

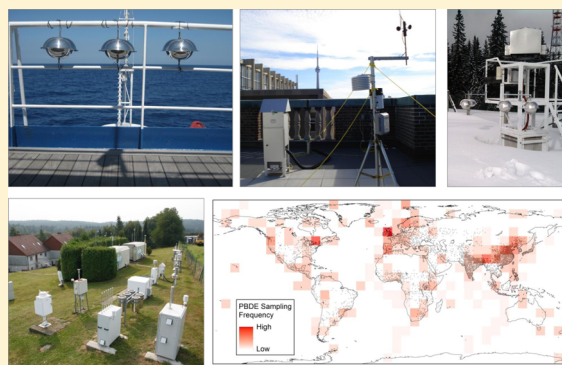
# Current Challenges in Air Sampling of Semivolatile Organic Contaminants: Sampling Artifacts and Their Influence on Data Comparability

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## S Supporting Information

**ABSTRACT:** With current science and policy needs, more attention is being given to expanding and improving air sampling of semivolatile organic contaminants (SVOCs). However, a wide range of techniques and configurations are currently used (active and passive samplers, different deployment times, different sorbents, etc.) and as the SVOC community looks to assess air measurements on a global scale, questions of comparability arise. We review current air sampling techniques, with a focus on sampling artifacts that can lead to uncertainties or biases in reported concentrations, in particular breakthrough, degradation, meteorological influences, and assumptions regarding passive sampling. From this assessment, we estimate the bias introduced for SVOC concentrations from all factors. Due to the effects of breakthrough, degradation, particle fractions and sampler uptake periods, some current passive and active sampler configurations may underestimate certain SVOCs by 30–95%. We then recommend future study design, appropriateness of sampler types for different study goals, and finally, how the SVOC community should move forward in both research and monitoring to best achieve comparability and consistency in air measurements.



## INTRODUCTION AND BACKGROUND

Recent scientific and policy discussion has addressed air sampling of semivolatile organic compounds (SVOCs)/persistent organic pollutants (POPs), particularly regarding long-term monitoring networks and the data needs of the SVOC community.<sup>1–3</sup> SVOCs are organic compounds with vapor pressures typically between  $\sim 1$  and  $10^{-10}$  Pa. Many of the SVOCs are classified as POPs, and are subject to international agreements and conventions such as the Aarhus protocol on POPs (1998) under the Convention on Long-Range Transboundary Air Pollution (LRTAP, 1979) (<http://www.unece.org/env/lrtap/>) and the Stockholm Convention (SC) on POPs (2001/2004) ([www.pops.int](http://www.pops.int)). These conventions aim to eliminate or restrict the production and emission of a range of SVOCs, notably organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), polycyclic aromatic hydrocarbons (PAHs), per- and polyfluorinated compounds (PFCs). To provide information on long-term trends and effectiveness of regulatory actions, air monitoring strategies have been established,<sup>1</sup> including the European Monitoring and Evaluation Programme (EMEP) for LRTAP compounds (1999) and the Global Monitoring Plan (GMP) for SC compounds (2008).<sup>1</sup> Monitoring networks require appropriate sampling strategies to provide reliable and broadly comparable air data and current

regional monitoring networks, with differences in sampling methodology and procedures, cannot adequately provide the data needed for global assessments, such as the GMP.<sup>1</sup> Furthermore, scientific concern is also growing regarding currently unregulated SVOCs such as endocrine disrupting compounds (EDCs).<sup>4</sup>

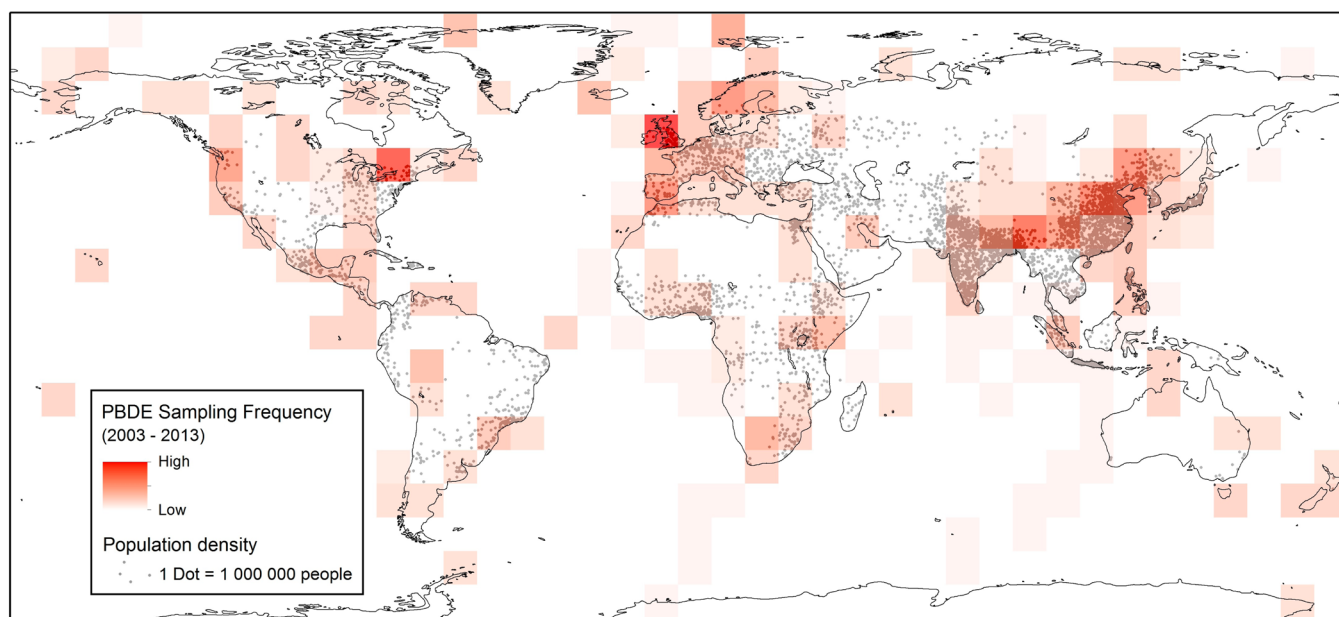
Beyond the policy demands of international conventions, the SVOC scientific community also requires air sampling to understand the fate and transport of SVOCs and to provide necessary information for scientific models and human exposure assessments.<sup>2</sup> This type of data is often produced through smaller-scale case studies or local- or regional-scale monitoring networks. While less standardized than long-term monitoring networks, some very critical knowledge of SVOCs has come from case studies, as they allow specific questions to be addressed in a focused manner. In particular, they provide a platform for testing samplers (e.g., polyurethane foam (PUF) passive air samplers,<sup>5</sup> XAD-passive air samplers<sup>6</sup>) and provide data in vulnerable areas that are not covered by long-term monitoring networks (e.g., e-waste sites in China<sup>7</sup> or Africa, intensive agricultural regions in India or South America<sup>8–10</sup>).

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**Figure 1.** Global distribution of PBDE measurements in air (active and passive) from 2003 to 2013, as an example of the unbalanced spatial distribution of SVOC sampling. Shading is used to aid in visualization of aggregated sampling distribution and frequency. Darker orange indicates a high density of sampling (e.g., regular sampling over many years), while the lightest orange indicates collection of a single event sample (e.g., ship cruises). Dots reflect global population density as of 2000 (<http://sedac.ciesin.columbia.edu/gpw>).

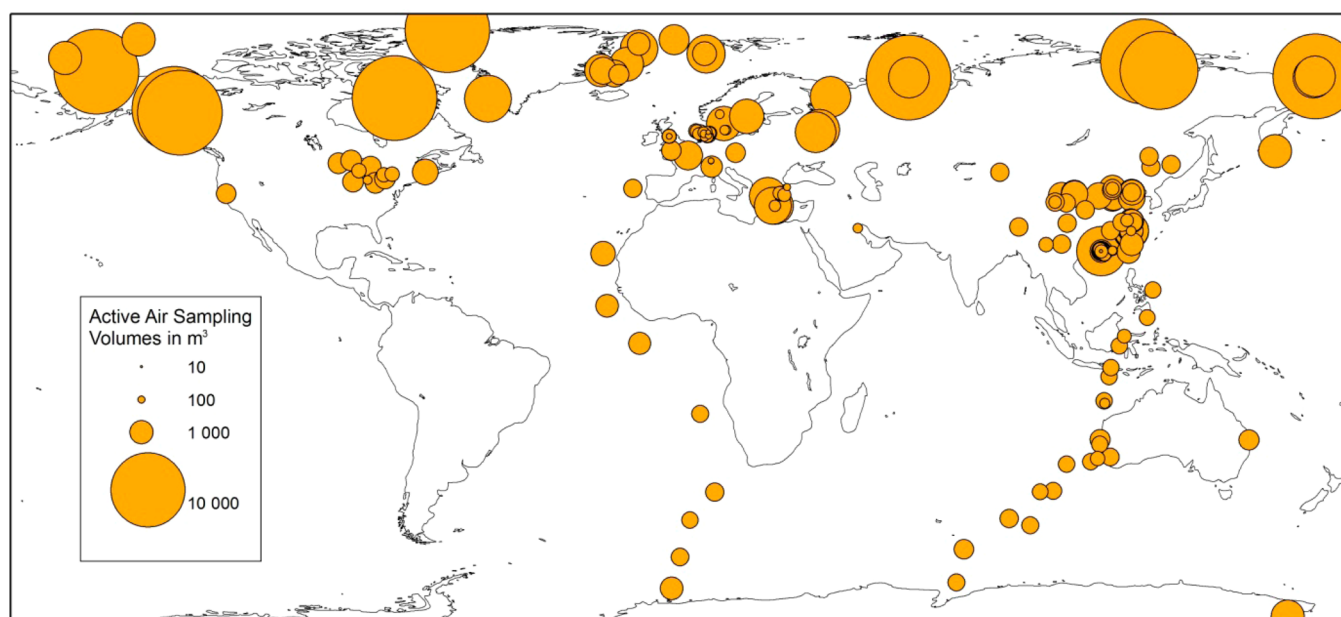
Together, monitoring networks and case studies provide our information on the global distribution of SVOCs, their atmospheric transport, fate, and relationship with sources. However, there are still crucial gaps and biases in this information which may lead to uncertainties in comparability of data, namely spatial distribution and temporal coverage of measurements, and lack of sampling standardization within and between networks/case-studies. Problems related to spatial distributions of established networks are discussed by Hung et al.<sup>2</sup> and Klánová and Harner.<sup>1</sup> The uneven spatial distribution is somewhat improved when one considers the contribution of case studies (Supporting Information (SI) Figure S1b) and new/planned monitoring networks in Australia, Southeast Asia, and South America,<sup>2</sup> but the issue of data comparability remains. Additionally, there are discrepancies in the spatial distribution of measurements and the spatial scale of concentration variations; SVOCs vary on small scales<sup>11–13</sup> and current sampling distributions infrequently address this. There are also discrepancies in the frequency of sampling at each site, with some regions having repeated continuous monitoring capturing seasonal trends and short-term variability, and others with only one or two reported measurements in the past ten years (Figure 1). Although individual monitoring networks are effective at accomplishing their respective goals (e.g., providing data for modeling exercises, or broad spatial coverage) the different network structures may lead to problems with the intercomparability of scientific results. With increasing international collaboration and data sharing (e.g., the GMP) the question of inter-network comparability is brought to the forefront.<sup>1</sup> There are a wide range of techniques used across different networks and case studies, including active and passive air samplers, and differences in sampling volumes, sorbents, sampling length and sampling frequencies. There has never been an agreed mandate to establish standardized procedures within and between SVOC networks and there is a lack of quality standard operating procedures for SVOC

sampling. While some studies have assessed comparability between samplers or sampling networks,<sup>14–21</sup> efforts never went beyond these to address the potential implications. Most current discussion focuses on the problems related to spatial distributions, as well as analytical quality assurance and quality control (e.g., interlaboratory or inter-network comparisons<sup>14,16,17,22,23</sup>), but little attention is given to sampling artifacts or spatial intercomparability. Herein, we review and discuss influences on the most frequently used SVOC air sampling methods/techniques in both established networks and case studies and analyze how they impact measurements and thus data comparability. We then make recommendations on what sampling techniques are appropriate for particular study goals, how to enhance data comparability, and what is needed to improve SVOC air measurements.

## ■ SAMPLING TECHNIQUES

**Active Air Sampling Methods.** Active air samplers (AAS) are currently perceived as the most accurate method of obtaining SVOC air concentrations as they accumulate both gas and particle phase compounds under a controlled flow. Despite identified sampling artifacts,<sup>24</sup> this technique is almost unchanged over the past 40 years.<sup>25–27</sup>

AAS are commonly classified as either high volume or low volume samplers, with the main differences being the flow rate and sample collection time. In high volume samplers, flow rates are typically 15–80 m<sup>3</sup>/hour<sup>16,28,29</sup> yielding total sample volumes of >400 m<sup>3</sup>, although there is a large variation in what is considered a high volume sample. For example, the Integrated Atmospheric Deposition Network (IADN) typically collects ~820 m<sup>3</sup> of air at American sites, and ~350 m<sup>3</sup> at Canadian sites,<sup>16</sup> while some Arctic sampling networks collect up to 13000 m<sup>3</sup>.<sup>30</sup> Low volume air samplers typically have flow rates of <3 m<sup>3</sup>/hour.<sup>15,31–34</sup> This often results in small sample volumes (e.g., <200 m<sup>3</sup>), but low volume samplers can also be used for longer deployment times, for example, 7–14 days of



**Figure 2.** Distribution of active air sampling volumes used in measurements of PBDEs from 2003 to 2013. Studies that did not report a sample volume are excluded. There is a general trend of larger volumes collected in remote areas, particularly the Arctic, however there is also significant variability in air volumes that is not directly related to the expected concentrations at a given site and this variability may affect what is reported as concentrations in a given location (e.g., occurrence of either breakthrough or lack of detection).

**Table 1.** Common Active and Passive Sampling Techniques for SVOCs

sampler	high volume sampler	low volume sampler	double-bowl PUF PAS	XAD PAS	SIP PAS
type of sampler	active	active	passive	passive	passive
typical sampling volume (m <sup>3</sup> )	600 m <sup>3</sup>	100 m <sup>3</sup>	80–400 m <sup>3</sup>	100–200 m <sup>3</sup>	100–500 m <sup>3</sup>
typical sampling rate/flow rate	15–80 m <sup>3</sup> /hour	<3 m <sup>3</sup> /hour	0.3–20 m <sup>3</sup> /day	0.4–0.8 m <sup>3</sup> /day	4–12 m <sup>3</sup> /day
sampling time	hours to month	days to weeks	weeks to months	months to year	weeks to months
gas-phase sorbent	PUF, XAD or combination of PUF, XAD	PUF, XAD or combination of PUF, XAD	PUF	XAD	XAD-impregnated PUF
particle-phase sampling	GFF or QFF	GFF or QFF	debatable. inconsistent. with lower sampling rate than gas-phase (10%).	no	debatable. inconsistent. with lower sampling rate than gas-phase (10%).
use in long-term monitoring networks?	yes (inter alia EMEP, IADN, AMAP, MONAIRNET)	rarely (selected OSPAR stations)	yes (GAPS, MONET)	yes (GAPS)	yes (GAPS)

continuous sampling resulting in air volumes of 500–1000 m<sup>3</sup>.<sup>31–33</sup> Low volume sampling is rarely used in long-term sampling networks; only the Coordinated Atmospheric Monitoring Programme of OSPAR and EMEP use low volume samplers at selected stations.<sup>31,35</sup>

Environmental parameters and SVOC concentrations vary widely, for example, very low concentrations in remote/polar regions or high temperatures in tropical regions, and thus it can be problematic to use identical sampling configurations in all locations. The use of different sampling configurations results in different sampling artifacts. Sampling events can only be compared if a sufficient measure of accuracy has been reached. Current sampling procedures/protocols have wide variations in sampled volumes that may not always reflect the best choice for the temperature and concentrations in a region, and rather may simply rely on established sampling protocols not tailored to specific sampling conditions (Figure 2). While these choices allow individual networks to have long-term temporal data continuity, they may reduce the accuracy of results and comparability between networks or studies. A greater analysis

of the influences of sample volume and sampling media is given in the following sections.

**Passive Air Sampling Methods.** Passive air sampling techniques for SVOCs were introduced in the end of 1990s to simplify and reduce the costs for air monitoring of SVOCs. Unlike AAS, passive air samplers (PAS) do not need electricity; instead chemicals are trapped by diffusive uptake to a sorbent material. PAS have enabled broader monitoring network distribution and, as a result, increased the spatial breadth of SVOC measurements.<sup>1,36</sup> Several types of PAS have been evaluated and used during the last 10–15 years, and a few of them have received greater attention and been implemented in monitoring networks (Table 1). Currently, the disk-shaped PUF–PAS,<sup>5</sup> and the XAD-resin based PAS<sup>6</sup> are most used in monitoring networks. Recently, an XAD sorbent-impregnated PUF (SIP) PAS has also been implemented in the Global Atmospheric Passive Sampling network (GAPS).<sup>37</sup> Other PAS samplers have been used (e.g., POGs,<sup>38</sup> SPMDs<sup>39</sup>), and new techniques are under development,<sup>40</sup> however these are largely used in case studies. The available PAS differ in characteristics



and applicability, which affects data comparability, as described below. For an in-depth review of PAS theory and application we recommend dedicated articles on theoretical framework,<sup>41</sup> calibration,<sup>42</sup> indoor use,<sup>43</sup> new developments and techniques.<sup>40,44</sup>

## SAMPLING INFLUENCES

Below, we describe and discuss some of the major sampling influences for both AAS and PAS. All air sampling techniques have biases that may affect measurements and thereby also the comparability of results between different sampling events. We consider: (i) is the sampling technique accurate—does it provide the real picture of atmospheric levels of the target contaminants, (ii) is the sampling technique robust—how sensitive is it to environmental conditions, and (iii) are data from different techniques comparable—do we get the same number when using different sampling techniques and different sampling approaches? A focus is often on analytical procedures and intercomparisons of chemical analyses;<sup>17,23</sup> comparisons of sampling procedures/methodologies/techniques are less common. Yet, given the range of sampling techniques, the parameters of sample collection (e.g., sorbent type, sample volumes) should be carefully considered, as they have the potential to introduce significant biases. A summary of the advantages and disadvantages of individual sampler configurations is given in SI Table S1.

**Sampling Influences—Active Air Sampling.** *Sampling Head.* The most commonly used sampling heads in AAS are the TSP (total suspended particulates) and PM<sub>10</sub> (particles with aerodynamic diameter <10  $\mu\text{m}$ ). TSP theoretically includes all airborne particulate matter, although in practice, the upper particle size cutoff of a TSP sampling head is between 50 and 100  $\mu\text{m}$ , dependent on flow rate and ambient conditions.<sup>45</sup> As a result of new legislations within the European Union (EU), recently PM<sub>2.5</sub> (particles <2.5  $\mu\text{m}$ ) has also been suggested as a sampling threshold for monitoring networks. Different sampling heads and a specific particle cut-point can be useful, as particles <10  $\mu\text{m}$  are most important for atmospheric chemistry and physics<sup>46</sup> while particles <2.5  $\mu\text{m}$  are most relevant for human health and risk assessment estimates,<sup>47</sup> but may result in lower data comparability. The choice of sampling head should not result in large differences in reported SVOC concentrations, as the majority of SVOCs are typically associated with the finest particles (e.g., <1.5  $\mu\text{m}$ ), which are sampled by the TSP, PM<sub>10</sub> and PM<sub>2.5</sub> sampling heads.<sup>48–52</sup> On average PM<sub>2.5</sub> represents >75% of TSP by mass and most of the SVOCs (>80%) are found in this fraction.<sup>51,52</sup> However, there may be circumstances when the use of different sampling heads leads to very different results, such as environments with high TSP, or industrial settings where SVOCs are found on coarser particles.

*Sorbent and Filter Type.* A range of different sorbent types are used for sampling gas-phase SVOCs in AAS (e.g., PUF, XAD, Tenax TA, polydimethylsiloxane), but published data on SVOCs is dominated by sampling with PUF and XAD, and we focus our discussion on these. PUF is a low density foam consisting of a polymer bound by urethane links that has been used in SVOC air sampling for over 40 years.<sup>25</sup> XAD is a styrene-divinylbenzene copolymer more recently used in AAS, either independently or in conjunction with PUF. Two types of XAD are commonly used in SVOC air sampling:<sup>53</sup> (i) Amberlite XAD-2, commonly used in AAS and XAD-PAS,<sup>6,54,55</sup> and (ii) Amberlite XAD-4, in active denuder

samplers and SIP-PAS.<sup>56,57</sup> The main difference between XAD and PUF is sorptive capacity; for equal amounts of sorbent material, PUF has a much lower capacity than XAD, largely due to differences in surface area. PUF has a specific surface area of 0.007–0.035  $\text{m}^2/\text{g}$  while the surface area of XAD-2 is 300–600  $\text{m}^2/\text{g}$ .<sup>53</sup> On a practical basis, this means that samplers using XAD as the gas-phase sorbent can collect larger volumes of air before breakthrough occurs (for AAS) or be deployed for longer periods of time before equilibrium is reached (for PAS). However, PUF does have the advantage of lower cost and ease-of-use compared to XAD, as manipulation of the PUF is simple and blanks are often lower.

There are also differences in the surface bonding of particular compounds to PUF and XAD.<sup>58,59</sup> XAD is a stronger sorbent for PFCs, current-use pesticides (CUPs), and other emerging chemicals,<sup>59,60</sup> yet the differences are not fully understood, and research is ongoing. Both sorbents are influenced by temperature and humidity, but the amount of variability introduced by these parameters is unclear and needs further research.<sup>53,59</sup> Generally, they are linked to changes in sorptive capacities,<sup>59</sup> and thus effects can be significant when large seasonal shifts are expected (e.g., monsoon-impacted areas). The choice of PUF vs XAD should be based on the choice of compound to be sampled and the sampling parameters, but is often due to previous regional practices (e.g., PUF is more commonly used in AAS in Canada and Europe, while XAD is more commonly used in the U.S.). PUF/XAD combinations are seeing increasing global use in recent years (SI Figure S2).

Three types of filters are used in AAS for SVOCs: quartz fiber filters (QFF), glass fiber filters (GFF), and Teflon/Teflon-impregnated filters. GFF and QFF are most common, and are perceived to give comparable results,<sup>61</sup> although specific studies assessing differences between them are limited. The recommendations on filter type instead suggest that choice of filter should consider what, if any, additional analyses will be completed in conjunction with SVOCs (e.g., PM, SO<sub>2</sub>, organic/elemental carbon, or metals).<sup>45,62</sup>

While the choice of sampling head determines the upper end of the particle sizes collected on the filter, the lower size cutoff is related to filter choice, but is more ambiguous. Typical GFFs or QFFs have a collection efficiency of >99%, but do not often have a specified fine particle cutoff. Particles <50 nm may pass through the filter and subsequently be trapped by the gas-phase sorbent material.<sup>63</sup> This might be an issue for ultrafine particles (typically <100 nm) which are of concern for human health.<sup>64,65</sup> Although numbers of ultrafine particles are high, their total mass is small and therefore they are challenging to quantify and require adaptations of current instrumentation or new sampler types. There is limited information on how ultrafine particles are distributed within an AAS, and this may contribute to uncertainty in gas-particle partitioning.

*Breakthrough.* An important consideration in AAS is what volume of air can be collected before the sampling medium experiences “breakthrough”, that is, the loss of compounds downstream of the sampling medium. This can be a result of a saturated sampling medium or desorption of compounds from the sampling medium. Sampling design must achieve the right balance between collecting sufficient sample for analysis of lower concentration SVOCs, while not collecting so much volume as to have breakthrough of more volatile SVOCs. In breakthrough estimates or controlled experiments <10% breakthrough is considered an acceptable threshold.<sup>66–68</sup>

The key factors affecting breakthrough are (1) type and geometry of sampling medium, (e.g., PUF vs XAD), (2) target compound properties and concentration, (3) competition for the sampling medium (i.e., from other gas-phase compounds), (4) sample volume, (5) sampler flow rate, (6) temperature, and (7) humidity. Of these, sampling medium, sample volume and sampler flow rate are the most easily controlled, and therefore breakthrough is most often discussed in terms of what sampling medium and sample volume are appropriate for a given class of compounds.

Basic chromatographic relationships can be used to estimate breakthrough,<sup>24,67</sup> but given the number of variables influencing breakthrough, it can be more reliable to conduct small breakthrough experiments with the exact study configurations. Results from early breakthrough studies<sup>67,68</sup> tend to be used as an accepted framework for present studies and little consideration is given to breakthrough in typical sampling set-ups. Despite this, measurements and calculations suggest that in a typical high-volume AAS breakthrough of more volatile compounds (e.g., PCB-28, HCB, HCHs, fluorene) can occur already at <600 m<sup>3</sup>.<sup>24,34,59,66,68–70</sup> For example, at tropical temperatures (e.g., around 30°C) a typical high volume AAS (2 PUF plugs, 600 m<sup>3</sup> of air, 24 h) can lose 10–15% of the PCB-28 due to breakthrough (calculations in SI). However, it should be noted that this is also highly temperature dependent: with the same sampling configuration at 5°C the breakthrough volume is >3000 m<sup>3</sup>. Many current AAS configurations may experience breakthrough for lower molecular weight SVOCs, leading to systematic underestimation of these compounds; consideration of this is warranted in interpretation of results.

**Filter Artifacts.** The filter within the AAS (GFF or QFF) can be the site of two sampling artifacts which influence measured concentrations: blowoff and filter adsorption. Blowoff is the volatilization loss of SVOCs from the filter, thereby disproportionately reducing SVOC filter masses, while filter adsorption is the adsorptive partitioning of gaseous compounds onto the filter, increasing the mass of SVOCs on the filter.

This is affected by sampler configurations (e.g., flow rate, sampling time, filter type) and occurs largely under three conditions: (i) when there are large variations in the SVOC concentration in incoming air, (ii) when there are large temperature variations, (iii) when there is very high particle loading to filters. Under these conditions, the gas-particle distribution of SVOCs in the AAS may no longer be in equilibrium with the influent air, and filter blow-off can occur in the case of higher temperatures/lower concentrations, or filter adsorption in the case of lower temperatures/higher concentrations. By using a higher flow rate or longer sampling time, surface-sorbed SVOCs can more easily be stripped from particles than those that are less available for exchange with the atmosphere. In large sample volumes or in areas of high PM, overloading of filters can cause further artifacts. If the filter becomes physically blocked by PM, sampler flow rates can be reduced and thus true sample volumes could be lower, resulting in an underestimate of concentrations.

Filter adsorption and blowoff further vary by compound, depending on partitioning coefficients, ionic interactions, and hydrophilicity.<sup>71,72</sup> For example, significant filter adsorption was identified for perfluorooctanesulfonate (PFOS), and certain perfluoroalkyl carboxylic acids (PFCAs) in a high-volume AAS, resulting in overestimation of particle-associated fractions by up to 80%, while other PFCs did not have significant filter adsorption.<sup>24</sup>

If filter blowoff/adsorption occurs, bulk air concentrations may be correctly characterized, but gas-particle partitioning estimates may be incorrect. This is expected to be most significant for compounds with short-term temporal variations in concentrations<sup>71</sup> (such as CUPs) which may not be in equilibrium between the gas and particle phases, and those with intermediate gas-particle partitioning that vary between largely gas- and largely particle-associated at ambient air temperatures.

**Degradation.** Degradation of atmospheric SVOCs occurs as a natural process, caused by reaction with atmospheric reactive species, in particular hydroxyl radicals, ozone, and NO<sub>3</sub>, or by photolysis (SI Figure S3). Degradation has been found to significantly affect ambient atmospheric concentrations, notably for PAHs through reaction with OH, ozone, and NO<sub>3</sub>,<sup>73,74</sup> for PCBs and pesticides through reaction with OH,<sup>75–78</sup> and for PBDEs and novel flame retardants (NFRs) through photolysis.<sup>79–81</sup> While a sampler should provide a snapshot of the atmospheric SVOC concentrations which may be already affected by degradation, there is also the possibility for degradation to continue within the sampler, as atmospheric reactive species are drawn into the sampling medium along with the SVOCs themselves. Within-sampler degradation is an unwanted sampling artifact that can result in underestimation of ambient concentrations.

UV radiation has a minimal direct influence on within-sampler degradation due to the protection provided by the sampler housings, but there is the potential for degradation due to ozone, hydroxyl radicals and other atmospheric reactive species to continue within the sampler. Significant within-sampler degradation has been observed for PAHs both on filters<sup>82,83</sup> and in gas-phase sorbents.<sup>84</sup> Particle-phase PAH concentrations can typically be underestimated by 20–40% due to degradative losses on AAS filters, with underestimates >70% for particularly reactive compounds (e.g., benzo[a]pyrene).<sup>82,83,85</sup> Gas-phase PAHs may also experience degradation within the sorbent, with losses of up to 50% due to reaction with both OH and ozone.<sup>84,86</sup>

The amount of potential within-sampler degradation depends on sampling conditions, site conditions, and compound, but the range of variability due to these factors is highly uncertain. For example, there are large spatial and temporal ranges in levels of atmospheric reactive species. On a global scale, ozone varies by a factor of 2–3, with higher levels in populated areas,<sup>87</sup> while OH varies by a factor of 6, with higher levels in tropical regions,<sup>75,88</sup> and there is potential for even higher local-scale variability in both ozone and OH.<sup>89</sup> Ozone can vary seasonally by a factor of 2 and diurnally to a lesser extent<sup>87</sup> while OH can vary up 10× both seasonally and diurnally.<sup>75,88,90</sup> Given the direct relationship between the amount of degradative losses and levels of atmospheric reactive species, within-sampler degradation may be significantly higher (up to 100%) if the concentrations of atmospheric reactant species are very high.<sup>84,85</sup> This can then affect the temporal (e.g., summer vs winter) and spatial comparability (urban vs remote) of measured concentrations. For example, estimates based on reaction with ozone<sup>74,91</sup> suggest that measured concentrations at an urban site in summer with 60 ppb ozone would be underreported by 30% due to particle phase reaction with ozone, while at a remote site in winter with 20 ppb ozone, there would be minimal within-sampler degradation. While site and season are very important for degradation, filter and sorbent type, sampling duration, amount and composition of PM, temperature and humidity also affect reactive losses.<sup>74</sup> The

length of sampler deployment may have a minor influence on degradation,<sup>74,85</sup> but more characterization of these processes is needed.

Experimental evidence only exists for PAHs, but within-sampler degradation should also be of importance for other reactive SVOCs, according to their susceptibility to degradation in the atmosphere. Gas-phase compound degradation is largely via reaction with the OH radical,<sup>73,86,92</sup> and thus we expect other gas-phase compounds with OH reaction rate constants in the same range as PAHs to also have potential within-sampler degradative losses (SI Table S2). In contrast, on-filter degradation is largely through reaction with ozone,<sup>82,86</sup> and thus degradative losses of particle-associated compounds are important mainly for PAHs (SI Table S3). Based on rate constants and gas-particle partitioning, we estimate that PAHs, CUPs and some NFRs may experience significant within-sampler degradative losses.

**Sampling Influences—Passive Air Sampling.** Despite the benefits and widespread use of PAS<sup>1</sup> they are still associated with challenges and limitations affecting the comparability of measurements. These are important to recognize and control, but few of them can be fully quantified in a field deployment setting.

**Calculation of Air Concentrations.** The most relevant limitation of PAS is their lower accuracy compared to AAS.<sup>5</sup> PAS have a semiquantitative nature, since air concentrations can only be derived if an estimated sampling rate ( $\text{m}^3/\text{day}$ ) is applied. The sampling rate is specific to the type of sampler (e.g., sorbent, sampler housing) and the environmental conditions (e.g., indoor, outdoor, meteorology), and can vary by orders of magnitude due to these differences.<sup>6,93–96</sup> In theory sampling rates should not vary by compound, but in practice large variations are found due to compound-specific behaviors or uncertainties in the methods of determining sampling rates. For example, measured sampling rates for PUF–PAS span 3 orders of magnitude (e.g.,  $0.02\text{--}20 \text{ m}^3/\text{day}$ ),<sup>32,33,94,95,97–99</sup> and some studies have observed systematic variations in sampling rates according to compound physical-chemical properties.<sup>32,33,93,100</sup> The choice of using one general sampling rate or nongeneric sampling rates is an important current discussion point within the PAS community. The use of nongeneric sampling rates (such as homologue-specific) can “correct” for some of the potential errors a general sampling rate may introduce under certain circumstances. For example, using a general sampling rate of  $\sim 4 \text{ m}^3/\text{day}$ <sup>36,101</sup> vs a nongeneric sampling rate of  $0.3 \text{ m}^3/\text{day}$  for benzo[a]pyrene<sup>94</sup> results in  $13\times$  concentration differences due to the choice of sampling rate alone. However, a general sampling rate for all SVOCs is often used in monitoring networks, as it is unclear whether the corrective potential of nongeneric sampling rates is significant considering the semiquantitative nature of PAS. It may not be a problem when the goal is to study the sum of compounds but may lead to errors if compound-specific concentrations or the SVOC fingerprint is of interest. The PAS community has not yet reached consensus regarding selection of appropriate sampling rates.

The methods for obtaining sampling rates add an additional level of uncertainty to their validity. Sampling rates are obtained from three methods: (1) use of depuration compounds (DCs)/performance reference compounds (PRCs),<sup>102,103</sup> (2) calibration studies with comparison to (i) continuous low volume AAS,<sup>31,33,104</sup> or (ii) intermittent high volume AAS,<sup>18,19,59,105</sup> or (3) modeling exercises<sup>106,107</sup> (e.g., applying a PUF-air

partitioning coefficient). Method (i) is considered most accurate, and is particularly advantageous when calibrating compounds with high short-term variability, which could be biased with intermittent high volume AAS depending on the timing of sampling.<sup>31</sup> DCs account for site-specific environmental conditions but do not cover the full-range of compounds, as they are not applicable for particle-associated compounds, and cannot be used for XAD samplers due to their high sorptive capacity.

PAS for SVOCs are used as time-integrated samplers, and sampling rates are only applicable when the sampler is in the linear uptake phase.<sup>41,95</sup> The length of the linear uptake phase varies for compounds within a SVOC class as well as between classes and it is important to keep deployment times within the reported linear time frames for each compound. While the conventional PAS model assumes uniform distribution of a compound within the sorbent,<sup>41,95</sup> recent studies have identified that kinetic resistance within the sorbent material may be limiting and as such, model-based calculations may overestimate the length of the linear uptake phase.<sup>59,100,108</sup> This contention is supported by experimental work.<sup>33,93</sup> For example, penta-hexachlorobenzene and low molecular weight PAHs and PCBs enter a curvilinear uptake after 6–9 weeks,<sup>93</sup> and thus air concentrations from a three-month PUF–PAS deployment may be underestimates. Furthermore, the length of the linear uptake phase may be affected by environmental conditions such as temperature, wind speed and air concentrations, but this is not yet fully characterized.

**Sorbent Material.** Two sorbent types are commonly used in PAS: PUF and XAD. As with AAS, other sorbents have been used but not applied on a large scale. Their specific characteristics result in different sampling potentials. The PUF sorbent has a lower capacity and higher sampling rate than the XAD sorbent (Table 1).<sup>31</sup> Typical deployment times in established air monitoring networks are months ( $\sim 1\text{--}4$  months) for PUF–PAS<sup>36,101,109</sup> and up to one year for XAD–PAS.<sup>6</sup> As a consequence, data from the two samplers are only comparable if sampling is conducted within the linear uptake phase of each sampler, and time weighted average concentrations from multiple PUF–PAS cover the same sampling period as XAD–PAS.

Another difference between the two sorbents is the type of compounds they can sample. While XAD is solely a gas-phase sampler, PUF is able to accumulate both gas-phase and particle-associated SVOCs, although particles are sampled with a lower accuracy and more variable sampling rates.<sup>93,97</sup> On the other hand, PUF–PAS have shown poorer or inconsistent performance for more volatile and polar SVOCs (e.g., CUPs, PFOS/PFOA), for which XAD perform well.<sup>31,56,59,110</sup> The low sorptive capacity of PUF–PAS for most PFCs<sup>60,110</sup> suggests different partitioning mechanisms for polar and nonpolar compounds. The SIP-PAS has been shown to be more effective for PFCs,<sup>56</sup> CUPs,<sup>37</sup> methyl siloxanes,<sup>111</sup> and phthalates.<sup>112</sup> However, consistency with SIP-PAS may be challenging, as XAD resin can be lost from the SIP disk during sampler deployment, particularly in windy, outdoor conditions,<sup>113</sup> thereby introducing added uncertainties.

PUF disks of different densities ( $0.021$ ,  $0.030$ , and  $0.035 \text{ g cm}^{-3}$ ) are currently used by different research groups.<sup>36,105,114,115</sup> Although density is included in the theoretical calculation of PUF-air partition coefficients, the comparability of results from different densities is not fully understood. A higher density PUF disk has higher capacity for



SVOCs and thus a longer linear uptake phase. However, kinetic resistance within the PUF also differs with density. This can result in different uptake scenarios, with lower density PUFs having enhanced rates of SVOC transfer into the interior of the disk, whereas higher density PUF has a rapidly filling “surface compartment” and slower filling of the interior of the disk (e.g., a two-phase uptake mechanism).<sup>114</sup> Additionally, particle uptake may be enhanced in a lower-density PUF, which could be a contributing factor in the discrepancies found for particle associated PAHs (0.1 vs 5.0 m<sup>3</sup>/day) in different studies.<sup>93,96</sup>

**Sampler Housing.** PAS sorbents are deployed inside a sampler housing (chamber) to reduce the influence of environmental factors that affect the performance of the PAS, such as wind speed and UV radiation. Studies have indicated that the PAS configuration, including the position of the sampling media (both PUF and XAD) inside the housing as well as the alignment of the housing (tight or open), affects uptake/accumulation and sampling rates.<sup>108,116,117</sup>

The housings used for PUF–PAS consist of two stainless steel bowls fixed on a common vertical axis around the PUF disk. This type of housing may vary slightly in geometry and deployment. Differences in the bowl geometries do not significantly affect uptake<sup>114</sup> but the way the housing is fixed results in different uptake scenarios, especially under windy conditions. A freely hanging sampler housing dampens the variation in external wind speed and results in small variations in sampling rates, while a fixed sampler results in up to 3× higher sampling rates under windy conditions.<sup>115,118</sup> The XAD-PAS housing consists of two parts: an inner stainless steel mesh tube in which the XAD is placed and an outer larger stainless steel cylinder acting as a protective shelter.<sup>6</sup> Differences in housing configuration for XAD-PAS and air movement within the sampler housing also cause significant variation in sampling rates (up to 50%).<sup>108</sup>

**Degradation.** No study has investigated degradation in PAS in detail. However, it is expected to affect the same compounds and be related to the same environmental variables as in AAS. Kennedy et al.<sup>119</sup> identified photodegradation when PUF–PAS were not shielded by a sampler housing and that this is reduced by the double bowl chamber; typical PAS housings should limit UV exposure. The long deployment times of PAS and thereby long exposures to atmospheric reactive species may exacerbate degradation, both of the SVOCs and the sorbent material itself. The effect on the structure and uptake capacity of the sorbent is unknown. Compound-specific degradation may also be a source of variability in sampler calibrations.

**Environmental Factors/Location.** The main causes of variability in PAS are environmental variables (e.g., wind speed, temperature, air concentrations) and most refinements to PAS aim to quantify/control these, through calibration of sampling rates, sampler housing design, use of DCs, etc. Despite these efforts, environmental factors continue to lead to bias/errors in estimated air concentrations.

Sampler housings are effective up to wind speeds of 4 m/s as they maintain the air flow within the chamber at less than ~1 m/s, which has a minor effect on sampling rates.<sup>115</sup> At wind speeds >5 m/s the sampler housing cannot sufficiently dampen outdoor winds, resulting in a higher air velocity within the chamber and a rapid increase in sampling rates.<sup>115</sup> This is supported by results from DCs, which have shown much higher sampling rates at windy, coastal, and mountain sites.<sup>36,99,101</sup> For XAD-PAS, sampling rates are also significantly higher under

windy conditions.<sup>106,120</sup> In contrast to the PUF–PAS, the XAD-PAS sampling rates double between winds of 0 and 1 m/s, but the effect on sampling rates is less with higher wind speed.<sup>6,120</sup>

Temperature affects PUF and XAD-PAS in similar ways. Temperature controls the gas-particle partitioning of SVOCs, thus affecting the sampling rate (discussed below). However, temperature also affects the sampling medium: for example, higher temperature leads to higher diffusivity and thus higher sampling rate<sup>95</sup> and higher temperature leads to lower sorptive capacity and thus shorter linear uptake phase. The effect of these two factors on the overall sampling rate is complex and varies by compound,<sup>106</sup> but can lead to underestimation of concentrations in warm/tropical conditions if deployment times are the same as in colder/temperate regions. Further complicating matters, variations in temperature also affect ambient air concentrations (e.g., higher temperature leads to higher volatilization and thereby higher air concentrations) which impacts one of the major assumptions of the PAS theory, that the air concentration is constant.

**Particle-Associated Compounds.** A big question when using PAS for SVOCs is their performance for particle-associated compounds. The XAD-PAS is considered a purely gas-phase sampler while the PUF–PAS also accumulates particle-associated compounds. Current findings are not consistent; some suggest similar PUF–PAS sampling rates for gas- and particle-phase compounds,<sup>33,96,121</sup> others show poorer performance and up to 100× lower sampling rates for the particle-associated compounds.<sup>93,105</sup> The reason for inconsistent results is not known but may be related to site characteristics, PUF types, or analytical differences. High TSP values and high wind speeds may favor the uptake of particle-associated compounds to a level similar to gas-phase compounds. Another possible reason may be differences in PUF density, as mentioned above.<sup>93</sup> The influence of particle-associated compounds on overall sampling rates can be exacerbated at colder temperatures when a higher fraction of SVOCs are associated with particles. The variable results imply large errors and low comparability for particle-associated compounds between sites, and it is difficult to draw a general conclusion that is applicable to all or most of the sites in monitoring networks.

The ability to use PAS for particle-associated compounds is a key need of the SVOC community, as regulated and emerging SVOCs (PAHs, PBDEs, NFRs, PFCs, CUPs) tend to have high particle fractions. The applicability of PAS for these compounds is uncertain, and the subject of ongoing research.

## ■ CHALLENGES AND LIMITATIONS

**Implications for Air Sampling.** Given the aforementioned sources of bias and potential error in AAS and PAS, it is clear that each individual measurement is associated with some degree of uncertainty which may be a bigger contribution than the analytical uncertainty. However, more importantly, the uncertainty, accuracy, and precision of the measured values vary widely by sampling technique and sampler configuration, and thus there may be poor comparability between different data sets.

Key issues for comparability are (i) sampling times, sample volumes and frequencies, (ii) PUF–PAS assumptions about particles, (iii) PAS sampling rates, (iv) spatial coverage, and the associated larger range of environmental variables as sampling is expanded to more geographic regions.<sup>2</sup>

Table 2. Percent of Ambient Air Concentration Captured by Given Sampler Configurations<sup>a</sup>

example compounds	vapor pressure (Pa) at 0 °C, 25 °C	log octanol-air partitioning coefficient ( $K_{OA}$ ) at 0 °C, 25 °C	atm. half-life (hrs) at 25 °C	estimated particle fraction at 0 °C, 25 °C	% of air concentration captured by sampler					
					high-volume sampler (24 h, 600 m <sup>3</sup> )		PUF-PAS (90 day deployment)		XAD-PAS (1 year deployment)	
					0 °C	25 °C	0 °C	25 °C	0 °C	25 °C
PFOS	0.0973, 0.981	5.23, 4.84	917	0.00, 0.00	70% (1)	6% (1)	1% (3)	1% (3)	50% (3,4)	0% (3,4)
fluorene	0.630, 0.819	8.03, 6.74	15	0.01, 0.00	4% (1, 2)	3% (1, 2)	20% (2,3)	4% (2, 3)	100%	80% (3)
$\alpha$ -HCH	0.105, 0.376	8.37, 7.37	224	0.01, 0.00	70% (1)	20% (1)	60% (3)	20% (3)	100%	90% (3)
PCB-28	0.0314, 0.123	9.28, 8.06	108	0.03, 0.00	100%	100% (1)	90% (3)	50% (3)	100%	100%
chlorpyrifos	0.00399, 0.00536	9.56, 8.41	1.4	0.04, 0.01	0% (2)	0% (2)	80% (2,3)	60% (2, 3)	70% (2)	70% (2)
endosulfan	$5.06 \times 10^{-4}$ $2.31 \times 10^{-5}$	10.58, 9.28	16	0.16, 0.03	90% (2)	90% (2)	80% (2, 3)	80% (2, 3)	80% (2)	80% (2)
PBDE-47	$4.91 \times 10^{-7}$ $2.19 \times 10^{-5}$	12.09, 10.54	128	0.64, 0.15	100%	100%	50% (4)	90% (4)	40% (4)	90% (4)
benzo[a]pyrene	$0.00550$ , $6.26 \times 10^{-6}$	12.29, 11.15	2.5	0.97, 0.76	60%	60% (2)	8% (2, 4)	20% (2, 4)	3% (4)	20% (4)
PBDE-209	$1.01 \times 10^{-8}$ $2.23 \times 10^{-4}$	16.51, 15.26	3810	1.00, 1.00	100%	100%	10% (4)	10% (4)	0% (4)	0% (4)

<sup>a</sup>The percentages represent the combined effects of breakthrough/degradation/exceedance of linear uptake phase at 0 and 25 °C and 50 ppb ozone. Causes of the losses corresponding to each compound are indicated by the numbers following the percentage. (1) indicates breakthrough, (2) is degradation, (3) is exceedance of the linear uptake phase, (4) is a high particle fraction. Full details on the estimates are given in the SI. References: PCB, HCH, and PAH physical-chemical properties and temperature adjustments are from Beyer et al.<sup>131</sup> and Paasivirta et al.<sup>132</sup> PBDE physical-chemical properties and temperature adjustments are from Harner and Shoeib,<sup>133</sup> Tittlemeier et al.,<sup>134</sup> and Wang et al.<sup>135</sup> PFOS, chlorpyrifos and endosulfan physical-chemical properties and temperature adjustments are from Odabasi and Cetin<sup>136</sup> and EpiSuite.<sup>137</sup> Particle-phase fractions were calculated using the methods of Harner and Bidleman<sup>126</sup> using the temperature-adjusted  $K_{OA}$  values. Breakthrough was calculated using the equations of Pankow.<sup>67</sup> Length of the linear uptake phase was calculated using the equations of Shoeib and Harner.<sup>95</sup> Degradation was estimated based on field study data from Armstrong et al.,<sup>138</sup> Schauer et al.,<sup>85</sup> Tsapakis and Stephanou,<sup>84</sup> Peters et al.,<sup>139</sup> Menichini,<sup>82</sup> and Goriaux et al.<sup>140</sup> Full details on all assumptions/estimates are provided in the SI.



For example, an intermittent AAS can easily be biased for compounds with short-term temporal concentration variability (e.g., CUPs, combustion-related SVOCs)<sup>31</sup> and a long-term time weighted average concentration from a PAS cannot provide information on episodic events. If intermittent sample timing results in sampling on the same weekday or period of a month, this can be biased by daily, weekly or monthly activity patterns (e.g., weekday traffic). This can lead to an over- or underestimation of concentrations if the sample either coincides with or completely misses a high concentration event. Furthermore, as we have moved to measurement of emerging compounds and lower concentration ranges (pg/m<sup>3</sup> and fg/m<sup>3</sup> levels), sample collection volumes have been pushed higher in order to achieve detection, particularly in remote environments, without thoroughly assessing the associated breakthrough potentials.

As described earlier, there is much uncertainty in how particles behave in PUF-PAS. Comparability issues are introduced because users of PUF-PAS make different assumptions about the fraction of the particle phase sampled by the PUF. The assumptions range from treating PUF-PAS as gas-phase only to assuming 1–10% of particles are sampled,<sup>93,105</sup> to assuming all particles are sampled.<sup>96</sup> If PUF-PAS are treated as bulk samplers when they are only sampling a fraction of particles, measured values may be biased low, particularly for higher molecular weight SVOCs.

The systematic variations in PAS sampling rates by physical-chemical properties identified in some studies,<sup>32,33,93,100</sup> reflect situations where the conventional PAS framework does not apply, such as when volatile compounds enter the curvilinear uptake phase, or when only a fraction of atmospheric particles are sampled. Thus, the use of a general sampling rate may introduce bias in either the low molecular weight or high molecular weight compounds and different compound/congener distributions.<sup>33</sup> It is also not well quantified how much sampling rates differ between different climate zones/seasons, thus considering the global range of average temperatures (SI Figure S4), large biases may be introduced when comparing PAS measurements from very different regions or seasons.

Spatial distributions of sampling networks further bias our global knowledge of air concentrations.<sup>1,2</sup> While coverage is somewhat improved when one also considers case studies, there continue to be areas of the world with limited measurement coverage (Figure 1). For example, if one considers available PBDE data for the period 2003–2013, only 2% of the global land mass is within 100 km of a reported PBDE air concentration, and 0.1% is within 20 km. By population, only 30% of people live within 100 km of a reported PBDE measurement, and only 6% within 20 km. Southeast Asia has some coverage for PBDEs measured by case study, but these largely consist of one-time measurements, thereby limiting temporal information. Additionally, land-based southern hemisphere sampling is largely PAS (SI Figure S1), furthering the spatial bias.

**Examples of Bias.** To demonstrate the potential combined effects of the aforementioned sampling artifacts and biases, we estimated the potential errors in measured concentrations for three typical sampler configurations: (1) a high-volume active air sampler with GFF or QFF and two PUF plugs, collecting ~600 m<sup>3</sup> of air over 24 h, (2) a PUF-PAS, deployed outdoors for 90 days, and (3) an XAD-PAS, deployed outdoors for one year, and two temperature scenarios: 0 and 25 °C. Estimates are

summarized in Table 2 and details are given in SI Table S4. These estimates have significant uncertainty, due to the very different data sources, but they emphasize the large possibility for sampling artifacts to influence measured concentrations.

The estimates suggest combined effects of breakthrough and/or exceedance of the PAS linear uptake phase lead to large underestimates in the reported values of the volatile SVOCs, notably PCB-28,  $\alpha$ -HCH, fluorene, PFOS, and by extension, other SVOCs with similar physical-chemical properties. This effect also influences XAD-PAS for more volatile SVOCs (e.g.,  $\alpha$ -HCH, fluorene, PFOS) at higher temperatures.<sup>59,106</sup> Within-sampler degradation, although not well-characterized, is also estimated to contribute to large losses, particularly for fluorene, benzo[a]pyrene, and chlorpyrifos. Similar degradation is expected for gas-phase compounds with short reactive atmospheric half-lives, which includes all PAHs, many CUPs and some NFRs (SI Table S2). The particle-associated SVOCs are under-sampled by PUF-PAS and not sampled by XAD-PAS. Estimates in Table 2 assume PUF-PAS collect 10% of the total particle fraction, but this may range from 1 to 100%. Thus, reported concentrations may vary between 15 and 100% of the actual concentration, depending on the fraction of particles that is truly collected by the PUF-PAS.

Attention is frequently given to issues of analytical comparability, but sampling comparability affects many compounds which we assume have minimal analytical uncertainties. For example, BDE-209, which has frequently been identified to have difficulties in laboratory analysis,<sup>122</sup> is “correctly” sampled, for example, 100% of the air concentration should be captured by a typical high volume air sampler, whereas PCB-28, a compound that has been consistently included in global monitoring networks and is one of the seven typical indicator PCBs, may experience losses of up to 15% based on breakthrough alone, and thus reported values may be biased low in many situations.

**Problematic Chemicals.** Many “emerging” SVOCs have different physical-chemical properties compared to the legacy SVOCs and this may introduce challenges in sampling. Current sampling networks and techniques were developed for legacy SVOCs and may not be appropriate for providing representative data on these newer SVOCs. For example, the use of PAS in the future may be more challenging because target compounds are either too volatile (volatile methylsiloxanes, phthalates) or too involatile (CUPs, NFRs) and thus have high uncertainty in conventional PAS. As a consequence of regulatory actions, newer compounds are often designed to be less persistent in the environment, but as a result are also less persistent in samplers (leading to more within-sampler degradation) and thus more difficult to correctly quantify. Degradation is also of concern when measuring nitro- and other substituted PAHs,<sup>123</sup> and existing data on these compounds is likely an underestimate. The lack of data on degradation and the potential importance for many emerging compounds highlights the need for more studies.

Furthermore, we must be aware that chemicals currently measured by the SVOC community are a small fraction of the chemicals in use that may be of environmental and/or human health concern.<sup>124</sup> Adding more chemicals to the lists of analytes without adapting current sampler configurations will introduce more uncertainty in measured concentrations.

## ■ RECOMMENDATIONS AND FUTURE DEVELOPMENTS

**Recommendations to Enhance Comparability.** Given the wide range of potential biases and uncertainties in air sampling identified above, it is clear that careful consideration must be given to sampling approaches. This consideration should first consider the study goals and outcomes. For example, what sampling designs are best suited to address global distributions vs data for human exposure assessments vs source identification, long-term vs short-term trends, and the target SVOCs? The sampler type, frequency, and sampling materials should correspond to the specific question and compounds to be addressed. But ultimately, as the GMP and other initiatives aggregate international data, study design should also aim for comparability with global data sets.

Overall, PAS are best for broad spatial coverage and long-term temporal trends, while AAS are best for short-term temporal trends and coverage of a broader set of compounds. When the intended result of a study is long-term integrated average concentrations (e.g., monthly to yearly scale), and particularly for largely gas-phase compounds, PAS have a clear advantage. The simplicity of PAS (no electricity, cheaper) make them best suited to resolve concentration gradients where levels vary by orders of magnitude. AAS are recommended when absolute concentrations are needed, smaller concentration variations are expected or high time resolution is needed. AAS are the only choice when gas-particle partitioning is important or particle-phase concentrations are expected to be dominant and when short-term trends (hourly to weekly) are of interest. Because congener/compound ratios can be biased in PAS, AAS are best for source identification/fingerprinting techniques. Regulations for human exposure assessment are often based on particle-associated SVOCs and the best sampler choice is a low volume AAS providing continuous gas- and particle-phase concentrations, while PAS are not as well suited. However, current research continues to demonstrate the broad applicability of PAS,<sup>96,97</sup> and, although they have higher uncertainty, particularly for particle-phase compounds, the uncertainty in a temporally integrated PAS could be lower than uncertainty in intermittent AAS for compounds with daily concentration variations.

Sorbent choice should be considered with respect to the length of sampling period and target compounds. In PAS, PUF is recommended for capturing seasonal trends for stable, legacy compounds, while XAD-PAS are recommended for longer term (e.g., yearly, decadal trends)<sup>31</sup> and also to cover emerging gas-phase SVOCs (more polar compounds). In AAS, for best applicability to a broad range of SVOCs and conditions, we recommend a combination of PUF and XAD, as this reduces breakthrough concerns and allows quantification of both polar and nonpolar SVOCs. While PUF and XAD are the current focus of the majority of the SVOC community, new sorbents should be investigated for their applicability to a wider range of compounds.

Although there is a need for standardization in SVOC air measurements, with large regional differences and equipment constraints, implementation of standardization can be challenging. This could be addressed in the long term through the development of international standards for SVOC sampling (e.g., an ISO standard), but in the short term resetting of all sampling campaigns and networks to the same configurations is not practical, nor necessarily useful. Many networks have long-

term established techniques and continuation of the same techniques allows for temporal comparisons. Furthermore, universal standardization of techniques would not be appropriate for all regions. For example, sampling in high temperatures tropical regions may require a different sampling approach to low temperature polar regions. However, when different techniques are used it is important for the SVOC community to understand the biases from techniques/configurations/approaches. Instead of implementing identical sampling techniques, data from different sampling configurations may be adjusted using standardization factors. Standardization factors can account for effects of breakthrough, temperature differences, wind, etc., and can be tailored to specific sites/sampler types/seasons/sampling approaches. For example, if degradation was better characterized, a standardization factor could be used to account for the underestimation caused at sites with high levels of reactive trace gases. For cases where large sample volumes are needed, standardization factors can be used to account for losses of the more volatile SVOCs. In fact, this is already done to a certain extent when compound-specific sampling rates are used for PAS; these rates account for nonlinear uptake of volatile SVOCs and lower sampling of particle-associated SVOCs.

One way standardization factors can be determined, particularly for long-term monitoring networks, is at “super-sites” where samplers and sampling approaches from different networks are used simultaneously.<sup>125</sup> Quality assurance techniques such as spiking samplers with labeled compounds should also be used periodically across different networks to further evaluate comparability.

However, standardization factors, once developed, should not be treated as a perfect solution. Better consideration of study design should be given in advance of sampler deployments. There is sufficient theoretical and experimental knowledge to allow researchers to estimate PAS linear uptake phases,<sup>41,95</sup> gas-particle partitioning of target compounds,<sup>126,127</sup> and AAS breakthrough<sup>67</sup> in advance of sampler deployment. A necessary part of sampling campaign should be estimating these effects and structuring the sampling campaign to reduce these artifacts. New monitoring networks and case studies should aim to harmonize, where possible, with existing networks to maximize data comparability.

**Recommendations for Future Work.** Extensive experimental, modeling and calibration work has and continues to be done on PAS techniques with the goal of improving the accuracy of measured concentrations and better understanding uptake processes. This should be continued. However, limited efforts have been made to improve AAS, despite knowledge of uncertainties from degradation, breakthrough, etc. and this should be an additional focus.

For PAS, there are some obvious improvements needed, particularly in the determination of sampling rates. Currently, sampling rates are determined either with calibration studies or DCs, but sampling rates could be improved by combining these two methods. Sampling rates (determined from calibration studies) could be adjusted according to differential losses of DCs between sampling sites to account for site-specific influences. Further studies should also focus on understanding the performance of PUF–PAS for particle-associated SVOCs under different conditions and for different PUF densities, to better understand why current studies obtain inconsistent results.

For AAS there are also clear improvements needed, particularly in the study of breakthrough and degradation. Current sampling configurations are based on information from breakthrough studies from 1980s and early 1990s<sup>24,67,128</sup> when different SVOCs were the primary concerns and concentrations were often higher. Today, larger volumes are used to detect compounds at the pg/m<sup>3</sup> and fg/m<sup>3</sup> level, particularly in low concentration regions (e.g., polar regions, Figure 2) without a good understanding of the associated impacts (breakthrough, degradation). Since the use of denuders in conjunction with AAS has yielded important information regarding the degradation of PAHs, this avenue should be further investigated to better understand within sampler degradation for PAHs and other reactive SVOCs. As the relationship between ozone levels and degradation appears relatively consistent,<sup>85</sup> it may be possible to estimate SVOC losses based on ozone levels, which could be especially important in locations/times of year when losses are expected to be large. Additionally, we should reconsider the paradigm that AAS provide more accurate results. We have summarized numerous well-known sampling artifacts associated with PAS and AAS, but due to limited experimental evidence, the question of the overall effect of these artifacts on the accuracy of reported concentrations remains a rough estimate (e.g., Table 2). The question of the overall significance of these artifacts on PAS vs AAS could be addressed with a well-designed PAS-AAS comparison.

In addition, as sampling expands to broader global coverage, a more thorough understanding of the effect of environmental conditions/meteorology on both AAS and PAS is needed. Currently, sampler evaluation and testing is largely performed in temperate regions; this may limit applicability in more extreme environments.

There is also room for innovation in sampling techniques. For example, source regions and the influence of specific air masses can be assessed using new directional AAS<sup>129</sup> and PAS.<sup>130</sup>

Finally, the SVOC community must be progressive and adaptable. How can sampling campaigns be designed to produce more comparable data without compromising the data needs of individual networks and case studies? What compounds are most important to continue monitoring, and what compounds should be added to global monitoring? We have established that there are big challenges in comparability between well-known SVOCs such as PAHs, PCBs, and PBDEs. These must be addressed, but the SVOC community should also move forward with air sampling methods that can meet the future challenges of new chemicals. We must also be prepared to address the future global developments, as the key questions in SVOCs shift, e.g., responding to climate change-induced meteorological shifts and new source balances due to melting of glaciers and polar ice caps<sup>1</sup> and the relationship between SVOCs and human health impacts, including consideration of possible synergistic effects.<sup>3</sup>

## ■ ASSOCIATED CONTENT

### ⑤ Supporting Information

Maps of global distributions of sampling networks and case studies, description of atmospheric degradation processes, atmospheric reactive half-lives for SVOCs, and details of calculations for Table 2. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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