

EVALUATION OF POLYURETHANE FOAM (PUF) PASSIVE AIR SAMPLERS (PAS) AS A TOOL TO ASSESS SEMI VOLATILE ORGANIC COMPOUNDS (SVOCs) IN OUTDOOR AND INDOOR ENVIRONMENTS

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Introduction

Passive air samplers (PAS) overtake many of the limitations related to active air samplers (AAS) by being cheap, easy to handle and tolerable, and as so they enable large-scale monitoring campaigns both outdoors and indoors. The stationary polyurethane foam (PUF) PAS, has in fact become a tool in regional and global monitoring networks of persistent organic pollutants (POPs) and other semi volatile organic compounds (SVOCs) (e.g. GAPS and MONET) as well as instrumental for the establishment of the global monitoring plan (GMP) of the Stockholm Convention (SC) of POPs¹⁻⁴. It has also been increasingly used for indoor monitoring of SVOCs⁵⁻⁷.

PUF-PAS was initially developed to collect SVOCs from the gas phase only but the range of SVOC classes for which it is nowadays applied has expanded during the last years to include also particle associated pollutants⁸⁻⁹. Whether they are capable of providing reliable and reproducible data on particle associated SVOCs remains a question¹⁰⁻¹¹. It has been shown that they can accumulate some particle-associated SVOCs but it is still not clear how consistent and quantitative, especially in relationship to different types of SVOCs, environmental conditions, and material composition and size stratification of atmospheric particles. The uptake efficiency of particle associated SVOCs in non-industrial indoor environments is expected to be even lower than in outdoor environments due to lower concentrations of suspended particulate matter, lower air flows, and lower sampling rates of PAS.

The application of PUF-PAS for a broad range of SVOCs appears as a critical aspect in the development of the PUF-PAS technique. Despite this and the fact that they are widely used and accepted, there is still a lack of in-depth characterization of compound specific sampling performance and critical analyses of its performance for SVOCs for which they are already being applied (e.g. polychlorinated dibenzo-p-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), novel brominated flame retardants (nBFRs/NFRs) and particle phase polycyclic aromatic hydrocarbons (PAHs)).

Herein we evaluate the sampling performance of PUF-PAS outdoors and indoors for seven SVOC classes (encompassing 90 compounds both in gas and particle phases) based on long-term comparison with co-deployed active air samplers (AAS).

Materials and methods

Polyurethane foam (PUF) disks; 15 cm diameter, 1.5 cm thickness, 424 cm² total surface area, 0.030 g cm⁻³ density (type T-3037 Molitan, a.s., Czech Republic), were used as stationary PAS. A stationary low volume AAS (LVS3, quartz fiber filter (QFF) and PUF plugs, flow 2.3 m³ h⁻¹, Sven Leckel Ingenieurbüro GmbH, Germany) was used as a reference sampler. The PUF-PAS' performance was evaluated in a calibration study lasting for 12 weeks in which PUF-PAS housed in protective chambers were deployed concurrently indoors (i.e. a university lecture room) and outdoors (i.e. the roof of the building) in Brno, Czech Republic. The reference AAS was co-deployed both indoors and outdoors, and continuously operated to provide weekly time integrated concentrations of the target SVOCs for the calibration study. One set of triplicate PUF-PAS was collected every 7th day throughout the calibration period. This generated in total 12 sets of triplicate PUF-PAS in each site with exposure periods progressively growing from one to twelve weeks. The QFF and PUF plugs of the reference active sampler were consistently substituted every 7th day. Samples were analyzed for polychlorinated biphenyls (PCBs, n=7+11), organochlorine pesticides (OCPs, n=8), polycyclic aromatic hydrocarbons (PAHs, n=16), polybrominated diphenyl ethers (PBDEs, n=10), novel brominated flame retardants (nBFRs, n=17) (also called

“novel” halogenated flame retardants (NFRs)), polychlorinated dibenzo-p-dioxins (PCDDs, n=7), and polychlorinated dibenzofurans (PCDFs, n=10)¹⁰. The PUF-PAS' performance was evaluated based on detection, precision, uptake pattern, and sampling rate (R_S).

Results and discussion

PUF-PAS performance for different SVOC classes

The results of the two calibration studies showed variable results for the studied SVOC classes (Table 1).

PCBs and OCPs: PUF-PAS works well 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.

PAHs: PUF-PAS works well for 3–4 ring PAHs, with a predominance in gas phase, concerning detection, precision and consistent R_S . The performance for 5-6 ring PAHs, with a predominance in particle phase, is more variable as they were detected to a lower extent and the variability of replicates was higher. The range of the obtained R_S for individual PAH compounds was bigger than between the compounds in the other SVOC classes showing a greater variability in accumulation pattern for the different PAH compounds. It is therefore important to be aware of a lower precision and need for compound specific R_S for the particle associated PAHs.

PBDEs: High particle distribution of the BDE compounds in the present study resulted in low detection frequency by PUF-PAS. Overall, satisfying results were only obtained for BDE 47, 99, 100 outdoors and BDE 28, 47, 99, 100 indoors.

nBFRs/NFRs: To our knowledge these studies present the first results on uptake calibration for nBFRs/NFRs in PUF-PAS. The results show inconsistent behavior in sampling performance between different nBFRs.

Satisfactory sampling performance was obtained for the gas phase nBFRs (n=10) while the nBFRs with a predominance in particle phase were detected to a low extent and/or did not show a linear accumulation pattern. R_S were consistent for the gas phase compounds. This suggest the potential for using PUF-PAS for gas phase nBFRs to increase the knowledge of their presence in the environment.

PCDD/Fs: PUF-PAS does not provide trustable results for PCDD/Fs as low detection, low precision, low consistency of compound profiles, and lack of a linear accumulation pattern (and thereby few R_S) was found for most of the PCDD/Fs. This was enhanced by low air concentrations and a predominance in particle phase at these sites. It suggests that PUF-PAS should be used with caution to assess PCDD/Fs and 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 and a better performance might be obtained at sites where levels are higher.

Table 1. Outdoor and indoor performance of PUF-PAS for some SVOC classes.

	Outdoors			Indoors		
	Sampling rate (m ³ /day)	Maximum linear uptake phase (weeks)	Variability (%RSD) of replicates	Sampling rate (m ³ /day)	Maximum linear uptake phase (weeks)	Variability (%RSD) of replicates
PCBs	2.4-6.6 (4.9)	8-12	15	0.9-1.7	12	14
OCPs	3.0-5.8 (4.6)	6-12	17	1.1-3.4	10-12	18
PAHs	0.2-5.1 (1.7)	9-10	21	0.03-5.5	9	20
PBDEs	0.7-2.4 (1.6)	9	20	0.9-2.9	12	42
nFRs	1.5-5.5 (3.5)	8-12	33	1.2-4.6	8-10	37
PCDD/Fs	0.5-2.5 (1.5)	9	60	0.6-1.5	-	80

PUF-PAS performance for particle associated SVOCs

The results from this study showed poorer performance of PUF-PAS for SVOCs with a predominance in the particle phase than compounds with a predominance in the gas phase in all assessment endpoints: detection frequencies in PUF-PAS were significantly lower ($p < 0.05$), precision was significantly lower ($p < 0.01$), and R_S were significantly lower ($p < 0.01$) and less consist (Table 2). In addition, no R_S could be obtained for 50% of the particle associated SVOCs compared to only 15% for gas phase SVOCs and the differences in detection frequencies between the two sampler types were bigger for particle associated SVOCs than for gas phase

SVOCs. These results confirm previous results from Klanova et al.¹⁰ but are in contrast to others that instead have reported similar sampling performance for gas phase and particle associated SVOCs¹². The reasons for such inconsistent results are unclear. Possible drivers may be searched for in the different conditions under which the studies were carried out, for example 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.

The results show that using a general R_S for all SVOC classes is questionable for SVOC classes including particle associated compounds. The findings instead call for the use of compound specific R_S over homologue specific and general R_S when including particle associated SVOCs in air measurements using PUF-PAS. The latter may hamper the results, possibly resulting in considerable under- or over-estimation of the concentrations.

Table 2. PUF-PAS performance for SVOCs in gas phase and particle phase

	Outdoors		Indoors	
	Gas phase compounds (>50% GP)	Particle associated compounds (<50% GP)	Gas phase compounds (>50% GP)	Particle associated compounds (<50% GP)
Detection frequency (%)	88	65	88	72
Variability (%RSD)	17	45	25	65
Sampling rate (m³/day)	4.7	1.1	1.6	0.6

General comments on sampling rates and linear uptake phases

Sampling rates (R_S) could not be obtained for some of the studied compounds. The reason for this was (i) low detection frequencies (including 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 (including most of the PCDD/Fs, and some nBFRs). The lack of a linear relationship suggests that these compounds do not behave as predicted by the mathematical model used to describe accumulation in PUF-PAS. 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; and/or (iv) confounding role of the accumulation of particles due to particle concentrations and distributions in different size classes.

For SVOCs with a significant uptake trend, the maximum length of the linear uptake phase was found to vary from 6 up to 12 weeks outdoors and from 8-12 weeks indoors (Table 1). The linear uptake phase was found to be longer indoors for most PCBs, HCB, PeCB and PBDEs. The results also show that PUF-PAS successfully provide detectable levels even after only two weeks of exposure time for PCBs, PeCB, HCB, Tri-Tetra BDEs, nBFRs, and gas phase PAHs (i.e. 3-4 ring PAHs) in low level indoor scenarios. In contrast, a longer exposure time (4-6 weeks) is required for DDTs and PCDFs, and Penta-Hepta BDEs, 5-6 ring PAHs, and PCDDs may not be detected at all with PUF-PAS under the conditions of this study. In general, a minimum exposure time of 4 weeks is recommended to avoid problem of detection and to obtain data for a broad range of compounds in indoor environments.

The obtained exposure time specific R_S were significantly higher (a factor of 2–5) ($p < 0.05$) for short exposure times (i.e. 1–3 weeks) than for longer exposure times (i.e. 4–12 weeks) for PCBs, OCPs, PAHs, and PCDD/Fs. For periods longer than 3-4 weeks the R_S tended to reach relative constant values. 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. It shows the need of using time specific R_S when deploying PUF-PAS for short exposure periods.

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