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Evaluation and guidelines for using polyurethane foam (PUF) passive air samplers in double-dome chambers to assess semi volatile organic compounds (SVOCs) in non-industrial indoor environments

Colour graphic:

Highlight text:

PUF passive air samplers perform well for gas phase SVOCs while inconsistent for particle associated SVOCs in non-industrial indoor environments.

Environmental Impact

This study presents recommendations and guidelines for using polyurethane foam (PUF) passive samplers (PAS) for monitoring of semivolatile organic compounds (SVOCs) in non-industrial indoor environments. The results provides an in-depth evaluation of PUF-PAS performance for seven SVOC classes including for the first time in a non-industrial indoor environment, novel brominated flame retardants (nBFRs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo-*p*-dioxins and furans (PCDD/Fs). Potential users will find guidance for choice of compounds, relevant exposure times, and sampling rates which can help to a more accurate application.

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Evaluation and guidelines for using polyurethane foam (PUF) passive air samplers in double-dome chambers to assess semi volatile organic compounds (SVOCs) in non-industrial indoor environments

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Pernilla Bohlin*[a], Ondřej Audy [a], Lenka Škrdlíková [a], Petr Kukučka [a], Šimon Vojta [a], Petra Přibylová [a], Roman Prokeš [a], Pavel Čupr [a], Jana Klánová* [a]

Abstract. Indoor air pollution has been recognized as an important risk factor for human health, especially in areas where people tend to spend most of their time indoors. Many semi volatile organic compounds (SVOCs) have primarily indoor sources and are present in orders of magnitudes higher concentrations indoors than outdoors. Despite this, awareness of SVOCs in indoor air and assessment of the link between indoor concentrations and human health have lagged behind that of outdoor air. This is partially related to challenges with indoor sampling of SVOCs. Passive air samplers (PASs), which are widely accepted in established outdoor air monitoring networks, have been used to fill the knowledge gaps on indoor SVOCs distribution. However, their applicability for indoor environments and the assessment of human health risks are lacking sufficient experimental data. To address this issue, we performed an indoor calibration study of polyurethane foam (PUF) PAS deployed in the double-dome chamber, covering both legacy and new SVOC classes. PUF-PAS and continuous low-volume active air sampler (AAS) were co-deployed for a calibration period of twelve weeks. Based on the results from this evaluation, PUF-PAS in double-bowl chamber is recommended for indoor sampling and health risk assessment of gas phase SVOCs, including novel brominated flame retardants (nBFR) providing sufficient exposure time is applied. Data for particle associated SVOCs suffered from significant uncertainties caused by low level of detection and low precision in this study. A more open chamber design for indoor studies may allow for higher sampling rates (R_S) and better performance for the particle associated SVOCs.

Introduction

Semi volatile organic compounds (SVOCs) include a wide range of compounds with potential or proved negative impacts on human health. They are present in non-industrial indoor environments (e.g. residential and public buildings) either in active primary sources (including: building materials and house appliances) or in temporary reservoirs acting as secondary sources[1-3]. The latter include indoor materials and appliances, originally not containing SVOCs, that over-time have adsorbed SVOCs from the indoor air and re-emit them under certain conditions in the indoor environment. As a result, many SVOCs are found at higher concentrations indoors than outdoors [4-6]. This in combination with an indoor lifestyle of most urban citizens make inhalation of indoor air a relevant human exposure pathway for some SVOCs [7, 8].

Indoor air, as a crucial medium for human risk assessment of SVOCs, has recently attracted growing attention of the scientists. However, there are still important knowledge gaps regarding the pattern of exposure, and contaminant fate and distribution indoors. Addressing those gaps require overcoming inherent challenges associated with the sampling of SVOCs: i) low concentrations (generally 1-3 orders of magnitude lower than many VOCs of regulatory interest) [2, 5, 9-11], ii) partitioning behaviour (significant association with the atmospheric particles), and iii) difficulties with performing proper calibration experiments under controlled conditions.

Active air sampling (AAS) techniques separating the gas and particle phases are recommended for quantification of the human exposure since the air quality guidelines for some SVOC classes (e.g. PAHs) are based on particle associated compounds[8]. However, deployment of AAS indoors is associated with major limitations since they i) are

intrusive; ii) are logistically demanding; iii) can cause sampling artefacts (e.g. depletion of air concentrations) and iv) can only provide data for short-term monitoring. These limitations have hampered the development of broad indoor monitoring programmes. On the other hand, passive air samplers (PAS) overtake many of these limitations by being cheap, easy to handle, and tolerable. They therefore have the potential for enabling large-scale indoor sampling campaigns.

PAS were initially developed to collect SVOCs from the gas phase only[12, 13] but during the last years, they have been increasingly used to report levels of particle associated SVOCs as well[14, 15]. Whether they are capable of providing reliable and reproducible data on particle associated compounds remains a question[16-19], since their behaviour in collecting particles can be affected by many factors that have not yet been fully characterized. These include particle size, material composition, wind velocity, air humidity, and others. In fact, the uptake efficiency of particle associated compounds in non-industrial indoor environments is expected to be even lower than in outdoor environments due to lower air flows, lower sampling rates of PAS, and in some environments, lower concentrations of particulate matter (PM)[42]. The most common PAS design for sampling of SVOCs, the stationary polyurethane foam (PUF) disk, has been proven to be suitable to assess spatial and temporal variability of SVOCs in outdoor environments[14, 20]. It is used in global monitoring networks as well as in local and regional case studies. It has been increasingly used also for indoor monitoring of SVOCs[4, 6, 21, 22] even though this application is critical due to a limited number of calibration studies as well as limited number of SVOC classes included in previous calibration exercises. The indoor application is further complicated by the use of different types of chamber designs. Originally, an open chamber design was suggested for indoor environments in order to minimize restriction of the low indoor air flows[6] while a more closed chamber design (i.e. the double-dome) was suggested for outdoor environments in order to reduce effects of high air flows etc. Despite this, the closed chamber design has also been used in many indoor measurements[21, 23, 25, 43, 3, 44]. There is therefore a clear demand for an in-depth evaluation of this kind of PUF-PAS as a valid tool for indoor monitoring and human exposure assessments of SVOCs.

In this study we evaluated in parallel the indoor and outdoor[16] performance of PUF-PAS in the closed double-dome chamber design for both legacy and new SVOCs. For the first time in a non-industrial indoor environment, the evaluation included novel brominated flame retardants (nBFRs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzo-*p*-dioxins and furans (PCDDs/Fs). The evaluation of PUF-PAS was based on long-term comparison with co-deployed AAS where detection limits, precision, fingerprinting (their ability to reflect true composition of the contaminant mixture in air), and sampling rate (R_S) were considered. The aim was to provide a guidance for the use of PUF-PAS for indoor sampling, i.e. for which SVOCs can PUF-PAS be applied indoor, which exposure time is appropriate for these compounds, and which R_S should be used when calculating the air concentrations. A concurrent outdoor evaluation enabled comparison of close chamber PUF-PAS' performance under indoor and outdoor conditions[16].

Materials and method

Sampling site

Passive and active air samplers were concurrently deployed indoors in a lecture room of the Research Centre for Toxic Compounds in the Environment (RECETOX), Masaryk University in Brno, Czech Republic. The room had a total volume of 150 m^3; was fully carpeted and contained chairs, tables, whiteboards, computers, and bookcases. Heating was provided by purely diffusive radiators, and air was circulated by natural ventilation. Temperature was constant around 20ºC throughout the experiment, and air velocity was negligible. Overall, the environmental conditions in the room were constant.

Passive samplers

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 Molitan, a.s., Czech Republic), were used as stationary 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). Depuration compounds (DCs)/Performance reference compounds (PRCs)[20] were not used in the PUF-PAS in order to avoid release of pollutants to the indoor environment.

Reference active air sampler

A low volume AAS (LVS3, Sven Leckel Ingenieurbüro GmbH, Germany) was continuously operated as a reference sampler to provide weekly time integrated concentrations of the targeted SVOCs. The low volume AAS 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 (QFF, Whatman) housed in an 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 Molitan, a.s., Czech Republic) were used as sorbents for SVOCs in the gas phase.

Sample preparation

Preparation and storage of the PUF-PAS disks, active PUF plugs, and QFFs followed previously published procedures[19] and is described in Supplementary Information.

Sample Cleanup and Analysis

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). See Table 1 for full names and abbreviations of compounds within each class.

Cleanup and analysis were performed at the RECETOX laboratories according to previously published procedures[19]. Details can be found in Supplementary Information.

Experimental design

The calibration was carried out during 12 weeks, from September to December 2010. PUF-PAS (n=36) and the reference AAS (n=1) were deployed side by side (~ 200 cm height) and sampling was conducted concurrently with the two sampler types. One set of triplicates PUF-PAS was harvested every seventh day throughout the 12 week calibration period. This generated 12 sets of triplicate PUF-PAS, each corresponding to a specific exposure time ranging from one to 12 weeks. The filter and PUF plugs of the reference AAS were simultaneously replaced every seventh day, generating 12 sets of reference samples, each with an exposure time of one week.

The size of the room and natural air ventilation was considered large enough to avoid depletion of SVOCs when sampling with many PUF-PAS and an AAS simultaneously. This was confirmed by the values of average weekly concentrations derived from the reference AAS (see following sections).

EVALUATION OF SAMPLING PERFORMANCE

i) Detection and minimum exposure times

Detection of target compounds after reasonable exposure times is a basic requirement when considering employment of a sampler and especially important when evaluating PAS performance indoors where the conditions (e.g. low air velocity, and low concentration of total suspended particles) may inhibit the uptake dynamics and restrict the window of applicability.

Three parameters were analysed to evaluate the PUF-PAS capability of detecting SVOCs indoors: A) compound specific method detection limits (MDLs) based on instrumental detection limits (IDL) and field blanks, B) lowest detectable concentrations (LDCs) estimated from MDLs and specific R_S for various exposure times, and C) detection frequencies based on accumulated amounts above MDLs in the PUF-PAS and the reference AAS respectively. Information from the three parameters was further used to assess the minimum exposure time for each compound.

ii) Precision

A comprehensive precision of parallel sampling and chemical analysis was determined based on the variance (expressed as relative standard deviation RSD in %) of accumulated amounts (ng sample^{-1}) of individual compounds in triplicate PUF-PAS samples. The analysis was repeated for each set of triplicates collected at various exposure times (i.e. 1-12 weeks).

iii) Fingerprinting

Evaluation of compound profiles or fingerprint of compounds is an important diagnostic parameter defined as the ability of PUF-PAS to provide consistent information on the relative abundance of different compounds within a given SVOC class with that obtained from the AAS.

Each compound's relative contribution to the total mass or concentration of its class (expressed as a percentage) was calculated for PUF-PAS (based on accumulated amounts in the PUF-PAS) as well as for gas phase, particle phase and bulk (gas+particle) phase of the reference AAS (based on concentrations). The level of agreement was assessed through linear regression analysis.

iv) Sampling rates (R_S)

R_S were calculated using two different methods commonly and interchangeably used in the literature for PUF-PAS; *Method 1* and *2*. Both methods are described in detail by Bohlin et al. 2014[16].

Method 1: Linear regression analysis of the equivalent air volume ($V_{eq,t}$) sampled by each PUF-PAS plotted against the corresponding exposure time (t) in days (Figure S1)[23-25]. The slope of the regression line provided information of the length of the linear uptake phase as well as the PUF-PAS R_S expressed in volume per time unit (i.e. m^3 day^{-1}). This method gives one overall R_S for the time frame of the linear uptake phase (i.e. time-integrated R_S).

Method 2: Comparison of the $n_{PUF\text{-}PAS,t}$ at each exposure time and the $C_{act,t}$ over the same exposure time[26, 27]. This method provides one R_S per individual set of triplicate and exposure time (i.e. exposure time specific R_S). These R_S should be constant with exposure time if the uptake is within the linear phase.

v) Sampling of particle associated compounds

The sampling performance for particle associated compounds was assessed by comparing results from all previous evaluation endpoints between: A) compounds mainly found in gas phase (i.e. more than 60% of their total concentration found in PUF plugs), and B) compounds mainly associated with particles (i.e. less than 60 % of their total concentration found in PUF plugs). The two categories were defined based on the results of the reference AAS.

APPLICABILITY FOR HUMAN HEALTH RISK ASSESSMENT

Human health risk resulting from lifetime indoor inhalation exposure of the targeted SVOCs was evaluated with respect to the risk of developing cancer. Quantification of the human health risk was based on results from the PUF-PAS and followed previously published methodology[28]. The exposure scenario was selected based on the goal of this paper: to compare human health risks derived from active and passive sampling techniques. Details are given in the Supplementary Information. The uncertainty of the risk assessment was estimated based on the results of the performance assessment of PUF-PAS as described above (e.g detection, precision and R_S).

Results and discussion

Indoor air concentrations and gas/particle partitioning

The reference AAS provided data on indoor air concentrations (gas and particle phase) and gas/particle distribution. The results showed consistent weekly air concentrations as well as gas/particle distributions throughout the 12 weeks sampling period for all SVOCs assessed in this study. This demonstrated that sampling did not result in progressively depleting concentrations of SVOC in the indoor air. Average air concentrations (gas + particle phase) are presented in Table S1

of the Supplementary Information together with information on fraction associated with the gas phase and detection frequencies. The concentrations were generally low, ranging from a few fg m^{-3} for PCDD/Fs and some nBFRs to tens of pg m^{-3} for PCBs, OCPs, BDEs and nBFRs, and in the lower range of ng m^{-3} for PAHs. These concentrations are up to one order of magnitude lower than those previously reported for residential indoor environments[3, 5, 29-31]. Results from a simultaneous assessment of outdoor air at the same site (reported elsewhere[16]) showed PCBs, PBDEs and nBFRs to be a factor of 3-8 higher indoors, and OCPs, PAHs, and PCDD/Fs to be a factor of 2-3 lower indoors. This is in agreement with results from previous studies carried out in other locations[4-6].

The gas/particle distribution data are in agreement with those from other indoor environments[3, 32, 33]. PCBs and DDTs were mainly found in gas phase (80-100%) while PBDEs, nBFRs and PAHs were more widely distributed between the two phases (0-100% in gas phase, depending on compound). Many of the PCDD/Fs compounds were below the MDL in one of the two phases and proper information could therefore not be obtained.

Performance of PUF-PAS

Detection

The obtained MDLs (pg $sample^{-1}$) and LDCs (pg m^{-3}) are shown in Table S2 together with the analytical limit of detection (LOD, pg $sample^{-1}$). It is important to emphasize that presented MDLs and LDCs are results of the instrumental sensitivity analysis and blank levels in this particular laboratory and not generally valid for other laboratories. However, the methodology adopted here followed strict QA/QC procedures consistent with those adopted by most of the reference users/developer of PUF-PAS[34].

Results for MDLs and LDCs obviously varied across compounds and SVOC classes. Generally, the obtained MDLs were in the same range as LODs indicating that the field blank manipulation was not a source of contamination for the PUF-PAS. Very high MDLs were however found both in the PUF-PAS and the reference AAS for HCHs, BDE 209, syn- and anti-DP and BEHTBP. These compounds were therefore omitted from further evaluation. MDLs higher than LODs were also found for many of the volatile compounds but the levels in PUF-PAS samples (with the exception of those listed above) were more than one order of magnitude higher than the MDLs.

The detection frequencies were generally high in the reference AAS (Table S1) except for a few compounds that were detected with low frequencies over the calibration period (i.e. 25-75%): BDE 154, 183, Hexa CDDs, and Tetra CDFs, or not at all (i.e. 0-17%): PCB 169, BDE 66, 85, 153, HCDBCO, and Tetra-Penta CDD. The latter group was excluded from further evaluation. The seven indicator PCBs were detected to the same high extent by PUF-PAS as the AAS. The rest of the SVOCs were detected to a significantly lower extent ($p<0.01$) by the PUF-PAS. The differences in detection frequencies between the two sampler types were bigger for particle associated compounds than for gas phase compounds. Compounds with low detection frequencies in PUF-PAS (i.e. <30%) were omitted from further evaluation. This group included PCB 126, BDE 154, 183, DPMA, BTBPE, DBDPE, Acenaphthylene, Acenapthene, Anthracene, Benzo(a)pyrene, Indeno(123cd)-pyrene, Dibenz-(ah)anthracene, Benzo(ghi)perylene, and Hexa CDDs.

The results show that even PUF-PAS in the double-dome chamber successfully provide detectable levels 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. These results show that for this set of compounds PUF-PAS can be employed in medium to long term human exposure studies where an averaged exposure over one to two weeks often is used. In contrast, a longer exposure time (4-6 weeks) is required for DDTs and PCDFs, while Penta-Hepta BDEs, 5-6 ring PAHs, and PCDDs may not be detected at all with the double-dome chamber PUF-PAS under the conditions of this study. A minimum exposure time of 4 weeks is recommended to avoid problem of detection and to obtain data for a broad range of compounds. The estimated minimum exposure times for individual compounds are presented in Table 1.

Precision

Starting from week 2, the precision for all SVOCs was independent on exposure time ($p<0.05$). An average precision, calculated using the variance of eleven sets of triplicates (week two to 12), was therefore used as representative for all exposure times (Table 1). The precision varied among the SVOC classes but generally good precision (<25% RSD) was found for PCBs, OCPs, PBDEs and PAHs (both in the gas and particle phase). Somewhat lower precision (20-50% RSD) was found for the detected nBFRs. Bad precision was found for the PCDD/Fs (>50%) as they were often found only in one of the three replicates indicating inconsistent accumulation of these compounds by PUF-PAS. High precision has previously also been reported for PCBs (7% RSD) in PUF-PAS deployed in the same double bowl chamber indoors[23]. Overall, the factors limiting PUF-PAS precision appeared to be: i) indoor air concentrations close to the MDL and ii) particle partitioning.

Fingerprinting

Table S3 reports the results of linear regression analysis between the compound specific relative abundances (in relation to the total sequester mass of all compounds of the same SVOC class) determined by the PUF-PAS and the reference AAS (bulk phase and gas phase, respectively). Slopes of 0.8-1.0 were obtained for PCBs and OCPs suggesting high fingerprinting capacity for these classes of SVOC. This result suggests that PUF-PAS can provide sensible information on the congener or compound pattern even without the need of correcting for possible different uptake behaviour of more particle-bound compounds. Poorer correlations were obtained for nBFRs, PAHs, and PCDDs showing the need of correcting for their particle-gas partitioning behaviour in order to determine the fingerprint for these compounds. No significant correlation was

found for SVOC classes with a higher content in the particle phase (i.e. PBDEs and PCDFs).

INDOOR SAMPLING RATES (R_S)

General remarks on R_S

In theory, the two methods used to calculate R_S should provide consistent data. Indeed, the two methods are used interchangeably in previous studies although the comparability of the results are rarely analysed or questioned.

The obtained exposure-time-specific R_S from *Method 2* was significantly higher (factor of 2-5) for short exposure times (1-3 weeks) than for longer exposure times. For periods longer than 3-4 weeks the R_S tended to reach relative constant values, in the same range as those obtained from *Method 1*. High initial R_S values were also found in a concurrent outdoor calibration study[16] and can be observed also by analysing data reported in some previous studies[23, 27]. This effect may be due to analytical issues as there is a greater uncertainty in derived sampling rates and potential bias for shorter exposure times when smaller amounts of compounds are collected by the PAS and data are near the MDL. However, the same effect was observed both for compounds well above MDL as well as those close to MDL which indicates that it may originate from a two-phase accumulation pattern with a rapid initial sorption onto the PUF-PAS surface in the first weeks of deployment followed by a slower diffusion into the interior of the PUF disk to approach equilibrium. Such a model is largely adopted in describing uptake of organic compounds in different hydrophobic environmental matrixes[27, 35, 36]. For PUF-PAS, it has not been described so far and would require further studies.

As a result of initial high R_S, the average R_S from *Method 2* is significantly higher than the time-integrated R_S from *Method 1* (factor of 2-5). This indicates that the two methods may provide inconsistent figures resulting in estimated air concentration deviating by a factor of two or more. This difference disappears when averaging R_S values from week 3 and up to end of the linear uptake phase (obtained by *Method 1*). It shows that the initial fast uptake by PUF-PAS is not seen by *Method 1* and should be taken into consideration if deploying PUF-PAS for short exposure times. In particular it is recommended to use *Method 2* when short exposure times of 2 weeks are used.

Compound specific R_S for indoor monitoring

Suggested compound specific R_S for PUF-PAS deployed in the closed double-bowl chamber in non-industrial indoor environments are presented in Table 1. It has to be noted that differences in apparent R_S of the individual chemicals are driven by their particle-gas partitioning behaviour. While a difference in the $R_S$of various gas phase-associated chemicals is not significant, particle-associated compounds are sampled less efficiently due to limited ability of the double dome PUF-PAS to capture the atmospheric particles. Data available from previous studies are not consistent which suggests that particle sampling efficiency of PUF-PAS can be affected by many site- and time-specific factors. It is an area of on-going research.

Results from *Method 1* were selected as a standard while results from *Method 2*, presented as the average of exposure-time-specific R_S, were chosen when *Method 1* could not be applied. *Method 1* provided valid and consistent R_S for the compounds of interest for indoor environments (Table 1), i.e. most PCBs, OCPs, and gas phase PBDEs, nBFRs and PAHs. The lack of R_S for the other compounds was due to: i) low detection frequencies (i.e. <30%), or ii) lack of a defined accumulation pattern with time (i.e. no appearing uptake curve). The second point was the main reason for lack of R_S for PCDD/Fs. This is explained by a random uptake caused by the low concentrations of PCDD/Fs and a high partition to particle phase.

Method 2 provided R_S for all compounds with a detection frequency above 20% (Table S4). Exceptions were Penta-Hexa PCDDs and Hepta-Octa PCDFs for which the exposure time specific R_S were inconsistent from week to week. The presented results for PCDD/Fs should be treated with caution as results from *Method 1* showed inconsistent accumulation pattern for these compounds in the PUF-PAS. Neither *Method 1* nor *Method 2* provided valid R_S for compounds with low detection frequency, e.g. PCB 126, BDE 154, particle associated PAHs, Tetra PCDDs, DPMA, and DBDPE. In total, R_S was obtained only for 60% of the total number of target compounds.

The R_S for individual compounds varied within each SVOC class as follows (Table 1): 0.9-1.7 m^3 day^{-1} for individual PCB congeners (PCB-7 and dlPCBs), 1.1-3.4 m^3 day^{-1} for OCPs (1.1-1.4 m^3 day^{-1} excluding PeCB and HCB), 0.9-1.2 m^3 day^{-1} for PBDEs, 1.2-4.6 m^3 day^{-1} for nBFRs (1.2-2.1 m^3 day^{-1} excluding p-TBX), 0.03-5.5 m^3 day^{-1} for PAH-16 (0.03-1.7 m^3 day^{-1} excluding fluorene), and 0.4-1.5 m^3 day^{-1} for PCDD/Fs. The R_S for individual PCBs and PBDEs are in agreement with previously reported data for PUF-PAS deployed in double-bowl chamber [23]. The results for the most volatile chemicals that may experience breakthrough in AAS (i.e. HCB, PeCB, fluorene), should be used with caution. When excluding these compounds the overall average R_S was 1.4±0.7 m^3 day^{-1}. This is almost a factor of 2 lower than the R_S (2.5 m^3 day^{-1}) obtained for PUF-PAS deployed in a more open chamber design and commonly used in many indoor monitoring studies[4, 6, 37]. The variability between compounds within each SVOC class was of a factor of 2-4 with the exception of PAHs for which a larger inter-class variability was found as a result of broad variance in gas/particle partitioning. The inter-class variability for all classes was smaller than the one obtained in the concurrent outdoor calibration study[16]. This was expected, since the meteorological conditions outdoors are more variable and the PUF-PAS is subjected to effects of wind speed and temperature variability.

Based on the obtained uncertainty ranges of the R_S for PCBs, DDTs, and some PAHs the expected relative error in concentration estimates does not exceed 20% while the error for nBFRs is up to 40%.

The length of the linear uptake phase (minimum to maximum) was estimated for all compounds using *Method 1*. Recommended ranges for exposure times are presented in Table

1. Generally, the uptake tended to be linear for most compounds during the full length of the sampling period (12 weeks). Exceptions were 3-4 ringed PAHs, nBFRs, and PCDFs for which the length of linear uptake phase lasted for 4-9 weeks. This is in agreement with previous publications[13, 24].

Table 1. Overview of results for PUF-PAS deployed in double-dome chambers: suggested indoor sampling rates (R_S, average ± 95% CI); exposure times within linear uptake phase; detection frequencies in PUF-PAS; average precision of triplicates for 1 to 12 weeks exposure times; and previously published R_S.

	Sampling rate (R_S, m^3 day^{-1}) ±95% CI	Linear phase (weeks)	Detection frequency (%) in PUF-PAS	Variability (%RSD) of PUF-PAS replicates	Sampling rate (R_S, m^3 day^{-1}) *Previously published* [6, 23, 25, 26]
Polychlorinated biphenyls (PCBs)					
PCB 28	1.0±0.2	1-12	100	10	0.75, 2.8
PCB 52	1.3±0.1	1-12	100	9	0.67, 2.3
PCB 101	1.7±0.2	1-12	100	9	0.8, 3.2
PCB 118	1.2±0.2	1-12	100	10	3.2
PCB 153	1.7±0.2	1-12	100	7	1.03, 2.4
PCB 138	1.7±0.2	1-12	100	7	1.18, 2.4
PCB 180	1.5±0.2	1-12	100	10	1.55, 2.2
PCB77	1.0±0.2	1-12	100	13	2.3
PCB81*	1.1±0.3*	-	36	25	2.3
PCB105	1.0±0.2	1-12	100	14	0.99, 3.2
PCB114	1.1±0.1*	4-12	59	22	3.2
PCB123	1.4±0.4	2-12	89	23	3.2
PCB156	1.1±0.2	1-12	100	15	2.4
PCB157	0.9±0.2*	4-12	50	25	2.4
PCB167	1.1±0.2	1-12	100	12	2.4
PCB189	1.1±0.4	4-12	71	23	2.2
Organochlorine pesticides (OCPs)					
PeCB	*3.4±0.8*	1-10	100	13	
HCB	*2.5±0.4*	1-12	100	16	
o,p'-DDE	1.3±0.2	1-12	100	10	
p,p'-DDE	1.3±0.5	5-12	61	24	
o,p'-DDD	1.4±0.3	5-12	54	31	
p,p'-DDD	1.2±0.4	2-12	100	16	
o,p'-DDT	1.2±0.3	1-12	100	15	
p,p'-DDT	1.1±0.5	1-12	100	21	
Polybrominated diphenyl ethers (PBDEs)					
BDE 28	1.2±0.2	1-12	100	19	1.74, 2.5
BDE 47	1.1±0.2	1-12	100	11	1.95, 2.5
BDE 99	0.9±0.3	2-12	67	45	1.12, 2.5
BDE 100	2.9±1.3	7-12	36	93	1.34, 2.5
Novel brominated flame retardants (nBFRs)					
2,4,6-Tribromophenylallyl ether (ATE)	1.4±0.5	1-8	83	48	
α,β,γ,δ-Tetrabromoethylcyclohexane (TBECH)	1.4±0.1	1-11	100	25	
2-Bromoallyl-2,4,6-tribromo-phenyl ether (BATE)	1.5±0.6	1-8	90	57	
1,2,5,6-Tetrabromocyclooctane (TBCO)	1.9±0.2	1-9	94	29	
2,3,5,6-Tetrabromo-p-xylene (p-TBX)	4.6±1.3	1-10	100	45	
Pentabromoethylbenzene (PBEB)	2.0±0.3	1-9	100	32	
2,3,4,5,6-Pentabromotoluene (PBT)	1.7±0.4	1-10	100	25	
2,3-Dibromopropyl-2,4,6-tribromophenyl ether (DPTE)	2.1±0.6	1-8	94	34	
Hexabromobenzene (HBB)	1.2±0.3	1-9	100	21	

	Sampling rate (R_S, m^3 day^{-1}) ±95% CI	Linear phase (weeks)	Detection frequency (%) in PUF-PAS	Variability (%RSD) of PUF-PAS replicates	Sampling rate (R_S, m^3 day^{-1}) *Previously published* [6, 23, 25, 26]
2-Ethylhexyl-2,3,4,5-Tetrabromobenzoate (EHTBB)	1.7±0.7*	1-10	86	55	
Polycyclic aromatic hydrocarbons (PAHs)					
Fluorene	*5.5±0.5*	1-9	100	14	1.9
Phenanthrene	1.7±0.1	1-9	100	12	1.9
Fluoranthene	0.9±0.1	2-9	83	17	4.2
Pyrene	0.8±0.1	2-9	83	10	7.8
Benz(a)anthracene	0.2±0.0	3-9	81	33	12.5
Chrysene	0.2±0.0	2-9	86	11	4.5
Benzo(b)fluoranthene	0.04±0.0*	-	100	41	3.5
Benzo(k)fluoranthene	0.03±0.0*	-	100	15	3.3
Polychlorinated dibenzo-*p*-dioxins (PCDDs)					
1234678-HpCDD	0.7±0.4*	-	61	82	
OCDD	0.4±0.1*	-	58	78	
Polychlorinated dibenzofurans (PCDFs)					
2378-TCDF	0.9±0.1*	-	64	72	
12378-PeCDF	1.0±0.3*	-	69	73	
23478-PeCDF	0.6±0.3*	-	78	55	
123478-HxCDF	1.2±0.7*	-	42	97	
123678-HxCDF	1.3±0.7*	-	69	82	
234678-HxCDF	1.0±0.8*	-	81	76	
1234678-HpCDF	1.5±1.1*	-	75	90	

*Sampling rate obtained from *Method 2.*
Italic means that results should be used with caution due to their high volatility.

PARTICLE ASSOCIATED COMPOUNDS

The evaluation of PUF-PAS performance for compounds with different gas/particle partitioning was based on two groups: A) gas phase compounds and B) particle associated compounds. The two groups encompass 55 and 30% of the total numbers of compounds respectively. The remaining 15% represent compounds below MDL in the AAS. The results confirm that PUF-PAS do collect, to some extent, particle associated compounds (group B), although with a less consistent performance compared to group A (Figure S2). The detection frequencies for group B in PUF-PAS (average=38%) were significantly lower than in the reference AAS (average=84%) and significantly lower than group A in PUF-PAS (average=84%). The precision for group B was significantly lower (average=75% RSD) than for group A (average=26% RSD). The results suggest inconsistent uptake behaviour for particle associated compounds in non-industrial indoor environments when using PUF-PAS in the closed double-bowl chamber design.

Time-integrated R_S (*Method 1*) could not be obtained for most of the particle associated compounds. The available R_S for group B were significantly lower (factor of 4) than for group A. The R_S for particle associated PAHs were up to a factor of 50 lower than for gas phase PAHs and the overall average R_S (1.4 m^3 day^{-1}). Additionally, a high uncertainty of R_S for group B (>50%) together with a low precision adds a significant overall error to estimated air concentrations. Lower R_S for particle associated compounds are in agreement with evaluations in urban and remote outdoor sites[16, 19, 24] but opposite to results from indoor and outdoor industrial sites[18, 26]. A better PUF-PAS performance at these industrial sites is probably due to a much higher level of total suspended particles, different particle size modes and enhanced air turbulence or flow in these environments.

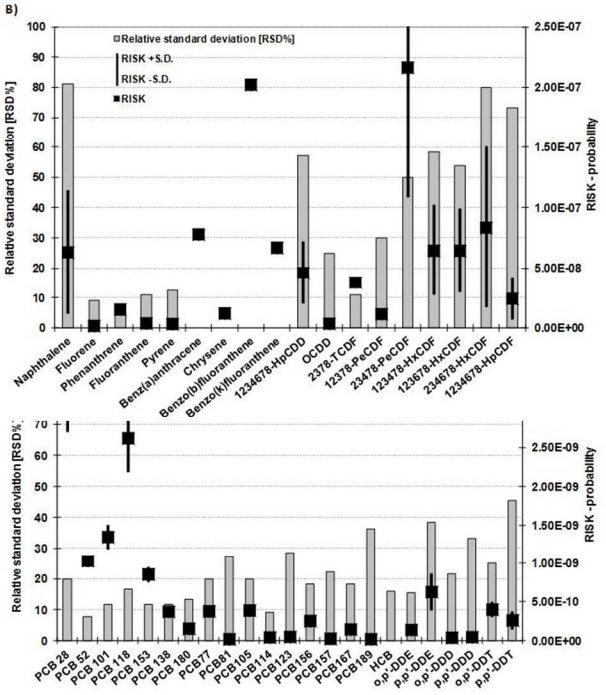
Better particle sampling efficiency may be achieved by deploying the PUF disks in a more open chamber design. This may either be open on all sides or covered only on the top[6, 4]. In any case we have to be aware that Rs values derived from the AAS-PAS co-employment studies are also affected by the AAS design. Active sampling of total suspended particles, PM10, PM5, PM2.5, or PM1 may result in slightly different Rs of particle-associated compounds.

Applicability for human health risk assessment

Human health risks were predicted for SVOCs with valid toxicity values (i.e. PCBs, OCPs, PAHs, and PCDDs/Fs) with a goal of assessing applicability of the double-dome PUF-PAS for human risk studies. The compound-specific human health risk level (i.e. estimated probability of developing cancer during lifetime) was calculated using the linear low-dose cancer risk equation and the total concentration of each compound obtained from the PUF-PAS[28].

Figure 1 shows the uncertainty of a PUF-PAS measurement (based on variability of replicates (%RSD)) and the quantified risk level (based on concentrations at this site) for individual SVOCs (boxes and whiskers). The influence of PUF-PAS uncertainty on the quantified risk is shown as the standard deviation of the risk probability level. The relative risk uncertainties were calculated from confidence intervals (± 95% CI) of indoor R_S (in Chapter "Evaluation of sampling performance") and are presented as ± S.D. (upper-bound and lower-bound values; Figure 2).

Figure 1. Summary of potential human cancer risks related to the individual SVOCs, and their uncertainties. Black boxes quantify risks estimated on the bases of the indoor passive



sampling. Black lines represent the upper-bound and lower-bound values of such risk predictions (right Y axis). Grey bars show relative standard deviations (RSD%) of the risk prediction (left Y axis).

The highest risk was predicted for several PCDD/Fs and PAHs (10^{-8}-10^{-7}). Quantification of their risk values, however, were also associated with the highest uncertainties. Relative standard deviations of PCDDs/Fs were high because PCDDs/Fs were found at very low levels. Among PAHs, the highest health risks were predicted for those only partially associated with particles while the high molecular PAHs gave inconsistent results. Most consistent risk estimates were obtained for PCBs and OCPs (Figure 1), for which the PUF-PAS performance is good. Among those, the highest (10^{-9}) risks were found for PCB 28 and PCB 118, while the risks associated with high molecular weight PCBs were an order of magnitude lower. The highest risk among the OCPs was assigned to p,p-DDE although still an order of magnitude smaller than those of PCB 28, 52, and 118.

Conclusions and recommendations

A double-dome PUF-PAS design was tested in this study as a tool for assessment of indoor concentrations and associated risks of various SVOC classes. It has been shown that even though this PAS design has been frequently applied indoors, results of such studies have to be interpreted with care. PUF-PAS can offer reasonable detection limits as well as precision for the gas phase associated SVOCs. It is also capable of providing representative compound fingerprints of their atmospheric mixtures. For the first time, it has been demonstrated that PUF-PAS performs well also for the gas phase nBFRs/NFRs indoors. Therefore, it can be used in future studies to enhance insufficient knowledge on indoor occurrence and distribution of these emerging contaminants measured previously only in house dust[39-41]. In contrast, a double-dome PUF-PAS did not perform well for particle associated SVOCs indoors as the results found: i) low detection frequencies, ii) low precision, iii) low ability to provide representative compound patterns, and iv) few valid R_S. While deployment of the same samplers outdoors allowed for estimation of particle-bound concentrations of many POPs, it was not ideal solution indoors.

Several knowledge gaps related to applicability of PUF-PAS for estimation of the atmospheric concentrations of high molecular weight chemicals have been identified previously. So far, we can only hypothesize on the particle size fraction that is efficiently sampled by the PUF-PAS. Particle sampling efficiency was reported to be between 10 and 100%[18, 19] indicating that it is probably affected by many factors including the amount, material composition and size distribution of the atmospheric particles at specific sites. Size-specific distribution of various SVOCs among the particulate fractions can be another factor driving uncertainties when estimating particle-bound concentration of SVOCs as well as using various sampling heads during AAS-PAS calibration studies.

Uncertainties of these measurements are further enhanced indoors when the particle concentrations tend to be generally lower and stagnant air is responsible for decreased sampling rates of the PUF-PAS.

Higher particle sampling efficiency may be achieved indoors when more open designs of the PUF-PAS (tripod chamber or no protective chamber at all) are applied. These designs, however, still have to be carefully tested as there are no systematic data on representativeness of the compound fingerprints detected in such samples for selected indoor environments. Not only various PUF-PAS but also AAS set ups have to be tested in the attempt of characterization of the particle size fractions captured by the PUF-PAS.

All of these uncertainties are complicating the use of the double-dome PUF-PAS for an assessment of human exposure and risk. While it works very well for estimation of the gas phase chemical exposure, an assessment of exposure to particle-bound compounds is affected by the large deviations. In addition, PUF-PAS does not provide information on the particle-size fractions crucial for assessment of inhalation risks.

However, PUF-PAS can still be used for a semi-quantitative screening of chemicals suspected to present most significant risks. To increase a level of confidence in such studies, PUF-PAS should be preferably applied i) for compounds >60% in gas phase; ii) with exposure times between 4 and 9 weeks using time-integrated R_S from *Method 1* (but R_S from *Method 2* whenever exposure times are 3 weeks or lower); and iv) applying a generic R_S for gas phase compounds and compound specific R_S for particle associated compounds. Specific recommendations for different SVOC classes are presented in Table 2.

Complementary sampling methods (for example, but not necessarily limited to dust or surface film sampling) should be also considered is an option to obtain a more reliable and quantitative picture of exposure to particle-bound contaminants in non-industrial indoor environments. These methods, however, also require further evaluation as there is a lack of consistent knowledge on best sampling approach, comparability to airborne particle concentrations and compound profiles.

Table 2. Summary of PUF-PAS' performance and recommendations for its indoor applications for the SVOC classes targeted in this study.

	Performance evaluation	**Recommendations for application**
PCBs	Good performance for all congeners except PCB 81, 126, and 169 due to low detection.	Expose between 2 and 12 weeks. Use generic R_S of 1.3 m^3 day^{-1}.
OCPs	Good performance for CBs and DDTs. No results obtained for HCHs due to high levels in blanks.	Expose between 2 and 12 weeks. Use generic R_S of 1.3 m^3 day^{-1}..
PBDEs	Good performance for gas phase compounds (i.e. 28, 47, 99). Poor performance for particle associated compounds due to low detection. No results obtained for BDE 209 due to high levels in blanks.	Expose between 2 and 12 weeks. Use generic R_S of 1.3 m^3 day^{-1}. Not recommended for particle-associated BDEs (i.e. Hexa-Hepta BDEs).
nBFRs/NFRs	Good performance for gas phase compounds. Poor performance for DPMA, HCDBCO, BTBPE, BEHTBP and DBDPE due to low detection. No results obtained for anti- and syn-DP due to high levels in blanks.	Expose between 2 and 9 weeks. Use compound specific R_S when detected at sufficient levels.,
PAHs	Good performance for gas phase compounds (i.e. 3-4 ring PAHs). Poor performance for particle associated compounds (i.e. 5-6 ring PAHs) due to low detection.	Expose between 2 and 9 weeks. Use generic R_S of 1.3 m^3 day^{-1} for gas phase (3-4 ring) PAHs. Use compound specific R_S for particle associated (5-6 ring) PAHs when detected at sufficient levels. Not generally recommended for particle-associated PAHs (i.e. 5-6 ring PAHs).
PCDD/Fs	Poor performance for most compounds. R_S only obtained for Tetra-Penta CDFs. Low precision.	Expose between 5 and 10 weeks. Use compound specific R_S when detected at sufficient levels.. Not generally recommended for PCDDs.

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Notes

[a] Research Centre for Toxic Compounds in the Environment (RECETOX), Faculty of Science, Masaryk University, Kamenice 753/5, CZ-625 00 Brno, Czech Republic. E-mail: bohlin@recetox.muni.cz, klanova@recetox.muni.cz; Tel.: +420 54949 5149; Fax: +420 54949 2840

Electronic Supplementary Information (ESI) available: details on sample clean up and analysis and health risk assessment, results from AAS, additional performance parameters.

References

1. J. C. Little, C. J. Weschler, W. W. Nazaroff, Z. Liu and E. A. C. Hubal, *Environ. Sci. Technol.*, 2012, 46, 11171-11178.
2. C. J. Weschler and W. W. Nazaroff, *Atmos. Environ.*, 2008, 42, 9018-9040.
3. X. M. Zhang, M. L. Diamond, M. Robson and S. Harrad, *Environ. Sci. Technol.*, 2011, 45, 3268-3274.
4. P. Bohlin, K. C. Jones, H. Tovalin and B. Strandberg, *Atmos. Environ.*, 2008, 42, 7234-7241.
5. E. Menichini, N. Lacovella, F. Monfredini and L. Turrio-Baldassarri, *Atmos. Environ.*, 2007, 41, 9518-9529.
6. B. H. Wilford, T. Harner, J. P. Zhu, M. Shoeib and K. C. Jones, *Environ. Sci. Technol.*, 2004, 38, 5312-5318.
7. J. A. Leech, W. C. Nelson, R. T. Burnett, S. Aaron and M. E. Raizenne, *J. Expo. Anal. Environ. Epidemiol.*, 2002, 12, 427-432.
8. WHO, *WHO guidelines for indoor air quality: selected pollutants*, World Health Organization, Copenhagen, Denmark, 2010.
9. D. Kotzias, O. Geiss, S. Tirendi, J. Barrero-Moreno, V. Reina, A. Gotti, G. Cimino-Reale, B. Casati, E. Marafante and D. Sarigiannis, *Fresenius Environ. Bull.*, 2009, 18, 670-681.
10. X. M. Zhang and F. Wania, *Environ. Sci. Technol.*, 2012, 46, 9563-9570.
11. J. P. Zhu, S. L. Wong and S. Cakmak, *Environ. Sci. Technol.*, 2013, 47, 13276-13283.
12. J. D. Petty, J. N. Huckins and J. L. Zajicek, *Chemosphere*, 1993, 27, 1609-1624.
13. M. Shoeib and T. Harner, *Environ. Sci. Technol.*, 2002, 36, 4142-4151.
14. C. Bogdal, E. Abad, M. Abalos, B. van Bavel, J. Hagberg, M. Scheringer and H. Fiedler, *Trac-Trends Anal. Chem.*, 2013, 46, 150-161.
15. Y. Moussaoui, L. Tuduri, Y. Kerchich, B. Y. Meklati and G. Eppe, *Chemosphere*, 2012, 88, 270-277.
16. P. Bohlin, O. Audy, L. Skrdlikova, K. P., P. P., P. R., V. S. and J. Klanova, *Environ. Sci.: Processes Impacts.*, 2014, 16, 433-444.
17. C. Chaemfa, E. Wild, B. Davison, J. L. Barber and K. C. Jones, *J. Environ. Monit.*, 2009, 11, 1135-1139.
18. 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.
19. J. Klanova, P. Eupr, J. Kohoutek and T. Harner, *Environ. Sci. Technol.*, 2008, 42, 550-555.
20. K. Pozo, T. Harner, S. C. Lee, F. Wania, D. C. G. Muir and K. C. Jones, *Environ. Sci. Technol.*, 2009, 43, 796-803.
21. S. Harrad, S. Hazrati and C. Ibarra, *Environ. Sci. Technol.*, 2006, 40, 4633-4638.
22. K. Kennedy, M. Macova, F. Leusch, M. E. Bartkow, D. W. Hawker, B. Zhao, M. S. Denison and J. F. Mueller, *Anal. Bioanal. Chem.*, 2009, 394, 1413-1421.
23. S. Hazrati and S. Harrad, *Chemosphere*, 2007, 67, 448-455.
24. L. Melymuk, M. Robson, P. A. Helm and M. L. Diamond, *Atmos. Environ.*, 2011, 45, 1867-1875.
25. C. Persoon and K. C. Hornbuckle, *Chemosphere*, 2009, 74, 917-923.
26. P. Bohlin, K. C. Jones and B. Strandberg, *Environ. Sci. Technol.*, 2010, 44, 749-754.
27. C. Chaemfa, J. L. Barber, T. Gocht, T. Harner, I. Holoubek, J. Klanova and K. C. Jones, *Environ. Pollut.*, 2008, 156, 1290-1297.
28. P. Cupr, Z. Flegrova, J. Francu, L. Landlova and J. Klanova, *Environment International*, 2013, 54, 26-34.
29. M. Frederiksen, H. W. Meyer, N. E. Ebbehoj and L. Gunnarsen, *Chemosphere*, 2012, 89, 473-479.
30. R. A. Rudel, R. E. Dodson, L. J. Perovich, R. Morello-Frosch, D. E. Camann, M. M. Zuniga, A. Y. Yau, A. C. Just and J. G. Brody, *Environ. Sci. Technol.*, 2010, 44, 6583-6590.
31. L. R. Wilson, P. M. Palmer, E. E. Belanger, M. R. Cayo, L. A. Durocher, S. A. A. Hwang and E. F. Fitzgerald, *Arch. Environ. Contam. Toxicol.*, 2011, 61, 530-538.
32. G. M. Currado and S. Harrad, *Environ. Sci. Technol.*, 1998, 32, 3043-3047.
33. E. Krugly, D. Martuzevicius, R. Sidaraviciute, D. Ciuzas, T. Prasauskas, V. Kauneliene, I. Stasiulaitiene and L. Kliucininkas, *Atmos. Environ.*, 2014, 82, 298-306.
34. A. K. Halse, M. Schlabach, S. Eckhardt, A. Sweetman, K. C. Jones and K. Breivik, *Atmos. Chem. Phys.*, 2011, 11, 1549-1564.
35. A. Delle Site, *J. Phys. Chem. Ref. Data*, 2001, 30, 187-439.
36. L. Nizzetto and J. A. Perlinger, *Environ. Sci. Technol.*, 2012, 46, 2699-2707.
37. P. Imm, L. Knobeloch, C. Buelow and H. A. Anderson, *Environ. Health Perspect.*, 2009, 117, 1890-1895.
38. 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.
39. N. Ali, L. Ali, T. Mehdi, A. C. Dirtu, F. Al-Shammari, H. Neels and A. Covaci, *Environment International*, 2013, 55, 62-70.
40. N. Ali, S. Harrad, E. Goosey, H. Neels and A. Covaci, *Chemosphere*, 2011, 83, 1360-1365.
41. A. Covaci, S. Harrad, M. A. E. Abdallah, N. Ali, R. J. Law, D. Herzke and C. A. de Wit, *Environment International*, 2011, 37, 532-556.
42. U. Matson, *Sci Total Environ*. 2005, 343(1-3):169–76.
43. S. Harrad and MA-E. Abdallah. *J Environ Monit*. 2008, 10(4):527–31.
44. D. Muenhor, S. Ali N. Harrad, A. Covaci. *Environ Int*. 2010, 36(7):690–8.