Using long-term air monitoring of semi-volatile organic compounds to evaluate the uncertainty in polyurethane-disk passive sampler-derived air concentrations

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Abstract
Much effort has been made to standardize sampling procedures, laboratory analysis, data analysis, etc. for semi-volatile organic contaminants (SVOCs). Yet there are some unresolved issues in regards to comparing measurements from one of the most commonly used passive samplers (PAS), the polyurethane foam (PUF) disk PAS (PUF-PAS), between monitoring networks or different studies. One such issue is that there is no universal means to derive a sampling rate ($R_s$) or to calculate air concentrations ($C_{air}$) from PUF-PAS measurements for SVOCs. $C_{air}$ was calculated from PUF-PAS measurements from a long-term monitoring program at a site in central Europe applying current understanding of passive sampling theory coupled with a consideration for the sampling of particle associated compounds. $C_{air}$ were assessed against concurrent active air sampler (AAS) measurements. Use of “site-based/sampler-specific” variables: $R_s$, calculated using a site calibration, provided similar results for most gas-phase SVOCs to air concentrations derived using “default” values (commonly accepted $R_s$). Individual monthly PUF-PAS-derived air concentrations for the majority of the target compounds were significantly different (Wilcoxon signed-rank (WSR) test; p < 0.05) to AAS regardless of the input values (site/sampler based or default) used to calculate them. However, annual average PUF-PAS-derived air concentrations were within the same order of magnitude as AAS measurements except for the particle-phase polycyclic aromatic hydrocarbons (PAHs). Underestimation of PUF-derived air concentrations for particle-phase PAHs was attributed to a potential overestimation of the particle infiltration into the PUF-PAS chamber and underestimation of the particle bound fraction of PAHs.

1. Introduction

Global and regional air monitoring networks have been established to monitor the progress of regulatory measures to reduce or eliminate emissions of pollutants, including a number of semi-volatile organic compounds (SVOCs), under the auspices of the Stockholm Convention (SC) on Persistent Organic Pollutants (POPs) and the Aarhus Protocol on POPs under the Convention on Long-Range Transboundary Air Pollutants (UN/ECE, 2010; UNEP, 2011).

Air is an important and effective transport route from sources of potential pollutants to the wider environment, and hence ambient air is a core matrix within the Global Monitoring Plan (GMP) framework as well as the European Monitoring and Evaluation Programme (EMEP) (UN/ECE, 1988; UNEP, 2011). Frameworks such as the GMP were established as a means to share information, create broad scale monitoring and to achieve some consistency (standardization or comparability) in monitoring procedures so that data are comparable (UNEP, 2011). Monitoring networks can also inform the understanding of the fate and transport of pollutants, which is essential in determining exposure in human and environmental health risk assessment.

Passive air samplers (PAS) have increasingly been used in regional and global scale air monitoring programs in the past.
decade to complement active air sampling, particularly the polyurethane foam (PUF) disk samplers (Hung et al., 2010; Jaward et al., 2004; Klánová et al., 2009). PAS are easy to use, do not require electricity and are relatively low cost compared to the alternative, active sampling (Harnet et al., 2006a). These characteristics make PAS such as the PUF disk PAS (PUF-PAS) suitable to increase the spatial coverage of air monitoring networks, particularly in countries with low available resources and in high need of information (Pozo et al., 2006). However, there are a number of factors that may affect the inter-comparability of passive sampling data between different monitoring networks or programs, as identified by Melymuk et al. (2014). For example, amongst the PAS most commonly used in monitoring networks (PUF-PAS, XAD-resin based PAS and XAD sorbent-impregnated PUF-PAS) (a) different deployment times, sample size and sampling frequencies, (b) PUF-PAS particle sampling assumptions, (c) the PAS sampling rate, as well (d) the spatial coverage of PAS networks are identified as key limitations for data compatibility (Melymuk et al., 2014).

In the present study we focused on the calculation of air concentrations of target compounds, which is currently perceived to be semi-quantitative, as a potential key limitation in ensuring inter-comparability of PAS measurements between monitoring programs (Melymuk et al., 2014). The amounts of compounds accumulated in PUF-PAS, for example, are routinely converted into air concentrations through application of sampling rates specific for a certain type of sampler (sorbent, housing). The sampling rates for PUF-PAS in particular can also be affected by physicochemical properties of compounds of interest (particle/gas partitioning), and environmental conditions at the site (temperature, wind speed) (Bohlin et al., 2014; Chaemfa et al., 2008; Klánová et al., 2008; Tuduri et al., 2006). For example, the sampling rates for PCBs increased by an order of magnitude between external wind speeds of 3.5–4 m s⁻¹ and 7 m s⁻¹ for the flying saucer configuration of the PUF-PAS (see Fig. S1 for a diagram of such a PUF-PAS configuration and Klánová et al. (2008) showed that the equivalent sample volume of the PUF-PAS for PAHs ranged from 300 m³ to 400 m³ at −6 °C and 150–250 m³ at 22 °C.

PUF-PAS sampling rates can be derived from (i) calibration studies based on parallel deployment of PAS and active air samplers (AAS) (Bohlin et al., 2014; Chaemfa et al., 2008, 2009a; Harnet et al., 2013; Hazrati and Harrad, 2007; Klánová et al., 2008; Melymuk et al., 2011), (ii) use of depuration compounds (DCs), also termed performance reference compounds (PRCs) (Bartkow et al., 2004; Bohlin et al., 2010; Gouin et al., 2005; Harnet et al., 2006b; Moeckel et al., 2009; Pozo et al., 2006, 2012) and (iii) theoretical models (Harnet, 2016; Petrich et al., 2013; Peverly et al., 2015). With the first method both gas-phase and particle-bound compounds are considered; however it can be influenced by the intermittent nature of many AAS records. For example, in some instances calibration studies are carried out using a high volume active air sampler (HVAAS) deployed for one 24-h period per week compared to month-long to three month-long periods, which are usual for PUF-PAS deployment (Harnet et al., 2013; Klánová et al., 2008). Added to this, most calibration studies are case studies, i.e. one study at a specific period of the year and for relatively short periods (e.g., weeks to months), and thus may not account for seasonal influences (Bohlin et al., 2014; Chaemfa et al., 2008, 2009a; Melymuk et al., 2011). In reality, PAS for established monitoring programs (GAPS, EMEP, etc.) are deployed over the entire year (across seasons) and monitoring with PAS-PAS occurs for long periods (decades). DCs account for site-specific environmental conditions but are not applicable for particle-associated compounds. In addition, typically only a few DCs are used to calculate sampling rates for a more extensive list of analytes.

The choice of method to derive sampling rates adds uncertainty to the determination of air concentrations, which can be compounded if the PUF-PAS has only partial efficiency for sampling particles, and hence particle-bound compounds (Melymuk et al., 2014). For example, for benzo[a]pyrene, a compound found primarily in the particle phase of the atmosphere, it has been estimated that only 8% of the air concentration may be captured by some PUF-PAS sampling configurations with potential losses possibly due to poor infiltration of particles into the PUF-PAS protective chamber, and hence under-sampling of particle-associated compounds by PUF-PAS (Melymuk et al., 2014). Therefore, our aim was to evaluate how well the theoretical PAS model (used to estimate the chemical-specific effective air sample volumes) described by Shoibeg and Harrar (2002) works to replicate the same levels and trends as seen in AAS at a long-term monitoring site. As passive sampling theory applies only to gas-phase chemicals a particle phase sampling rate as a fraction of the gas-phase sampling rate was estimated using long-term monitoring data or derived from the literature. In addition, and an occtanol-air partition coefficient (KOA) based model was used to estimate the fraction of compounds that might be associated with particles entering the PUF-PAS protective chamber and settling on or infiltrating into the PUF disk. PAS monitoring sites are globally distributed and a variety of PUF-PAS configurations are used by different monitoring programs, and hence there exist a variety of potential site- and sampler-based influences that contribute uncertainty to the calculation of air concentrations calculation from PAS measurements. Therefore, in this study a particular focus is given to how the choice of site- and sampler-based parameters, such as sampling rate and PAS particle-sampling efficiency affect the calculation of these air concentrations.

Air concentrations were calculated from PUF-PAS measurements using two sets of input variables including, (i) “site-based” variables, where up to nine years of PUF-PAS and HVAAS measurements from the sampler deployment site were used to first derive the gas-phase sampling rate (Rg), a particle-phase sampling rate (Rp) and, from these, Cin and (b) a set of “default” input variables, where typical values of Rg based on PAS theory (Shoibeg and Harrar, 2002) and Rp derived from the literature, i.e., field measurements (Harnet et al., 2013; Markovic et al., 2015) were used to calculate Cin. The method used to determine air concentrations of SVOCs from PUF-PAS measurements was a template provided by the GAPS network (Harnet, 2016) using calculations and theory originally described in Shoibeg and Harrar (2002), Finizio et al. (1997) and Harrar and Bidleman, 1998. Cin were compared to HVAAS measurements from the same period, i.e., a set of reference values.

2. Materials and methods

2.1. Sampling site

Passive and active air samplers were deployed at the Košetice observatory, located in central Czech Republic (N49°35’; E15°05’) (Fig. S1, SM). The site is operated by the Czech Hydrometeorological Institute and ambient air monitoring has been carried out at Košetice since 1988 (Holoubek et al., 2007b). The Košetice observatory is part of the European Monitoring and Evaluation Programme (EMEP), and hence, the monitoring design is based on the EMEP POP monitoring strategy (EMEP; 2009; Holoubek et al., 2007b). It is a background site located in a region with a moderately warm, moderately humid, highland climate (Váňa et al., 2001).

2.2. Air sampling, meteorological and particle data

HVAAS and PUF-PAS measurements for a range of SVOCs
(including polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs)) and for sampling periods from 2003 to 2012 (PAHs) and 2006–2012 (PCBs and OCPs), were used in the current study. PCB and OCP measurements from 2003 to 2005 were excluded from the present study due to a change in analytical methods in 2006; we wanted to reduce the associated analytical uncertainty in order to focus specifically on uncertainties related to sampler performance and air concentration calculations. All meteorological data (temperature and wind), particle (particulate matter <10 µm in size (PM10), organic carbon (OC) and elemental carbon (EC)) information was obtained upon request from the Czech Hydrometeorological Institute (CHMI).

In brief, PUF-PAS of the MONET-CZ design and HVAAS measurements were deployed at the Kostice observatory for 28 days and 24 h for 1 day each week (each Wednesday), respectively (Klánoř et al., 2008). While in most instances PUF-PAS were deployed for 28 days there were two exceptions; one PUF-PAS deployment was for 34 days and one for 55 days. There were also a few instances (2–3 times) where HVAAS data were missing (sampling error, sampling maintenance, etc.). Characteristics of the PUF-PAS (density, volume, surface area and effective film thickness) and the PUF plug component of the HVAAS are included in Table S1, SM. A detailed description of the air sampling techniques is included in Section S1.1.1 of the Supporting Material (SM).

2.3. Sample analysis

All PAH, OCP and PCB analyses were carried out at the accredited Trace Analytical Laboratories, Research Centre for Toxic Compounds in the Environment (RECETOX), Brno, Czech Republic, using methods developed there. Analytes are listed in Table S2 and included: 16 United States Environmental Protection Agency Priority PAHs (NAP, ACY, ACE, FLU, PHE, ANT, FLA, PYR, BAA, CHRY, BBE, BKF, DBAHA, BAP, JPY and BGP), 7 PCBs (28, 52, 101, 118, 138, 153, 180), and 12 organochlorine pesticides (α-HCH, β-HCH, γ-HCH, p,p′-DDE, p,p′-DDE, p,p′-DDE, p,p′-DDT, p,p′-DDT, PeCB and HCB). Sample extraction, clean-up and analysis for PAH, PCBs and OCPs was similar to previous studies (Klánoř et al., 2009; Lammel et al., 2015; Lohmann et al., 2012) and are described in the SM, section S1.1.2.

2.4. Study design

The main objective was to investigate how air concentrations derived using the theoretical understanding of PAS, as well as theoretical understanding of gas–particle partitioning, compare with long-term AAS-determined concentrations. Under this objective we examined how the choice of input parameters, such as \( R_s \), influences the estimated air concentration calculation. We also estimated particle-phase sampling of the MONET-CZ PUF-PAS and investigated whether this had a significant influence on the calculation of air concentrations from PUF-PAS measurements.

For this study, gas-phase compounds were defined as those that had on average > 70% of their total concentration in the PUF plug of the HVAAS, and particle-phase compounds were defined as those that had on average > 70% of their total concentration on the QFF of the HVAAS. Two out of a total of twenty compounds did not fit the gas or particle-phase categories: fluoranthene (FLA) and pyrene (PYR), and were termed ‘intermediate’ compounds, i.e., average 33% and 44% of their total concentration in the PUF plug of the HVAAS, respectively. The gas, particle and intermediate compounds are indicated in Table S2, Fig. S2, Supporting Material (SM) provides a chart showing the time periods for data collection.

Two types of input data, summarized in Table 1 and further described below, were used to calculate air concentrations.

### 2.5. Theory and calculations

The compound specific gas-phase sampling rates were calculated using the following:

\[
R_s = \frac{1}{n} \sum_{i=1}^{n} \left[ \frac{M_{\text{PAS}} / C_{\text{CAAS}}}{t} \right]
\]

(1)

where \( M_{\text{PAS}} \) is the mass of the compound in the PUF disk (ng sampler\(^{-1}\)) accumulated over a deployment period lasting 28 days (in most cases); \( C_{\text{CAAS}} \) is the average bulk air concentration (ng m\(^{-3}\)) of four weekly 24-h HVAAS measurements during the same sampling period as the PUF-PAS measurements (i.e., HVAAS measurements cover ~14% of the time of the PAS deployment) and \( t \) is the PUF-PAS deployment period (days).

Passive sampling theory applies only to gas-phase compounds. Yet, particles are known to infiltrate into the PUF-PAS sampling chamber and to penetrate into to PUF disk (Chaemfa et al., 2009b).

A larger proportion of the particle-bound SVOCs captured by active and passive samplers are associated with fine (aerodynamic diameter \( d_p \) of <2.5 µm) and ultrafine \( (d_p \) of <0.1 µm) particles, due to their high surface area on a mass basis (Degrendele et al., 2014; Heo and Lee, 2014; Luo et al., 2014; Odabasi et al., 2015; Ren et al., 2008). These fine and ultrafine particles may behave like gas-phase molecules in air in terms of their movement and delivery or capture on PUF disks (Chaemfa et al., 2009a; Harner et al., 2006a; Heo and Lee, 2014; Klánoř et al., 2008). Particle-capture by PUF disks has been characterized (Chaemfa et al., 2009b) and there is evidence of particle-phase compound sampling by the PUF-PAS (Böhlin et al., 2014; Chaemfa et al., 2009a, b; Harner et al., 2013; Klánořová et al., 2008; Pozo et al., 2015). Yet, the uptake mechanism for particle-phase compounds by the PUF disk, which likely involves a combination of process such as diffusion, deposition, impaction, electrostatic interactions and entrainment of particles in the PUF pores, is not yet fully understood. The approach to dealing with particle-associated SVOCs in this study was to use PAS and HVAAS field measurements to first derive a ‘sampling rate’ for these compounds using the same formula as for \( R_s \) (Equation (1)). Following this a particle-phase sampling rate as a fraction of the gas phase sampling rate was calculated using Equation (2), which was consequently used to calculate the PUF disk equivalent air volume (\( V_{\text{EQ}} \)).

\[
\phi_{R/P} = \frac{R_P}{R_s}
\]

(2)

\[
V_{\text{EQ}} \text{ (m}^3) \]

\[
C_{\text{air}} = \frac{M_{\text{PAS}}}{V_{\text{EQ,TRUE}}}
\]

(3)

where \( M_{\text{PAS}} \) is the mass of compound in the PUF disk (ng sampler\(^{-1}\))
\[ V_{EQ,TRUE} = (1 - \phi + \phi \times \phi_{R,P}) \times V_{EQ} \]  
where \( \phi \) is the fraction of compound in the particle phase and

\[ V_{EQ} = (K'_{PUF,A}) \times (V_{PUF}) \times \left\{ 1 - e^{-K_{PM10}(fom)/(\Delta mlm)} \right\} \]

where, \( V_{PUF} \) is the volume of the PUF disk (\( m^3 \)), \( k_A \) is the air-side mass transfer coefficient (\( R_s/\text{surface area of the PUF disk} \)) and \( \delta_{\text{flm}} \) is the effective thickness of the PUF disk (\( \text{volume of the PUF disk}\div\text{PUF disk surface area} \)) \( K'_{PUF,A} \) is the PUF-air partition coefficient \( (K_{PUF,A}) \) multiplied by the PUF disk density (\( g m^{-3} \)) and log \( K_{PUF,A} = 0.6366 \times \log K_{OA} - 3.1774 \).

The fraction of compounds in the particle phase was calculated using the following equations from Finizio et al. (1997) and Harner and Bidleman (1998):

\[ \phi = K_p \times PM_{10}/(K_p \times PM_{10} + 1) \]

where log \( K_p = log K_{OA} + log f_{om} - 11.91 \). \( K_{OA} \) is the \( K_{OA} \) at the average temperature over the sampling period and \( f_{om} \) is organic matter fraction of particles.

2.6. Input data used in air concentration calculations

MONET-CZ PUF disk specifications, PUF-PAS deployment times at Kosetice from 2003 to 2012 (PAHs) and 2006–2012 (PCBs and OCPs), and average temperatures at Kosetice over each deployment period were common to all air concentration calculations. The average temperature over the deployment periods was calculated using average daily values and ranged from -71 °C to 21 °C.

Two sets of values were used to calculate air concentrations:

(a) A set of site-based/sampler-specific variables: \( C_{air} \) 1

All of the following site-based or sampler-specific values were used to calculate air concentrations \( (C_{air} \) 1). Approximately nine years of PUF-PAS and HVAAS measurements of ACE, FLU, PHE, PCBs 28, 52, 101, 138, 153 and 180; \( \alpha, \beta, \gamma \) and \( \delta \)-HCH, \( \gamma \)-DDD, \( \gamma \)-DDE, \( \gamma \)-DDD and HCB from Kosetice were used to calculate \( k_A \) with Equation (1). \( R_p \) was calculated using Equation (1) with PUF-PAS and HVAAS measurements of BAA, CHY, BBF and BKE. The \( R_s \) and \( R_p \) were then used to determine particle-phase sampling rate as a fraction of the gas-phase sampling rate \( (\phi_{R,P}) \) (Equation (2)). Also, site-specific particle data (~18 years of \( PM_{10} \) and ~6 years of OC measurements) along with a factor of 1.4 for converting the OC to OM from Yttri et al. (2007), were used to calculate an average \( PM_{10} \) and average organic matter fraction of particles \( (f_{om}) \) for use in Equation (6). \( PM_{10} \) has been used instead of total suspended particles (TSP) as (a) for part of the sampling period (2011–2012) only particles <10 \( \mu \)m diameter were collected by the HVAAS (Digitel DH-77) and (b) target compounds, particularly the particle-phase PAHs, were expected to play a major role in this size fraction of the particulate matter (Gutierrez-Daban et al., 2005; Keyte et al., 2013).

(b) A set of default (literature) variables: \( C_{air} \) 2

A default gas-phase sampling rate was derived from a calibration study where a sampling rate of 4 \( m^3 d^{-1} \) was observed when using GAPS network PUF disks (Shoeib and Harner, 2002). In consideration of the surface area of the MONET PUF disk, which in turn affects the calculation of the mass transfer coefficient (Harner, 2016), this was adjusted to a default \( R_s \) of 4.6 \( m^3 d^{-1} \) and this value was used to calculate air concentrations \( (C_{air} \) 2) from PUF-PAS measurements. The assumption in deriving this value is that air flow through the sampler housing for GAPS and MONET PUF-PAS are similar, however this was not tested in the present study. Similar sampling rates have been widely observed in studies where DCs have been used for the GAPS-type sampler (Harner et al., 2004; Motelay-Massei et al., 2005; Pozo et al., 2006, 2009). Default values for total suspended particle (TSP) concentration (25 \( \mu g m^{-3} \), \( f_{om} \) of 0.2) and \( \phi_{R,P} \) of 1 were also used to calculate \( C_{air} \) 2 (Harner, 2016; Harner and Bidleman, 1998; Harner and Shoeib, 2002). An \( \phi_{R,P} \) of ~1 has been observed elsewhere using PUF-PAS for the GAPS network (Harner et al., 2013; Pozo et al., 2015). It is important to note that the most recent investigations of particle infiltration into PUF-PAS housing suggest that MONET-type samplers have lower particle infiltration than those used elsewhere (Markovic et al., 2015). However, there is still very limited data on the true particle sampling rate of MONET PUF-PAS and our aim was to demonstrate whether using default values to characterize a particular sampler, when not enough specific information is available, can affect the calculation of air concentrations.

2.7. Data treatment

Prior to any calculations data were cleaned up in an attempt to reduce the potential influence of analytical uncertainties. Compounds that were excluded from data analysis because >50% of PUF-PAS measurements were below the limit of quantification (<LOQ) were BAP, IPY, BGP, DBAHA, -HCH, PCB 118 and PCB 180. ANT was excluded due to potential analytical uncertainties caused by co-elution with PHE. PeCB, NAP and ACY were excluded due to potential for breakthrough of sampling media (PUF plug) in the HVAAS (Melymuk et al., 2016). \( p,p'-DDD \) was also excluded due to its relatively low detection in the PUF-PAS compared to the other isomers and metabolites of DDT (DDx), as well as the low levels of this compound in PUF-PAS samples. All compounds used for air concentration calculation subsequent to data treatment are indicated in bold in Table S2.

Prior to data comparison between \( C_{air} \) and HVAAS measurements, the four 24-h HVAAS measurements (ng m\(^{-3}\)) taken during the same sampling period as the PUF-PAS were averaged to give one HVAAS measurement per PUF-PAS measurement, covering on average 14% of the PUF-PAS sampling period. If any one of the HVAAS measurements was <LOQ then the batch of four associated 24-h HVAAS data points were excluded from the study.

2.8. Data analysis

The methods used for comparing air concentrations calculated using PUF-PAS measurements and HVAAS measurements:

(a) Linear regression analysis was carried out using the “least squares” method to fit a line through a set of observations (using Microsoft Excel) with 95% confidence intervals; two-tailed ANOVA was used to test the significance of the regression with a significance level of \( \alpha = 0.05 \) and all data were log-transformed (natural log - ln) to reduce the skewness of the data-set. Slopes were obtained from raw (non-log-transformed) \( C_{air} \) and HVAAS data (Figs. S10-S12, SM). Coefficients of determination (\( R^2 \)) and significance values (\( p \)) were obtained from log-transformed \( C_{air} \) and HVAAS data. Plots of log-transformed air concentrations of PUF-PAS versus average HVAAS measurements from the same period are shown in Figs. 2–4.
(b) Wilcoxon signed-rank (WSR) test with \( \alpha = 0.05 \) for comparing paired samples. WSR is a non-parametric method to test whether data distribution populations are identical, i.e., whether any difference between \( C_{\text{air}} \) calculated from PUF-PAS and HVAAS measurements is due to chance. The WSR test for comparing paired samples was performed using R Statistical Software.

3. Results and discussion

3.1. HVAAS measurements

A summary of the HVAAS measurements taken during the same period as the PUF-PAS measurement is included in Table S4 and Figs. S7-S9, SM. Results (levels and seasonal trends) are similar to long-term monitoring using a HVAAS at Kosetice from 1996 to 2007 (Dvorska et al., 2008; Holoubek et al., 2007a; Klánová et al., 2008). Clear seasonal trends were observed for PAHs in the current study, with higher concentrations of PAHs in the winter months than during summer, due to an increase in combustion emissions. PCB and OCP concentrations were higher in spring/summer compared to winter, attributed to volatilization from environmental sinks (soils and sediments) or stored wastes.

3.2. Sampling rates derived from a site specific PAS and HVAAS data

3.2.1. Gas-phase sampling rate (\( R_g \)) of the PAS

The average \( R_g \), derived using concurrent PUF-PAS and HVAAS measurements from Kosetice was 8.7 m\(^3\) d\(^{-1}\) (standard deviation (SD): 9.5 m\(^3\) d\(^{-1}\)) (Table S5). The range of \( R_g \) for all individual compounds from the present study was 0.53—170 m\(^3\) d\(^{-1}\). Given the range of values and the log-normal distribution of the data, the median and interquartile range (IQR) was used for the \( R_g \) (6.8 m\(^3\) d\(^{-1}\) and 4.5—10 m\(^3\) d\(^{-1}\)) as a site-based input for air concentration calculations (\( C_{\text{air}} \); as discussed in the proceeding sections). Large chemical-specific deviations in sampling rates are thought to be partly attributed to sampling and analysis artifacts (Ahrefs et al., 2013; Bohlin et al., 2014; Chaemfa et al., 2009a, 2009b; Hazrat and Harrad, 2007; Melymuk et al., 2016, 2014, 2011; Person and Hornbucke, 2009) and to extreme conditions at the sampling sites (e.g. high wind speeds) (Klánová et al., 2008; Tuduri et al., 2006).

The large ranges for \( R_g \) in this study may be partially explained by temporal variation in meteorological conditions and the intermitent nature of the HVAAS. There was a significant decrease in \( R_g \) with temperature for half the target gas-phase compounds: ACE, PHE, PCB 28, 52 and 101, as well as OCPs – \( \gamma \)-HCH, \( p,p' \)-DDE and HCB (Fig. S3, SM). Also a significant increase was observed in \( R_g \) with wind speed, but for less than half of the gas-phase target compounds: PHE, FLU, PCBs 28, 52 and 101, \( \alpha \)- and \( \gamma \)-HCH and \( p,p' \)-DDE (Fig. S4, SM). Where significant linear relationships were observed, temperature or wind speed only explained a small fraction of the variability in \( R_g \) (\( R^2 < 0.20 \); Figs. S3 and S4, SM). Klánová et al. (2008) have previously shown a relationship between temperature and wind speed and the effective sample volume of the PUF-PAS at Kosetice, with these meteorological conditions accounting for a two-fold variation in sampling rate for gas-phase compounds (Klánová et al., 2008). Wind speed and temperature at Kosetice are strongly correlated with higher wind speeds observed at colder temperatures, which may be why there was higher \( R_g \) at lower temperatures (Klánová et al., 2008). Because of a negative correlation between temperature and wind speed at Kosetice (Spearman \( r = 0.23, p < 0.001 \)) it is difficult to distinguish between the influence of these meteorological variables, however wind speed may be a more important factor for sampling rates at sites that are windier; for example, at high ambient wind speeds (>4.5—6.5 m s\(^{-1}\)), sampling rates may be significantly enhanced (Thomas et al., 2006; Tuduri et al., 2006). Another factor potentially driving the variability in the gas-phase sampling rates derived from Kosetice data is the intermittent nature of the HVAAS, which may be biased by short term variability in compound concentrations. As air concentrations may vary over orders of magnitude over a short period of time (e.g., diurnally or weekly), taking one HVAAS every seven days, as is the case at Kosetice, may not always be representative of average atmospheric levels. The greatest variability in sampling rates has been observed at sites where HVAAS have been used in the calibration and this has led to recommendations elsewhere that use of low-volume active air samplers may be more appropriate for PAS calibration (Melymuk et al., 2014). Although measures were taken to reduce the influence of analytical uncertainty or error it is also likely to be a factor here, potentially leading to outliers in \( R_g \).

The median \( R_p \), calculated using site-based data, i.e., PUF-PAS and HVAAS measurements from Kosetice, is similar to the default \( R_p \) of 4.0 m\(^3\) d\(^{-1}\) determined using the GAPS default value (Harner et al., 2013; Shoeb and Harner, 2002); and is similar to average sampling rates from other studies (Bohlin et al., 2014; Chaemfa et al., 2008; Harner et al., 2013; Klánová et al., 2008; Melymuk et al., 2011; Persoon and Hornbucke, 2009; Pozo et al., 2012; Santiago and Cayetano, 2007).

3.3. Particle-phase sampling rate (\( R_p \)) and sampling efficiency of the PAS

It is important to highlight that the particle sampling rate for \( C_{\text{air}} \) was derived using data from field measurements for only a few particle-bound PAHs and this is likely to have added some uncertainty to these calculations. The lower detection of particle-phase PAHs is due to lower atmospheric levels of these compounds relative to the gas-phase PAHs, but is also likely due to the poorer efficiency of the MONET PAS at sampling particle-phase PAHs. It has been observed that there is a poorer infiltration of particles into the MONET PUF-PAS chamber compared to those from other monitoring networks (Markovic et al., 2015) and a lower particle-phase sampling rate compared to the gas-phase sampling rate has previously been observed for MONET PUF-PAS (Bohlin et al., 2014; Klánová et al., 2008). As a result, we were limited to four particle-phase PAHs for determining the particle-phase sampling rate and in the calculation of \( \phi_{pR} \) (BAA, CHRY, BBF and BKF). Other particle-phase PAHs (e.g., BAP) monitored at Kosetice were <LOQ more than 50% of the time and, according to our data-processing criteria, were excluded from air concentration calculations (Table S2).

The average \( R_p \) for the four particle-phase compounds was 1.6 m\(^3\) d\(^{-1}\) (±SD: 2.6 m\(^3\) d\(^{-1}\)) (Table S5) and ranged from 0.11 to 24 m\(^3\) d\(^{-1}\) with a greater range in \( R_p \) for BAA, CHRY than for BBF and BKF (Fig. 1). The greater range in sampling rates for BAA and CHRY may be due to the effect of temperature on partitioning of these compounds, with lower partitioning to particles in warmer months (Fig. S5, SM). On average BAA, CHRY, BBF and BKF were found 93%, 83%, 99% and 100% in the QFF of the HVAAS. There is clear decrease in the percentage of these compounds in the QFF during warmer months. There were some instances of lower % in the QFF of the HVAAS in months that expected to have lower temperatures and this was potentially due to analytical uncertainty (Fig. S5, SM).

\( R_p \) increased significantly with temperature (Fig. S6, SM), suggesting that it is not a purely particle-phase sampling rate, but has some contribution from gas-phase sampling in warmer months. This observation is at odds with the assumption that \( \phi_{pR} = 1 \) but support the assumption that \( \phi_{pR} < 1 \). Using the KQ model (Finizio et al., 1997) (and KQf from Harner (2016), a TSP of 22 \( \mu \)g m\(^{-3}\) and a
The gas-phase would be 0.03, 0.12 and 0.69 at sampling rate (\(R_p\)) of 0.22 we estimated that the fraction of BAA and CHRY in the gas-phase would be 0.61, 0.85 and 0.98 at \(-10^\circ\text{C}, 0^\circ\text{C}\) and \(20^\circ\text{C}\), respectively. For BBF and BKF the fraction of these compounds in the gas phase would be 0.03, 0.12 and 0.69 at \(-10^\circ\text{C}, 0^\circ\text{C}\) and \(20^\circ\text{C}\), respectively. Yet, when assessing the correlation between temperature and \(R_p\), temperature accounted for only a portion of the variability in \(R_p\) (\(R^2\) ranging from 0.22 to 0.4, i.e., 22–40\% explained variability; Fig. S6). Therefore, as with the gas-phase sampling rate we suspect that the variability in the particle-phase sample rate is also due to the intermittent sampling of the HVAAS and short term variability in compound concentrations. As with \(R_p\) there may also be some influence from analytical uncertainties on the large range in \(R_p\).

Some of the variability in \(R_p\) could also be related to the poor particle infiltration into the MONET PUF-PAS chamber, which may result in low sampling of the particle-phase compounds — values used to derive \(R_p\) were low and close to LOQ, thus more affected by analytical uncertainty and, only four of the particle-phase compounds were detected with sufficient frequency to be included in air concentration calculations.

Using the other particle-phase PAHs that were excluded due to low detection (e.g., BAP, IPY and BGP) to calculate the particle-phase sampling rate may have led to estimation of a different rate. For instance, if BAP, IPY and BGP were used along with BAA, CHRY, BBF and BKF, to derive the \(R_p\), then the average value would be 1.4 m\(^3\) d\(^{-1}\), which is lower but not significantly different to the average calculated using BAA, CHRY, BBF and BKF, i.e., 1.6 m\(^3\) d\(^{-1}\).

The particle phase sampling rate as a fraction of the gas-phase sampling rate (\(\phi_{p} = 0.13, 13\%\)), used for \(C_{air}\) 1 calculations, was calculated using Equation (3) and median gas-phase and particle-phase sampling rates. The median particle-phase sampling rate over the colder months of winter at Kosice (21st December – 21st March), when concentrations of BAA, CHR, BBF and BKF data in the QF were greater than 81%, 67%, 95% and 95% was calculated to test whether our approach of choosing a sampling rate of all data over all seasons was valid. If the median “winter” sampling rate for the particle-phase PAHs was used to calculate \(\phi_{p}\) it would lower —

\[C_{air} = \frac{C_{gas}}{\phi_{g} + \phi_{p}}\]

Therefore our approach of using a median \(R_p\) calculated across all seasons may have contributed to the underestimation of air concentrations for the particle-bound compounds. The sampling of particle-phase compounds of the PUF-PAS is still an area of high uncertainty, and this will be discussed in more detail in proceeding sections. The limited information that does exist on the sampling phase compounds by the PUF-PAS suggests there are large differences depending on the sampler configuration/geometry (Bohl et al., 2014; Harner et al., 2013; Klánová et al., 2008; Markovic et al., 2015; Pozo et al., 2015).

### 3.4. Estimation of air concentrations (\(C_{air}\)) from PUF-PAS measurements

There was a significant linear relationship between each estimated \(C_{air}\) and HVAAS measurements for most of the compounds included in the present study regardless of which set of input variables were used (site-based/sampler-specific or default) (Figs. 2–4). Exceptions included PCB 101, 138 and 135, and p,p’-DDE. For the PCBs and OCPs, estimated air concentrations (\(C_{air}\)) tended to be less than HVAAS measurements at the low end of the concentration range and greater than HVAAS measurements at the high end of the concentration range (Figs. 2 and 3). The only exception was HCB, where the site-based/sampler-specific air concentrations were generally higher than measurements and using default variables to calculate air concentrations (\(C_{air}\)) were in closer agreement with HVAAS along the whole concentration range. In general, PUF-PAS-derived \(C_{air}\) (i.e., using site-based and sampler-specific variables) for the gas-phase and intermediate PAHs were higher than HVAAS measurements but \(C_{air}\) 1 were lower than HVAAS measurements. For the four particle-phase PAHs, which were considered in the present study, \(C_{air}\) 1 and 2 were not HVAAS measurements.

Individual measurements of air concentrations (i.e., individual, month-long PUF-PAS measurements) for PCBs, OCPs and PAHs (\(C_{air}\) 1 and \(C_{air}\) 2) were significantly different to paired HVAAS measurements taken during the same period (WSR test; \(\alpha = 0.05\)) for most of the compounds (Table S6, SM) with some exceptions (e.g., PCB 28, 52 and 101, as well as, \(\alpha\), \(\beta\) and \(\gamma\)-HCH, PHE and FLU for \(C_{air}\) 1, in addition to \(\beta\)-HCH and PYR for \(C_{air}\) 2). However, we note that is a comparison of (in most cases) a 28-day average versus four 24-h samples, and thus the paired HVAAS is only sampling 14% of time of the PUF-PAS. Over longer time-scales (e.g., annual) average PUF-PAS-derived air concentrations were within the same order of magnitude as the HVAAS for the PCBs, OCPs and gas-phase PAHs regardless of the set of input variables used to calculate them in the present study. For PCBs and OCPs, the annual average \(C_{air}\) was within a factor of 2 or 3 of annual average HVAAS (Fig. 5 and Figs. S13 and S14, SM). Annual average \(C_{air}\) were also within a factor of ~2–3 of the HVAAS measurements for the more volatile, gas-phase PAHs (ACE, FLU, PHE, FLA and PYR — Fig. 5), regardless of whether site-based/sampler-specific or default input values were used. However, for the less volatile, particle-phase PAHs (BAA, CHRY, BBF and BKF) PUF-PAS-determined air concentrations were up to 23 times lower than annual average HVAAS measurements (Fig. 5 and Fig. S15, SM).

For the HVAAS measurements we observed that PCB levels were generally higher in warmer months, but this pattern is not congruous with PUF-PAS-derived \(C_{air}\) (Fig. 5, SM). This is a reflection of the raw PUF-PAS measurements, where no distinct seasonal patterns were observed for PCBs, rather than an issue related to the air concentration estimation. Temporal trends for \(\alpha\) and \(\gamma\)-HCH, p,p’-DDE and HCB were similar for PAS-\(C_{air}\) and HVAAS measurements (Fig. S8, SM) with higher values in spring and summer compared to winter. Seasonal patterns were not clear for
p,p'-DDT and β-HCH, most likely because levels of these compounds in PUF-PAS and HVAAS were low and frequently below limits of detection. PUF-PAS-derived air concentrations for the gas-phase and intermediate PAHs showed expected seasonal trends that matched what was observed for the HVAAS measurements, with higher air concentrations in colder months than in summer and spring (Fig. S9, SM). Moreover, despite >10 fold difference between HVAAS and \( C_{\text{air}} \) for the particle-phase PAHs, the same seasonal trends were captured by the PAS and HVAAS (higher levels in colder months).

There are only a few other studies that compare PUF-PAS derived air concentrations of SVOCs with AAS. In general there has been good agreement between PUF-PAS derived air concentrations of SVOCs with AAS in these studies and a few studies that compare the chemical profiles of PUF-PAS and AAS (Ahrens et al., 2013; Bohlin et al., 2014; He and Balasubramanian, 2010; Peverly et al., 2015; Yoonki et al., 2014). However, these studies were generally conducted over much shorter time periods, i.e., the present study is the first to our knowledge that compares PUF-PAS and AAS from a long-term dataset. For example, individual PUF-PAS derived air concentrations for per- and polyfluoroalkyl substances from a 1 year sampling campaign were found to be within a factor of 2 of HVAAS (Ahrens et al., 2013). Average PUF-PAS concentrations of flame retardants, PAHs, and pesticides across up to 13 sites, were in close agreement with HVAAS measurements, but not for all compounds (e.g., brominated benzenes, which were at relatively low concentrations), but this comparison was made across only 6 weeks (Peverly et al., 2015). Bohlin et al. (2014) also found a good agreement between PUF-PAS and low volume active air samples for the PCBs and OCPs but a less than ideal match was found for the PAHs. However, in this study profiles for SVOC classes from a 3 month sampling campaign were compared rather than comparing PUF-PAS derived air concentrations with AAS measurements (Bohlin et al., 2014). The >10 times discrepancy between PAS and HVAAS for the particle-bound compounds in the present study is a major source of uncertainty in PAS application, and therefore warrants further investigation. The approach used to account for sampling of particle-phase SVOCs by the PUF-PAS and the particle-

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**Fig. 2.** In\( [C_{\text{air}}]\) determined using site-based/sampler-specific and default input values (\( C_{\text{air}} \) 1 and \( C_{\text{air}} \) 2, respectively) for PCBs plotted against ln[HVAAS measurements]. HVAAS measurements represent an average of 3–5 24-h sampling events. Included in the boxes in this figure, as well as those in Fig. 3 and 4, are (a) the slope (m), which was taken from the linear regression analysis performed in Excel using non-log-transformed data, (b) the R\(^2\) = coefficient of determination of the regression using log-transformed data and (c) the p value for the regression (\( \alpha = 0.05 \)) determined with log-transformed data.
phase sampling rate as a fraction of the gas-phase sampling rate \((\phi_{RP})\), i.e., estimated using empirical data, likely contributed to the underestimation of \(C_{air}\) for particle-phase PAHs. A \(\phi_{RP}\) of 1, which originated from previous studies using the GAPS-type sampling chamber (Harner et al., 2013; Markovic et al., 2015), was used as a default input value for \(C_{air}\) calculation, but it is unlikely that the MONET PAS used for the present study had a particle-phase sampling rate equivalent to that of the gas-phase sampling rate given that MONET PAS have previously shown that particle filtration into the protective housing of the PUF-PAS (the sampler configuration) is ~50% (Markovic et al., 2015) and the particle phase sampling rates for MONET PAS have been estimated previously, using the same approach as the present study, at ~10%–20% of the gas-phase sampling rate in the present and previous studies (Bohlin et al., 2014; Klánová et al., 2008). As highlighted previously, particle infiltration into the protective chamber of the PUF-PAS can vary depending on the PAS sampler design (Markovic et al., 2015), and hence the discrepancy in \(C_{air}\) for particle-phase compounds may be unique to some samplers/sampling networks. PUF disk density can also affect particle accumulation of the fine particle fraction (Chaemfa et al., 2009b). However, questions remain as to the true particle-phase sampling rate for MONET PAS and for PAS of different design. There is also a lack of information on how significant site-based factors such as wind speed and direction, as well as particle concentration, are for particle infiltration into the PAS, which in turn influences particle sampling by the PUF, and hence particle-phase sampling rates. Other factors may affect also the estimation of PUF-PAS-derived air concentrations when the particle-phase sampling rate is less than the gas-phase sampling rates, leading to annual average PUF-PAS-derived air concentrations that are significantly lower than the HVAAS measurements, including the method used for estimation of the particle-bound fraction of compounds (Holt et al. (submitted)).

4. Conclusions

The present study used the current understanding of passive sampling theory, as well as consideration of the sampling of particle associated compounds by the PAS, to calculate air concentrations using PUF-PAS measurements, through the readily accessible GAPS network template (Harner, 2016). A main objective of the present study was to assess how the choice of input parameters affects the calculation of air concentration; whether using as much site-specific (sampling rate) and sampler-specific (particle-phase
sampling efficiency) information as possible is important or if it is sufficient to use default/literature data.

Differences between PUF-PAS-derived air concentrations and the reference HVAAS may be, in part, due to the intermittent HVAAS (leading to bias due to short term fluctuations in air concentrations) and, in spite of efforts to reduce the influence of this factor in our calculations, analytical uncertainty in the long-term monitoring data. However, despite differences in individual

**Fig. 4.** $\ln(C_{air})$ determined using site-based/sampler-specific and default input values ($C_{air 1}$ and $C_{air 2}$, respectively) for PAHs plotted against $\ln$[HVAAS measurements]. HVAAS measurements represent an average of three to five 24-h sampling events.
measurements, annual average air concentrations determined from PUF-PAS measurements were generally within the same order of magnitude as HVAAS for gas-phase compounds, while not for particle-phase compounds, regardless of whether site-based/sampler-specific or default/general information (e.g., sampling rate, particle-phase sampling) was used in calculations. Although the results observed in the current study may be generally applicable to similar sampling sites, they may not be applicable in all cases, as some studies have reported large deviations in sampling rates, sometimes within the same class of compounds. However, large variation in sampling rate for SVOCs may result from factors other than those that are site-based (e.g. windy sites), such as sampling and analysis artifacts.

PAS-determined air concentrations for particle-phase PAHs were at least an order of magnitude less than HVAAS measurements. Two main factors may be responsible for this underestimation, namely, accounting for (1) particle infiltration into the protective chamber of the MONET-CZ PUF-PAS so that particles are able to penetrate into and settle onto the PUF-disk and (2) the estimation of particle-partitioning of PAHs. MONET-CZ design PUF-PAS were used in the present study and particle infiltration can vary between PUF-PAS sampling designs (Markovic et al., 2015). At the moment there is too little information on the particle infiltration into the protective chamber of the PUF-PAS and how particles can penetrate into or settle onto the PUF-disk given the large range of potential sampling configurations, and hence there is a need to better characterize this prior to the calculation of air concentrations. The suitability of the $K_{OA}$ model for estimating particle-partitioning of PAHs may also need to be assessed for potential uncertainties, i.e., whether the $\phi$ is underestimated, leading to a $V_{EQ}$ that is higher than expected and a $C_{air}$ that is underestimated.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.envpol.2016.11.030.

References


