compound under the same temperature conditions and is therefore identical. Accordingly, if we substitute the right side of eqn (22) for SR, eqn (16) simplifies to:

$$V_{\text{air}} = K_{SG} V_s \left(1 - \frac{m_s}{m_{s0}}\right) \quad (23)$$

The ratio  $m_s/m_{s0}$  should be in the range from approximately 0.2 to 0.8, if the estimated SR should not have too high an uncertainty.<sup>48</sup> This implies that the DC should not be lost too much (more than 80%) or too little (less than 20%). Because the extent of loss of a DC depends on  $K_{SG}$ ,  $T_d$ , wind speed and deployment length, it requires considerable prior knowledge of the deployment conditions to choose the right DC. In practice, multiple DCs with variable  $K_{SG}$  are used, as this increases the likelihood, that at least one of them is lost to the appropriate extent. In the case of low temperature deployments, DC would have to be considerably more volatile than the target compounds to achieve losses of 20% during deployment. In fact, typically applied DCs spiked onto PUF-PASs deployed at low temperatures often do not experience sufficient loss.<sup>126</sup> In the case of passive water sampling, the information contained in DCs being lost less than 20% and more than 80% should not be ignored, which likely also applies to passive air sampling.<sup>270</sup>

It is important to keep in mind that the assumption of air-side resistance-controlled uptake is underlying the use of DCs. Even if this assumption may not be valid, DCs can often give a semiquantitative measure of the wind exposure that a PAS sorbent experienced during a particular deployment and make some allowance for how this affects the SR. However, it would not be appropriate to use DCs in PAS, where the sampler-side resistance is clearly contributing to the exchange kinetics (XAD-PAS, SIP-PAS, PUF-PAS under some conditions). In any case, most SVOCs would not be lost appreciably from the sorbent of the XAD-PAS during normal deployments, because of its very high uptake capacity (Section E.3).

Disadvantages of the use of DCs are the considerable cost of isotopically labelled compounds and restrictions on their use during indoor deployments, *i.e.* it may not be possible to get approval to deliberately release potentially toxic compounds into indoor living environments. They can also not be used, when the PAS extract is to be used for toxicological characterisation with *in vitro* bioassays (see Section G.5.5) (*e.g.* ref. 271). Furthermore, the often very considerable uncertainty in the  $K_{SG}$  of the DCs propagates directly to the estimated SR.

## F.5 Theoretical estimation of sampling rates

There have been several efforts to describe the uptake of SVOCs in PASs using numerical simulation models.<sup>21,126,190,204,207,272</sup> Whereas the models by Zhang and Wania<sup>207</sup> and Armitage *et al.*<sup>21</sup> could be applied to any sampler with a porous sorbent and have been parameterised for the XAD-PAS and the PUF-PAS, the model by Petrich *et al.*<sup>272</sup> and Herkert *et al.*<sup>126,204</sup> is specific to

the PUF-PAS, because it relies on a sampler-specific empirical fitting constant. These efforts have a variety of motivations, including confirming a comprehensive understanding of the processes and factors controlling the uptake in a PAS,<sup>207</sup> aiding the interpretation of calibration studies and monitoring data (*e.g.* by estimating whether the PAS is operating in the linear or the curvi-linear uptake phase), and informing the design of PAS campaigns (*e.g.* in terms of deciding on the appropriate deployment length or the selection of DCs that will experience the desired extent of loss).<sup>21,126,190,204</sup>

These models can also be used for estimating the uptake of a particular target compound during a particular deployment, *e.g.* by using data on variable temperatures, external wind speeds and ambient air concentrations.<sup>21,204</sup> If the model aims to simulate the mass transfer kinetics between atmospheric gas-phase and PAS sorbent, they can be used to predict deployment-specific, inherent SR during the linear uptake phase.<sup>21,272</sup> If the model additionally allows for calculation of uptake in the curvi-linear and equilibrium part of the uptake curve, it can be used to calculate what is either called an apparent SR<sup>21,190</sup> or an effective sampling volume.<sup>126,204</sup> The effective sampling volume is simply the product of the apparent SR and the deployment time.

The models vary widely in terms of the processes being considered. The first such model by Zhang and Wania was the most comprehensive in terms of treating the uptake process as a sequential diffusion through a stagnant air-side boundary layer and a porous sampling sorbent followed by the reversible sorption onto the sorbent.<sup>207</sup> The PAS-SIM model<sup>21</sup> does not explicitly consider the kinetics of the sorption process, because numerical values for the parameterization of this process for SVOCs on PUF or XAD generally do not exist. The model by Petrich *et al.*<sup>272</sup> and Herkert *et al.*<sup>204</sup> furthermore does not include a description of transport within the sorbent (specifically the pores of the PUF), *i.e.* disregards the possibility of the importance of a sampler side resistance and uses as a starting point that the "uptake of PCBs on a PUF-PAS can be modelled as a function of the air-side mass transfer coefficient". This is somewhat questionable, considering both empirical<sup>205</sup> and theoretical evidence<sup>207</sup> to the contrary.

The models have also a number of things in common. They require input of temporally resolved wind speed and temperature data during a PAS's deployment period and calculate time-variant  $K_{SG}$  for the target compound from these temperature data using the van't Hoff equation. Armitage *et al.*<sup>21</sup> directly estimate  $K_{SG}$  at a reference temperature and the internal energy of phase transfer between sorbent and the gas-phase  $\Delta U_{SG}$  using ppLFERS<sup>215,223</sup> (see Section E.2.2). Herkert *et al.*<sup>204</sup> estimate the  $K_{OA}$  and  $\Delta U_{OA}$  for the PCBs first and then use the empirical single parameter linear free energy relationships between  $K_{\text{PUF-G}}$  and  $K_{OA}$  by Shoeib and Harner<sup>24</sup> (see Section E.2.1) assuming that  $\Delta U_{OA}$  equals  $\Delta U_{\text{PUF-G}}$ . For the PCBs, these two approaches give reasonably consistent results.<sup>204</sup>

Zhang and Wania<sup>207</sup> and Armitage *et al.*<sup>21</sup> estimate the mass transfer coefficient through the air-side boundary layer using molecular diffusivity  $D$  (estimated using the semi-empirical Fuller-Schettler-Giddings equation) and the thickness of that



layer  $\Delta z$ . Armitage *et al.*<sup>21</sup> propose a  $\Delta z$  of 1.5 cm for stagnant air conditions as it provides SRs for the XAD-PAS consistent with observations.<sup>191</sup> They then apply an empirical function to scale the SR of the XAD-PAS with wind speed based on measurements.<sup>191</sup> This function shows a stronger dependence on wind speed below 1 m s<sup>-1</sup> than above, which is also consistent with studies on other PASs using an effectively wind-sheltered sorbent.<sup>273-276</sup> A similar approach is used to parameterise the PAS-SIM model<sup>21</sup> for the PUF-PAS relying on the relationship between SR and windspeed by Thomas *et al.*<sup>132</sup>

Petrich *et al.*<sup>272</sup> and Herkert *et al.*,<sup>126,204</sup> on the other hand, estimate the mass transfer coefficient through the air-side boundary layer using an equation for laminar flow along a flat plate, which includes molecular diffusivity, the kinetic viscosity of air, the length of mass transfer (taken to be the diameter of the PUF disk), and the wind speed inside the PAS chamber. The latter is obtained from ambient wind speed using an empirical linear relationship determined in wind tunnel experiments.<sup>128</sup> This approach further requires a fitted dimensionless constant, the so-called advective mass transfer coefficient  $\gamma$ , presumably because the flow along the PUF disk is not really laminar. Different values of  $\gamma$ , all based on fitting empirical data of the loss of DCs, have been presented.<sup>126,204,272</sup> The  $\gamma$  value depends on the precise formulation of the laminar flow equation, the data set of DC loss rates being used (in particular the range of wind speeds encountered during deployment) as well as the source of the meteorological data being used (e.g. measurements at the nearest airport or meteorological station or data estimated from a global weather reanalysis).<sup>126</sup>

In summary, both approaches ultimately rely to some extent on fitting to parameterise the mass transfer through the boundary layer. PAS-SIM uses empirical data to fit the boundary layer thickness under stagnant conditions,<sup>21</sup> whereas Herkert *et al.* use the observed loss of DCs to fit  $\gamma$ .<sup>126</sup>

Herkert *et al.* argue that models in combination with readily available meteorological data can be used to derive SR when DC-derived SRs are not available or are implausible.<sup>126</sup> Mapping model-estimated SRs on a global scale suggests that wind speed is the decisive factor responsible for variable SRs, with higher values over the oceans and lower values within forests. This is consistent with the discussion in Section C.1. They also claim to be able to use their model to estimate effective air sampling volumes  $V_{\text{air}}$  for compounds in the curvi-linear uptake regime.<sup>126</sup> Incidentally, the PAS-SIM model could be similarly combined with meteorological data to estimate apparent SRs or  $V_{\text{air}}$  for specific deployments, while also taking the sampler side resistance into account. It is important to note, however, that such estimations of deployment-specific  $V_{\text{air}}$  will inevitably require the assumption of constant air concentrations during deployment, the implications of which were discussed in Section F.3 and illustrated in Fig. 9.

Different approaches have been chosen to evaluate a model's ability to predict the uptake behaviour of SVOCs in a PAS. PAS-SIM has been evaluated by comparing theoretically determined uptake curves with those obtained from a year-long calibration study of the XAD-PAS for PCBs and PAHs<sup>21</sup> and pesticides.<sup>190</sup> Herkert *et al.*<sup>204</sup> compared concentrations of PCBs obtained

using model-derived SRs for the PUF-PAS with those obtained by HiVol sampling in three different studies.

For completeness sake, we also note that there have been attempts to predict SRs using quantitative structure property relationships. Van Mourik *et al.* linearly regressed empirically determined SR for the XAD-PAS against molecular mass in order to estimate SRs for chlorinated paraffins.<sup>277</sup> Empirical SRs in SPMs were regressed against quantum-chemical descriptors by Zhu *et al.*<sup>278,279</sup> However, these are statistical relationships not based on a mechanistic understanding of the sampling process.

## F.6 Sampling of SVOCs in the particle phase

As was mentioned in Section F.2, sorption of SVOCs to the atmospheric particle phase contributes to the variability in empirically determined SRs. Whether a PAS is taking up particle-bound SVOCs or not appears to be quite strongly dependent on the sampler housing. For example, there is no evidence of the uptake of particle-bound SVOCs in the XAD-PAS; substances that are predominantly particle-bound in the atmosphere, such as PAHs with five or more fused rings or more highly brominated PBDEs, tend to have levels below the limit of detection in XAD-PASs.<sup>280</sup> On the other hand, the PUF-PAS is much more likely to take up particles, because the double bowl housing does not block wind very effectively. Chaemfa *et al.* used microscopy to study the entrapment of particles within the PUF disks deployed in the double bowl housings.<sup>131</sup> The PUF disk mostly sampled the fine particle fraction (<1  $\mu\text{m}$ ) and the size distribution of particles in the PUF was found to diverge strongly from that obtained with an aerosol spectrometer. On the other hand, Markovic *et al.* reported that particle numbers and size distributions measured with a particle spectrometer in empty double bowls were similar to those measured outside, suggesting that the housing does not discriminate between different particles.<sup>281</sup>

An extensive evaluation of the PUF-PAS for different particle-associated SVOCs suggested a poorer performance than for gaseous compounds, which was attributed to "unpredictable accumulation behaviour of particles".<sup>245</sup> SRs were reported to be much lower and more variable for particle-bound substances than for gas-phase compounds,<sup>25,129,245</sup> which contrasts with other studies that have reported similar SR for particle-bound and gaseous polycyclic aromatic compounds.<sup>247,257</sup> Because of the propensity to sample particles, the PUF-PAS has even been used as a sampler for atmospheric trace metals.<sup>282,283</sup> However, SR for different metals differed widely, presumably because of their different size distributions and the different SR of particles of different size.

Overall, the evidence as to the capability of the PUF-PAS to sample particle-bound substances reliably and reproducibly is still inconclusive.<sup>284</sup> The largest study evaluating the performance of the PUF-PAS for compounds in the particle phase concluded that in all assessment endpoints (detection, precision, fingerprinting performance, and SR consistency and magnitude) the performance was poorer than for gas-phase compounds.<sup>245</sup>



Table 13 Studies using PASs to measure the spatial variability of SVOCs around major suspected emission sources

Sampler	Location, number of sites	Time frame	SVOCs	Ref.
SPMD	13 sites around DEZA chemical plant, Valasske Mezirici, Czech Republic	Sep. 1998, 4 weeks	PAHs	36
PUF-PAS	9 sites around chemical factory, Neratovice, 11 sites around coal tar and mixed tar oils processing plant, Valasske Mezirici, Czech Republic	Jan. to Jul. 2004, six 28 day periods	PCBs, OCPs, PAHs	289
PUF-PAS	4 sites around municipal solid waste incinerator and power plant, Barcelona, Spain	Mar. to Jun. 2005, 3 months	PCDD/Fs, PCBs, PCNs	236
PUF-PAS	8 sites around a municipal solid waste incinerator, Tarragona, Spain	Mar. to Jun. and Sep. to Dec. 2010 and 2011, 3 months	PCDD/Fs, PCBs, PCNs	285
PUF-PAS	8 sites around a petrochemical and a chemical complex, Tarragona, Spain	Nov. 2014 to Jan. 2015, one 2 month period	PAHs	290
Membrane-enclosed copolymer sampler	6 sites around steel complex, Pohang, Korea	Aug. to Sep. 2005, 37 days	PAHs	53
PUF-PAS	15 sites around an iron and steel making plant, Pohang, Korea	Sep. 2006 to Jul. 2007, four 3 month periods	PCBs	291
SIP-PAS	12 sites around a municipal wastewater treatment plant and 4 sites close to two municipal solid waste landfill sites, Ontario Canada	Jul. to Sep. 2009, 63 days Jun. to Aug. 2009, 55 days	PFAS	144
SIP-PAS	1 site at eight wastewater treatment plants and 1 reference site each	Aug. to Nov 2013, Jan. to Mar. 2014, two 2 month periods	PFAS, VMS, UV-filters Synthetic musks	287 288
PUF-PAS	15 to 17 sites around oilsands region, Fort McMurray, Alberta, Canada	Nov. 2010 to Jan. 2016, thirtyone, 2 month periods	PAHs, alkylated PAHs, dibenzothiophenes	247, 292 and 293
PUF-PAS PAS-DD	5 sites in oilsands region, Fort McMurray, Alberta, Canada	Oct. to Nov. 2015, 2 month period	PAHs, alkylated, nitrated and oxygenated PAHs	294
PUF-PAS	5 sites around a secondary copper and aluminum metallurgical facilities, China	Apr. to Oct. 2011, two months	PCDD/Fs, dlPCBs, PCNs	295
PUF-PAS	13 sites around a municipal solid waste incinerator, China	May to Aug. 2012, Oct. 2012 to Jan. 2013, two 3 month periods	PCDD/Fs, PCBs	286
PE-PAS	23 sites close to natural gas extraction wells, Carroll County, Ohio, USA	Feb. 2014, one 3 to 4 week period	PAHs	69
PUF-PAS	23 sites near ship-breaking activities, Chittagong, Bangladesh	Feb. 2013, one 1 week sample (7 to 9 days)	PAHs, PCBs, DDTs, HCB, SCCPs	296
PUF-PAS	7 sites in an e-waste dismantling region, Taizhou, China	Sep. 2009 to Aug. 2010, four 3 month periods	Dechlorane plus	297
PUF-PAS	5 sites around hazardous waste landfill, Sabiñánigo, Aragon, Spain	Summer 2014 to autumn 2016, twenty-three consecutive 1 month periods	HCHs	298
PUF-PAS	Municipal solid waste landfill, Novi Sad, Serbia	Jun. and Oct. 2012, Jan. and Apr. 2013, four 1 month periods	PAHs, PCBs, OCPs	299
PUF-PAS	5 sites within a chemical manufacturing plant, China	Sep. to Oct. 2016, one 1 month period	SCCPs	300
PUF-PAS	12 sites around a coal-fired power plant on south-west coast of India	2014/2015, four seasonal samples	PAHs	301
XAD-PAS	18 or 20 sites in different waste handling facilities, Norway	2013/2014, 2 to 3 month periods	PBDEs, PCBs	302 and 303
PUF-PAS	16 sites in urban area and vehicular waste processing areas, Northern Vietnam	Jan. to Mar. 2013 and Sep. to Nov. 2015, two 2 month periods	>1000 micro-pollutants, incl. PCBs, PBDEs, PAHs, BFRs methylated PAHs	304 and 305



Instead of looking at the uptake of particle-bound substances by the sorbent meant for gaseous compounds, others have sought to add a GFF to a PAS to explicitly sample particle-bound substances.<sup>155–157,168,199</sup> This is discussed in more detail in Section D.3.1.3. Yet others have proposed PASs solely dedicated to particle-bound substances<sup>158</sup> or to use different sampler orientation and sorbents to distinguish total atmospheric load from gaseous contributions.<sup>200</sup>

## G. Applications of PASs for SVOCs

### G.1 PAS networks

One of the most common uses of PASs is the recording of the spatial variability in time-averaged air concentrations of SVOCs. This can take the form of networks of samplers. These networks vary widely in scale.

**G.1.1 Local and urban PAS network studies.** Among the PAS network studies with the smallest scale are those that seek to characterise the influence of a known or suspected point source on local atmospheric SVOC concentrations (Table 13). The use of PAS networks for mapping concentration variability close to sources makes intuitive sense, because it is in those areas that substantial heterogeneity of air concentrations can be expected to occur. The facilities that have been studied this way include chemical plants, steel plants, power plants, petrochemical extraction areas, waste incinerators, sewage treatment plants, and landfills. The target chemicals are often focused on the SVOCs that are expected to be emitted by the studied facility, for example combustion-related SVOCs such as PCDD/Fs, PCBs, PCNs from municipal waste incinerators,<sup>236,285,286</sup> volatile PFAS, VMS and musk compounds from waste water treatment plants<sup>144,287,288</sup> or parent PAHs and alkyl-PAHs in the oilsands region of Alberta, Canada<sup>247</sup> and in the vicinity of natural gas extraction wells.<sup>69</sup>

With more than 30 studies, networks of PASs across urban areas are very common (Table 14). This is not surprising as urban areas with their multitude of potential sources and large gradients in land cover and human activities are likely to experience large heterogeneity in SVOC air concentrations. A diverse set of urban areas around the world has been studied, including major metropolitan areas in the USA, such as Philadelphia<sup>306</sup> and Chicago,<sup>307,308</sup> a number of Chinese cities, including Beijing,<sup>309</sup> Shanghai,<sup>310</sup> Tianjin,<sup>311–313</sup> and Harbin,<sup>314</sup> as well as major cities in developing countries such as Bangkok,<sup>46</sup> Manila,<sup>315</sup> Alexandria,<sup>73,74</sup> Karachi and Lahore.<sup>316</sup> However, some PAS networks have also been used to measure air concentration variability in less well-known, mid-size cities, such as Manizales, Colombia,<sup>317,318</sup> Ulsan, South Korea<sup>319,320</sup> and Aliaga, Turkey.<sup>321</sup> PUF-PASs are most commonly used, but SPMDs, XAD-PASs and PE-PASs have also been employed.

**G.1.2 Regional PAS network studies.** Studies involving networks of PASs in a region are also very common and have been conducted around the world (Table 15). A region can be an administrative unit, such as a Chinese province<sup>251,346–348</sup> or an Italian region<sup>349–351</sup> or it could be a country's coastal area<sup>352–355</sup> or an entire or partial watershed.<sup>356–359</sup> These types of studies have almost exclusively relied upon the PUF-PAS, with a few

exceptions. PAHs are most frequently measured, but OCPs and PCBs are also commonly targeted. Occasionally, more unusual target substances have been studied, such as short-chain chlorinated paraffins (SCCPs) in the Yangtze River Delta<sup>360</sup> or three monosaccharides in the province of Guangdong.<sup>251</sup> While many studies only sampled for one or two periods, some seek to observe temporal patterns by sampling during multiple seasons. The number of sampling sites varies widely and ranges from as little as three to more than 30.<sup>361–364</sup>

**G.1.3 National PAS network studies.** A number of studies involved networks of sampling sites across a country (Table 16). The scale of these studies varies obviously with the size of the country, ranging from as little as five sampling sites in Luxembourg<sup>385,386</sup> to more than 90 sites within China.<sup>387,388</sup> A number of these studies were conducted in countries with no prior measurements of SVOCs in the atmosphere and the PAS network served as an initial reconnaissance of atmospheric SVOC contamination. Examples are Kuwait,<sup>389</sup> Costa Rica,<sup>280,390,391</sup> Botswana,<sup>210</sup> Ghana<sup>392,393</sup> and Azerbaijan.<sup>394</sup> Some studies focus on a particular type of sampling environment, *e.g.* on cities<sup>239,395</sup> or national parks,<sup>396</sup> whereas most national scale studies include a mix of remote, rural and urban sampling locations. Whereas most of these studies analyzed classical SVOCs, such as PCBs and OCPs, some had a focus on chemicals, for which the national database of atmospheric measurements may have been inadequate. Examples are studies on specific CUPs in Canada,<sup>397,398</sup> on dechlorane plus in China<sup>399</sup> and SCCPs and MCCPs in Australia.<sup>277</sup> These studies typically relied on PUF-PASs and XAD-PASs, with deployment periods ranging from 1 month to 1 year.

**G.1.4 International regional network studies.** Table 17 compiles information on studies with PAS sampling sites across an international region. Most of these have been done in parts of Europe, but there are also two in Western Africa<sup>421,422</sup> and a number in East Asia.<sup>423,424</sup> One network, relying on SPMDs, has been measuring SVOC concentrations at 10 to 12 sites along a transect from Southern UK to Northern Norway from 1994 to 2008, with an unusually long deployment period of 2 years.<sup>40,42–45</sup> Most of the other studies of this type used PUF-PASs and sampling periods ranging from 1 to 3 months. High capacity sorbents, *i.e.* XAD-PAS and SIP-PAS, find use when a year-long deployment is used.<sup>150,423</sup> The studies using PE-PASs around the Laurentian Great Lakes also could be classified as international regional studies, but they are discussed separately in Section G.8.1, because they include paired air and water passive samplers.

**G.1.5 Continental PAS network studies.** A few international studies were sufficiently large in scope to categorise them as continental in scale (Table 18). An early network of XAD-PASs ranged from the High Canadian Arctic to Central America and from the Pacific to the Atlantic coast of North America.<sup>29,432,434</sup> A number of studies were Pan-European in scale<sup>95,434–436</sup> or covered large parts of East Asia.<sup>143,437–439</sup> Two studies reported data on African networks<sup>440,441</sup> and a regional Global Atmospheric Passive Sampling (GAPS) effort<sup>31,442,443</sup> focussed on the group of Latin American and Caribbean countries. While an Australian national study<sup>277,414</sup> could also be classified as



Table 14 Studies using PASs to measure the spatial variability of SVOCs in the urban atmosphere

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS	20 sites in Brno, Czech Republic	Oct. to Nov. 2004, 28 days	PCBs, OCPs, PAHs	322
SPMD	2 sites in Genoa, Italy, industrial area	April 2007 to May 2008, nine 1 month periods (28 to 36 days)	PAHs	59
PUF-PAS	7 sites in Liberec, Czech Republic	Dec. 2005 to Dec. 2006, thirteen 28 day periods	PAHs	323
PUF-PAS	23 sites in Zurich, Switzerland	Spring 2011 and spring 2013, two periods	PCBs	324
XAD-PAS	3 sites in Strasbourg, France	Every spring between 2013 and 2016, eleven 2 week periods	PAHs, PCBs, OCPs, CUPs	325
PUF-PAS	6 sites in Ottawa, Ontario, Canada	Dec. 2002 to ar. 2003, 3 months	PFAS	162
PUF-PAS	32 sites in Philadelphia/ Camden, USA	Apr. to Jul. 2005, 96 to 98 days	PCBs	306
PUF-PAS	5 sites in Fairbanks, Alaska, USA	Dec. 2008 to Mar. 2009, 4 months	PAHs	326
XAD-PAS	26 sites in Toronto, Ontario, Canada	Jul. to Oct. 2012, 65 to 92 days	VMS	28
PUF-PAS	21 sites in Cleveland, Ohio and 17 sites in Chicago, Illinois, USA	Aug. to Sep. 2008, 20 to 22 days (Cleveland) and 13 to 47 days (Chicago)	PCBs	307
PUF-PAS	13 sites in Chicago, Illinois, USA	Jan. 2012 to Jan. 2014, 180 samples of $43 \pm 11$ days.	PAHs, BFRs, OPFR, OCPs	308
PUF-PAS	8 sites in Toronto, Ontario, Canada	Aug. 2016 to Aug. 2017, six 2 month periods	PAHs, alk-PAHs, nitro-PAHs, Oxy-PAHs, dibenzothiophene (DBT), alk-DBTs	327
PUF-PAS	6 sites in Concepcion, Chile	Jan. to Mar. 2007, 2 months	PCBs, PAHs, OCPs	328
PUF-PAS	6 sites in Temuco, Chile	Apr. 2008 to Apr. 2009, three 4 month periods	PAHs	329
PUF-PAS	5 sites in Santiago, 6 sites in Concepcion, 6 sites in Temuco, Chile	Apr. 2008–Aug. 2009, four 4 month periods	PCBs, OCPs	330
PUF-PAS	4 sites in Santiago de Cali, Colombia	May to Sep. 2011, one 4 month period	PCBs, OCPs, PAHs	331
PUF-PAS	4 sites in Manizales and 1 site in Bogota, Colombia	June 2012 to Nov. 2014, total of 27 periods (90 to 120 days)	PCDD/Fs, dlPCBs	317,318
PUF-PAS	11 sites in Mendoza, Argentina	Dec. 2010 to Apr. 2011, ~90 days	PCBs, HCB DDTs, PBDEs,	332
SPMD	6 sites in Bangkok, Thailand	Mar. to Apr. 2000, 3 weeks	PAHs	46
PUF-PAS	6 sites in and around Manila, Philippines (3 urban, 3 rural)	May to Dec. 2005, four periods of 42 to 56 days	PAHs	315
PUF-PAS	3 sites in Manipur, India	Jan. to Dec. 2009, one month for a year	OCPs	333
PUF-PAS	5 sites in Kolkata, 1 site in Sundarban, India	Dec. to Mar. 2014, one 3 month period	PAHs	334
XAD-PAS	6 sites in Karachi and 4 sites in Lahore, Pakistan	Jan. to Oct. 2011, 10 months	PBDEs, OCPs, PCBs	335
PUF-PAS	6 sites in Kathmandu, 4 sites in Pokhara, 3 sites in Hetauda in Nepal	Kathmandu and Pokhara: Aug. 2014 to Aug. 2015, Hetauda: Nov. 2015 to Aug. 2016, six 2 month periods	PAHs	336
PUF-PAS	6 sites in Shanghai, China	Aug. 2006 to Jun. 2007, three 3 month periods	PCBs, OCPs	337
PUF-PAS	6 sites in Tianjin, China	Jul. 2006 to Jun. 2008, one 8 months & five 3 month periods	PAHs	310
PUF-PAS	8 sites in Harbin, China	Feb, 2007 to Jan. 2008, four 3 month periods	OCPs, PCBs	311
			PAHs	314



Table 14 (Contd.)

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS	11 sites in Tianjin, China	Jun. 2008 and Jan. 2009, two 1 month periods	PCBs, PCDD/Fs	312
PUF-PAS	13 sites in Beijing, China	Feb. 2011 to Mar. 2012, four seasonal periods	PCDD/Fs, dlPCBs, PBDEs	309
PUF-PAS	28 sites in Nanjing, China	Jan. to Oct. 2015, four 2 to 3 month periods	PAHs	338
PUF-PAS	7 sites in Ningbo, China	Nov. 2014 to Oct 2015, twelve 1 month periods	PAHs	339
PUF-PAS	8 sites in Ezhou, Wuhan, Hubei, China	Jun. to Aug. 2015, one period	PAHs	340
PUF-PAS	20 sites in Dalian, Liaoning, China	Jul. to Sep. 2017, one 40 day period	PAHs	341
PUF-PAS	33 sites in Tianjin, China	Jul. to Sep. 2016, Nov. 2016 to Jan. 2017, two 90 day periods	OPEs	313
PUF-PAS	20 sites in Ulsan, South Korea	Jan. to Feb 2011, 49 days	PAHs	319
PUF-PAS	20 sites in Ulsan, South Korea	Mar. to May 2013, 84 days	PAHs, Cl- PAHs, Br-PAHs	320
PUF-PAS	36 sites in Seoul, South Korea	Aug. to Sep. 2006, Jan. to Feb. 2007, two 1 month periods	PAHs	342
PUF-PAS	7 sites in Tangshan, China	Jul. to Oct. 2010, 3 months	OCPs	343
PUF-PAS	22 sites in Istanbul, Turkey	Sep. to Dec. 2014, four 1 month periods	PAHs, PCBs	344
PUF-PAS	40 sites in Aliaga, Turkey	Jul. 2009 to May 2010, four 2 month periods	PAHs, PCBs	321
PUF-PAS	8 sites in Bursa, Turkey	Feb. to Dec. 2014, five 2 month periods	PCBs	345
XAD-PAS	15 sites in Minneapolis, Minnesota, USA	2013–2015, several 3 month periods	PAHs	253
PE-PAS	11 sites in Alexandria, Egypt	Jul. 2010 to Jan. 2011, 21 days	PAHs alkyl-PAHs, thiophenes OCPs	73
				74

continental, we have listed those studies in Table 16 in Section G.1.3 above.

**G.1.6 Global PAS network studies.** Table 19 lists the PAS network studies that were truly global in scale. Most of these were conducted as part of the Global Atmospheric Passive Sampling (GAPS) project, which is relying on PUF-PASs,<sup>127,208,444–447</sup> XAD-PASs<sup>197,448,449</sup> and SIP-PASs.<sup>139,147,151–153</sup> Another global scale study with a focus on Africa, Latin America, the Caribbean, and the Pacific Islands also relied on the PUF-PASs.<sup>450</sup> In some cases, first long-term time trends could be derived from samples taken in different years.<sup>153,197,448</sup>

## G.2 PAS transects

Another common application of PASs involves a transect of sampling sites along which a change in air concentration may be expected. Again, the scale of such transects varies widely. At the smallest scale, PASs have been used to quantify the impact of roadways and other traffic arteries on the concentrations of SVOCs.<sup>451,452</sup> Some of the local scale studies in Section G.1.1 seeking to quantify the influence of specific point sources (Table 13) have relied on linear transects. Quite frequently, the air concentration variability along urban to rural transitions (Table 20) has been studied, with most of these studies sampling North

of Toronto, likely because this is an area of such clear transition in population density and industrial and agricultural activity.<sup>453–458</sup> Harrad *et al.* sampled a transect across the Birmingham region.<sup>459,460</sup> There is obviously some overlap between transect studies sampling along an urban-rural gradient and the urban network studies in Section G.1.1, if those networks include urban, suburban and rural sites (Table 14).

At the largest scale, PAS transects explore air concentration variability with latitude. These studies have already been mentioned in the context of network studies in Section G.1. Most notable among those are the transects in Northern Europe,<sup>40,42–45,150</sup> along the length of Chile,<sup>195,400</sup> and across North America.<sup>29,432,433</sup> The northern part of the latter transect from Southern Canada to the High Arctic is particularly useful because there are few, if any, emission sources that would confound the recorded air concentration gradient. This transect thus constitutes a gradient of source proximity or remoteness<sup>449,461</sup> and lends itself to the derivation of empirical travel distances.<sup>29</sup>

## G.3 PAS vertical gradients

Another frequent theme of PAS studies for SVOCs is their use in the determinations of vertical concentration gradients. Again, these studies have a range of spatial scales.



Table 15 Studies using PASs to measure the spatial variability of SVOCs in a region

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
<b>Europe</b>				
PUF-PAS	6 sites in Northern Estonia	Mar. to Aug. 2006, four 4 week periods	PCBs, OCPs	353 and 354
PUF-PAS	19 sites in Tuscany, Italy	Apr. to Jul. 2008, 60 to 160 days	PAHs, OCPs, PBDEs, PCBs	349
PUF-PAS	10 sites in Tuscany, Italy	Apr. 2008 to Jul. 2009, four 3 to 5 month periods	PCBs, OCPs	351
PUF-PAS	4 sites in Puglia, Italy	Jan. 2009 to Feb. 2010, four periods of 2 to 5 months	PCBs, PAHs	350
PUF-PAS	8 sites in Sicily, Italy	Jul. to Dec. 2007, two 2 to 3 month periods	PCBs, OCPs, PBDEs	365
PUF-PAS	7 sites in Molise, Italy	Apr. to Jul. 2011, one 3 month period	PAHs	366
PUF-PAS	6 sites around the Mar Menor lagoon, Cartagena, Spain	2010, four 1 month periods in each season	PAHs, CUPs	237
PUF-PAS	3 sites around Bothnian Bay, Sweden	Jul. 2011 to Jan. 2013, five 3 to 5 month periods	OCPs, CUPs, brominated anisoles	367
PUF-PAS	150 sites in Naples, Campania, Italy	Jul. 2015 to Apr. 2017, three-four 3 month periods	OCPs, PCBs, PAHs	368
PUF-PAS	4 sites in Sabiñánigo, Aragón, Spain	Feb. 2016 to Nov. 2018, 29 consecutive 1 month periods	HCHs, PeCB, HCB	369
<b>Africa</b>				
PUF-PAS	3 sites in Northern Algeria	Jul. 2008 to Nov. 2009, 28 to 56 days	PCBs, CUPs, PCDD/Fs	370
PUF-PAS	3 sites along coastal zone of Ghana	Jan. to Dec. 2008, 4 weeks and 12 weeks	OCPs	355
PUF-PAS	4 sites in Gauteng Province, South Africa	May 2016 to Jan. 2017, two 100 day periods	PBDEs, novel BFRs	371
<b>Americas</b>				
PUF-PAS	4 sites in Southern Mexico	2002 to 2004, 31 to 116 days	OCPs, PCBs	372
PUF-PAS	23 sites in the Yakima valley, Washington, USA	Mar. to Apr. and Jun. to Aug. 2011, 5 to 30 days	CUPs	244
PUF-PAS	8 sites in Bahia Blanca, Buenos Aires province, Argentina	2006–2007, 105 to 155 days, 191 to 230 days	PCBs, OCPs	373
PUF-PAS	6 sites in Córdoba, Argentina	Nov. to Dec. 2014, one period (44 to 50 days)	PAHs, PCBs, OCPs, PBDEs	374
XAD-PAS	10 sites in Quequén Grande basin, Buenos Aires province, Argentina	May 2013 to Sep. 2014, three 4 month periods	OCPs, CUPs, PCBs	357
XAD-PAS	9 sites around Bahia Blanca, Buenos Aires province, Argentina	Jan. to Dec. 2015, four seasonal samples	PAHs	375
<b>Asia (other than China)</b>				
PUF-PAS	10 sites in Punjab, Pakistan	Jan. to Mar. 2011, one 8 week period	OCPs	376
PUF-PAS	6 sites in the Indus Basin, Pakistan	Sep. to Oct. 2013, 56 days	OCPs	356
PUF-PAS	6 sites in the Indus Basin, Pakistan	Oct. to Dec. 2012, 8 weeks	PCBs	377
PUF-PAS	32 sites in Azad Jammu and Kashmir region, Pakistan	Nov. 2016 to Jan. 2017, 8 weeks	OCP, PCBs	364
PUF-PAS	Unknown number of sites in Punjab, Pakistan	Unknown number of consecutive 56 day periods	PAHs	378
PUF-PAS	32 sites in Tamil Nadu, India	Apr. 2009 to Jan. 2010, three seasonal periods	PAHs	361
PUF-PAS	9 sites within the Ganga River basin, India	Apr. to Sept. 2013 (3 to 4 months) and Feb. to May 2014 (1 to 2 months)	PAHs	358
PUF-PAS	7 sites at lower reaches of Ganga River, India	Mar. to Apr. 2015, one 40 day period	OCPs	359
PUF-PAS	19 sites along the south coast of South Korea	Jan. to July 2006, two 3 month periods	Coplanar PCBs, PCNs, PBDEs	352



Table 15 (Contd.)

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS	10 sites in Gyeonggi Province, South Korea	Mar. 2011 to Feb. 2013, 80 to 100 days	PCBs, PCDD/Fs	379
PUF-PAS	20 sites in Ulsan, South Korea	Feb. 2011 to Feb. 2012, four 3 month periods	PAHs	380
PUF-PAS	41 sites in Kutahya, Turkey	Jan. to Mar. and Jun. to Aug. 2014, two 2 month periods	PAHs, PCBs	363
PUF-PAS	4 sites in Kumluca, Antalya, Turkey	May to Nov. 2013, 11 periods (1 to 3 months) at one site, two 3 month samples at three sites	OCPs, PCBs	381
PUF-PAS	23 sites in Dilovasi district, Kocaeli, Turkey	Feb. 2015 to Feb. 2016, twelve 1 month periods	PAHs, PCBs	382
<b>China</b>				
PUF-PAS	40 sites in Hebei province	2007 to 2008, 46 to 123 days	PAHs	346
PUF-PAS	7 sites in Hubei province	Apr. 2012 to Mar. 2013, four seasonal samples	OCPs	347
PUF-PAS	14 sites in Gansu province	Nov. 2010 to Mar. 2011, Jun. to Sep. 2011	PAHs	348
PUF-PAS	10 sites along the Lanzhou valley, Gansu province	2013, two periods of 107 and 100 days	PAHs	383
PUF-PAS	31 sites in Yangtze River Delta, Jiangsu province	Jul. 2011 to Jun. 2012, four seasonal periods	PAHs	362
PUF-PAS	11 sites within Guangdong province	Jan. to Apr. and Jul. to Sep. 2015, two 2 month periods	SCCPs Levoglucosan, mannosan, galactosan	360 251
PUF-PAS	18 sites along the Lanzhou valley, Gansu province	Winter 2014, summer 2015, two 12 week periods	Nitrated PAHs	384
PAD-DD				

**G.3.1 Small scale gradients above soil.** A number of research groups have sought to quantify small scale (<2 m) vertical gradients of SVOCs above soil (Table 21). The rationale is to deduce the direction and extent of diffusive air-soil exchange. This is a particularly challenging application of PASs, because the concentration differences on such a small scale may be too small to be confidently established, considering the limited precision of most PASs. This is particularly so, because wind speeds decrease close to the ground, and therefore the SR of a PAS will also decrease. It thus needs to be confirmed that sequestered amounts that increase with PAS deployment height are not due to a gradient in the uptake kinetics, but truly reflect a depositional flux of the SVOC. In most cases, this will require the use of DCs to quantify the extent to which wind exposure of the PASs varies with height.

This application of PASs has spawned a whole range of custom-designed PAS, presumably because the most commonly used PASs are too bulky and their sampling height too poorly constrained for finely resolved measurements. In particular, the PUF-based samplers used for fine-scale vertical gradients have small housings that envelop the foam disk and are only open at the bottom. As a result, they have lower SRs than the regular PUF-PAS.<sup>169–171</sup>

Zhang *et al.* observed levels that decline with height at contaminated site and levels that increase with height at two other sites, but those gradients were only apparent very close to the soil surface (<3 cm).<sup>169</sup> They were interpreted as indicating

volatilisation and deposition, respectively. No attempt was made to account for the possibility that the SR is reduced so close the ground surface, even though a photograph of one of the sampling sites shows a vegetation cover. Wang *et al.* used a slightly modified version of that sampler with double the surface area to record concentration gradients above a Tibetan pasture, but did use DCs to correct for differences in the SR with height.<sup>171</sup> Strangely, while SRs varied considerably (ranging from 1 to 3 m<sup>3</sup> per day), they showed no apparent relationship with height. *o*-HCH and *o,p'*-DDT showed lower levels close to the ground during both summer and winter, indicative of deposition.

Since the largest concentration difference can be expected to occur between the bulk atmosphere and the air right next to the soil surface, Donald and Anderson proposed to only sample at those two heights using PE strips placed in custom-made metal boxes.<sup>70</sup> DCs are used to correct for variable atmospheric turbulence in the boxes, which was much higher in air than in soil air samplers. Above two contaminated soils, air concentrations at ground were found higher than at height, indicative of a potential for evaporation. At one site, the gradient was reversed, indicating that PAHs and PCBs are likely to deposit. Air-soil exchange fluxes were estimated using molecular diffusion across a stagnant boundary layer presumed to be 1 mm thick. More recently, this approach has been used to measure potential emissions of chemicals from artificial turf.<sup>71</sup>



Table 16 Studies relying on PAS network for SVOCs on a national scale

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS	6 sites in Chile	Dec. 2002 to Feb. 2003, 2 months	OCPs, PCBs	400
XAD-PAS	20 sites in Chile	Feb. 2006 to Jul. 2007, 1 year	OCPs, CUPs, PAHs, PCBs	195
PUF-PAS	14 sites in Kuwait	Feb. to Apr. 2004, 6 weeks	PBDEs and PAHs	389
XAD-PAS	23 sites in Costa Rica	Feb. 2004 to Feb. 2005, 1 year	OCPs	390
			PAHs	280
			CUPs	391
XAD-PAS	7 sites in Costa Rica	Oct. 2005 to Oct. 2006, 1 year	OCPs, CUPs	401
			PFAS	197
PUF-PAS	11 sites in Mexico	2005–2006, up to four consecutive 3 to 4 month periods	OCPs	402
PUF-PAS	8 sites in Canada (PEI, QC, ON, SK, BC)	2004 to 2005, 1 month	Dacthal	397
PUF-PAS	10 sites in Central and Northern Canada (SK, AB, NV, NWT)	May to Aug. 2005, May to Aug. 2007, 78 to 106 days	Herbicides	398
PUF-PAS	97 sites in China	Jul. to Oct. 2005, 3 months	PCBs	387
			Dechlorane plus	399
PUF-PAS	40 sites in China	Feb. to Mar., Apr. to May, Jul. to Aug., Sep. to Nov. 2005, 8 weeks	PAHs	403
PUF-PAS	90 sites in Northern China	Jun. to Oct. 2011	OCPs	404
			PBDEs, TBE, DBDPE	388
			PCNs	405
			Bromomonoo-aromatics	406
			PAHs, nitro-PAHs	407
PUF-PAS	18 sites in coastal India	Jul. to Sep. 26, 2006, 6 weeks	PCBs, PBDEs	408
PUF-PAS	68 sites in 7 Indian cities	Dec. 2006 to Mar. 2007, 28 days	OCPs	395
	20 sites in 3 Indian cities,	Winter 2006 (India)	SCCPs, MCCPs	409
	10 sites in Pakistan	Winter 2011 (Pakistan)	PCNs	410
			PBDEs	411
PUF-PAS	9 sites in Indian agricultural areas	2006–2007, four 3 month periods	PCBs, OCPs	412
PUF-PAS	8 sites in Australia (WA, QLD, SA)	Jan. to Feb. and Jul. to Aug. 2007, 40 to 50 days	PAHs	268
			PCBs	413
XAD-PAS	15 sites in Australia	Jan. 2012 to Mar. 2013, 1 year (325 to 414 days)	OCBs, PCBs	414
XAD-PAS	15 sites in Australia	Jan. 2016 to Jun. 2017, 1 year (302 to 408 days)	SCCPs, MCCPs	277
XAD-PAS	15 sites in Botswana	May 2006 to May 2007, 1 year	OCBs	210
			PFAS	197
XAD-PAS	36 sites in 19 USA National parks	Summer 2005-summer 2006, 1 year	OCPs, CUPs, PAHs	396
PUF-PAS	13 locations in Azerbaijan	Nov. to Dec. 2008, 4 weeks	PCBs, OCPs	394
SIP-PAS PUF-PAS	10 cities in Korea	Apr. to Jul. 2009, 90 days	PFAS	239
PUF-PAS	55 sites in Japan	Mar. to May, Aug. to Oct., Nov. 2008 to Jan. 2009, 8 weeks	PCBs, PCNs	415
PUF-PAS	13 sites in Ghana + 2 e-waste sites	May to Jul. 2010, 56 days	PCNs	392
			OCPs	393
			PCBs	416
XAD-PAS	5 sites in Luxembourg	Jun. to Oct. 2008, 6 to 87 days	Pesticides	385
PUF-PAS	15 sites in Vietnam	Jun. to Aug. 2012, Dec. 2012 to Feb. 2013, two 6 week periods	PAHs	386
PUF-PAS	34 sites in 4 Nepalese cities (Kathmandu, Pokhara, Birgunj, Biratnagar)	Aug. 2014 to Oct. 2014, one 8 week period	PCBs, OCPs	417
PUF-PAS	32 sites in 16 provinces in Turkey	May 2014 to Apr. 2015, four 3 month periods	OCPs, PCBs, PBDEs	419
PUF-PAS	62 sites in China	2016–2017, three periods of 7 to 8 weeks	Unintentionally produced PCBs	420

Liu *et al.* used PE strips covered by a metal plate to sample PAHs in air at numerous heights above the ground.<sup>76</sup> SRs derived from DCs were strongly dependent on height, ranging from 2 to 3 m<sup>3</sup> per day at the lowest sampling heights to 20 m<sup>3</sup> per day and higher for PASs deployed more than 50 cm above ground. Concentration gradients indicated deposition of lighter PAHs and volatilisation of heavier PAHs. Relatively large variations in the reported air concentrations at greater heights,

where the air should be reasonably well-mixed, indicate a fairly high uncertainty of the recorded concentrations.

Wang *et al.* used the PUF-PAS to measure concentrations of OCPs and PAHs above and below the canopy of a rice crop, using DCs to allow for different SRs.<sup>463</sup> Following expectations, SRs were notably lower below the canopy than above it. Both lower and higher concentrations were observed below the canopy when compared to those measured above.



Table 17 Studies relying on PAS network on a regional scale involving multiple countries

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS	15 sites in the Laurentian Great Lakes region (USA, Canada)	Jul. 2002 and Jun. 2003, four 3 month periods	PCBs, PBDEs, OCPs PCNs Chiral pesticides	425 426 427
XAD-PAS	8 sites in Northeast Asia (South Korea, Mongolia, China)	2007 to 2008, 1 year	PCBs, OCPs, dechlorane plus	423
SPMD	10 sites from South of the UK to the north of Norway	Summer 1994 to summer 1996, 2 years	PCBs, $\alpha$ -HCH and $\gamma$ -HCH	40
SPMD	12 sites from South of the UK to the north of Norway	Summer 1998 to summer 2000, 2 years	PCBs, HCB	42
SPMD	11 sites from South of the UK to the north of Norway	Summer 2000 to summer 2002, 2 years	PCBs, PBDEs, OCPs	43
SPMD	11 sites from South of the UK to the north of Norway	Summer 2002 to summer 2004, 2 years	PCBs, OCPs PBDEs, PAHs	44
SPMD	11 sites from South of the UK to the north of Norway	Summer 2004 to summer 2008, two 2 year periods	PCBs, PBDEs	45
SIP-PAS	10 sites from South of the UK to the north of Norway	Jul. 2008 to Jun. 2009, 1 year	PCBs, PBDEs, HCB	150
SPMD	40 sites in 5 European countries (Austria, Czech Republic, Poland, Slovakia, Sweden)	Sep. to Dec. 1999 and Jun. to Aug. 2000, 21 days	PAHs, nitro-PAHs	47
PUF-PAS	23 sites in 8 Northern European countries (Ireland, UK, Denmark, Norway, Sweden, Russia, Finland, Estonia)	Aug. to Oct. 2004, 56 to 82 days	PCBs, PAHs, PBDEs, HCB, <i>p,p'</i> -DDT, <i>p,p'</i> -DDE	428
PUF-PAS	11 sites around the Aegean Sea (Greece, Turkey)	Jul. to Aug. 2012, one 1 month period	OCPs, PCBs, PBDEs, PAHs	103
PUF-PAS	5 sites Mexico City, Mexico, Gothenburg, Sweden and Lancaster, UK	Mar. to Apr. 2006, 42 to 50 days	OCPs, PCBs, PBDEs	429
PUF-PAS	15 sites in 4 West African Countries (Ghana, Gambia, Sierra Leone, Ivory Coast)	May to Jul. 2008, 90 days	PCBs	421
PUF-PAS	19 sites in 4 West African countries (Togo, Benin, Nigeria, and Cameroon)	2012, one 8 week period in rainy season, two 8 week periods in Cameroon	OCPs	422
PUF-PAS	155 sites in 22 Central and Eastern Europe countries	2006–2008; 6 periods of 28 day	PAHs, OCPs, PCBs	430
PUF-PAS	45 sites in 3 East Asian countries (China, South Korea and Japan)	Mar. to May, 2008, Aug. to Oct. 2008, 51 to 90 days	PBDEs	424
PUF-PAS	6 sites in 4 East Asian countries (The Philippines, Japan, Malaysia, Vietnam)	2011–2012, two ~2 month periods (46 to 98 days)	PCBs	431

The modified Bowen ratio method for flux estimation, which relies on vertical concentration gradients, can become problematic when the time resolution of the concentration measurements is too coarse.<sup>464</sup> In particular, if during the sampling period, the air–soil exchange flux changes direction, the concentration gradient cannot be interpreted in terms of a flux.<sup>464</sup> In the case of SVOCs, it is quite likely that air–soil exchange fluxes experience day and night differences. PAS sampling periods are almost always longer than a day. If, however, it can be assumed that the direction of net flux does not change during the sampling period, the performance of the modified Bowen ratio method is not strongly affected by the length of sampler deployment.<sup>464</sup> The condition to measure meaningful vertical concentration differences with PASs is therefore most likely fulfilled when sampling above a highly

contaminated soil, because (i) a wind speed/SR gradient would only counter and not create a decrease in the sequestered amounts with PAS deployment height, *i.e.* a measured contamination gradient is less likely to be a sampling artefact, and (ii) SVOC evaporation is likely to occur continuously, *i.e.* it is less likely that the net flux direction changes during a deployment. None of the studies reporting SVOC concentration gradients above soil measured with PASs seems to be aware of the limitations of deriving fluxes from long term average concentrations.

**G.3.2 Gradients on towers.** At a somewhat larger scale, five studies have used towers to make vertical SVOC concentration measurements with PASs<sup>34,130,135,465,466</sup> (Table 22). The issue of wind speed gradients possibly resulting in an SR gradient (as discussed in Section G.3.1) applies here as well. For example, Chaemfa *et al.* attributed lower sequestered amounts of PCBs at



Table 18 Studies involving continental scale PAS networks for SVOCs

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
XAD-PAS	40 sites in North and Central America (Canada, USA, Mexico, Belize, Costa Rica)	May to Jul. 2000 to May to Jul. 2001, 1 year	OCPs $\alpha$ -HCH, $\gamma$ -HCH PCBs, PBDEs	29 432 433
PUF-PAS	71 sites in 22 European countries	Jun. to Jul. 2002, 6 weeks	PCBs, PBDEs, OCPs PAHs, PCNs	434 435
POG	38 sites in 19 European countries	Jun. 2002, 1 week	PCNs, PCBs, PAHs	95
PUF-PAS	86 sites in 34 European countries	Summer 2006, 3 months	PCBs, OCPs, PAHs	436
PUF-PAS	77 sites in East Asia (China, South Korea, Singapore)	Sep. to Nov. 16, 2004, 56 days	PCBs, OCPs, PBDEs	437
SIP-PAS	46 sites in East Asia (China, Taiwan, Japan, India)	Mar. to Aug. 2009, 100 days	PFAS	143
PUF-PAS	106 sites in East Asia (Japan, China, Korea, Taiwan)	Mar. to May 2008, 8 weeks	PCBs, PCNs	438
PUF-PAS	176 sites in Asia (China, India, Japan, Vietnam, South Korea)	Sep. 2012vAug. 2013, 4 seasonal periods	PAHs, alkylated PAHs	439
PUF-PAS	26 sites in 15 African countries	Jan. to Jun. 2008, 28 days to 3 months	PAHs, PCDD/Fs, PCBs, OCPs	440
PUF-PAS	20 sites in 12 African countries (166 samples)	2010–2018, 2 to 3 month periods	CUPs	441
PUF-PAS	7 sites in Latin America	2014, two to four 3 month periods	OPFRs	442
PUF-PAS, SIP-PAS	9 sites in Latin America	2014/2015, up to eight 3 month periods, SIP for one period	HCBD, PCA, dicofol, OCPs, PCBs BFRs, OFRs in PUFs, cVMS, PFAS in SIPs	31 443

the lowest sampling height to differences in wind speed with height.<sup>135</sup> Moeckel *et al.* quantified the gradient in SR with the help of DCs and noted a four-fold increase of the SR of the PUF-PAS between ground level and 100 m (2 to 8 m<sup>3</sup> per day).<sup>130</sup> Similarly, Li *et al.* noted an increase in SR from around 7 m<sup>3</sup> per day at 15 m to 11 to 12 m<sup>3</sup> per day at 320 m.<sup>466</sup> Using height-

specific SRs to derive air concentrations largely eliminated a gradient of increasing sequestered amounts of PCBs and OCPs with elevation in a Swedish forest.<sup>130</sup> On a tower in Beijing, levels were still slightly higher closer to the ground, suggestive of urban ground sources.<sup>466</sup> Both of these studies suggest that DC-corrected SRs are imperative when trying to measure vertical

Table 19 Studies involving global scale PAS networks for SVOCs

Sampler	No. of sites	Time frame	SVOCs	Ref.
PUF-PAS	7 sites	2002, 2 to 7 months	OCPs	444
PUF-PAS	41 sites in 28 countries	Dec. 2004 to Mar. 2005, ~3 months (70 to 232 days)	OCPs, PCBs, PBDEs PCNs	208 445
PUF-PAS	41 sites in 36 countries	Dec. 2004 to Dec. 2005, 4 consecutive 3 month periods	OCPs, PCBs, PBDEs	127
SIP-PAS and PUF-PAS	20 sites	Mar. 2009 to Oct. 2009, 86 to 130 days	PFAS, PCBs VMS OCPs, PBDEs CUPs	139 147 151 152
XAD-PAS	36 to 46 sites	2005 to 2008, 4 consecutive 1 year periods	OCPs, CUPs	448
XAD-PAS	34 to 35 sites	2005 to 2006, two 1 year periods	PAHs	449
PUF-PAS	31 sites in 11 countries	3 to 6 months	PCBs, PCDD/Fs, DDT-compounds	450
XAD-PAS	17 to 46 sites	2006 to 2011, six consecutive 1 year periods	PFAS	197
PUF-PAS	40 sites	2005 to 2006, four consecutive seasonal periods	BFRs	446
PUF-PAS	48 sites	2014, several consecutive ~3 month periods	PBDEs, HBCD, BFRs, chlorinated FRs, OPEs	447
SIP-PAS	21 sites	Apr. to Jul. 2015, one 3 month period, 2013, four consecutive ~3 month periods	PFAS, VMS	153



Table 20 Studies deploying PASs along urban to rural transects

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
PUF-PAS SPMD	7 sites North of Toronto, Canada	Jul. to Oct. 2000, 120 days	PCBs, OCPs	453
PUF-PAS	7 sites North of Toronto, Canada	Jun. 2000 to Jul. 2001, three 4 month periods	PAHs, PCBs, OCPs	454
PUF-PAS	7 sites North of Toronto, Canada	Apr. to May 2002, 1 month	PBDEs	456
PUF-PAS	8 sites North of Toronto, Canada	May to Oct. 2003, seven consecutive 1 month periods	CUPs	457
PUF-PAS	10 sites across Birmingham, UK	Aug. 2003 to Oct. 2004; eleven 1 month periods	PBDEs	459
PUF-PAS	19 sites North, East and West of Toronto, Canada	Oct. 2007 to Oct. 2008, four 3 month periods	PCBs	460
			PCBs, PBDEs, PAHs	458

Table 21 Studies using PASs to measure air concentration gradients of SVOCs above soil

Sampler	Location/time frame	Sampling height	SVOCs	Ref.
SPMD	1 contaminated site in landfill, Bitterfeld, Germany	20 and 150 cm	HCHs, HCB, DDTs	462
PUF disks in stainless steel can with open mesh-covered bottom (3 cm diameter opening)	1 contaminated and 2 uncontaminated sites, Beijing, China, one 2 month period	0.5, 2, 3, 4, 5, 8, 12, 15, 170, 20, 25, 30, 40, 45 cm, 6 per height	PAHs	169
Regular PUF-PAS	1 rice paddy field, Guangzhou, China, two ~6 week periods	Above (120 cm) and below (40 cm) the rice crop canopy, 6 per height	PAHs, OCPs	463
PUF disks in ABS can with bottom that has holes	Sealed PVC chamber within greenhouse over soil spread on the ground, six 10 day periods	5–8, 15–18, 30–33 cm, no replicates	HCHs, DDTs	170
PUF disk in stainless steel housing with open mesh-covered bottom (4 cm diameter opening)	Pasture in Tibet, two 2 month periods	2, 3, 5, 8, 10, 15, 20, 50, 80, 120, 200 cm, 3 per height pooled	OCPs	171
PE strip, 5 per metal box with open bottom over soil, 5 per box in upright metal chimney in air	3 historically contaminated sites (Anniston, Alabama Wyckoff, Washington, Mosie, Oregon) in USA, one 14 day period	4 replicates right above soil and 3 replicates at <i>ca.</i> 150 cm above it	PAHs, PCBs	70
PE strips placed beneath a metal plate	1 urban green space, Shanghai, China, seven 2 to 8 week periods	5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 150, 200 cm	PAHs	76

gradients with the PUF-PAS, whose SR becomes highly susceptible to wind at the wind speeds encountered at height.<sup>130,466</sup>

**G.3.3 Vertical gradients in mountains.** At an even larger vertical scale, PASs have been used repeatedly to study air concentration gradients along mountain slopes (Table 23). Often, those studies could also be classified as transects as defined in Section G.2 above. Studies have been conducted on mountains in Europe,<sup>467,468</sup> Western Canada,<sup>452,469–471</sup> South American mountains,<sup>195,472–475</sup> the Southern and Eastern slope of the Himalayas,<sup>65,194,476–481</sup> as well as on the island of Hawaii.<sup>482</sup> The largest elevational range exceeds 5000 m on the Southern slope of the Himalayas.<sup>476,479</sup>

The issue of SR variability with elevation can also arise along mountain transects, where the wind speed may vary between sites at different elevation. The majority of these studies used

the XAD-PAS, but the PUF-PAS and SPMDs have also found use. Because DCs cannot be used with the XAD-PAS, other ways to correct for variable SRs may be required. Sites where a PAS is exposed to very high wind can often be identified when all target chemicals have elevated sequestered amounts.<sup>194</sup> The deployment time-normalised sequestered amount of a chemical that can be assumed to have uniform air concentrations along the elevation gradient has been used to adjust SRs. The amounts of HCB sequestered by a XAD-PAS can often serve this purpose, as long as there are no major sources of HCB in the vicinity of the transect.<sup>194,195,482</sup>

A common theme among those studies is the investigation of mountain cold-trapping, especially when combined with measurements of concentrations in soils (e.g. ref. 391, see also Section G.8.2). Remarkably, air concentrations of endosulfan



Table 22 Studies involving PASs measuring vertical gradients of SVOC concentrations on a tower

Sampler	Location, sampling heights	Time frame	SVOCs	Ref.
POG	CN Tower, Toronto, Canada 6 heights (30, 90, 150, 210, 270, 360 m)	Oct. 2001, three 1 week periods	PAHs, PCBs, OCPs	94
PUF-PAS	CN Tower, Toronto, Canada 5 heights (30, 90, 150, 210, 270 m)	May to Sep. 2005, five 1 month periods	OCPs	465
PUF-PAS	Meteorological tower Hazelrigg field station, Lancaster, UK 5 heights (3, 5, 10, 20, 30 m)	Apr. to Jun. 2006, one 54 day period	PCBs, OCPs	135
PUF-PAS, SPMD	Norunda Common, Sweden 8–9 heights (2.5, 9, 14, 19, 25, 44, 68, 73, 96 m)	May to Jul. 2007, one 40 day period	PCBs, OCPs	130
PUF-PAS	Meteorological tower, Beijing, China 9 heights (15, 47, 80, 120, 160, 200, 240, 280, 320 m)	Dec. 2006 to Jan., May to Jul., Jul. to Aug. 2007, three 2 month periods	PCBs, OCPs	466

are often found to increase with elevation,<sup>65,195,470</sup> consistent with its high potential for mountain cold trapping.<sup>195,391</sup> Some studies compare forested sites with sites in clearings to explore the influence of vegetation.<sup>65,468,471,478</sup> Others compare the levels from sampling sites on different sides of a mountain.<sup>65,471</sup> In many cases, source proximity is found to govern the air concentration variability along such transects.<sup>471</sup> For example, proximity to traffic arteries is the main variable controlling PAHs concentrations in Canadian mountain air<sup>452</sup> and on Hawaii, the highest concentrations of many OCPs occur in the vicinity of major towns.<sup>482</sup>

#### G.4 Spatial variability in indoor air concentrations and inhalation exposure

Air concentrations vary of course also in different indoor environments, depending mostly on the presence and strength of indoor sources, but also on characteristics of the indoor environment, such as room ventilation rate or the availability of sorbing compartments. Interest in air concentration variability in indoor environments is driven by the desire to characterise human inhalation exposure to SVOCs, considering that most humans spend the majority of their time indoors. While for most SVOCs, exposure routes other than inhalation are considered dominant and health-relevant, inhalation exposure can be an important contributor to total exposure, *e.g.* if concentration levels are very high.<sup>485</sup> Occupational environments are particularly susceptible to having high indoor concentrations of SVOCs.

PASs have been used in several studies seeking to measure air concentrations of SVOCs indoors (Table 24). While access to electricity is usually not difficult in indoor environments and the use of active air sampling techniques is often feasible,<sup>486</sup> PAS-based approaches tend to be less noisy and obtrusive and allow for cost-effective sampling in a larger number of locations,<sup>487</sup> *e.g.* in various locations within a room<sup>108</sup> or within a building,<sup>488</sup> or, more typically, in a number of different buildings.<sup>145,161,489</sup> A common theme is also the use of PASs to compare levels in different types of indoor environments, such

as offices and residences,<sup>489</sup> or between the indoors and outdoors.<sup>146,161,490</sup> The ultimate goal is often the assessment of personal inhalation exposure for large, epidemiological health studies.<sup>491,492</sup> In this context, there is also interest in portable, personal PASs that measures concentrations of SVOCs in the breathing zone of an individual.<sup>166,167</sup>

A wide variety of PASs have been used indoors, including SPMDs,<sup>24,49,488,493</sup> PE-based PASS,<sup>490,494</sup> SIP-PASS,<sup>145,146,495</sup> the original PUF-PAS<sup>24</sup> or modification of it with different types of housing.<sup>156,163,164</sup> Most recently, also a number of PASs based on PDMS have been introduced<sup>112,114</sup> and used.<sup>496</sup> While some studies compared different PASs with each other,<sup>113</sup> others compared PAS-derived indoor air concentrations with concentrations in other media that may serve for exposure assessment, such as surface wipes, window films or house dust.<sup>497</sup>

#### G.5 Aspects related to using PASs for probing spatial variability

**G.5.1 Reporting amounts sorbed per time period *vs.* volumetric concentrations.** As shown in eqn (5), an SR is required to convert the amount of an SVOC quantified in the sorbent of a PAS operating as a kinetic sampler into a volumetric air concentration. As discussed in Sections F.2 and F.3, SRs often have considerable uncertainty. If the main objective of a study is the recording of spatial patterns, as may be surmised for most of the studies listed in Sections G.1 to G.4 above, the conversion of sequestered amounts into volumetric air concentrations may not always be necessary. The key question then is whether the spatial concentration differences that a study seeks to resolve are larger than the uncertainty in the SR. If that is the case, the uncertainty in the SR is less of a concern and it may be sufficient to report the concentration patterns in units of mass sequestered per unit of time (*e.g.* per day or per the nominal deployment period such as one month or one year). Especially, if a generic SR is to be applied *i.e.* not one that is specific to a particular deployment, it may in fact be more transparent to not report volumetric air concentrations: the time-normalised sequestered amount has less uncertainty than the calculated



Table 23 Studies using PASs to record gradients in SVOC air concentrations along mountain slopes

PAS	Location, no. of sites	Time frame	SVOCs	Ref.
SPMD	3 sites (1600, 2240, 2600 m) in the Pyrenees, Catalonia, Spain	Mar. 2002 to Jun. 2003, 85, 161 and 210 days	HCB, PCBs	467
PUF-PAS	12 or 13 sites at four elevations (700, 1010, 1420, 1790 m) on Mont Mars, Alps, Italy	Sep. to Oct. and Oct. to Nov. 2003, 52 and 33 days	PCBs, HCB, <i>p,p'</i> -DDE, <i>p,p'</i> -DDT	468
XAD-PAS	8 sites (570–1951 m) on Mount Revelstoke, BC, Canada 6 sites (1109–2561 m) in Yoho National Park, BC, Canada 8 sites (1402–2902 m) on Observation Peak, Banff National Park, Alberta, Canada	Aug. 2003 to Aug. 2004, one 1 year period	OCPs PAHs	469 452
XAD-PAS	5 sites (800–2740 m) in Canadian Rocky and Purcell Mtns., British Columbia, Canada	Mar. to Aug. 2004, one 5 month period	PFAS, HCHs, endosulfan	470
PUF-PAS	4 sites (1820, 2600, 4650, 5200 m) on east side of the Andes, Bolivia	Feb. 2005 to Jan. 2006, four 3 month periods	OCPs, PCBs	472
XAD-PAS	9 sites (1242–4485 m) on Balang Mtn., Wolong Nature Reserve, Sichuan, China	2005 to 2008, five 6 month periods	OCPs, PCBs	194
PUF-PAS	4 sites (400–2200 m) in Serra dos Orgaos National Park, Brazil 4 sites (600–1800 m) in Sao Joaquim National Park, Brazil	Jun. to Aug. 2007 and Dec. 2007 to Mar. 2008, two 90 day periods	PCBs, PBDEs OCPs	473 474
XAD-PAS	6 sites (135–5100 m) on the Southern slope of the Himalayas in Nepal	May to Nov. 2012	OCPs, PCBs PAHs	476 477
PUF-PAS	3 sites (3800, 4200, 4400 m) on S-slope, 2 sites (4200, 4400 m) on N-slope of Sygera Mtn., Tibet, China	Jan. 2008 to Jan. 2012, sixteen 3 month periods	OCPs, PCBs	478
XAD-PAS	18 sites (1983–4553 m) on Shergyla Mtn., Tibet, China	Jul. 2010 to May 2011, two periods of 4 and 7 months	OCPs, PCBs, PBDEs, HBCD	65
XAD-PAS	6 sites (48–4405 m) in Northern Chile 7 sites (10–1874 m) in Central Chile 5 sites (50–760 m) in Southern Chile	Feb. 2006 to Jul. 2007, one 1 year period	OCPs, CUPs, PAHs, PCBs	195
XAD-PAS	3 sites (500, 1310, 2052 m) in Swiss Alps, Switzerland	Jul. 2006 to Oct. 2006, one 4 month period	OCPs, PCBs	483
XAD-PAS	9 sites (0 to 3400 m) on Hawaii Big Island	May to Sep. 2011	OCPs, PAHs, PBDEs	193 and 482
XAD-PAS	18 or 20 sites (1983–4553 m) on Shergyla Mtn., Tibet, China	Jul. 2012 to Jul. 2015, one 1 year period	SCCPs, MCCPs	480 and 481
LDPE-PAS	4 sites (700 to 2400 m) on Serra do Mar and 4 sites on (990 to 1700 m) on Serra Geral, Brazil	May to Jun. 2012, one 30 to 40 day period	PAHs	484
XAD-PAS	4 sites (60–600 m) on Mt. Anderson, BC, Canada 4 sites (350–950 m) on Grouse Mtn. 4 sites (90–700 m) on Four Brothers Mtn. 3 sites (400–800 m) on Blue Grouse Mtn. 1 site on Chilkoot Trail (435 m)	Aug. 2007 to Aug. 2008, 1 year period	PAHs, PCBs	471
XAD-PAS	8 to 9 sites (100–5200 m) on the S-slope of the Himalayas in Nepal	May 2012 to Nov. 2014, five half year periods	OCPs, PCBs	479

concentration, because the latter inherits the uncertainty of the SR. Several early PAS studies had reported spatial results in amount per sampler or amount per sampler per time,<sup>29,280,390,391,432,433,448,469</sup> but only recently has there been a re-emergence of support for not necessarily reporting volumetric air concentrations.<sup>514–517</sup> This approach is clearly advisable when using a PAS whose SR under a given set of circumstances is not well established or even unknown. A good example is the study attaching a PAS to a gull, where it was entirely possible to

compare the exposure of different birds using time-normalised sequestered amounts.<sup>518</sup>

The issue of SR uncertainty becomes paramount when small concentration differences are to be discerned. This issue is further compounded if the concentration differences occur along a spatial gradient where factors with an influence on the SR (most notably wind speed, but possibly also temperature) may be expected to vary systematically. Examples are:



– Comparing indoor and outdoor deployments:<sup>490,492</sup> indoor environments tend to experience much lower air turbulence and therefore lower SRs, which could lead to the underestimation of indoor concentrations when compared to outdoor deployment.

– Elevational transects of any scale (see Section G.3) can be expected to experience gradients of wind speed, with wind speeds increasing with height. This is particularly problematic when trying to observe air concentration gradients that increase with elevation.

– Comparing deployments under a forest canopy to deployments in unsheltered locations.<sup>65</sup> The SR for the PUF-PAS is predicted to be much lower in forested regions and much higher over the ocean.<sup>126</sup>

When concentration differences between sites with different wind exposure are small, it is necessary to derive deployment-specific SRs, *e.g.* through the use of DCs, or choose a sampler design with an SR that is not, or at least less, dependent on wind speed. For example, the application of DC-derived, elevation-specific SRs changed the concentration gradient with height along a tower.<sup>130</sup>

It is important to realise that during the interpretation of spatial PAS data, one is not limited to comparing concentrations or time-normalised sequestered amounts, but it is possible to investigate compositional changes. If wind speed influences SRs, it does so for all target chemicals and not just for one. Compositional patterns thus are not, or at least less, affected by spatial variability in wind. Cluster analysis is particularly useful when interpreting compositional changes across a PAS network.<sup>477,519,520</sup>

Of course, there are often objectives of PAS studies that go beyond deciphering of spatial patterns and these may require the calculation of volumetric air concentrations. Examples are: (i) data obtained from different sampling methodologies are to be compared,<sup>521</sup> (ii) PAS data are to be combined with data from adjoining environmental media such as water or soil in order to derive information on air–surface exchange, which is discussed in detail in Section G.8 below, or (iii) PAS-derived data on inhalation exposure are to be used in risk assessment, which is discussed in Sections G.4 and G.5.5.

**G.5.2 Sampling site representativeness and scale.** The number of sites in PAS networks varies widely from less than a handful to more than 100. No matter how large the number of sites within a network may be, the issue of representativeness of sites is important. This is particularly relevant for large scale networks, where a site is often meant to represent a large area. In some of the continental or global networks listed in Sections G.1.5 and G.1.6, an entire country may often be represented by a single sampling site. Depending on the nature of that site, completely different results could be obtained. For example, within GAPS, the French site often shows the highest concentrations, merely by virtue of being located within Paris.<sup>127,447</sup>

Gawor *et al.*<sup>197</sup> analyzed PASs from a global and two national networks for PFAS and used it to assess to what extent one site from the global GAPS network in each of Botswana and Costa Rica represents the national average as obtained from national networks in those two countries. In both cases, the levels of PFAS measured at the GAPS site were lower than the levels

measured across the country, suggesting that these sites are representative of the more remote parts of Botswana and Costa Rica.

One potential application of a PAS network is in fact to assist in the selection of a representative sampling site or in the determination of the number of sites that is required to appropriately represent a particular area. For example, the purpose of a PAS network across Chicago was to establish how representative an active air sampling site is of the city as a whole.<sup>308</sup> A network of PASs across the Czech Republic was used to address the issue of representativeness more comprehensively by not only comparing absolute concentration levels of different SVOCs but also time trends obtained from those sites.<sup>516</sup> Cluster analysis based on levels and trends revealed that the fourteen sites belonged to one of three types, whereby sites belonging to a cluster share characteristics related to remoteness, landscape, population, and pollution sources and therefore also their pollution profile. An analysis like this could assist in optimizing the elimination of sampling sites from a network, by finding the number and location of sites that yield the most information with the least number of sites.<sup>516</sup>

**G.5.3 Mapping and interpolation.** Related to this issue of site representativeness is the question of whether it is justified to interpolate the levels measured by PASs at different sampling sites, *e.g.* by geo-statistical methods, such as kriging. This is likely only appropriate if it can be assured that there are no major sources of an SVOC between any pair of sampling sites, *e.g.* in a small-scale network with one or a few clearly dominant emission sources (*e.g.* for some of the studies summarised in Table 13). A few studies have attempted to create urban concentration maps through interpolation (Fig. 10A).<sup>342,360</sup> The results are not always very convincing,<sup>301,340</sup> mostly because relatively large concentration differences can occur over small distances and the number of sampling sites is generally insufficient. When seeking to map urban air pollution, a minimum number of sampling sites of 0.29 multiplied with the urban surface to be monitored in  $\text{km}^2$  has been recommended, based on work with VOCs and  $\text{NO}_2$ .<sup>522</sup> None of the urban PAS networks for SVOCs (Table 14) comes close to fulfilling this criterion. A more defensible way of displaying the spatial variability of PAS networks is to use a map that visualises the variability in the measured levels, but does not seek to interpolate values in areas where no sampling was done (see Fig. 10B for a good example).

A more sophisticated strategy for urban pollution mapping is land use regression analysis, where air pollution monitoring data are combined with stochastic models that rely on predictor variables that are typically obtained through geographic information systems.<sup>523</sup> While quite common for classical air pollutants (such as VOCs,  $\text{PM}_{2.5}$  and  $\text{NO}_2$ ), land use regression has, to the best of our knowledge, only been applied once to PAS data for SVOCs, namely to identify potential sources of PCBs, PBDEs, PAHs, and polycyclic musk compounds in Toronto.<sup>524</sup> A large fraction of the observed variability in PCB air concentrations could be related to the distribution of PCBs in use/storage/building sealants, whereas that of the musk compounds was strongly related to population density.<sup>524</sup>



Table 24 Studies using PASs to study SVOC air concentrations indoors

PAS	Location, no. of sites	Time frame	SVOCs	Ref.
SPMDs	10 homes and outdoor sites in Makwanpur region, Nepal	One 11 day period	PAHs	493
PUF-PAS w/o double bowl	74 homes and 7 outdoor locations in Ottawa, Ontario, Canada	One 3 week period (outdoor 3 months)	PBDEs	161
	59 homes for FOSE/FOSA		MeFOSE, EtFOSE, EtFOSA, MeFOSEA	162
SPMDs	52 homes for FTOHs		10:2 and 8:2 FTOH	136
PUF-PAS	15 homes in Hagfors, Sweden	One 2 week period	PAHs, PCBs	49
	31 homes, 33 offices, 25 cars, 3 public indoor spaces in Birmingham, UK	One 28 day period	PCBs, PBDEs	489
PUF-PAS w/o DB	35 homes and 11 outdoor locations in Mexico City, Mexico, Gothenburg, Sweden and Lancaster, UK	One 6 to 7 week period	PAHs, OCPs, PCBs, PBDEs	429
SPMDs	52 homes situated along the border between Arizona and Mexico (four locations in each home, pooled)	One 30 day period	PAHs, PCBs, OCPs, some non-target	488
SIP-PAS	59 homes and 6 outdoor locations in Vancouver, Canada	One 4 week period (outdoor 3 months)	Neutral and ionic PFAS	145
SIP-PAS	6 homes, 2 public indoor spaces and 6 outdoor sites in 3 major cities	One 20 day period (indoor) one 90 day period (outdoor)	Neutral PFAS	239
PUF-PAS	17 indoor and 18 outdoor sites in 10 cities in South Korea			
SIP-PAS	20 homes, 12 offices, and 10 outdoor locations in Birmingham, UK	One 1 month period, 12 monthly periods at 8 sites	Neutral and ionic PFAS	146
PUF-PAS	20 homes, laboratories and offices in Toronto, Canada	One 27 to 38 day period	PCBs, PBDEs	498
Triolein coated vial	2 car interiors, 4 occupational indoor, 12 outdoor sites in Malaysia	One 37 day period	Synthetic musk PAHs	288 499
PUF-PAS (single bowl in North America)	63 homes in Bloomington, Indiana, United States, Toronto, Canada, Brno, Czech Republic, 1 or 2 rooms per home, 23 homes in Toronto, Canada, 20 homes in Brno, Czech Republic	One 28 day period	PBDEs, BFRs 13 OPFRs OCPs, PCBs	500 501 502
PUF-PAS	Inside and outside of 6 schools in East Chicago, Indiana and Columbus Junction, Iowa, USA	Multiple periods of 48 days average (22 to 114 days)	PCBs, hydroxylated PCBs	492
PUF-PAS	Indoors and outdoors at schools and homes ( $n = 293$ ), Greater Chicago Metropolitan Area, USA	Quarterly (homes), bi-quarterly (schools), 45 days	PCBs	491
PUF-PAS	20 homes, offices, 10 outdoor in suburban and urban in Shanghai, China	Two 56 day period	PBDEs	503
PUF-PAS	15 indoor samples (university, hospital, school) and 2 outdoor samples (playing area at university) in Ouargla city, Algeria	One 61 day period	PAHs, phthalate	504
PUF-PAS	34 homes in Pokhara, Birgunj, Biratnagar and Kathmandu, Nepal	One 2 month period	PBDEs, HFRs	505
PUF-PAS	20 homes (20 living rooms and 13 bedrooms) and 20 offices in Hangzhou, China	One 90 day period	PBDEs	506
PUF-PAS	Three offices (low-use, medium-use and high-use) in Beijing, China	Three consecutive 28 day periods	BFRs	507
PUF/GFF-PAS				



Table 24 (Contd.)

PAS	Location, no. of sites	Time frame	SVOCs	Ref.
SIP-PAS	57 homes in Kuopio, Finland	One 21 day period	PFAS	508
PUF-PAS	16 sites in offices and residential buildings in Beijing, China	Two 60 day periods	SCCPs, MCCPs	509
PUF-PAS	16 residences in Iowa City, Iowa	One 6 week period	PCBs	165
PUF-PAS and PDMS	51 homes in Ottawa and Toronto, Canada	One 3 week period	Phthalates, PBDEs, novel BFRs, OPFRs	112
LDPE-PAS	33 apartments, 33 car interiors, 60 offices, 30 outdoor locations in Alexandria, Egypt	One 2 month period	OPFRs	494
SIP-PAS	3 buildings in Uppsala, Sweden	One 140 day period	FTOHs, cVMS, BFRs, OPFRs	495
LDPE-PAS	6 urban sites with matched indoor and outdoor samples in Eugene, Oregon	Seven 24 hour samples for 1 week	63 PAHs	490
PUF-PAS modified	14 residential houses and 14 offices in Brisbane and Canberra, Australia	One 2 to 3 month period	PAHs, PCBs, OCPs, CUPs	163
PUF-PAS	25 homes in Harbin, China	One 30 day period	PAHs, phthalates, PBDEs, OPEs	510
PUF-PAS	8 residential buildings and 3 outdoor locations in Bursa, Turkey	Two 44 to 45 day periods	PCBs	511
PDMS	63–71 apartments in Toronto, Canada	Two 1 week periods	PBDEs, PAHs, BFRs, phthalates	496
PUF-PAS (PUF-cyl)	Two Swedish vessels (Icebreaker and cruise ship)	Two 6 to 7 day periods	PAHs, alkylated PAHs	512
PUF-PAS	11 biological, 15 chemical and 14 physical laboratories, 3 offices	One 21 day period	Phthalates	513

While not quite a land use regression, several PAS studies have sought to regress PAS-derived concentration data for PAHs with spatially resolved data on population density. PAHs concentrations measured at different sites of the global GAPS network have been regressed against four different means to quantitatively express the proximity of those sites to people.<sup>449</sup> The remoteness index, which is derived from a global atmospheric transport model, explained as much as 60% of the variability in the concentration of fluoranthene. Despite the simplicity of this variable, the number of people living within 20 km of a sampling site explained even more of the variability in the concentrations of the sum of PAHs measured around the lower Great Lakes.<sup>82</sup> Concentrations of SCCPs measured across Australia also correlated well with a number of variables, including population density, number of roads and site classification (*i.e.* remote, rural and urban).<sup>277</sup>

**G.5.4 PAS networks and spatial modelling.** There have been several studies that used the spatial information from PAS networks in modelling studies. Sometimes this involves the comparison of the measured spatial distribution with one obtained from models. Fine-scale emission estimates and a dynamic atmospheric model have been used to simulate the distribution of acenaphthene in the atmosphere of Nanjing, China,<sup>338</sup> and of DDTs, HCB, PCBs and PBDEs in Mendoza, Argentina.<sup>332</sup> Empirical travel distances could be estimated from the air concentration variability across a latitudinal transect in North America to evaluate the characteristics travel

distances of OCPs calculated with models designed to assess a chemical's long-range transport potential.<sup>29</sup> At other times, models are used to describe the observed spatial variability. For example, a radial dilution model was applied to fit the SVOC concentration variability across Toronto and to probe the relative importance of sources within and outside of the city's central business district.<sup>458</sup>

**G.5.5 PAS networks and human exposure and toxicity.** One of the motivations for interpolating PAS measurements of air pollution levels is their potential use for human exposure assessment and therefore use in epidemiological research. However, not for all air pollutants can a stationary network of PASs allow for a reliable prediction of personal exposure levels.<sup>525</sup> For many SVOCs, air concentrations generally are less pertinent for human exposure and health effects, as inhalation is rarely a dominant pathway for exposure. The PAHs are an exception. Accordingly, numerous PAS studies have sought to estimate inhalation exposure and the health risk associated with exposure to airborne PAHs.<sup>336,348,361–363,439,526</sup> This is typically done by summing the products of the concentration of carcinogenic PAHs with their relative potency factors in order to obtain an equivalent concentration of benzo[*a*]pyrene, which in turn can be converted into a chronic daily inhalation intake rate. Sometimes, a value for the cancer risk due to inhalation is derived as well.

Even though inhalation is generally not believed to represent a large fraction of the total intake of compounds with dioxin-



like toxicity, some studies similarly calculate a toxic equivalence concentration (TEQ) using the product of the concentrations of the toxic PCDD/Fs, PCBs, and PCNs congeners and their toxic equivalent factors (TEFs), which in turn is used to calculate the TEQ intake by inhalation.<sup>309,312,345,382,416,527</sup> In other studies, the inhalation exposure and risk are estimated for individual substances<sup>285,299</sup> rather than for equivalent concentrations. Some studies performed probabilistic exposure-risk modeling.<sup>363,382</sup> Again, often a cancer risk is estimated for dioxin-like substances. In other studies, the estimated inhalation exposure is compared with reference doses to estimate risk.<sup>304</sup>

In the above studies, the health risk assessment is based on the SVOC air concentrations measured with the PAS. Another approach to probing the spatial variability in inhalation toxicity is to perform *in vitro* bioassays using the extracts and dialysates obtained from PASs (Table 25). In the nine studies we found in the literature, either SPMDS, PUF-PASs or PE-PASs were deployed mostly in areas with elevated SVOC levels, namely urban location<sup>271,322,413,528-530</sup> or sites impacted by industrial activity.<sup>327,531,532</sup> The bioassays explored genotoxicity,<sup>322,327,413,528,529,531</sup> dioxin-like toxicity modulated *via* the aryl hydrocarbon receptor (AhR),<sup>271,413,530,532</sup> estrogenicity,<sup>530,532</sup> and cytotoxicity.<sup>327</sup>

The PAS extracts were in most cases also subjected to chemical analysis, most frequently for PAHs. In some cases, more extensive chemical characterisation was undertaken, *e.g.* in addition to PAHs, extracts have been analysed for PCBs and OCPs,<sup>322</sup> alkylated PAHs and benzothiophenes,<sup>327</sup> and alkylated PAHs and OPE.<sup>271</sup> By subjecting the extracts to  $H_2SO_4$  treatment prior to the bioassay, it is possible to investigate whether recalcitrant or degradable compounds in the extracts are responsible for the detected biological activity.<sup>413,530</sup> Eventually, the biological activity of samples deployed in different locations or during different seasons<sup>413</sup> is compared. Studies typically also investigate whether biological activity and SVOC concentrations in samples correlate.

PASs have also been used for the assessment of exposure of birds to SVOCs. Stationary PUF-PAS deployed in Hamilton harbour were used to assess the exposure of double-crested cormorant colonies to PAHs,<sup>533</sup> whereas a miniaturised sampler strapped to the back of gulls was used to observe that PASs attached to birds foraging in or around landfills accumulated higher levels of PBDEs, but not of three other BFRs.<sup>518</sup>

While the applications described in Sections G.1 to G.5 in some way take advantage of the ability of PASs to efficiently provide spatial information on SVOCs in the atmosphere, not all PAS studies are motivated by the need for characterisation of spatial variability. Some of the other application areas of PASs are discussed in Sections G.6 to G.8.

## G.6 Extreme remote region monitoring (polar regions, Tibet, mountains)

Because they do not require power, PASs have found use in the monitoring of SVOCs in very remote or otherwise difficult to access locations. Examples are high mountain areas, and polar research stations and field camps. One challenge for sampling in such locales is often that access is very difficult and expensive and it may be only possible to visit sampling sites once a year. Long term deployments require a PAS with long  $t_{\text{linear}}$ , *i.e.* a high uptake capacity and the capability to work at extremely low temperatures. DCs often do not work well at low temperatures, because of insufficient loss rates,<sup>126</sup> yet these remote sites often experience very high winds and are therefore in particular need of deployment-specific SRs. Its high uptake capacity explains why the XAD-PAS is frequently used in such situations.<sup>520,534-540</sup> It is probably not by coincidence that PE, PUF and SIP-PASs are only used during the short and milder summer seasons.<sup>90,541,542</sup>

Another challenge for passive sampling in remote areas are the often very low SVOC concentrations, which, when combined with relatively low SRs, can result in sequestered amounts below detection limits. The FTS can achieve sampling volumes in the 1000s of  $\text{m}^3$  and is therefore used when regular site access is

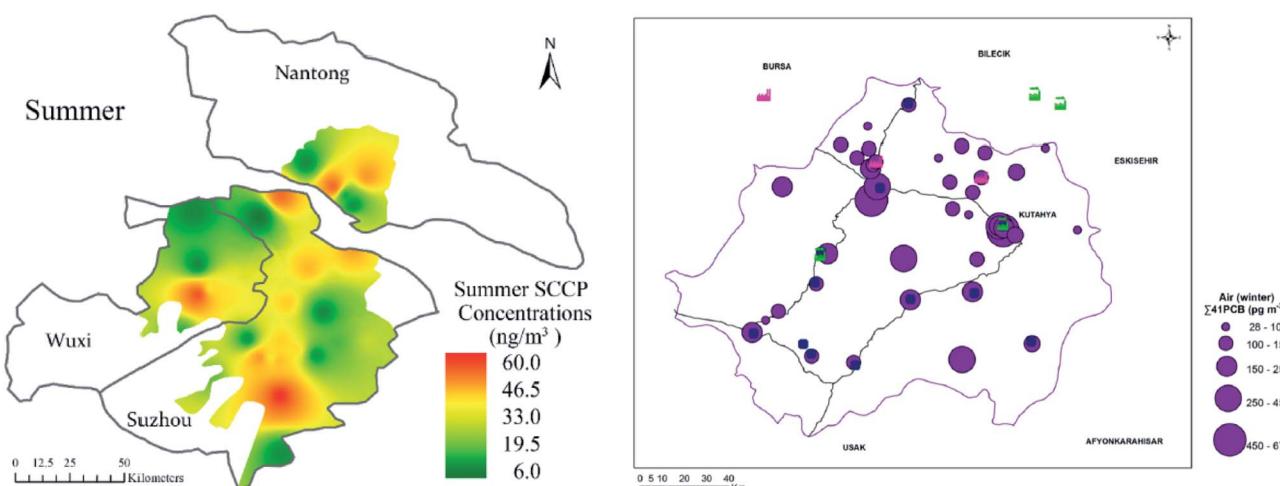


Fig. 10 Two examples of how spatial variability in air concentrations as determined by PAS networks has been displayed, either using interpolation<sup>360</sup> (left) or not<sup>363</sup> (right). Reproduced from ref. 360 and 363 with permission from Elsevier, Copyright 2017 and 2020.



Table 25 Studies that use assays to probe the biological activity of extracts obtained through passive air sampling

Sampler	Location, no. of sites	Bioassays	Ref.
SPMDs	5 sites in Caserta, Italy, One 3 week period	Microtox (inhibition of bioluminescence of <i>V. fischeri</i> ) Mutatox (genotoxic reversion of dark mutants of <i>V. fischeri</i> ) Bacterial genotoxicity test using <i>E. coli</i> sulA::lacZ	528
PUF-PAS	20 sites across Brno, Czech Republic, one 28 day period in Oct./Nov. 2004	Bacterial genotoxicity test using <i>E. coli</i> sulA::lacZ	322
SPMDs	4 sites in Vilnius, Lithuania, four 8 week periods in different seasons in 2002–2003	Chromosome aberrations and sister chromatid exchanges (SCEs) in human blood lymphocytes <i>in vitro</i> SMART: somatic mutations and recombination in <i>Drosophila melanogaster</i> wing cells <i>in vivo</i> Comet assay ( <i>in vitro</i> DNA-damaging activity in human cells) Mutagenicity (Ames test TA98 strain, w/o S9)	529
SPMDs	6 sites in an occupational setting of a coke plant, incl. an office as a control, one 24 day period in winter	Estrogenic (E-SCREEN-MCF7- BOS) AhR (CAFLUX-H4G1.1c2)	531
PUF-PAS	6 offices and inside and outside of a suburban home in Brisbane, Queensland, Australia, one 40 to 50 day period in Apr. to Aug. 2007	Indirect acting genotoxicity (umuC assay) AhR	413
PUF-PAS	4 urban, 3 rural, and 1 background sites across Australia, two 40 to 50 days periods in Jan. to Feb. 2007 and Jul. to Aug. 2007	AhR (anti-)estrogenicity, (anti-)androgenicity	532
PUF-PAS	1 background and 1 urban/industrial site in each of Lithuania, Slovakia, Romania, and Serbia, one 5 month period in Mar. to Aug. 2006	Salmonella mutation Mammalian lactate dehydrogenase cytotoxicity AhR	327
PUF-PAS	15 sites across the Athabasca Oil sands region, one 60 day period in Apr. to May 2014		
PE-PAS	9 sites in the Cleveland, Ohio area, one 60 day period in Jul. to Sep. 2013		271

possible (e.g. in research stations that are operating year-round), but electricity supply is difficult. Even if a research station has electric power, it is often desirable to sample at a site sufficiently removed from station buildings and human activities (and therefore electricity) to avoid the possibility of contamination. The FTS has been used on the Tibetan plateau and in Arctic, sub-Arctic and Antarctic research stations.<sup>176–181</sup>

Table 26 summarises studies that have used PASs in extremely remote environments. A vertical mountain transect is a particular type of study in remote regions. These studies are discussed in Section G.3.3 above and summarised in Table 23. Some of the studies in extremely remote regions have been going on for several years and allow for the observation of time trends,<sup>181,539</sup> which is further discussed in Section G.7 below.

## G.7 Time trend monitoring

Long term time trends in the air concentrations of SVOCs are an important method to assess the effectiveness of measures to reduce emissions of those compounds. Traditionally, this is being done using active air sampling campaigns. However, such campaigns require a long-term commitment of fairly significant resources in terms of personnel and finances. With the Stockholm Convention, there is a greatly increased need for such time trend monitoring in the context of the Convention's effectiveness evaluation. An important motivation for

developing PASs for SVOCs therefore was the prospect to determine long-term, interannual temporal trends in air concentrations much cheaper and with less effort. One of the advantages of PASs in this regard is that they can provide time-averaged concentrations over long time periods. The challenge of deriving long term trends from active sampling campaigns is that the latter usually sample only during a small fraction of time and therefore the time periods of active sampling need to be representative, which requires a relatively large number of samples.<sup>448</sup>

On the other hand, atmospheric concentration changes over time may be quite subtle and, considering the uncertainty of SRs for many PASs, it may be questioned whether the precision of PASs is sufficient to detect such changes. Shunthirasingham *et al.* have argued that the uncertainty of the SR is of diminished concern when the main interest is in the trend and not in the absolute concentration levels and if the PAS sampling sites are not changed.<sup>448</sup> The reason is that the factors that result in SR variability (most notably wind speed) should be reasonably constant from year to year at the same site. Therefore, the uncertainty of the SR is not propagated to the uncertainty of the temporal trend. In fact, time trends can be derived from time-normalised sequestered amounts, *i.e.*, no SRs are required at all.<sup>448,515,516</sup>



Table 26 Studies using PASs in extremely remote environments

Sampler	Location, no. of sites	Time frame	SVOCs	Ref.
SPMD	3 sites (Weissfluhjoch, Switzerland, Zugspitze, Germany, Sonnblick, Austria)	May to Nov. 2005, Dec. 2005 to May 2006, May 2005 to May 2006, Three periods	OCPs	60
XAD-PAS	3 sites at each of Ny-Ålesund and King George Island, Antarctica	Aug. 2005 to Aug. 2006 (Ny-Ålesund), Dec. 2004 to Dec. 2005 (King George)	PCBs, OCPs	534
XAD-PAS	3 sites at each of King George Island, Ny-Ålesund, and Chuuk, South Pacific	Dec. 2004 to Dec. 2007 (Ny-Ålesund), Aug. 2005 to Jun. 2007 (King George), Feb. 2006 to Oct. 2009 (Chuuk), three 1 year periods	PCBs, OCPs	535
XAD-PAS	1 site at Cape Vera, Devon Island, Nunavut, Canada	2006 to 2008, two 1 year periods	HCB, <i>p,p'</i> -DDE, $\alpha$ -HCH, heptachlor epoxide, PCBs	537
XAD-PAS	16 sites on the Tibetan Plateau, China	Jul. 2007 to Jun. 2008, 1 year period	PCBs, OCPs, PBDEs	536
	13 sites		PAHs	543
	16 sites	2007 to 2012, five 1 year periods	PCBs, OCPs	520
SIP-PAS	16 sites on the Tibetan Plateau, China	May to Jul. 2011, May to Jul. 2013, two 3 month periods	VMS, PFAS	544
FTS	1 site at Nam Co Lake, Tibet, China	Oct. 2006 to Feb. 2008, fifteen 1 month periods	PCBs, PAHs, OCP	180
FTS	1 site at Alert, Nunavut, Canada	Oct. 2007 to Dec. 2008, eleven consecutive one-month periods	PBDEs, TBPH, EHTeBB, BTBPE	176
FTS	1 site at Little Fox Lake, Yukon, Canada	Aug 2011 to Dec. 2014, 42 consecutive one-month periods	OCPs, PBDEs, TBPH, EHTBB, BTBPE	177
FTS	2 sites at Toolok field station, Alaska, USA	Jul. to Aug. 2013, three consecutive 18 day periods	PBDEs	178
FTS	1 site at Casey station, Antarctica	Dec. 2009 to Nov. 2014, thirty-three consecutive samples (4 to 6 weeks, some 3 months)	PCBs, OCPs	181
PUF-PAS	5 sites on King George Island, Antarctica	Dec. 2009 to Feb. 2010, 2 months	PCBs, PBDEs	541
XAD-PAS	4 sites on King George Island, Antarctica	2009–2010, 1 year	PCBs	538
PUF-PAS	2 sites in National Parks Itatiaia (2470 m) and Serra dos Orgaos (2200 m), Brazil	Sep. 2013 to Oct. 2015, eight ~3 month periods	OCPs, CUPs	475
XAD-PAS	7 sites on King George Island, Antarctica	Dec. 2010 to Jan. 2018, 7 consecutive 1 year periods	PCBs, OCPs, PBDEs	539
LDPE	1 site at Cape Bounty, Melville Island, Nunavut, Canada	Aug. 2015, 21 days, Jun. to Aug. 2016, 59 days	PCBs, HCB, $\alpha$ -HCH, <i>p,p'</i> -DDE	90
SIP-PAS	6 sites, Terra Nova Bay, East Antarctica	Dec. 2010 to Jan. 2011, One 1 month period	OCPs, PCBs	542
XAD-PAS	5 sites, Ny-Ålesund and London Island, Svalbard	Aug. 2014 to Aug. 2015, 1 year	OPEs	549

Kalina *et al.* investigated to what extent PAS-derived long-term trends agree with those derived from active air sampling campaigns.<sup>515,517</sup> The first comparison involved 534 active air samples and 132 PUF-PASs taken over a period of more than 10 years in Košetice in the Czech Republic.<sup>515</sup> The trends obtained from the two sampling methods generally agreed well, except when break-through of lighter SVOCs in the active sampling occurred or when levels of high molecular weight PAHs were too

uncertain because of low levels close to the detection limit. In particular, the study confirmed that time-normalised sequestered amounts can be used for trend determination from PASs and suggested that it can be advantageous to use annually averaged PAS values. Kalina *et al.* expanded on this work by comparing time trends from active and passive air sampling at five additional sites in Northern Europe.<sup>517</sup> While again good agreement in the trends from both sampling method was noted,



the comparison was limited somewhat by the shorter time periods of side-by-side sampling.

By now several multi-year trends obtained by PASs have been reported. Table 27 lists the studies that have derived temporal trends from at least four consecutive years of passive sampling. The longest such trend so far could be obtained from the transect of SPMD deployments at 11 sites in the UK and Norway, which comprises 12 years of sampling between 1994 and 2008.<sup>150</sup> This study clearly established declining trends of both PCBs and PBDEs in Northwestern Europe. Interannual time trends could also be derived from the XAD-PAS deployed within the global GAPS project for pesticides<sup>448</sup> and neutral perfluoroalkyl substances.<sup>197</sup> Somewhat confusingly, there are two national networks in Spain deriving temporal trends of SVOCs in the atmosphere. These networks, which have been sampling over the same time frame, using the same PUF-PAS, the same seasonal resolution, the same target compounds and even at a similar number of urban and rural locations, reported preliminary results from five years of sampling in 2016.<sup>545,546</sup> More recently, one of the networks has reported on seven years of continuous monitoring for PCBs, PBDEs, PCDD/Fs and selected OCPs at 12 locations across the country.<sup>548</sup> Among the findings are divergent trends for different PBDE congeners belonging to different technical mixtures,<sup>547</sup> as well as significant declines in the levels of dioxin-like PCBs and PCDD/Fs.<sup>548</sup>

Time trends of OCPs, PAHs, and PCBs have been derived from PUF-PASs deployed for multiple years at 14 sampling sites across the Czech Republic.<sup>516</sup> Levels for most PCBs and HCHs

declined significantly, but those of *p,p'*-DDE did not show trends and HCB and the PAH chrysene even showed increasing levels. Having time trends from multiple sites within a relatively small area allowed for the investigation of the spatial variability in those trends: three types of sampling sites could be identified which differ from each other in terms of the absolute levels and time trends. For example, four remote mountain sites were characterised by low levels of all SVOC types and decreasing levels of PAHs.<sup>516</sup>

PASs have particularly been useful for time trend determination in remote regions, where active sampling campaigns are often not feasible. Examples are Antarctica,<sup>181,539</sup> Tibet<sup>520</sup> or Mongolia.<sup>549</sup> In Antarctic air, concentrations of PCBs, HCHs, DDTs and endosulfans declined over a seven-year period, whereas those of HCB did not.<sup>539</sup> At a site in Mongolia, levels of HCB even increased, those of HCHs and DDTs declined, whereas there was no significant trend for the PCBs.<sup>549</sup> Over a five-year period, concentrations of HCB and HCHs declined on the Tibetan plateau, but no such trend was apparent for DDT-related substances.<sup>520</sup>

In some cases, while there may not be an extended period of continuous sampling, it can be possible to infer time trends if sampling sites are revisited after a hiatus of several years. For example, levels of pesticides measured with PASs in Brazilian mountains in 2014/15 could be compared<sup>475</sup> with those measured with the same technique in 2008.<sup>474</sup> Similarly, time trends of cVMS and PFAS could be derived<sup>443</sup> by comparing

Table 27 Studies deriving interannual time trends in atmospheric SVOC contamination from PASs

Sampler	Location, no. of sites	Time frame	Compounds	Ref.
SPMDs ( <i>n</i> = 66)	11 sites along UK-Norway transect	1994–2008, 14 years, two-year resolution, gap: 1996–1998	PCBs, PBDEs	45
XAD-PAS ( <i>n</i> = 60)	15 sites distributed globally	2005–2008, 4 years, annual resolution	OCPs, CUPs	448
XAD-PAS ( <i>n</i> = 78)	13 sites distributed globally	2006–2011, 6 years, annual resolution	PFAS	197
XAD-PAS ( <i>n</i> = 80)	16 background sites in Tibet, China	2007–2012, 5 years, annual resolution	PCBs, OCPs	520
PUF-PAS ( <i>n</i> = 17)	1 urban site in São Paulo, Brazil	2010–2015, 5 years, seasonal resolution	PCBs, PCDD/Fs, OCPs	550
PUF-PAS ( <i>n</i> = 211)	4 urban and 7 background sites across Spain	2008–2013, 5 years, seasonal resolution	DDTs, HCHs, HCB, PCBs, PBDEs, PCDD/Fs	545
PUF-PAS	5 urban and 7 background sites across Spain	2008–2013, 5 years, seasonal resolution	DDTs, HCHs, HCB, PCBs, PBDEs, PCDD/Fs	546
PUF-PAS ( <i>n</i> = 132)	1 site in the Czech Republic	2003–2013, 10 years, monthly resolution (28 days)	OCPs, PCBs, PAHs	515
PUF-PAS	14 sites in the Czech Republic	At most: 2004–2014 At least: 2007–2010, monthly resolution (28 days)	OCPs, PCBs, PAHs	516
PUF-PAS	5 sites in Northern Europe	2012–2016, min. of 5 years, seasonal resolution	PCBs, OCPs, PBDEs	517
FTS ( <i>n</i> = 33)	1 site in Antarctica	Dec. 2009 to Nov. 2014	PCBs, OCPs	181
PUF-PAS ( <i>n</i> = 321)	5 urban and 7 background sites across Spain	2008–2015, 7 years, seasonal resolution	PBDEs	547
XAD-PAS ( <i>n</i> = 44)	6 to 7 sites on the Fildes Peninsula, Antarctica	2007–2017, 7 years, annual resolution	dlPCBs, PCDD/Fs	548
PUF-PAS ( <i>n</i> = 35)	1 site at Lake Hovsgol, Mongolia	2008–2015, 8 years, three to five 2 month periods per year	PCBs, PBDEs, HCB, HCHs DDTs, endosulfans PCBs, OCPs	539



levels in PASs from 21 GAPS sites in 2013 and 2015 with those reported at the same sites in 2009.<sup>139,147</sup>

### G.8 PASs in studies of air-surface exchange

Quite regularly, surface compartments, such as soil and water, are sampled at PAS deployment sites, often with the intention to learn something about the equilibrium status of SVOCs between the atmosphere and these compartments and possibly estimate air-surface exchange fluxes.

**G.8.1 PASs in studies of air-water exchange.** The very first field study of a PAS involved the placement of SPMDs in the water and the overlying atmosphere of a coastal lagoon.<sup>35</sup> Another early study also deployed SPMDs in air and water in the vicinity of a chemical factory to record the levels of PAHs<sup>36</sup> and while both these studies estimated concentrations, no attempt was made to relate the concentration in different media with each other. On the other hand, Booij and van Drooge used four simultaneous deployments of SPMDs in air, water and within the sea surface microlayer to probe the equilibrium status of HCB and PCBs in the Western Wadden Sea of the Netherlands.<sup>37</sup> The study indicated no enrichment of these SVOC at the water surface and a phase distribution close to equilibrium.

PE was first used to sample both air and water at the same location and derive an activity or fugacity gradient for PCBs and PAHs in Narragansett Bay.<sup>72,77</sup> Differences in the activity or fugacity of a chemical between different compartments indicate deviations from thermodynamic equilibrium and therefore the potential for diffusive exchange between those compartments. Another early study using this approach was for PCDD/Fs in Newark Bay, New Jersey, USA, and revealed very strong fugacity gradients favouring volatilisation from the bay to the atmosphere.<sup>78</sup> The approach is also suitable for sampling from a moving ship by deploying the PE-PAS on the ship's mast and sampling the water either by towing a PE strip behind the ship or pumping sea water through a pipe containing the PE strip.<sup>79</sup> This approach was applied to study the air-water exchange of PBDEs along a cruise track across the tropical Atlantic Ocean.<sup>79</sup>

PE has been deployed in paired air and water passive samplers along the shores and on several on-lake locations of Lakes Ontario and Erie (number of sites varied from 13 to 22) during several ~2 month long periods in 2011 and 2012 (number of deployments varied from 3 to 4 depending on location). Those samples have been analyzed for PAHs,<sup>82</sup> OCPs,<sup>80</sup> PCBs,<sup>81,85</sup> PBDEs and other BFRs<sup>83</sup> and musk compounds.<sup>84</sup> In a similar set-up, PE samplers were deployed at eleven coastal and three open-lake sites on Lake Superior during three deployments in 2011, with quantification of PAHs, PBDEs<sup>87</sup> and PCBs and OCPs.<sup>88</sup> Error propagation analysis and Monte Carlo simulations have been used to estimate the uncertainty of air-water exchange fluxes that have been calculated from the air and water concentration obtained from PE-based passive samplers.<sup>86</sup>

PE-PASs have more recently been used to confirm the net deposition of OCPs and PAHs from the atmosphere to mountain lakes in Brazilian National Parks<sup>89,484</sup> and to assess the air-

water equilibrium of PCBs and OCPs in the Canadian High Arctic.<sup>90</sup> While studies involving paired air and water samples have been dominated by PE-based PAS, not all studies used them. PUF-PAS-derived air concentrations have been combined with water concentrations obtained from a passive water sampler based on PDMS sheets to derive air-water fugacity ratios for selected PAHs, PCBs, OCPs, and PBDEs at three sites in the Aegean Sea.<sup>103</sup> Accounting for the gas-phase fraction of the air concentration measured by PUF-PAS was possible, because active air sampling conducted at the same time allowed for the derivation of that fraction. Atmospheric concentrations measured by PUF-PAS have also been combined with grab water samples to estimate air-water fugacity ratios of several OCPs in the lower Ganga River.<sup>359</sup>

**G.8.2 PASs in studies of air-soil exchange.** It is quite common to analyze soil samples taken at or in the vicinity of passive air sampling sites,<sup>301,353,364,377,459,460,476,551</sup> for example to compare the relative composition of PCB mixtures in different media.<sup>387</sup> In particular, spatial trends of concentrations in air and soil along elevation gradients have been used to study the occurrence of mountain cold trapping.<sup>390,391,452,471</sup>

Measured air-soil concentration ratios can be compared with those that might be expected if air and soil were in equilibrium.<sup>280</sup> It is also possible to calculate fugacity gradients between soil and air and infer the likely flux direction from that gradient. Daly *et al.* were the first to do this with air concentrations derived from PASs and also explored the considerable uncertainty inherent in this approach.<sup>390</sup> Not only is the estimation of a fugacity from a soil concentration dependent on numerous assumptions and possibly quite uncertain partition coefficients, the uncertainty of the SR of a PAS directly propagates to the uncertainty of the air fugacity value. Therefore, only calculated fugacity gradients that deviate strongly from equilibrium should be interpreted as indicating the potential for volatilization or deposition.<sup>390</sup> This approach has since been adopted repeatedly,<sup>340,341,344,346,347,356,363,375,376,394,543</sup> not always with full awareness of the significant uncertainties it entails. It is also important to stress that only the gas-phase concentration contributes to a chemical's fugacity in air. Since there is now considerable evidence that the PUF-PAS samples particle-bound substances (Section F.6), an air concentration derived from a PUF-PAS should only be used to calculate a fugacity if the chemical is entirely in the gas-phase.

Sometimes, generic mass transfer coefficients are applied to the fugacity gradient to estimate fluxes across the air-soil interface.<sup>346,394</sup> This is quite questionable, as (1) air concentration averaged over extended periods of time may not be appropriate for flux estimation, considering that the fugacity gradient will undergo significant changes as air concentration and temperature are variable at a time scale shorter than the PAS deployment period,<sup>464</sup> (2) the mass transfer coefficients are highly site-specific, and (3) the uncertainty of the fugacity ratio is directly propagated to the flux. Such flux values should therefore not be interpreted as anything but rough order of magnitude estimates.

Another approach to measuring soil-air exchange fluxes is not based on the analysis of soil samples, but on recording



a gradient of air concentrations above the soil. These studies were reviewed in Section G.3.1.

## H. Recommendations and outlook regarding PASs for SVOCs

### H.1 Comprehensive and quantitative evaluation of PASs for SVOCs

It is now more than 25 years since the first PAS for SVOCs has been introduced<sup>34</sup> and since then well in excess of 300 studies have used PASs for SVOCs in a wide range of applications (see Section G). Some of these applications include governmental monitoring programs, such as the programs for Global Atmospheric Passive Sampling (GAPS)<sup>208</sup> and Joint Oilsands Monitoring (JOSM),<sup>292</sup> as well as large epidemiological investigations such as the Airborne Exposure to Semi-volatile Organic Pollutants (AESOP) study.<sup>192</sup> One would think that this represents a mature field, where the community of PAS developers and users has a solid understanding of the strengths, limitations and uncertainties of this sampling technique. However, it is only as a result of a number of comprehensive evaluation studies conducted during the past few years<sup>254,262,514,552</sup> that increased awareness and a better quantitative understanding of these limitations and uncertainties have emerged.

Holt *et al.* used the long time series of concurrent air samples taken in Košetice in the Czech Republic to assess the agreement between a PUF-PAS deployed for one month and four one-day HiVol samples taken during the same time.<sup>514</sup> For most PCBs, OCPs and PAHs, concentrations obtained from the two sampling techniques were statistically significantly different from each other, irrespective of whether the effective air volume  $V_{\text{air}}$  was derived using site-specific or generic SRs and what assumptions were made concerning the relative SR of particle-bound substances. Correlations between concentrations obtained from passive and active sampling were often poor and linear regressions hardly ever showed a slope close to 1. While the average of 12 monthly PUF-PASs and the average of the 48 active air samples taken during the same year were generally within the same order of magnitude, for less volatile PAHs discrepancies larger than an order of magnitude were common. Some of these discrepancies may be attributed to uncertainties introduced during analytical quantification and the different temporal coverage of the two sampling approaches (14% overlap), but they are too large to be fully explained by these sources of uncertainty.<sup>514</sup>

When trying to calibrate the PUF-PAS for a number of perfluorinated substances, Karásková *et al.* often failed to observe an increase in the sequestered amount with increasing deployment time indoors.<sup>552</sup> Also, the uptake curves obtained for outdoor deployments showed poor replicate precision and a very large range in  $SR_e$  (0.7 to 30  $\text{m}^3$  per day). Because many of these perfluorinated compounds are charged and have extremely limited volatility, these results hint at the large variability in the uptake of non-gaseous substances in PAS, especially indoors, where air turbulence is very limited and/or highly spatially variable. Melymuk *et al.* found much lower levels of several PAHs and BFRs in PUF-PASs deployed for one month

than were taken up cumulatively in four PUF-PASs deployed sequentially for one week each at the same time and place.<sup>262</sup> Together the studies by Holt *et al.*,<sup>514</sup> Melymuk *et al.*,<sup>262</sup> and Karásková *et al.*<sup>552</sup> are a sobering illustration of the large uncertainties one might expect even from one of the most thoroughly characterised PAS when deployed and analyzed by a highly experienced group.

Melymuk *et al.* summarised many of the challenges besetting the passive air sampling for SVOCs and highlighted the appreciable uncertainties and biases to which they give rise.<sup>284</sup> It is important that the community of PAS researchers and users is responding appropriately to the repercussions of the findings of these evaluation studies. For the community of PAS researchers, it means that future effort should be dedicated to quantifying and reducing the uncertainties of the passive air sampling of SVOCs based on a comprehensive understanding of how it works. New sampler designs and modifications of existing designs should be targeted to address the identified shortcomings of the existing designs. This is further discussed in Section H.2. For the community of PAS users, it implies the need to become aware of, and knowledgeable about, the limitations of the tools they apply and consequently to become more transparent and explicit in reporting the uncertainties of the results they report. Section H.3 expands on this further.

### H.2 Recommendations and outlook regarding the design of PASs for SVOCs

This review revealed a surprisingly large number of designs for PASs for SVOCs. Tables 1, 2, 4 and 5 list almost 40 different designs that have been proposed. Many of these designs are only the subject of one or two publications, *i.e.* these designs remain for the most part poorly characterised and find only very limited, if any, applications. On the other hand, there are a number of PAS designs for which a large body of work exists, that created valuable information on SRs and their variability, *e.g.* with respect to the influence of wind or to the differences between different types of SVOCs (see Section F), as well empirical quantitative data and estimation techniques on the uptake capacity of their sorbent materials (see Section E). Some of these have also been rigorously evaluated (Section H.1). As a result, it is possible to apply these PASs with a reasonably clear understanding of their limitations and the expected uncertainty of the data they yield.

This is not to say that these PAS designs could not be improved upon. On the contrary, some of the most frequently used PAS designs are quite compromised. The first PAS for SVOCs, the SPMD, has turned out to have too complex and too variable an uptake kinetic and to pose too many analytical challenges that it has ceased to be a competitive choice for most applications, despite a fairly substantive body of work characterising it. Even the PUF-PAS, which has become the default choice of many PAS studies, leans heavily on the side of high SRs in the balancing of the conflicting objectives of high *vs.* tightly controlled SRs and therefore these SRs are variable and highly uncertain (see Section C.1). While PUF is a popular choice as a sorbent because of its ease of handling and low cost, its low uptake capacity necessitates complex SR estimations for



more volatile SVOCs that introduce considerable uncertainty (see Section F.3).

Introducing a new sampler design only makes sense, if two conditions are fulfilled. There has to be a:

(1) Clear motivation for proposing a new design, *i.e.* it has to fundamentally improve on the existing, well-characterised PAS designs for at least one type of application. Sadly, the evidence suggests that some of the researchers proposing new designs are not even always aware of the full slate of PAS designs that have been described in the literature and therefore may be ill-equipped to make a genuinely useful contribution.

(2) Commitment to undertake the experiments that are required for comprehensive characterisation of a new design. At a minimum that needs to include (i) a calibration study with replicated samplers being retrieved after various lengths of time and with simultaneous measurement of air concentration with active air sampler, as this is what is necessary to obtain information on  $t_{\text{linear}}$  and  $t_{\text{equilibrium}}$  for SVOCs of different volatility and at different temperatures, (ii) an exploration of the variability in SRs that can be expected in different types of deployments.

There is certainly a need for a PAS for SVOCs that can generate air concentrations with a much smaller uncertainty than the current slate of sampler designs. Such a PAS would be useful for applications where small concentration differences need to be discerned (*e.g.* when measuring vertical gradients, see Section G.3) or when highly accurate numbers are required (*e.g.* when the potential for diffusive air-surface exchange of SVOCs is to be deduced, see Section G.8). Such a sampler would almost certainly need to apply effective wind sheltering and a diffusive barrier in order to achieve the tightly controlled SRs necessary for high precision (see Section B.4). Because that would inevitably lead to small SRs, the analysis of the amount of SVOC on the sorbent of such a sampler will need to achieve very low LODs. There are now several studies that have shown that an analytical approach that thermally desorbs the sequestered chemical from a sorbent onto a GC-MS is capable of delivering such low LODs. This is most easily achieved by a sorbent that can be placed in the tubes used by commercial thermal desorption instruments. Sorbents that have been thermally desorbed include silicone coated stir bars,<sup>52,55,108-110</sup> Tenax TA-coated GFFs,<sup>199,200</sup> and commercially available Tenax TA filled cartridges.<sup>201</sup>

Often and maybe surprisingly, there has been no attempt to control the diffusion distance to these sorbents. In studies where this was attempted, *e.g.* by using different types of PE-based diffusive barriers,<sup>55</sup> this has not been successful, as evidenced by high and unexplained SR variability. Interestingly, some of the thermally stable sorbents that have been proposed, such as the commercially available Tenax TA-filled cartridges and silicone rods, would be compatible with the commercial Radiello diffusive barriers, which for example finds use for passively sampling VOCs.<sup>273</sup> Yet, there appears to have been no study that explored the feasibility of a PAS for SVOCs that combines a thermally stable sorbent in rod-shaped form with a Radiello diffusive barrier. It is possible, and maybe even likely, that the sorptive capacity of the

PE of the Radiello is itself too large and would interfere with the diffusion of the SVOC to the sorbent. However, it may be feasible to construct a radial diffusive barrier from material that has less capacity to sorb SVOCs than PE.

Apart from their potential analysis by thermal desorption, PDMS-based PASs show considerable promise for indoor applications, because of the ease of handling and because fast diffusion within the polymer should assure that diffusion across the air boundary layer is rate-limiting uptake. A hurdle to their credibility currently is a general disregard of the need to constrain the thickness of that air boundary layer to a small range, which even in indoor settings would be required to increase precision, and the failure to observe the theoretically expected quantitative relationship between surface area and uptake rate, at least when the results of various studies are compared (see Table 3). If that issue could be resolved, it should be quite easily possible to modify the surface area to volume ratio of the PDMS sorbent in order to tailor a PAS for a particular set of deployment conditions (*i.e.* a specific set of SVOCs sampled for a particular length of time, given a particular LOD of the detection technique).

### H.3 Recommendations and outlook regarding applications of PASs for SVOCs

As Section G illustrates, PASs for SVOCs now find use for a wide variety of applications. A perusal of those studies reveals that the considerable uncertainty of results obtained with most currently used PASs is often profoundly underappreciated. Partly, this may be attributable to an overestimation of the performance capability of a PAS. More typically, it is a result of the reluctance of many PAS users to quantify or even consider that uncertainty. Going forward, there should be an expectation that certain elements are present in a PAS-based study, if it is to be published in the peer-reviewed literature or if the generated data serve regulatory purposes.

A good PAS study will replicate at least some of the sampler deployments and have a large number of field blanks. When targeting SVOCs that are known to be susceptible to blank contamination (*e.g.* cvMS) and/or when sampling very low concentrations (see *e.g.* Section G.6), it may be advisable to have a field blank for every deployed sampler.

Importantly, the uncertainty of the reported results needs to be explicitly stated. If results are reported in sequestered amounts (normalised to time), it may be sufficient to estimate that uncertainty from the standard deviation of replicated sampler deployments. If volumetric air concentrations are reported, the uncertainty of the applied SRs or effective sampling volumes needs to be considered in addition to the sampling and analytical uncertainty. As Section F.3 illustrates the uncertainty of SRs is often very large. If an effective sampling volume is estimated for a PAS operating in the curvi-linear uptake regime, the uncertainty of the variables going into that estimation need to be propagated to the final reported air concentration. These variables include the  $K_{\text{SG}}$  value, which is often estimated from a highly uncertain empirical regression equation and then adjusted to the temperature of deployment using an equally



uncertain energy of sorption,<sup>263</sup> and it includes the intrinsic SR determined from the loss of depuration compounds. The study by Liu *et al.* illustrates how this can be done.<sup>86</sup>

An honest and comprehensive appraisal of uncertainty will most likely reveal that in many instances a PAS-derived air concentration for SVOCs may essentially be an order of magnitude estimate. This is especially true for particle-bound substances. It is important to stress that this does not invalidate the usefulness of PASs as in many applications even highly uncertain data are perfectly sufficient to meet the project objectives. As was discussed in Sections G.5.1 and G.7, amounts sequestered in a PAS have much less uncertainty than air concentrations and are often appropriate to answer the questions related to spatial variability and temporal trends that PASs are frequently called upon to address. However, honest uncertainty estimates will also reveal that some of the interpretations of PAS-based studies will have to be questioned. Small differences in levels measured at forested and open sites may be caused by SRs that depend on wind and not necessarily be an indication of the forest filter effect.<sup>65,468,478</sup> The same applies to small differences in paired indoor/outdoor PAS deployments. Even air-soil or air-water fugacity fractions of 0.1 or 0.9 may not be confidently distinguished from equilibrium, if the air concentration is derived from a PAS. If efforts to develop a high precision PAS for SVOCs, as advocated in Section H.2, should succeed it will be time to revisit those PAS applications that rely on measured air concentrations with small uncertainty.

## I. Acronyms, abbreviations, variables

### I.1 Variables

$A$	Geometric surface area of the sorbent exposed to the gas-phase
$A_S$	Specific surface area of an adsorbent
$C_G$	Concentration of chemical in the gas-phase
$C_S$	Concentration of chemical in the sorbent of a passive air sampler
$D$	Molecular diffusivity in the gas-phase
$\Delta H_{SG}$	Enthalpy of transfer from the sorbed phase to the gas-phase
$k_l$	Rate constant describing chemical loss from a passive air sampler
$k_u$	Rate constant describing chemical uptake in a passive air sampler
$K_{SG}$	Equilibrium sorption coefficient between a sorbent and the gas-phase
$m_S$	Amount of chemical taken up in the sorbent of a passive air sampler
$R$	Ideal gas constant
$SR$	Inherent sampling rate of a passive air sampler
$SR_e$	Empirical sampling rate of a passive air sampler
$\Delta t$	Deployment time of a passive air sampler
$t_{\text{linear}}$	Length of the linear uptake period of a passive air sampler
$t_{\text{equilibrium}}$	Time needed to approach equilibrium between sorbent and gas-phase
$T$	Temperature

$\Delta U_{SG}$	Internal energy of transfer from the sorbed phase to the gas-phase
$V_{\text{air}}$	Effective sampling volume of a passive air sampler
$V_S$	Geometric bulk volume of a passive sampling sorbent
$\Delta z$	Thickness of the stagnant air boundary layer surrounding a sorbent

### I.2 Abbreviations for different samplers and sorbent materials

ACF	Activated carbon felt
AL	Artificial leaf
EVA	Ethyl vinyl acetate
FTS	Flow through sampler
GFF	Glass fibre filter
HiVol	High volume sampler
LoVol	Low volume sampler
MECOP	Membrane-enclosed copolymer
PAS	Passive air sampler
PAS-DD	Passive dry deposition sampler
PDMS	Polydimethylsiloxane
PE, LDPE	Polyethylene, low-density polyethylene
PES	Passive emission sampler
POG	Polymer-coated glass
PUF	Polyurethane foam
SBSE	Stir bar sorptive extraction
SIP	Sorbent impregnated polyurethane
SPMD	Semi-permeable membrane device
SPME	Solid phase micro extraction
VERAM	Versatile, easy and rapid atmospheric monitor
XAD	Styrene–divinylbenzene co-polymer

### I.3 Abbreviations for compounds and compound groups

SVOCs	Semi-volatile organic chemicals
VOCs	Volatile organic chemicals
BFRs	Brominated flame retardants
CUPs	Current use pesticides
HFR	Halogenated flame retardants
MCCPs	Medium chain chlorinated paraffins
OCPs	Organochlorine pesticides
OPE	Organophosphate esters
OPFRs	Organophosphate flame retardants
PAHs	Polycyclic aromatic hydrocarbons
PBDEs	Polybrominated diphenyl ethers
PCBs	Polychlorinated biphenyls
PCDD/Fs	Polychlorinated dibenzo- <i>p</i> -dioxins and dibenzofurans
PCNs	Polychlorinated naphthalenes
PFAS	Perfluorinated and polyfluorinated alkyl substances
SCCPs	Short-chain chlorinated paraffins
VMS	Volatile methyl siloxanes



ADBI	Celestolide
AHTN	Tonalide
ATE	2,4,6-Tribromophenylallyl ether
ATII	Traseolide
BATE	2-Bromoallyl-2,4,6-tribromo-phenyl ether
BTBPE	1,2-Bis(2,4,6-tribromo-phenoxy)ethane
D3	Hexamethylcyclotrisiloxane
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DBDPE	Decabromodiphenylethane
DDT	Dichlorodiphenyltrichloroethane
DDE	Dichlorodiphenyl dichloroethylene
DPTE	2,3-Dibromopropyl-2,4,6-tribromophenyl ether
EHTBB	2-Ethylhexyl-2,3,4,5-tetrabromobenzoate
EtFOSA	<i>N</i> -Ethyl perfluoroctane sulfonamide
EtFOSE	<i>N</i> -Ethyl perfluoroctane sulfonamidoethanol
8:2 FTOH	Perfluoroctyl ethanol
10:2 FTOH	Perfluorodecyl ethanol
GEM	Gaseous elemental mercury
HBB	Hexabromobenzene
HBCD	Hexabromocyclododecane
HCBD	Hexachlorobutadiene
HCB	Hexachlorobenzene
HCH	Hexachlorocyclohexane
HHCB	Galaxolide
MCPA	2-Methyl-4-chlorophenoxyacetic acid
MDM	Octamethyltrisiloxane
MD2M	Decamethyltetrasiloxane
MD3M	Dodecamethylpentasiloxane
MeFOSA	<i>N</i> -Methyl perfluoroctane sulfonamide
MeFOSEA	<i>N</i> -Methylperfluoroctane sulfonamidethylacrylate
MeFOSE	<i>N</i> -Methyl perfluoroctane sulfonamidoethanol
PBEB	Pentabromoethylbenzene
PBT	2,3,4,5,6-Pentabromotoluene
PCA	Pentachloroanisole
PeCBz	Pentachlorobenzene
TBBP-A	Tetrabromobisphenol-A
TBE	1,2-Bis(2,4,6-tribromophenoxy)ethane
TBECH	Tetrabromoethyl-cyclohexane
TBCO	1,2,5,6-Tetrabromocyclooctane
<i>p</i> -TBX	2,3,5,6-Tetrabromo- <i>p</i> -xylene
TBPH	Bis-(2-ethylhexyl)tetrabromophthalate

## Conflicts of interest

There are no conflicts of interest to declare.

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