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Polyurethane foam passive air sampler shows large inter-compound variability in sampling performance for semivolatile organic compounds in outdoor environment.

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Environmental Impact

This study shows potentialities and limitations of using polyurethane foam (PUF) passive samplers for monitoring of semivolatile organic compounds (SVOCs) in outdoor air. The results provides an in-depth evaluation of PUF-PAS performance for seven SVOC classes including particle associated compounds, novel brominated flame retardants (nBFRs) and polychlorinated dibenzo-*p*-dioxins/furans (PCDD/Fs). Potential users will find guidance for choose of compounds, relevant exposure times, and sampling rates which can help to a more accurate application.

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Outdoor passive air monitoring of semivolatile organic compounds (SVOCs): a critical evaluation of performance and limitations of polyurethane foam (PUF) disks

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Abstract. The most commonly used passive air sampler (PAS) (i.e. polyurethane foam (PUF) disk) is cheap, versatile, and capable of accumulating compounds present both in gas and particle phases. Its performance for particle associated compounds is however disputable. In this study, twelve sets of triplicate PUF-PAS were deployed outdoors for exposure periods of 1-12 weeks together with continuously operated active samplers, to characterize sampling efficiency and derive sampling rates (R_S) for compounds belonging to 7 SVOC classes (including particle associated compounds). PUF-PAS efficiently and consistently sampled polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polycyclic aromatic hydrocarbons (PAHs), and eight novel brominated flame retardants (nNBFR) compounds. Low accuracy and lack of sensitivity was observed for most polychlorinated dibenzo-p-dioxins/furans (PCDD/Fs) and polybrominated diphenyl ethers (PBDEs) (under the conditions of this study), with the exception of some congeners which may be used as qualitative markers for their respective classes. Application of compound specific R_S was found crucial for all compounds except PCBs. Sampling efficiency of the particle associated compounds was often low.

Introduction

The use of passive air samplers (PAS) is becoming increasingly frequent in regional and global scale monitoring of persistent organic pollutants (POPs) and other semi volatile organic compounds (SVOCs) in outdoor air. PAS offer several advantages over active air samplers in terms of possibility for long time integrated sampling, cost reduction and simplified field operations. In fact, before the introduction of PAS, monitoring networks could only provide fragmentary regional scale information on air concentrations of POPs due to limitations for active samplers to implement large scale integrated sampling. As a result, PAS have been instrumental for the establishment of the Global Monitoring Plan of the Stockholm Convention for POPs.[1-4]

Basically, two types of PAS techniques are currently being used for SVOC sampling in monitoring networks; i.e. the polyurethane foam (PUF) disk[4-6] and the XAD-resin[7, 8] (hereon defined as PUF-PAS and XAD-PAS). Despite their broad acceptance within the POP community, both sampler types present some clear limitations. The most relevant (and common to other PAS techniques) is the lower accuracy in delivering air concentration data compared to conventional active samplers. PUF-PAS and XAD-PAS are semi quantitative since the air concentration can only be derived if an estimated sampling rate (R_S, m^3 day^{-1}) is applied.[9] For this reason they have mainly been used to detect and resolve variability in air levels across broad ranges where levels may vary within orders of magnitude.[10-14] For studies where more quantitative comparison and greater confidence in air concentrations are required, such as the assessment of human exposure or flux estimations (e.g. air-soil or air-water exchange), the accuracy of PAS may not be always sufficient. While XAD-PAS accumulates SVOCs from the gas phase, the PUF-PAS can also accumulate some particle-associated compounds.[15-17] It is however still not clear how quantitative and consistent sampling of particles by PUF-PAS

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is, especially in relationship to different types of SVOCs,[16] as well as to material composition and size stratification of atmospheric particles. Although PUF-PAS was originally introduced as a gas phase sampler the range of SVOC classes for which it is nowadays applied has expanded during the last years to include also particle associated pollutants, even in the absence of detailed calibration studies.[10, 13, 18-20] This may result in the use of PUF-PAS beyond the boundaries within which it was originally conceived, possibly resulting in a generalized uncritical acceptance of delivered data.

The lack of in-depth characterization of compound specific sampling performance (or R_S) and critical analyses of their performance for broad range of contaminant classes also appears as a critical aspect in the development of the PAS techniques. R_S and data on sampling performance for PUF-PAS and XAD-PAS are still sparse or lacking for some SVOCs for which they are already being applied (e.g. polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), novel brominated flame retardants (nBFRs) and particle phase polycyclic aromatic hydrocarbons (PAHs)). In addition, many users tend to use a generic R_S for different SVOC classes as well as for all the compounds within one class.[10, 18, 20-22] This is the case when using depuration compounds (DCs)/performance reference compounds (PRCs) to attain R_S values, since this method gives one or few generic values which then are applied for a wide range of compounds.[4] It has however been shown that R_S may vary significantly between classes and between individual compounds within each class.[15, 17, 23-26] Recent publications therefore recommend the use of homologue specific R_S over generic R_S.[26, 27] Consequences of using generic R_S are: reduced accuracy, poor comparability of data, and loss of reliable information on compound fingerprints in the air. This complicates/prevents key analysis on contaminant mixture fingerprint, including: source apportionment, age of contamination analysis, and global fractionation analysis.

The goal of this study is to characterize sampling performance of PUF-PAS for seven different SVOC classes (encompassing 90 compounds both in gas and particle phases). PUF-PAS was selected due to its potential for sampling of particle associated compounds but also because it is currently the most commonly adopted technique. An outdoor environment with moderate temperatures typical for mild climates was chosen to evaluate its applicability for real air monitoring. The end-points for this evaluation were: i) screening performance (e.g. success in detecting a pollutant), ii) precision, iii) ability to provide fingerprint/compound profile, iv) inter-compound variability of R_S and v) performance in detecting particle-bound compounds.

Materials and methods

Sampling site

Passive and active samplers were deployed on the roof (6th floor) of the Research Centre for Toxic Compounds in the Environment (RECETOX), at Masaryk University in Brno, Czech Republic. The site can be characterized as urban background. The area is open to air circulation from all directions. Wind speed and temperature data were collected from the Czech Hydrometeorological Institute in Brno on a daily basis. Sampling was performed during fall season from September to December (2010). The conditions at this site reflect an environment with moderate temperatures typical for mild climates.

Passive samplers

Polyurethane foam (PUF) disks; 15 cm diameter, 1.5 cm thickness, 424 cm^2 total surface area (A_{PUF}), 0.030 g cm^{-3} density (type T-3037 Molitana.s., Czech Republic), were used as stationary passive air samplers (PAS). The PUF-PAS disks were deployed in protective chambers consisting of two stainless steel bowls (upper 30 cm diameter and lower 24 cm diameter) to form a protective chamber. The different size of chambers compared to those used in previous outdoor calibration studies have been shown not to affect the accumulation.[25]

Reference active sampler

A low volume air sampler (LVS3, Sven Leckel Ingenieurbüro GmbH, Germany) was continuously operated during deployment of the PUF-PAS as a reference sampler to provide weekly time integrated concentrations of the target compounds for the calibration study. The low volume sampler consisted of a sampling head connected to a pump with a flow of 2.3 m^3 h^{-1}. SVOCs in the particulate phase were collected by a 47 mm quartz filter (QMF, Whatman) housed in a PMX Inlet equipped with PM10 jet tubes (CEN standard EN 12341, the EU Council Directive 1999/30/EG). Two PUF plugs (55 mm diameter, 50 mm length, 0.030 g cm^{-3} density, type T-3037 Molitana.s., Czech Republic) were used as sorbents for SVOCs in the gas phase. The PUF plugs were analyzed separately to check for breakthrough of gas phase compounds.

Experimental design

A total number of 36 PUF-PAS were simultaneously deployed at ~100 cm height at the sampling site in September 2010. One set of triplicate PUF-PAS was harvested every seventh day throughout a 12 week calibration period. This generated 12 sets of triplicate PUF-PAS with exposure periods progressively growing from one to twelve weeks.

An active reference sampler was co-deployed at similar height in the vicinity to the PUF-PAS. Sampling was conducted concurrently with the two sampler types. The filter and PUF plugs of the active reference sampler were changed every seventh days concurrently with the harvesting of each set of PUF-PAS. This generated 12 sets of reference active samples (QMFs and PUF plugs), each with an exposure time of one week.

The performance of PUF-PAS was studied concerning:

I) DETECTION

The ability for PUF-PAS and the active reference sampler to detect individual compounds was studied by comparing

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accumulated amounts to the method detection limit (MDL). MDL (pg sample^{-1}) was calculated for each compound as the mean mass measured in the field blank plus 3 times standard deviation. The number of samples (PUF-PAS or active) with levels above MDL divided by the total number of samples provided detection frequencies for individual compounds in each sampler type. Values below or close to the MDL were considered as not detected and excluded from further analysis.

As a method performance evaluation, the MDLs were also compared to the analytical limit of detections (LOD). MDLs were further converted into concentration units (e.g. pg - ng m^{-3}) by dividing them by R_S and exposure time to obtain a value of the lowest detectable concentrations (LDC). The LDC represents the lowest air concentration at which a compound can be detected in a PUF-PAS at a specific exposure time under the conditions of this study. LDCs were obtained for each compound and for each exposure time (1-12 weeks). The obtained MDLs and corresponding LDCs are dependent on the specific conditions at this site and the analytical methods, quality assurance and control measures adopted in our laboratory (see Supplementary Information). These measures are consistent with the state of the art analytical method and QA/QC procedure adopted in by international reference laboratories.[11] The LDCs are presented here as a simple tool to guide PUF-PAS users in the definition of appropriate exposure times under expected air concentrations.

II) PRECISION

Precision of PUF-PAS (expressed as relative standard deviation of replicates, %RSD) was calculated weekly for all exposure periods (1-12 weeks). %RSD was calculated from the amounts accumulated in individual PUF-PAS within each set of triplicates as:

$$\%RSD = \frac{SD}{MEAN} \cdot 100 \qquad \text{Eq. 1}$$

where SD is the standard deviation of triplicates and MEAN is their mean value. Weekly compound specific %RSD values (using N=3 replicates) were also compared among each other to look for the influence of exposure time on precision. Finally, whenever no time trends in %RSD values were observed, an average precision value was calculated from the full twelve week dataset (N=12).

III) FINGERPRINTING

The ability of PUF-PAS to provide representative compound profiles or fingerprints within a given class (based on accumulated amounts in the PUF-PAS) was analysed by comparison to compound profiles obtained from the reference active sampler. Compound profiles for each SVOC class were obtained from accumulated amounts in the PUF-PAS and the bulk phase (gas+particle) of the reference active sampler, respectively, by calculating individual compound's contribution to the total mass of compounds from the same class. The profiles in PUF-PAS and reference active sampler were compared by linear regression analysis between individual compound's contribution in PUF-PAS and reference active sampler. The results from this analysis emphasize whether it is important or not to correct by using compound specific R_S to achieve meaningful fingerprint results.

IV) SAMPLING RATES (R_S)

Compound specific R_S were obtained using two methods (1 and 2), both commonly used in the literature for PUF-PAS.

Method 1 used the results (N=36) from all exposure periods to perform a linear regression analysis between the equivalent volume of air ($V_{eq,t}$, m^3) "seen" by the PUF-PAS and exposure time (t, days). $V_{eq,t}$, for each exposure time was calculated as follows:

$$V_{eq,t} = \frac{n_{PUF-PAS,t}}{C_{act,t}} \qquad \text{Eq. 2}$$

where $n_{PUF-PAS,t}$ is the amount of a given compound (pg) accumulated in the PUF-PAS at a given exposure time and $C_{act,t}$ (pg m^{-3}) is the average bulk air concentration (gas+particle phase) measured by the reference active sampler over the same time (calculated by averaging concentration data for all the exposure periods preceding the harvesting of a given PUF-PAS triplicate set). The obtained regression analysis provides information on the duration of the linear uptake phase whereas the slope of such a linear uptake curve is directly equivalent to the R_S (m^3 day^{-1}). This method provides one single time-integrated R_S for each individual compound, and the uncertainty of the R_S is calculated from the confidence boundaries of the slope values.

Method 2 calculated exposure time specific R_S (Eq. 3) for each compound by dividing $n_{PUF-PAS,t}$ by $C_{act,t}$ multiplied by the corresponding exposure time (t, days), as follows:

$$R_S = \frac{n_{PUF-PAS,t}}{C_{act,t} \times t} \qquad \text{Eq. 3}$$

This provides exposure time specific R_S which preferably should be applied to sampling events of different length as is the case for PAS of volatile organic compounds (VOCs) and inorganics[28]. In this case the uncertainty boundaries for R_S were derived from the variance of the triplicate set.

V) PARTICLE ASSOCIATED SVOCS

The PUF-PAS performance for the particle associated compounds was studied following the four previously defined endpoints, by grouping all the analysed compounds into two groups:

1. Gas phase compounds; compounds present mainly in the gas phase (i.e. more than 50% of their total concentration was detected in the PUF plugs in the active reference sampler). These encompassed 41 compounds, about 46% of the total number of the analytes.

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2. Particle associated compounds; compounds present mainly in the particle phase (i.e. less than 50% of their total mass found in the PUF plugs). These encompassed 37 compounds, about 41% of total number.

Twelve compounds (13% of total) were excluded due to lack of detection in the reference active sampler.

Sample preparation

Preparation and storage of the PUF–PAS disks and active PUF plugs followed previously published procedures for PUFs[17] and is described in Supplementary Information.

Sample Cleanup and Analysis

Data were provided for polychlorinated biphenyls (PCBs, N=7+11), organochlorine pesticides (OCPs, N=8), polycyclic aromatic hydrocarbons (PAHs, N=16), polychlorinated dibenzo-*p*-dioxins (PCDDs, N=7), polychlorinated dibenzofurans (PCDFs, N=10), polybrominated diphenyl ethers (PBDEs, N=10), and novel brominated flame retardants (nBFRs, N=17). See Table 1 for full names and abbreviations of compounds within each class.

Cleanup and analysis were performed at the laboratory of RECETOX, Masaryk University according to previously published procedures.[17] Details in Supplementary Information.

Table 1. Overview of obtained sampling rates (R$_S$, m^3 day^{-1}) (average ± 95% CI) with Method 1, exposure times within linear phase (weeks), detection frequencies in PUF-PAS (% of PUF-PAS>LOD), average precision of triplicates for 12 weeks sampling, and previously published R$_S$.

	Sampling rate (R$_S$, m^3 day^{-1}) ±95% CI	**Linear phase (weeks)**	**Detection frequency (%) in PUF-PAS (N=84)**	**Variability (%RSD) of PUF-PAS replicates**	**Sampling rate (R$_S$, m^3 day^{-1}) *Previously published***
Polychlorinated biphenyls (PCBs)					
PCB 28	3.3±0.5	1-12	100	17	2.5-4.1[19, 23, 24]
PCB 52	4.0±0.5	1-12	100	14	3.8- 6.7[19, 23, 24]
PCB 101	4.7±0.6	1-12	100	17	4.3- 9.8[19, 23, 24]
PCB 118	5.5±1.4	1-8	100	23	2.1-6.3[19, 23]
PCB 153	5.5±0.9	1-8	100	16	4.4-6.8[19, 24]
PCB 138	5.8±0.9	1-8	100	15	4.2-5.9[19, 23]
PCB 180	4.1±0.8	1-8	100	17	6.1-7.3[23, 24]
PCB77	6.3±1.3	1-8	100	16	
PCB81	5.3±2.9*	4-8	81	14	
PCB126	4.7±0.7	4-8	81	15	
PCB169	-	-	0	-	
PCB105	6.1±0.6	1-8	100	10	
PCB114	5.6±1.0	3-10	75	27	
PCB123	6.6±1. 6	2-7	90	17	
PCB156	5.3±0.7	1-8	100	17	
PCB157	4.6±0.6	2-8	90	9	
PCB167	5.3±0.5	1-8	100	7	
PCB189	2.4±0.7	1-8	100	16	
Organochlorine pesticides (OCPs)					
Pentachlorobenzene (PeCB)	5.8±1.2	1-6	100	14	
Hexachlorobenzene (HCB)	3.0±0.9	1-6	100	16	7.0[23, 29]
***o,p'*-DDE**	4.5±0.4	1-12	100	12	
***p,p'*-DDE**	5.6±0.8	1-12	100	12	2.6-4.32[23, 29]
***o,p'*-DDD**	4.1±0.5	2-12	100	13	
***p,p'*-DDD**	3.0±0.4	2-12	100	14	3.75[23, 29]
***o,p'*-DDT**	6.1±1.5	1-12	100	27	
***p,p'*-DDT**	4.6±1.6*	2-12	100	30	2.1-3.73[23, 29]
Polycyclic aromatic hydrocarbons (PAHs)					
Naphthalene	31.0±17.4*	1-2	81	30	1.66[29]
Acenaphtylene	5.5±0.7*	1-2	81	19	2.58[29]

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Acenapthene	3.8±1.1	1-10	100	16	1.33[29]
Fluorene	3.8±0.9	1-10	100	16	3.14[29]
Phenanthrene	5.1±0.9	1-10	100	14	1.77[29]
Anthracene	3.3±0.7	1-10	100	16	1.46[29]
Fluoranthene	4.0±0.9	1-9	100	14	1.66[29]
Pyrene	3.4±0.7	1-9	100	14	2.51[29]
Benz(a)anthracene	0.6±0.1	1-9	100	16	1.99[29]
Chrysene	0.9±0.2	1-9	100	15	2.68[29]
Benzo(b)fluoranthene	0.3±0.1	1-9	100	23	2.28[29]
Benzo(k)fluoranthene	0.3±0.1	1-9	100	18	4.50[29]
Benzo(a)pyrene	0.2±0.0	1-10	94	28	2.43[29]
Indeno(123cd)pyrene	0.3±0.1	3-10	78	46	3.07[29]
Dibenz(ah)anthracene	-	-	0	-	3.29[29]
Benzo(ghi)perylene	0.3±0.1	3-10	81	37	3.70[29]
Polychlorinated dibenzo-*p*-dioxins (PCDDs)					
2378-TCDD	-	-	8	-	
12378-PeCDD	-	-	28	103	2.05[19]
123478-HxCDD	-	-	33	124	1.5[19]
123678-HxCDD	-	-	41	79	1.3[19]
123789-HxCDD	**	-	55	80	
1234678-HpCDD	0.7±0.2*	-	100	44	1.2[19]
OCDD	0.5±0.1*	-	94	39	3.0[19]
Polychlorinated dibenzofurans (PCDFs)					
2378-TCDF	2.5±0.3	2-9	100	7.4	2.1[19]
12378-PeCDF	2.0±0.6	2-9	100	24	1.7[19]
23478-PeCDF	1.3±0.3	2-9	100	19	1.8[19]
123478-HxCDF	1.0±0.3*	-	83	54	2.1[19]
123678-HxCDF	1.1±0.7*	2-9	100	37	1.7[19]
234678-HxCDF	1.1±0.6	2-9	100	35	
123789-HxCDF	**	-	44	120	0.7[19]
1234678-HpCDF	0.9±0.3*	-	100	45	1.4[19]
1234789-HpCDF	**	-	94	76	1.1[19]
OCDF	1.7±0.8*	-	92	60	0.7[19]
Polybrominated diphenyl ethers (PBDEs)					
BDE 28	-	-	0	-	10[24]
BDE 47	2.4±0.3	1-9	100	10	1.8-8.2[24, 25]
BDE 66	-	-	0	-	
BDE 100	2.4±1.3*	-	31	31	2.9-5.8[24]
BDE 99	0.7±0.3*	1-9	71	19	2.6-4.7[24, 25]
BDE 85	-	-	0	-	
BDE 154	-	-	0	-	
BDE 153	-	-	0	-	1.2[24]
BDE 183	-	-	8	-	5.7[24]
Novel brominated flame retardants (nBFRs)					
2,4,6-Tribromophenylallyl ether (ATE)	1.5±0.3	1-12	100	21	
α,β,γ,δ-Tetrabromoethyl-cyclohexane (TBECH)	3.8±0.6	1-12	100	16	

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2-Bromoallyl-2,4,6-tribromo-phenyl ether (BATE)	-	-	0	-
1,2,5,6-Tetrabromocyclooctane (TBCO)	4.8±1.0	1-12	100	17
2,3,5,6-Tetrabromo-p-xylene (p-TBX)	3.9±0.8	2-12	94	28
Dechlorane plus monoadukt (DPMA)	-	-	0	-
Pentabromoethylbenzene (PBEB)	4.8±2.7*	1-8	100	29
2,3,4,5,6-Pentabromotoluene (PBT)	5.5±1.3	1-10	100	18
2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE)	1.5±0.3	1-12	94	41
Hexabromobenzene (HBB)	3.3±1.8	1-12	100	31
Hexachlorocyclopentadienyl-dibromocyclooctane (HCDBCO)	-	-	0	-
2-Ethylhexyl-2,3,4,5-Tetrabromobenzoat (EHTBB)	2.5±0.5	2-10	100	27
1,2-Bis(2,4,6 tribromo-phenoxy)ethane (BTBPE)	2.7±1.7*	-	33	130
Bis(2-ethylhexyl)-3,4,5,6-tetrabromophthalate (BEHTBP/TBPH)	-	-	0	-
Decabromodiphenylethane (DBDPE)	3.4±2.6*	-	49	105

*R^2<0.4
**Inconsistent results

Results and Discussion

Environmental conditions at sampling site

During the measurement period the air temperatures ranged from -8 to +12ºC with the minimum during week 9, 10 and 12. Averaged wind speed was generally below 4 m s^{-1} with SE as prevalent direction.

Reference air concentrations at sampling site

The average total air concentrations (gas + particle phase), detection frequencies and gas particle distribution of individual compounds measured with the reference active sampler during all of the sampling period are presented in Table S1. Most of the target compounds (75% of total) were detected during all sampling weeks in the active air samples (full names and abbreviations are presented in Table 1). 13% of the compounds were detected with lower frequency; i.e. PCB 169, BDE 154, 153 and 183, Tetra-Penta CDDs, various CDFs and some nBFRs (i.e. DPMA, HBB and BEHTBP). Four compounds (namely BDE 28, 66, 85, and HCDBCO) were always below detection limits. HCHs, BDE 209 and anti+syn-DP were excluded from further analysis due to problems with high MDLs.

The average total air concentration of each SVOC class measured by the active sampler were: 17 pg m^{-3} (sum of 7 PCB compounds, ΣPCB_7), 1 pg m^{-3} (dioxin like PCBs, dl-PCBs), 26 pg m^{-3} (sum of 6 DDTs, ΣDDTs), 85 ng m^{-3} (sum of 16 EPA PAHs, ΣPAH_{16}), 0.7 pg m^{-3} (sum of 7 PCDD compounds, ΣPCDD), 0.5 pg m^{-3} (sum of 10 PCDF compounds, ΣPCDF), 8 pg m^{-3} (sum of 9 PBDE compounds, $\Sigma PBDE_{10}$), and 15 pg m^{-3} (sum of 17 nBFR compounds, ΣnBFR). The concentrations of PCBs, PCDDs, PCDFs, and PBDEs were in the same range as in other outdoor PUF-PAS calibration studies.[19, 23-26] The OCPs were similar to those measured in a calibration site in Europe (United Kingdom) but lower than those observed in a tropical site (Singapore).[23, 29] 3-4 ring PAH concentrations were similar to previous calibration conditions while comparison for 5-6 ring PAHs could not be accurately performed since previous studies only provide information on gas phase concentrations. Continuous active sampling provided information on variability of air concentrations throughout the sampling period. PCBs, OCPs, particle associated PAHs, PBDEs, and nBFRs were stable with minima and maxima ranging within the same order of magnitude. Larger variability between weekly air concentrations (factor of 10-100) was observed for a few PCDD/Fs, and some gas phase PAHs. This may have resulted in not optimal conditions for the calibration purposes; however this exposure scenario reflected real environmental conditions. The influence of varying concentrations was reduced during the calculation of R_S by calculating time averages of the weekly atmospheric concentrations over the preceding exposure periods (1 to 12 weeks).

Compounds with a major fraction in the gas phase (>50% in gas phase, Group 1), included tetra to hepta PCB, OCPs, 2-4 ring PAHs, and 60% of the nBFRs. Compounds mainly in particle phase (<50% in gas phase, Group 2) included 5-6 ring PAHs, PCDD/Fs, PBDEs, and 40% of the nBFRs. These distributions were constant until the last two weeks of sampling when a small shift towards a higher particle phase association was observed for each compound, converging with the lowest temperatures. This was taken into consideration when evaluating time of linear uptake phase and R_S (Method 1) as the

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accumulation pattern may have been affected by the higher particle association.

General comments on R_S results

Method 1 (Table 1): The linearity between $V_{eq,t}$ and t was considered valid when t explained at least 80% of the $V_{eq,t}$ variance (namely, when the regression analysis provided $P<0.01$ and $R^2>0.65$). The R^2-values for all of the SVOCs were lower than in recent indoor calibration studies[30] likely due to a larger variability of environmental conditions outdoors than indoors. Lower R^2-values here than in other outdoor calibration studies[26] were basically due to the higher number of observations (including N=3 replicates in each sampling period) in this study.

R_S could not be obtained for some compounds (Table 1) due to i) low detection frequencies (i.e. some PCDD/Fs, BDEs, and nBFRs) or ii) lack of a clear accumulation pattern which resulted in a non-significant relationship between $V_{eq,t}$ and t (i.e. most of the PCDD/Fs, and some nBFRs). The lack of linear relationship suggests that these compounds do not behave as predicted by the mathematical model used to describe accumulation in PUF-PAS.[6, 9] This can be the result of different factors (alone or in combination and depending on the compounds) including: i) low air concentrations resulting in challenging conditions for consistent significant detection by the PUF-PAS, ii) degradation in the PUF-PAS, iii) short equilibration time in PUF-PAS;[31] and/or iv) confounding role of the accumulation of particles due to particle concentrations and distributions in different size classes. A further assessment of the influence of each of these factors on the low PUF-PAS performance for these classes of compounds cannot be performed on the basis of the present dataset, and is therefore left to a future study.

For chemicals with a significant uptake trend, the maximum length of the linear uptake phase was found to vary from 6 up to 12 weeks (Table 1). Recommendations for adequate exposure times are shown in Table 1 and discussed in the following sections. The length of the linear uptake phase for all SVOCs in this study did not vary or show any trend with gas/particle distribution or molecular weight. This is contrary to previous findings and the background theory saying that a shorter linear uptake phase is expected for compounds purely in gas phase with lower equilibrium PUF-air partition coefficients (K_{PUF-A}) than for more particle associated compounds, with higher K_{PUF-A}.[6, 23, 29] The reason is unclear but might depend on the lower temperature during last weeks of sampling.

Method 2 (Table S2): Significantly higher (a factor of 2-4) R_S ($p<0.05$) were found for short exposure times (i.e. 1-2 weeks) than for long exposure times (i.e. 4-12 weeks) for PCBs, OCPs, PAHs, and PCDD/Fs. The same trend, but not as strong (factor of 1-2), was seen for PBDEs and nBFRs. The trend was found both for compounds close to MDL and for compounds well above MDL. This behavior is well known within the PAS community for VOCs[28, 32, 33] but still not explicitly recognized for the PUF-PAS for SVOCs. Results from some outdoor and indoor calibrations[15, 23, 30, 34] are consistent with these findings while some other outdoor studies have not shown the same. Explanations for high initial R_S may be a more efficient uptake in the initial stage of the exposure facilitated by a maximum concentration gradient between PUF-PAS and surrounding air and/or a two-phase uptake mechanism in the PUF-PAS encompassing a rapid sorption to the surface followed by a slower diffusion into the interior of the sampler. If sampling continues for sufficient time, these initial variations in R_S tend to become negligible since PUF surface equilibrates with air and the slow uptake phase become dominant. This shows that exposure time specific R_S are of critical importance for short term monitoring where the lower time-integrated or average R_S will overestimate the air concentrations.

Comparison of the obtained R_S with previous results is complicated by differences in experimental design between different calibration studies due to the following factors: i) calculation using either Method 1 or Method 2, ii) calculation based on either gas phase or bulk phase from the reference active sampler or iii) calculation using DCs.

PUF-PAS performance for specific SVOC classes

PCBs and OCPs

PCBs and OCPs are the most evaluated SVOC classes for PUF-PAS and the ones most frequently monitored using the PUF-PAS.[4-6, 11, 12, 14, 21, 23, 26, 27, 35-37] Results from this study confirm that PUF-PAS works well for PCBs and OCP compounds both concerning detection, precision, and ability to provide reliable compound fingerprints. Linear accumulation patterns were obtained and R_S were defined with satisfactory levels of confidence. The compounds' predominant distribution in the gas phase (>50%) clearly played in favour of the good sampling performance.

Most of the PCB and OCP compounds were detected in PUF-PAS already after 1 week exposure. Exceptions were PCB 81, 126, and 114 (3 weeks) and PCB 169 (not detected). The lower detection frequency of these compounds was due to their low concentrations at this site (Table S1). Blank values (MDLs) were negligible for PCBs and most OCP compounds. Only p,p'-DDE had an elevated MDL. The estimated lowest detectable concentrations (LDC) for one week exposure were below or in the same range as typical urban and rural air concentrations. According to our results the minimum exposure times for PCBs and OCPs are 2 weeks while the maximum length of exposure range between 6 and 12 weeks depending on the compound. Overall, this suggests that PUF-PAS can provide time-integrated results over one to two months for PCBs and OCPs. Long-term monitoring (e.g. three months or more) may be critical due to equilibrium approach.

The precision of PCB and OCP determination was good(%RSD<25) and constant throughout the sampling period showing stable accumulation patterns in PUF-PAS. A lower level of precision (a factor of 2-3 higher %RSD) was observed during the week when all compounds shifted towards higher distribution in particle phase. This result is an evidence of the sensitivity of PUF-PAS performance on gas/particle distribution.

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Regression analysis between fingerprints obtained by PUF-PAS and the active sampler provided highly significant correlation with mean slope values undistinguishable from 1 and high R^2-values (0.86-0.99) for PCBs and OCPs. This shows that PUF-PAS can deliver the same information as the reference active sampler for the full range of analyzed PCB and OCP compounds even using generic R_S.

The compound specific R_S for PCBs and OCPs (Table 1) varied within a factor of 2-6 among compounds. The results for PCBs (2.4-6.6 m^3 day^{-1}, average 4.9±1.1) agree well with previous results obtained from time integrated calibration with active and passive samplers.[19, 23] The corresponding R_S for OCPs (3.0-6.1 m^3 day^{-1}, average 4.6±1.2) agree with results from He et al.[29] and Chaemfa et al.[23] Results from DC calibrations (PCBs and OCPs) are also in the same range (2.7-8.2 m^3 day^{-1}).

PAHs

PUF-PAS have been used to monitor PAHs outdoors in various studies.[11, 13, 36, 38, 39] A few publications also present outdoor calibration data, both from applications of DCs and comparison to active samplers.[17, 26, 29, 39] The results from this study shows trustable performance of PUF-PAS for 3-6 ring PAHs but the need of using compound specific R_S.

All PAH compounds were detected in 100% of the reference active samplers. 3-5 ring PAHs were detected to 100% also in the PUF-PAS already after one week exposure. Two of the 6 ring PAHs were detected to a lower extent in PUF-PAS than in the reference active sampler (~80%) and required 3-4 weeks of exposure to rise above MDL. The PAH compound with lowest air concentration (i.e. dibenz(ah)anthracene) was not detected at all in PUF-PAS.

MDLs were elevated for most 3-4 ring PAHs but did not affect the detection. MDLs for the 5-6 ring PAHs were instead negligible compared to the accumulated amounts in the real samples. The estimated LDCs for one week exposure were below the air concentrations at our site. However, detection of air concentrations in the range of the air quality guideline for benzo(a)pyrene (i.e. 0.1 ng m^{-3}),[40] according to the estimated LDCs will require more than two weeks of exposure. Altogether these results suggest a minimum exposure time of two weeks for gas phase PAHs (3-4 ring PAHs) and at least 4 weeks for the particle associated PAHs (5-6 ring PAHs). The accumulation deviated from linearity after nine or ten weeks for all PAHs and therefore long-term monitoring (e.g. three months or more) might result in larger bias in the results. This relatively short equilibrium time may be the result of low persistency (degradation) of the PAHs in the PUF-PAS.

The precision for 3-4 ring PAHs was good and stable throughout the sampling period (%RSD<20). The precision for 5-6 ring PAHs was a factor of 2-3 lower as well as more variable from week to week than for 3-4 ring PAHs. This is consistent with the poor precision observed for the particle associated compounds discussed below.

The compound profile in PUF-PAS matched poorly with the compound profile in the bulk phase of the reference active sampler (R^2=0.81, slope=1.2). The regression for PAH_{16} was influenced by an overrepresentation of Naphthalene in PUF-PAS compared to the active sampler. By excluding naphthalene from the analysis, a better regression (R^2=0.94, Slope=1.4) was obtained. The slope of the regression is however significantly different from 1.0 showing a skewed profile of the compounds in the PUF-PAS. This is mainly due to the underrepresentation of 5-6 ring PAHs in PUF-PAS. In fact, the relative abundance of 5-6 ring PAHs in the PUF-PAS was only 2-10% of that observed in the bulk phase from the active sampler. This can be compared to 90-110 % for the 3-4 ring PAHs. This aspect however does not affect the R^2-value of the regression since the gas phase PAHs contribute to ~80% of the total PAHs. These results emphasize the need of using compound specific R_S for the PAHs to obtain meaningful fingerprint information potentially useful for source apportionment.

The results for the 2-ringed Naphthalene deviated from the other PAH compounds in having low precision, very short linear uptake phase (two weeks) and high R_S. A reason for the high R_S may be breakthrough and thereby underestimation of real concentration in the active reference sampler. The contribution of Naphthalene to the PUF-PAS compound profile also decreased with exposure time showing equilibrium or degradation in PUF-PAS. In addition, MDLs and LDCs were elevated due to its high volatility and fast equilibrium time resulting in high levels in field blanks. This gives a narrow range of applicability of PUF-PAS for the purpose of monitoring 2-ring PAHs (1-2 weeks).

The obtained compound specific R_S for the PAHs (excluding Naphthalene) varied widely: around a factor of 30 for the time-integrated R_S (0.2-5.5 m^3 day^{-1}, average 1.7±1.7). The variability between the PAH compounds was higher than between the compounds in the other SVOC classes showing a greater variability in accumulation pattern for the different PAH compounds. In addition, R_S were dependent on gas/particle distribution and 3-4 ring PAHs had significantly higher R_S than 5-6 ring PAHs (factor of 10). These results are in agreement with results from background outdoor sites using the same PUF-PAS type.[17] Contrasting results are however found in calibration studies performed in industrial sites; i.e. R_S were found to be similar for both gas phase and particle associated PAHs.[15, 41] The R_S for gas phase PAHs from the present study (3.3-5.5 m^3 day^{-1}, average 4.1±0.8) are similar to recently published data obtained under similar climate conditions (average 5.0±3.6 m^3 day^{-1}) but a factor of 2-3 higher than data obtained in warm tropical area (1.3-3.1 m^3 day^{-1}, average 1.97±0.65).[29, 41] R_S for particle associated PAHs (0.2-0.9 m^3 day^{-1}, average 0.4±0.2) were a factor of 10 lower than previously published R_S for particle associated PAHs.[29, 41] It has however to be remarked that the method used to calculate R_S differs between the different studies. In He et al.[29] only the gas phase concentrations from the reference active sampler were used.

PCDD/Fs

PCDD/Fs are mainly monitored using active samplers but a few recent publications have presented PCDD/Fs data also from PUF-PAS.[10, 18-20, 42] The published results are based on a fixed R_S of 3.5 m^3 day^{-1}. Only one publication has presented

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calibration data for PCDD/Fs.[19] The results for the PCDD/Fs from our study generally show low detection, low precision, low consistency of compound profiles, and lack of a linear accumulation pattern in PUF-PAS which suggest that the use of a general R_S may not be valid. Acceptable sampling performance was however obtained for a few compounds that might act as markers for this class.

All PCDD/F compounds, except 2378-TCDD and 12378-PeCDD, were detected in almost all of the active reference samples (83-100%). PUF-PAS were able to detect Hepta-Octa CDDs and most PCDFs to the same extent as the active sampler. Tetra-Hexa CDDs and one of the Hexa-CDF compounds were however detected to a lower extent in PUF-PAS and the most toxic compound 2378-TCDD was the least common compound in the active sampler and below MDL in PUF-PAS for all exposure times. Low levels were found in all field blanks resulting in low MDLs for PCDD/Fs. The results suggest the need of exposure times longer than four weeks in order to achieve detection. For some compounds 12 weeks may not be sufficient. The compounds displaying a linear accumulation patterns (namely: Tetra-Penta CDFs) started to deviate from linearity after nine weeks. It is therefore not recommended to exceed this exposure time.

Good and constant precisions were only found for Tetra-Penta CDFs. Generally bad and inconsistent precision was found for all the other congeners. The poor results for detection and precision did not depend on low air concentrations or a high particle distribution as inconsistent results were observed for congeners in different ranges of air concentrations and gas phase distributions.

Compound fingerprint from the PUF-PAS and the reference active sampler were not consistent for PCDFs (R^2=0.46, slope=0.6). These results enhance the need of using compound specific R_S for this class.

Method 1 provided R_S for only four PCDF compounds (1.1-2.5 m^3 day^{-1}, average 1.7±0.6). No R_S could be obtained for PCDDs and most of the Hexa-Hepta CDFs since they were not displaying a clear accumulation pattern.

Method 2 routinely provided exposure time specific R_S for PCDFs and Hepta-Octa CDD (Table S2). The R_S were varying within a factor of 3 between the compounds (0.9-2.5 m^3 day^{-1}, average 1.5±0.6). These values are similar to PCDF compound specific R_S from Mari et al. (0.4-3.3 m^3 day^{-1}).[19] Consistently to the present results, Mari et al. showed a poor performance of PUF-PAS for the PCDDs and R_S for PCDDs in the range of 0.5-0.7 m^3 day^{-1} (average 0.6±0.1).[19]

PBDEs

Monitoring reports of atmospheric PBDEs using PUF-PAS are increasingly frequent in literature,[7, 11, 18, 43-46] however only two publications addressed calibration issues.[25, 26] This is critical since the relatively higher affinity of PBDEs for particles may result in challenging conditions for PUF-PAS performance. High particle distribution of the BDE compounds in the present study resulted in low detection frequency by PUF-PAS. Six of the ten analysed BDEs were detected by the reference active sampler; three congeners (i.e. BDE 47, 99 and 100) with a 100% frequency and three (i.e. BDE 154, 153 and 183) with a frequency between 25 and 67%. The remaining congeners were not detected at all. The PUF-PAS in turn could only detect three of these BDEs (namely: BDE 47, 99 and 100). BDE 47 was detected in 100% of the PUF-PAS while BDE 99 and 100 only in 71 and 31%, respectively. Overall, satisfying results were only obtained for BDE 47 and 99.

Blanks, MDLs and LDCs were very low for all BDEs except for BDE 47, and 99. For these congeners, however air concentrations were sufficiently high to allow detection by PUF-PAS. The results suggest a minimum exposure time of at least two weeks and a maximum exposure time of nine weeks for BDE 47 and 99.

The average precisions were good for BDE 47, 99, and 100 (%RSD<31) while weekly results varied to a large extent for the more particle associated BDE 99 and 100. In agreement with the findings from the other chemical classes, these results confirm a less predictable accumulation pattern for particle associated compounds in PUF-PAS.

The compound fingerprint in PUF-PAS did not match with the one from the active sampler (R^2=0.55, slope=1.3), meaning that congener specific R_S should be used. This was clearly determined by high particle distribution and to a certain extent to the low atmospheric concentrations characterizing this site.

Time-integrated R_S (Method 1) could only be obtained for two compounds (BDE 47 and 99) while exposure time specific R_S (Method 2) were also obtained for BDE 100. The R_S (0.7-2.4 m^3 day^{-1}, average 1.6±1.2) are within the range of previously published R_S (0.7-11 m^3 day^{-1}) for PBDEs.[25, 26]

NOVEL BFRS

Data on nBFRs in the atmosphere are still limited as this is a relatively new SVOC class. The interest in these pollutants is however growing, since they are used as substitutes for regulated BDEs.[47] To our knowledge this is the first report on uptake calibration for a range of nBFRs in PUF-PAS. One previous study presented detection frequencies of nBFRs in PUF-PAS after 3 months exposure globally.[48] The results from the present study show inconsistent behavior in sampling performance between different nBFRs. This is not surprising since nBFRs encompasses substances with very different structure and characteristics.

Nine of the individual nBFRs (namely ATE, TBECH, TBCO, p-TBX, PBEB, PBT, DPTE, HBB, and EHTBB (see Table 1 for full names)) were detected already after one week of exposure and to a similar high extent in PUF-PAS as the reference active sampler. Three compounds (namely BATE, BTBPE, and DBDPE) were detected to a lower extent in PUF-PAS (<50%) and five compounds (namely: DPMA, HCDBCO, BEHTBP, s-DP and a-DP) were detected to low extent or not at all by the two sampler types. The low detection frequency of some compounds might have been determined by degradation in the PUF media under the current environmental conditions, although no data, to this regard are currently available in the literature.

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The amounts in field blanks and the corresponding MDLs varied widely between the nBFRs. 50% of the compounds had low MDL (similar to LOD) while the remaining had elevated MDL. Especially high MDLs were found for s-DP and a-DP which therefore were excluded from further evaluation. The results for the nine nBFRs successfully sampled shows that exposure times of 2-10 weeks are ideal to sample within the boundaries of detectability and linear uptake phase.

Bad precision and a high week-to-week variability were found for the nBFRs with low detection frequencies. Good average precision (RSD 16-40%) was found for most of the remaining nBFRs.

The profile in PUF-PAS did not correlate with the one in the reference active sampler suggesting the use of compound specific uptake rate is crucial. A large scatter (R^2=0.50) showed a random contribution of compounds. This was not caused by any specific compound being over- or underrepresented in the PUF-PAS as with PBDEs. In general, however, the most abundant compound in the active sampler (TBECH) was also the most abundant in the PUF-PAS.

Time-integrated R_S (Method 1) could only be obtained for compounds with detection frequency above 50% (namely: ATE, TBECH, TBCO, p-TBX, PBT, HBB, EHTBB) although some compounds with high detection frequencies (namely: PBEB and HBB) showed poor linear accumulation pattern (R^2~0.4) in PUF-PAS. Reasons can be rapid equilibrium and/or fast degradation in the PUF. R_S were therefore obtained for 40 and 65% of the compounds with Method 1 and Method 2 respectively. Their value ranged 1.5-5.5 m^3 day^{-1} (average 3.5±1.4). The obtained R_S varied within a factor of 4-8 between compounds. These are the first published R_S for nBFRs.

Performance for particle associated compounds

Several studies have shown that particles and particle associated SVOCs accumulate in PUF-PAS and some studies even suggested equal uptake rates for particle and gas phase SVOCs.[15, 16, 41] The results from this study however showed poorer performance of PUF-PAS for compounds in the particle phase than compounds in gas the phase (Figure 1) in all assessment endpoints: detection, precision, fingerprinting performance, and R_S consistency and magnitude.

Gas phase and particle associated compounds were detected to the same extent by the reference active sampler (96±13%). Detection frequencies in PUF-PAS were significantly lower ($p<0.05$) for the particle associated compounds (65%) than for the gas phase compounds (88%) (Figure 1A). The variability of detection frequencies among replicates was also bigger for the particle associated compounds.

The precision was significantly worse ($p<0.01$) for particle associated compounds (45% RSD) than for gas phase compounds (17% RSD) (Figure 1B). Weekly results on replicate were also less consistent among the particle phase compared to gas phase compounds. The lower detection frequency for many particle associated compounds was a major contributor to low precision among replicates. These differences probably stem from different accumulation pattern for gas phase and particle associated compounds, substantially determining unpredictable accumulation behaviour of particles, especially under normal to low levels of total suspended particles (as in the conditions of the present study).

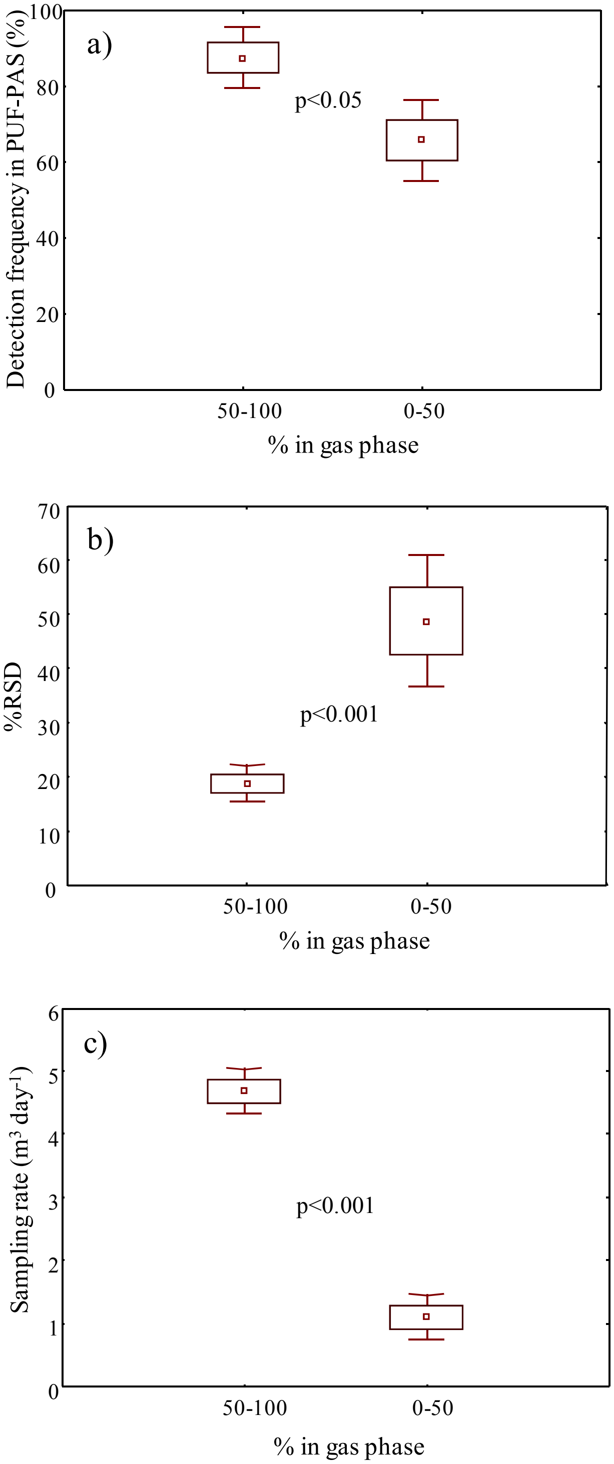

Figure 1. a) Detection frequencies in PUF-PAS (%), b) Precision of weekly triplicates (%RSD), and c) Sampling rates (m^3 day^{-1}) for gas phase congeners (50-100%) and particle associated congeners (0-50%), respectively. Mean values, standard errors and confidence intervals are given.

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The R_S (Method 1 and 2) were significantly lower ($p<0.01$) for the particle associated compounds (1.1±0.80 and 1.3±1.0 m^3 day^{-1}) than for the gas phase compounds (4.7±1.0 and 6.3±3.3 m^3 day^{-1}) (Figure 1C). These results confirm previous results from Klanova et al.[17] In addition, no R_S could be obtained for 50% of the particle associated compounds compared to only 15% for gas phase compounds. Other authors have instead reported similar sampling performance for gas phase and particle associated compounds.[41] The reasons for such inconsistent results are unclear. Possible drivers must be searched in the different conditions at which the studies were carried out. In particular different concentrations of TSP, different types and sizes of particles, and possibly different PUF densities. Understanding the reasons for such contrasting results will be the matter for future studies.

Compound specific R_S versus general or homologue R_S

Most published results on R_S for SVOCs in PUF-PAS are based on the use of DCs and not on comparison to active reference samplers. The average R_S from all SVOCs assessed in this study (3.5±1.9 m^3 day^{-1}) is similar to the average R_S reported from DCs and applied in the GAPS network (3.9±2 m^3 day^{-1}).[4] The analysis presented above shows however that using a general R_S for all SVOC classes is questionable for some classes of contaminants. In fact, the average R_S comprises compound specific R_S differing up to a factor of 40-150. In addition, the present results showed variable performance for different SVOC classes or even individual compounds within one class in all the performance endpoints considered here. This variability is not detected by DCs since only a small set of compounds are used to calculate R_S. The use of a general R_S could thereby amplify the uncertainty to the end-point results of a PUF-PAS.

The homologue specific R_S for PCBs in this study did not differ significantly from the compound specific R_S (Figure S1a). Homologue grouped R_S for PAHs were statistically different between 3-, 4- and 5-ring PAHs while no difference was found between 5- and 6-ring PAHs. Additional grouping into 3+4-ring PAHs and 5+6-ring PAHs resulted in significantly lower R_S ($p<0.01$) for the 5+6-ring PAHs (0.4±0.37 m^3 day^{-1}) compared to 3+4-ring PAHs (3.4±1.50 m^3 day^{-1}) (Figure S1b). The differences between homologue groups however did not reflect the wide ranges of compound specific R_S within each group.

These findings call for the use of compound specific R_S over homologue specific and general R_S as the latter may hamper the results for compounds, possibly resulting in considerable under- or over-estimation of the concentrations.

Conclusions

This study confirmed that PUF-PAS is an efficient sampler for PCBs, OCPs, and gas phase PAHs. For these classes the sampler displayed high detection frequency, high sensitivity (detection can be achieved already after two weeks exposure in a typical semirural area), low LODs, high precision, good fingerprinting performance, and consistent R_S. Good performance was also observed for eight of the 17 analysed nBFRs showing the potential of using PUF-PAS to increase the knowledge of their presence in the environment. For sampling of particle associated PAHs it is however important to be aware of a lower precision and need for compound specific R_S. For most of the compounds belonging to the PCDD/Fs, and PBDEs the PUF-PAS showed unsatisfactory results under the conditions of this study, possibly due to a range of factors (alone or in combination) including: poor consistency in collecting the particle associated fraction, very low or very variable air concentrations, possible degradation of compounds in the PUF medium. Within each of these classes, however, some exceptions were spotted for which the PUF-PAS may provide usable results (namely tetra-penta CDFs, and BDE 47, 99 and 100). These compounds can be used as qualitative markers of contamination for their respective classes.

Results for particle associated compounds showed that expanding the application of PUF-PAS outside the domain of solely gaseous SVOCs (for which this sampler was originally conceived) is critical and can lead to very uncertain/inconsistent results, unless calibration parameters are provided for the very same conditions of the monitoring area. Finally, the use of compound specific R_S is highly recommended to significantly increase precision of air concentration estimates. In the case of PCBs however, and in accordance to previous findings, homologue specific R_S can also be used.

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Notes

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References

1. *Guidance on the Global Monitoring Plan for Persistent Organic Pollutants (www.pops.int/documents/meetings/cop_3/meetingdocs/inf14/GMP%20Guidance%20CD/Guidance.pdf)*, 2007.
2. J. Klanova and T. Harner, *Trac-Trends Anal. Chem.*, 2013, 46, 139-149.

Environmental Science: Processes & Impacts Accepted Manuscript

3. H. A. Leslie, B. van Bavel, E. Abad and J. de Boer, *Trac-Trends Anal. Chem.*, 2013, 46, 85-97.
4. K. Pozo, T. Harner, S. C. Lee, F. Wania, D. C. G. Muir and K. C. Jones, *Environ. Sci. Technol.*, 2009, 43, 796-803.
5. T. Harner, K. Pozo, T. Gouin, A. M. Macdonald, H. Hung, J. Cainey and A. Peters, *Environ. Pollut.*, 2006, 144, 445-452.
6. M. Shoeib and T. Harner, *Environ. Sci. Technol.*, 2002, 36, 4142-4151.
7. L. Shen, F. Wania, Y. D. Lei, C. Teixeira, D. C. G. Muir and H. Xiao, *Environ. Pollut.*, 2006, 144, 434-444.
8. F. Wania, L. Shen, Y. D. Lei, C. Teixeira and D. C. G. Muir, *Environ. Sci. Technol.*, 2003, 37, 1352-1359.
9. M. E. Bartkow, K. Booij, K. E. Kennedy, J. F. Muller and D. W. Hawker, *Chemosphere*, 2005, 60, 170-176.
10. C. Bogdal, E. Abad, M. Abalos, B. van Bavel, J. Hagberg, M. Scheringer and H. Fiedler, *Trac-Trends Anal. Chem.*, 2013, 46, 150-161.
11. A. K. Halse, M. Schlabach, S. Eckhardt, A. Sweetman, K. C. Jones and K. Breivik, *Atmos. Chem. Phys.*, 2011, 11, 1549-1564.
12. T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2004, 38, 4474-4483.
13. K. Pozo, T. Harner, A. Rudolph, G. Oyola, V. H. Estellano, R. Ahumada-Rudolph, M. Garrido, K. Pozo, R. Mabilia and S. Focardi, *Atmos. Pollut. Res.*, 2012, 3, 426-434.
14. E. C. Santiago and M. G. Cayetano, *Bull. Environ. Contam. Toxicol.*, 2011, 86, 50-55.
15. P. Bohlin, K. C. Jones and B. Strandberg, *Environ. Sci. Technol.*, 2010, 44, 749-754.
16. C. Chaemfa, E. Wild, B. Davison, J. L. Barber and K. C. Jones, *J. Environ. Monit.*, 2009, 11, 1135-1139.
17. J. Klanova, P. Cupr, J. Kohoutek and T. Harner, *Environ. Sci. Technol.*, 2008, 42, 550-555.
18. X. M. Li, Y. M. Li, Q. H. Zhang, P. Wang, H. B. Yang, G. B. Jiang and F. S. Wei, *Chemosphere*, 2011, 84, 957-963.
19. M. Mari, M. Schuhmacher, J. Feliubadalo and J. L. Domingo, *Chemosphere*, 2008, 70, 1637-1643.
20. Y. Moussaoui, L. Tuduri, Y. Kerchich, B. Y. Meklati and G. Eppe, *Chemosphere*, 2012, 88, 270-277.
21. V. H. Estellano, K. Pozo, T. Harner, S. Corsolini and S. Focardi, *Atmos. Pollut. Res.*, 2012, 3, 88-94.
22. J. N. Hogarh, N. Seike, Y. Kobara, A. Habib, J. J. Nam, J. S. Lee, Q. L. Li, X. Liu, J. Li, G. Zhang and S. Masunaga, *Chemosphere*, 2012, 86, 718-726.
23. C. Chaemfa, J. L. Barber, T. Gocht, T. Harner, I. Holoubek, J. Klanova and K. C. Jones, *Environ. Pollut.*, 2008, 156, 1290-1297.
24. C. Chaemfa, J. L. Barber, K. S. Kim, T. Harner and K. C. Jones, *Atmos. Environ.*, 2009, 43, 3843-3849.
25. C. Chaemfa, J. L. Barber, C. Moeckel, T. Gocht, T. Harner, I. Holoubek, J. Klanova and K. C. Jones, *J. Environ. Monit.*, 2009, 11, 1859-1865.
26. L. Melymuk, M. Robson, P. A. Helm and M. L. Diamond, *Atmos. Environ.*, 2011, 45, 1867-1875.
27. C. Persoon and K. C. Hornbuckle, *Chemosphere*, 2009, 74, 917-923.
28. E. Gallego, F. J. Roca, J. F. Perales and X. Guardino, *J. Environ. Monit.*, 2011, 13, 2612-2622.
29. J. He and R. Balasubramanian, *Atmos. Environ.*, 2010, 44, 884-891.
30. P. Bohlin, O. Audy, L. Skrdlikova, P. Kukucka, S. Vojta, P. Cupr and J. Klanova, *Submitted.*
31. M. Shoeib, T. Harner, S. C. Lee, D. Lane and J. P. Zhu, *Anal. Chem.*, 2008, 80, 675-682.
32. B. Strandberg, A. L. Sunesson, K. Olsson, J. O. Levin, G. Ljungqvist, M. Sundgren, G. Sallsten and L. Barregard, *Atmos. Environ.*, 2005, 39, 4101-4110.
33. C. Walgraeve, K. Demeestere, J. Dewulf, K. Van Huffel and H. Van Langenhove, *Atmos. Environ.*, 2011, 45, 5872-5879.
34. S. Hazrati and S. Harrad, *Chemosphere*, 2007, 67, 448-455.
35. F. M. Jaward, A. Di Guardo, L. Nizzetto, C. Cassani, F. Raffaele, R. Ferretti and K. C. Jones, *Environ. Sci. Technol.*, 2005, 39, 3455-3463.
36. A. Motelay-Massei, T. Harner, M. Shoeib, M. Diamond, G. Stern and B. Rosenberg, *Environ. Sci. Technol.*, 2005, 39, 5763-5773.
37. K. Pozo, T. Harner, S. C. Lee, R. K. Sinha, B. Sengupta, M. Loewen, V. Geethalakshmi, K. Kannan and V. Volpi, *Environ. Pollut.*, 2011, 159, 646-653.
38. P. Bohlin, K. C. Jones, H. Tovalin and B. Strandberg, *Atmos. Environ.*, 2008, 42, 7234-7241.
39. E. C. Santiago and M. G. Cayetano, *Atmos. Environ.*, 2007, 41, 4138-4147.
40. WHO, *Air Quality Guidelines for Europe*, World Health Organization, Copenhagen, Denmark, 2000.
41. T. Harner, K. Su, S. Genualdi, J. Karpowicz, L. Ahrens, C. Mihele, J. Schuster, J. P. Charland and J. Narayan, *Atmos. Environ.*, 2013, 75, 123-128.
42. Z. Y. Ren, B. Zhang, P. Lu, C. Li, L. R. Gao and M. H. Zheng, *J. Environ. Sci.*, 2011, 23, 228-235.
43. M. A. E. Abdallah and S. Harrad, *Environ. Sci. Technol.*, 2010, 44, 3059-3065.
44. T. Harner, M. Shoeib, M. Diamond, M. Ikonomou and G. Stern, *Chemosphere*, 2006, 64, 262-267.
45. Y. M. Li, D. W. Geng, F. B. Liu, T. Wang, P. Wang, Q. H. Zhang and G. B. Jiang, *Atmos. Environ.*, 2012, 51, 140-145.
46. B. H. Wilford, T. Harner, J. P. Zhu, M. Shoeib and K. C. Jones, *Environ. Sci. Technol.*, 2004, 38, 5312-5318.
47. A. Covaci, S. Harrad, M. A. E. Abdallah, N. Ali, R. J. Law, D. Herzke and C. A. de Wit, *Environ. Int.*, 2011, 37, 532-556.
48. S. E. Lee SC, T. Harner, J. Schachtschneider, D. Zaruk, M. DeJong, E. Barresi, *BFR 2010 abstract.*, Kyoto, Japan, 2010.

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