



Research article

Comparisons of indoor active and passive air sampling methods for emerging and legacy halogenated flame retardants in Beijing, China offices

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ABSTRACT

One active and two passive air sampling configurations were deployed simultaneously in three offices in Beijing, China to test their comparability for sampling emerging and legacy halogenated flame retardants spanning a large range of octanol–air partition coefficients (K_{OA}). Sampling in each office was carried out for three consecutive 28-day periods in the spring–summer of 2013. The active sampler was run for 2.5 h at different times every day for 28 days to parallel the passive samplers and sample a total volume comparable to that sampled by the passive samplers ($\sim 20 \text{ m}^3$). At the end of each 28-day sampling period, a separate active air sample was taken by running the sampler pump continuously for about 2.5 days. The comparability of measured concentrations varied between the air sampling configurations and for different compounds. The predominant compound measured in nearly all samples was BDE-209, a compound known to have heavy use in China. Several emerging flame retardants were also detected including DBE-DBCH, PBT, HBB, DDC-CO, and DBDPE. Very little of the tetra-hexabrominated BDEs associated with the technical PentaBDE product was observed.

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1. Introduction

Brominated flame retardants (BFRs) constitute a diverse group of compounds used in consumer products to reduce the flammability of those products. In particular, legacy BFRs such as polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecanes (HBCDDs) are known to be ubiquitous pollutants in indoor environments [1–3]. Recent studies have also shown the presence of a range of emerging flame retardants (EFRs) in indoor samples as well [4–6]. Many studies have focused on BFRs in indoor dust, however,

atmospheric transport has been recognized as a major route of global BFR distribution and indoor air has been found to be a major source of emissions to outdoor air [7,8]. Furthermore, inhalation is a route of human exposure to BFRs and may be of particular importance if the exposure is continuous [9,10]. There is thus a need for reliable and cost-effective monitoring of BFRs in indoor air.

Both active and passive air sampling methods have been used for measuring BFRs in indoor and outdoor air [1]. However, the comparability of the data that these sampling methods produce is not well studied, especially indoors and data for EFRs in particular are few [11]. Passive air samplers (PAS) offer a convenient sampling method for BFRs in air because they do not require electricity, are less researcher intensive, and are quiet, which increases acceptance by study participants. Furthermore, PAS give an integrated concentration over a longer time period than active air samplers (AAS). PAS are deployed typically for 1–3 months whereas AAS are typically deployed for several hours to a few days. This makes PAS less susceptible to biases caused by short term variability or spikes in concentrations than AAS. There are drawbacks to using PAS,

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though. Factors influencing uptake rates of passive samplers are not fully understood and uptake rates for different compounds can be uncertain [11]. Uptake rates for indoor PAS also differ from those for outdoor PAS due to different meteorological conditions (wind, changes in humidity, temperature). Because of these uncertainties, PAS are often considered only semi-quantitative [12]. PAS are believed to estimate the “true concentrations” within a factor of 2–3 and are considered to not yet have reached a stage of maturity to approach the accuracy of AAS for the measurement of persistent organic pollutants (POPs) [13]. Sample volumes of AAS though, can be measured directly by a flow meter so measured concentrations are considered closer to “true concentrations” [13]. Furthermore, the air flow of an AAS can be directed through a filter to capture particles separated from a gas-phase adsorbent, while the particle-capturing capabilities of PAS are not well understood [14]. Generally, PAS are usually used to sample gas phase contaminants but recently, Abdallah and Harrad [15] introduced a PAS fitted with a glass fiber filter to capture particle-bound contaminants as well.

AAS is often used simultaneously to obtain sampling rates for PAS but few studies have been conducted to compare their performances after the initial calibration. This is sometimes done by periodic AAS sampling throughout the PAS sampling period. This approach has given comparable results outdoors while atmospheric concentrations are stable but was less satisfactory when concentrations were unstable, as for current-use pesticides [16,17]. Little is known about the daily or weekly variability of BFR concentrations in indoor air. However, UK data on month to month variation indicate that although indoor air concentrations of Penta-BDE congeners in warmer months usually exceed those in colder months, seasonal variability in indoor contamination appears less significant than observed previously for outdoor air [18].

This study investigated the comparability of indoor air sampling methods for a range of BFRs using two different PAS configurations simultaneously and an AAS configuration set up to mimic PAS by sampling air for short periods daily over the entire span of the PAS period. This AAS method was also compared to a more typical short-term AAS method of sampling continuously for a shorter period (2.5 days).

2. Materials and methods

2.1. Materials

Polyurethane foam (PUF) disks for the passive samplers were obtained from PACS, Leicester, UK and were 140 mm diameter, 12 mm thickness, 360.6 cm² surface area, 0.07 g cm⁻³ density. PUF plugs for the active samplers were obtained from Specialplast AB, Gillinge, Sweden (diameter 15 mm, thickness 15 mm). Glass fiber filters (GFF) for the passive samplers were obtained from Whatman, UK (12.5 cm diameter, 1 μm pore size) and for the active samplers from Pall Corp., MI, USA (binder-free A/E borosilicate, 25 mm diameter). Dichloromethane (DCM) and n-hexane (both Lichrosolv) were obtained from Merck (Darmstadt, Germany); diethyl ether and iso-octane (both HPLC-grade) from LabScan (Gliwice, Poland); acetonitrile and methanol (B&J Brand) from Honeywell (Seelze, Germany); and sulfuric acid (AnalaR, BDH) from VWR International (Pennsylvania, USA). Water was obtained from a Milli-Q water purification unit (Millipore AB, Solna, Sweden). Other materials used were silica gel 60 (0.0063–0.200 mm) from Merck; anhydrous Na₂SO₄ (reagent grade) from Scharlau (Barcelona, Spain); ISOLUTE aminopropyl columns (0.5 g), empty reservoirs and frits from Biotage (Uppsala, Sweden). The vacuum evaporator was a Syncore[®] Line from Büchi (Flawil, Switzerland). Information about the origin and purity of the surrogate and reference standards can be found in the [Appendices \(Tables A1 and A2\)](#).

2.2. Sampling

Three offices in the same building at Tsinghua University, Beijing, China, were sampled simultaneously with two passive and one active air sampling configurations. Offices were selected to represent different levels of activity. The low-use office had two occupants, little furniture and lots of open space (area, 21 m²). The medium-use office had 6–8 occupants but was still fairly large because half of the space was a laboratory that was seldom used (84 m²). The high-use office had approximately 30 occupants in small cubicles with almost no unoccupied space (99 m²).

One AAS and two different PAS configurations were used simultaneously in each office. Both passive samplers consisted of two stainless steel bowls of different sizes, 18 cm in diameter for the bottom and 23 cm for the top. One passive sampler was fitted with a PUF disk in the center between the two bowls (referred to as the “PUF Only PAS” described elsewhere [19]) and the other was fitted with a GFF in the center and a PUF disk positioned against the top of the upper bowl (referred to as the “Combo PAS” and described in Abdallah and Harrad [15]) (Fig. 1). The active sampler consisted of four sampling trains, each with a GFF followed by two PUFs [20] (Fig. 1). The four sampling trains were attached in parallel to a low volume pump as described in Thuresson et al. [21]. The passive samplers were placed on the top of book shelves or cabinets about 2 m above the floor and the active sampler was placed in close proximity with the sampling trains pointing downward.

In order to sample in a time-weighted average fashion akin to a passive sampler, the active sampler pump was run at different times of day for approximately 2.5 h per day for 28 days (flow rate of 5 L min⁻¹, total sample volume of approximately 20 m³, referred to as the “28-day Active”). After 28 days, the passive samplers were harvested and the active sampling trains replaced with new ones. The active sampler was then run for 2.5 days continuously at a flow rate of 5 L min⁻¹ (referred to as the “Snapshot Active”) in order to compare the 28 day sampling with the shorter term sampling that is more often performed in indoor air sampling studies. The air sampling regime was then repeated for two more 28 day periods in the same three offices to give three samples for each air sampling configuration in each office. All samples were wrapped in aluminum foil and two plastic bags and stored in a freezer at approximately -20 °C until transport from Beijing, China to Stockholm, Sweden where they were stored in a freezer at -20 °C until analysis.

2.3. Sampling rates

Where available, calibrated uptake rates were taken from Harrad and Harrad [19] for the PUF Only PAS and from Abdallah and Harrad [15] for the Combo PAS sampler. PBDE sampling rates for the Combo PAS were correlated ($R^2 = 0.99$) with estimated particle bound fraction (ϕ) based on a K_{OA} adsorption model up to BDE-153 ($\phi = 0.95$, $\log K_{OA} = 12.1$) and declined rapidly above 0.95 (BDE-183 and BDE-209, Fig. 2). The linear range was used to estimate sampling rates for EFRs for this sampler based on the EFR $\log K_{OA}$ values [22–25]. More information about how the particle-bound fraction was estimated can be found in the Appendices. Some uncertainty exists with the sampling rates of DBE-DBCH, PBT, and HBB as these compounds have lower particle-bound fractions (0.002, 0.078, and 0.25, respectively) than the lowest PBDE used to construct the calibration curve (BDE-47, $\phi = 0.38$). It is possible that compounds with low ϕ (e.g. <0.25) approach the same sampling rate and thus the curve depicted in Fig. 2 should approach a horizontal asymptote at or slightly above 2.0. This would mean that the sampling rates for these three compounds are actually slightly lower than the extrapolated values in Table 1. However, the extrapolated sampling

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