Calibration of two passive air sampler configurations for monitoring concentrations of Hexabromocyclododecanes in indoor air

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Introduction

PUF (Polyurethane Foam) disk passive air samplers are increasingly employed for monitoring of POPs in ambient air[1]. The benefits of using passive samplers are that they are easy to handle, more cost effective than active monitors and do not require electricity, thus facilitating simultaneous monitoring in many spatially distinct locations[2]. Furthermore, their noise-free operation and relative unobtrusiveness, makes them ideal for the determination of indoor air quality. Although passive samplers have relatively low sampling rates necessitating long sampling times, they provide time weighted average concentrations which are more appropriate with respect to exposure assessment given that the health impacts of POPs and related compounds in the general population arise predominantly from chronic exposures[1]. Despite their proven track record for monitoring concentrations of related contaminants such as PBDEs and PCBs[3] in indoor air, the fact that PUF disks effectively sample only the vapour phase, renders them inappropriate for contaminants that exist primarily in the particle phase. To the authors' knowledge, there have been no reports of concentrations of HBCDs in indoor air and the only study to address the vapour:particle partitioning of HBCDs in (outdoor) air, found them to be present largely in the particulate phase[4]. Furthermore, in order to obtain quantitative data on airborne contaminant concentrations from passive samplers, one needs to know not only the mass of contaminant sequestered by the sampler over the course of its deployment, but the volume of air sampled over the same period.

In light of the above, the objectives of the current study are:

- To investigate the feasibility of employing PUF disk passive samplers for monitoring HBCDs in indoor air via determination of the atmospheric phase distribution of HBCDs in indoor air using active air sampling.
- To carry out a calibration experiment to determine the passive air sampling rates for the three principal HBCD diastereomers using 2 different passive air sampler configurations.
- To compare the concentrations of HBCDs derived for indoor environments using conventional active air sampling apparatus, with those obtained using the PUF disk sampling configurations for which air sampling rates were obtained.

Materials and Methods

Active air sampling for determination of vapour:particle phase distribution of HBCDs in indoor air was conducted in two offices using a Graseby–Andersen Hi–Vol sampler fitted with a total suspended particulate (TSP) inlet modified to hold a standard PTFE back coated glass-fiber filter (GFF, 0.8 mm pore size, Whatman) and a pre-cleaned polyurethane foam (PUF) plug (827 cm^3 volume).

PUF disk passive samplers calibration was conducted in September 2007 in a temporarily vacant office microenvironment (distinct from the two offices monitored earlier, and for consistency, identical to that employed in our earlier calibration for PBDEs and PCBs). Fully-sheltered passive samplers (n = 8) were deployed over a 50 d period at a height of 150 cm with a minimum distance between samplers of 50 cm. PUF disks were harvested at 10 d intervals over the 50 d of the experiment. To ensure that detectable concentrations were provided by the passive samplers at the 10 and 20 d sampling intervals, three and two samplers were harvested and combined for analysis at these times respectively. The analyte masses present in these combined samples were subsequently normalized to a single PUF disk equivalent mass for the purposes of the calibration. Concurrent with the deployment of the passive air samplers, a single active air sample was taken covering the full 50 d duration of the experiment. The calibration was also conducted in identical fashion simultaneously in the same room, but using "part-sheltered" PUF disk samplers with the bottom housing removed. Active air sampling for the PUF disk calibration was performed using a low volume pump (Capex L2X) was operated at a flow rate of 6 L min^{-1} to yield a single sample comprising approximately 430 m^3 air. The designated flow rate of 6 L min^{-1} was achieved and maintained by using a flow meter (Platon 12 L min^{-1}) connected to an adjustable valve. The flow meter was calibrated at the start

and the end of each sample using a Gilibrator air flow calibrator (Gilian) which is classified as a primary standard device. The particulate phase was collected by employing a 47 mm membrane filter (1.0 μm pore size, Whatman) housed in a standard open face 47 mm filter holder airside of the PUF plug sorbent. Two PUF plugs (4 cm diameter × 8 cm length) housed by a glass holder (3 cm diameter × 25 cm length), were used as a gas phase sorbent. Samples were Soxhlet extracted, and extracts purified by washing with H_2SO_4 and Florisil chromatography prior to analysis using LC/ESI/MS/MS. Further details can be found elsewhere[2].

Results and discussion

Concentrations, Diastereomer Patterns, and Vapour:Particle Phase Distribution of HBCDs:
The majority (~65%) of each HBCD diastereomer is present in the vapour phase (table 1). This suggests that PUF disk passive samplers are likely to be appropriate for sampling HBCDs in indoor air. The HBCD isomer distribution pattern reported here (~65% γ−, 20% α−) more closely reflects that observed in the technical HBCD formulations (bearing in mind the interconversion of HBCD stereoisomers at elevated temperatures -predominated by transformation of γ-HBCD to α-HBCD- encountered in technical processes required to incorporate HBCD into goods[5]); those in the US outdoor samples[4] displayed a far greater abundance of α-HBCD (32-81%) in five out of the seven samples reported.
The concentrations reported here (239 and 283 pg ΣHBCD m^{-3}) exceed substantially those reported in outdoor air from the US (range 2.1-11 pg ΣHBCD m^{-3})[4]. This apparent indoor:outdoor gradient may be attributable to the greater European usage of HBCD – two outdoor air samples from Stockholm contained 76 and 610 pg ΣHBCD m^{-3} [6]- but may also indicate a substantial indoor:outdoor gradient for HBCDs, similar to those observed for PCBs and PBDEs[3].
The predominantly γ−HBCD pattern observed in indoor air, differs from that observed in our study of indoor dust samples[7], where 14-67% (average 32%) of ΣHBCD was the α-diastereomer.
There is no obvious explanation for the disparity between our results regarding the vapour:particle phase distribution of HBCDs and that of US outdoor air[4], as the US outdoor samples included some taken in summer, thus eliminating the possibility that the absence of vapour phase HBCDs in the US samples was temperature-related.

PUF Disk passive sampler uptake rates:
To determine the passive sampling rates of each diastereomer, the equivalent air volumes sampled by each PUF disk over a given exposure period, Veq (cm^3), were calculated using equation 1.

$$V_{eq} = \frac{M}{C_A} = k_A \, A_{PUF} \, \Delta t \qquad (1)$$

where M is the mass of compound sequestered by the PUF disk (pg) within the deployment period, C_A is the concentration (pg cm^{-3}) of the target analyte in the air being sampled, k_A is the air side mass transfer velocity (cm sec^{-1}), A_{PUF} is the exposed macro surface area of the PUF disk (cm^2), and Δt is the sampling period (sec).
The Veq values were converted to m^3 units and plotted against the exposure time of the PUF disks (days). The slope of the linear regression plots obtained (Figure 1) is defined as the passive air sampling rate (R, m^3 d^{-1}) of the PUF disk samplers for the corresponding diastereomer. Strong correlation (R values >0.987) between values of Veq and PUF disk exposure time for each diastereomer regardless of sampler configuration demonstrate linear uptake of HBCDs over the 50 d calibration period. PUF disk passive sampling rates for the part-sheltered configuration were 1.38, 1.54, and 1.55 m^3 d^{-1} for α-, β-, and γ-HBCD respectively. These were nearly double those derived for the fully-sheltered configuration – 0.87, 0.89, and 0.91 m^3 d^{-1} for α-, β-, and γ-HBCD respectively.
Finally, we calculated air side mass transfer coefficients (k_A) for each diastereomer and sampler configuration, given that $k_A = R/A_{PUF}$. For the part-sheltered configuration these were 0.044, 0.049, and 0.050 cm s^{-1} for α− , β− and γ-HBCD respectively, and for the fully-sheltered configuration – 0.028, 0.029, and 0.029 cm s^{-1} for α− , β− and γ-HBCD respectively. These can be used to estimate passive air sampling rates for the same sampler configuration but fitted with PUF disks of different macro surface areas.

Comparison of Concentrations Derived Using PUF Disk Samplers with those Derived via High Volume Active Sampling

The passive sampler-derived concentrations are approximately one third (table 1) lower than those derived using high-volume active air samplers (sum of both vapour and particulate phases). This may be due partly to the difference in the monitoring periods. However, it is evident that the PUF disk-derived concentrations approximate very closely to the concentrations recorded in the vapour phase only by the high volume sampler. This indicates that the PUF disk samplers "capture" only those HBCDs associated with the vapour phase, and suggests that PUF disk samplers may not be appropriate for use at low temperatures where the majority of airborne HBCDs may be expected to reside in the particulate phase.

References

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Table 1: Concentrations (pg m^{-3}) of HBCDs in Indoor Air

Sample id	α-HBCD	β-HBCD	γ-HBCD	ΣHBCD
	Concentration of…			
Office 1 Active HiVol particle phase	16	11	53	80
Office 1 Active HiVol vapour phase	32	21	106	159
Office 1 Passive sampler	32	23	116	171
Office 2 Active HiVol particle phase	19	10	65	94
Office 2 Active HiVol vapour phase	38	20	131	189
Office 2 Passive sampler	39	22	138	199
Office 3[a] Active LoVol particle phase	30	22	69	121
Office 3 Active LoVol vapour phase	57	42	139	238

[a]Office 3 is location in which calibration experiment was conducted.

Figure 1: Plot of Equivalent Air Volume (V$_{eq}$, m^3) versus Exposure Time (days) for γ-HBCD and the Part-Sheltered PUF Disk Passive Sampler Configuration. Slope = Passive Air Sampling Rate (m^3 d^{-1}).