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## 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 cm<sup>2</sup> surface area, 0.07 g cm<sup>-3</sup> 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 Na<sub>2</sub>SO<sub>4</sub> (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<sup>®</sup> 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

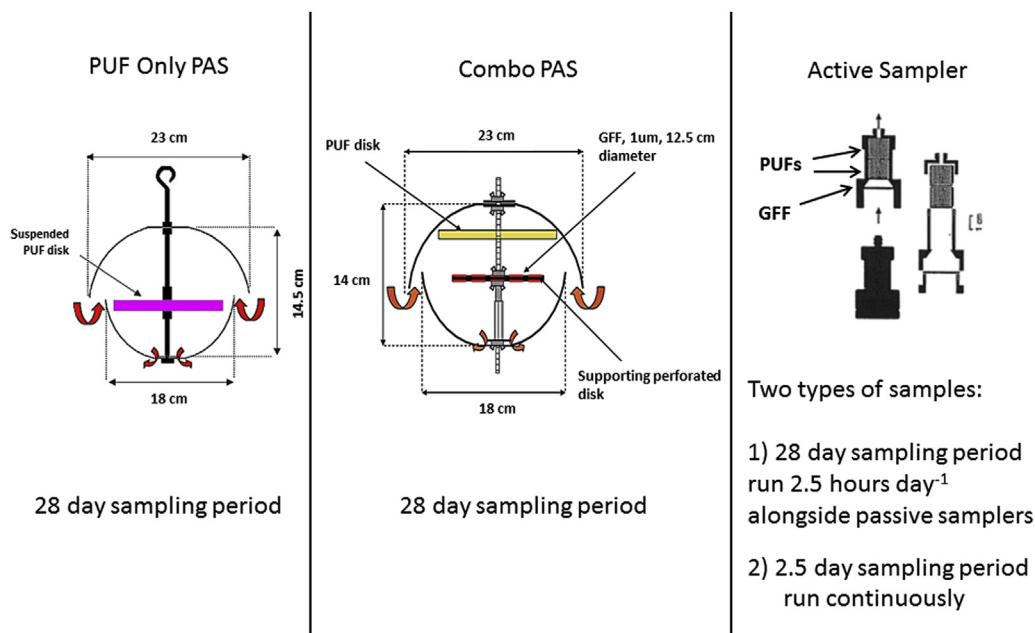
Three offices in the same building at Tsinghua University, Beijing, China, were sampled simultaneously with two passive and one active air sampling configurations. Offices were selected to represent different levels of activity. The low-use office had two occupants, little furniture and lots of open space (area, 21 m<sup>2</sup>). 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 m<sup>2</sup>). The high-use office had approximately 30 occupants in small cubicles with almost no unoccupied space (99 m<sup>2</sup>).

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<sup>-1</sup>, total sample volume of approximately 20 m<sup>3</sup>, 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<sup>-1</sup> (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 ( $\phi$ ) 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  $\phi$  (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

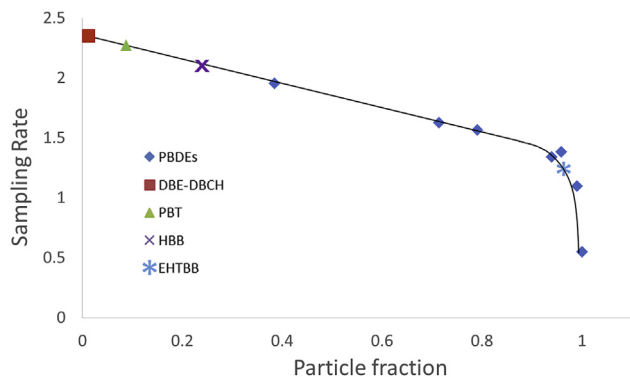


**Fig. 1.** Schematic of the samplers and the sampling design: PUF Only PAS from Hazrati and Harrad [19] reprinted with permission of Elsevier, Combo PAS schematic from Abdallah and Harrad [15] reprinted with permission of the American Chemical Society, and active sampler schematic reprinted with permission from Östman et al. [20].

rates do not differ significantly to that of BDE-47, with only an 18% difference between the most gaseous compound (DBE-DBCH) and BDE-47. Uptake rates for the PUF Only PAS were taken from other studies that employed similar samplers and used active samplers rather than depuration compounds to calibrate their uptake rates, as the former method is considered to be most accurate [26] (Table 1). EFRs with high  $K_{OA}$  values ( $\log K_{OA} > 14$ ) were assigned the same uptake rate as BDE-209 ( $0.55 \text{ m}^3 \text{ day}^{-1}$ ) as these compounds are expected to be particle-bound and thus behave similarly. In support of this, a comparison of 42 paired active and passive air samples for particle-bound polycyclic aromatic hydrocarbons (PAHs) using a PUF only PAS similar to the one in this study resulted in a sampling rate of  $0.7 \text{ m}^3 \text{ day}^{-1}$  [27]. A similar sampling rate of  $0.5 \text{ m}^3 \text{ day}^{-1}$  was used in a Chinese study [28] for DDC-CO ( $\log K_{OA} > 14$ ) based on the above-mentioned PAH study.

#### 2.4. Extraction, clean-up, and instrumental analysis

Sample extraction, clean-up and analyses were performed at Stockholm University, Sweden. All samples were spiked with  $^{13}\text{C}$ -



**Fig. 2.** Calibration curve derived from PBDE sampling rates and particle bound fraction used to estimate sampling rates of several EFRs for the Combo PAS.

**Table 1**  
Sampling rates ( $\text{m}^3 \text{ day}^{-1}$ ) used for passive samplers,  $\log K_{OA}$  used, and particle bound fractions ( $\phi$ ). How sampling rates were obtained: a) derived from calibrated PBDE values as shown in Fig. 2; b) taken from Bohlin et al. [11]; c) assigned the same rate as BDE-209; d) taken from Abdallah and Harrad [15]; e) taken from Hazrati and Harrad [19]. All  $K_{OA}$  values taken from Refs. [22–25]. NA = not applicable (compound not used in calibration).

	Combo PAS rate	PUF only PAS rate	$\log K_{OA}$	$\phi$
DBE-DBCH	2.4 <sup>a</sup>	1.4 <sup>b</sup>	8.01	0.002
PBT	2.3 <sup>a</sup>	1.7 <sup>b</sup>	9.66	0.078
HBB	2.1 <sup>a</sup>	1.2 <sup>b</sup>	10.26	0.25
EHTBB	1.3 <sup>a</sup>	1.7 <sup>b</sup>	12.3	0.97
DDC-CO	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
DBDPE	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
$\alpha$ -HBCDD	1.4 <sup>d</sup>	0.87 <sup>e</sup>	NA	NA
$\beta$ -HBCDD	1.4 <sup>d</sup>	0.89 <sup>e</sup>	NA	NA
$\gamma$ -HBCDD	1.4 <sup>d</sup>	0.91 <sup>e</sup>	NA	NA
BDE-47	2.0 <sup>d</sup>	2.0 <sup>d</sup>	10.53	0.38
BDE-99	1.6 <sup>d</sup>	1.1 <sup>e</sup>	11.31	0.79
BDE-100	1.6 <sup>d</sup>	1.1 <sup>e</sup>	11.13	0.71
BDE-153	1.4 <sup>d</sup>	1.1 <sup>e</sup>	12.1	0.96
BDE-183	1.1 <sup>d</sup>	1.0 <sup>e</sup>	13	0.99
BDE-196	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
BDE-203	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
BDE-206	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
BDE-207	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
BDE-208	0.55 <sup>c</sup>	0.55 <sup>c</sup>	>13	>0.99
BDE-209	0.55 <sup>d</sup>	0.55 <sup>c</sup>	>13	>0.99

labeled surrogate standards of BDEs –155, –183, –197, and –209, *syn*-, and *anti*-DDC-CO,  $\alpha$ -,  $\beta$ -, and  $\gamma$ -HBCDD, and  $^{13}\text{C}_6$   $^2\text{H}_{17}$ -labeled EHTBB and BEH-TEBP before being extracted. The clean-up procedures are from Sahlström et al. [29] and only described briefly here. Active air samples (small PUFs and filters) were extracted in 18 mL dichloromethane (DCM) and passive air samples (larger PUFs and filters) were extracted in 40 mL DCM in an ultrasonic bath for 30 min. The extraction was repeated twice for active and thrice for passive samples. All extracts were reduced to 1 mL and the solvent changed to *n*-hexane before fractionation on an SPE column containing 2 g silica (deactivated with 2.5%  $\text{H}_2\text{O}$ ) and 1 g  $\text{Na}_2\text{SO}_4$ . Fraction 1 was eluted with 30 mL *n*-hexane and contained PBDEs,

DBDPE and also some EFRs not included in the original method (DBE-DBCH, PBT, HBB, DDC-CO, hexachlorocyclopentadienyl-dibromocyclooctane (DBHCTD) and octabromo-1,3,3-trimethyl-1-phenylindane (OBTMPI)). Fraction 2 was eluted with 10 mL 5% diethyl-ether (DEE) in *n*-hexane and contained EHTBB, BEH-TEBP, and BTBPE. Fraction 3 was eluted with 10 mL 50% DEE in *n*-hexane and contained the HBCDDs. Fractions 1 and 3 were further cleaned up using concentrated sulfuric acid while fraction 2 (containing acid sensitive analytes) was eluted through a 0.5 g aminopropyl (NH<sub>2</sub>) column with 12 mL *n*-hexane. Results for validation of the extraction and fractionation method used here can be found in Sahlström et al. [29] and Newton et al. [5].

Instrumental analysis of fractions 1 and 2 was performed using a Trace GC Ultra coupled to a DSQ II MS (Thermo Scientific, Waltham, USA) operating in ECNI mode with ammonia as the moderating gas. A 15 m HT 5 fused silica column (Thermo Scientific, Waltham USA, 0.25 mm inner diameter, 0.1 µm film thickness) was used for separation. HBCDDs were analyzed using ultra performance LC (ACQUITY UPLC) coupled to a tandem-quadrupole MS (Xevo™ TQ-S). A UPLC column (ACQUITY UPLC HSS C18, 1.8 µm; 2.1 mm × 100 mm), with a pre-column (ACQUITY UPLC HSS C18; 1.8 µm VanGuard 2.1 × 5 mm) was used for separation. The UPLC instrument and columns used were from Waters (Milford, USA). Ions monitored for all compounds can be found in Tables A1 and A2 (appendices).

### 2.5. Quality assurance/quality control

All glassware (including Pasteur pipettes) was heated to 450 °C for 4 h and rinsed with acetone before use. To minimize photolytic degradation of the analytes, ultraviolet-light protection was mounted on windows and light fixtures in the laboratory and samples were shielded from light using aluminum foil whenever possible. Low volume sampling trains were cleaned by sonication in 30% ethanol in water and air dried. PUFs for active sampling were pre-cleaned by Soxhlet extraction for 24 h in toluene or DCM and 24 h in acetone. PUFs for passive sampling were cleaned by extraction with *n*-hexane:DCM 9:1 for two cycles in a pressurized liquid extractor (Dionex, UK). Both types of GFFs (for PAS and for AAS) were pre-cleaned by baking in an oven at 450 °C for 24 h.

Field blanks and laboratory blanks were analyzed with each batch of samples. Air field blanks for active samples were collected by loading the sampler with PUFs and GFF, attaching it to the air pump and turning the pump on and then immediately off. For passive samples, the sampler was loaded with the sampling media (a PUF for the PUF Only PAS and a PUF and a GFF for the Combo PAS), placed in its sampling location and then the sampling media were immediately removed.

The method limit of quantification (mLOQ) for a compound was estimated by quantifying it in a sample where the peak was close to a 10:1 signal-to-noise ratio. The method limit of detection (mLOD) was estimated as mLOQ divided by 3. For compounds detected in the blanks, mLODs and mLOQs were calculated as the mean blank level plus 3 or 5 standard deviations, respectively. Furthermore, the ratio of a compound's retention time to its internal standard could not differ by more than 0.01 between the standard and sample. Field blanks were used to blank-correct samples in cases where an analyte was present in blanks. For statistical calculations, concentrations below the mLOD or mLOQ were replaced with the mLOD or mLOQ divided by the square root of two. Levels of nonaBDEs (BDEs -206, -207, and -208) were corrected for possible degradation of BDE-209 in the samples by measuring the peak area of <sup>13</sup>C nonaBDEs in each sample formed from the degradation of <sup>13</sup>C BDE-209 and assuming native BDE-209 had degraded in the same proportions. At least 20% of the original native nonaBDE peak had to remain after correction for the compound to be considered quantifiable.

## 3. Results and discussion

Mean measured concentrations of selected BFRs using the various samplers are shown in Tables 2 and 3, Fig. 3, and more detailed data (amounts in filters and PUFs and all air concentrations) are given in Tables A6–A9 (appendices). The predominant compound in all offices was BDE-209 with concentrations at least an order of magnitude greater than any other PBDE (Tables 3 and A8) and higher than most EFRs (Tables 2 and A8). Most of the congeners associated with the PentaBDE or OctaBDE technical products were observed at very low concentrations (BDEs -47, -99, -100, -153, -183, -196, -203, -206, -207, and -208). The only exception was BDE-206, which is present in the OctaBDE formulation. However, it is also present in the DecaBDE technical product [30] and may also be present due to debromination of BDE-209 [31]. BDE-206 was significantly correlated with BDE-209 (Pearson's  $r = 0.60$ ,  $p = 0.01$ ) indicating the main source to be the DecaBDE technical product and/or the debromination of BDE-209.

The most commonly detected EFR was HBB (97% detection frequency) but it was found at low concentrations (most samples were below the mLOQ) (Table 2, Table A8). Other commonly found EFRs were PBT, DDC-CO, DPTE, and EHTBB (94, 81, 64, and 46% detection frequencies, respectively). DDC-CO was found in the highest concentrations of any EFR, surpassing those of BDE-209 in one office. The highest levels of BDE-209 were observed in the low-use office. This office contained the least amount of furniture and electronics so it is suspected that the source was building materials, especially because two new walls had recently been constructed, converting a previously open area into the low-use office. The high-use office contained the highest levels of the EFRs DBE-DBCH, HBB, PBT, and DDC-CO but the lowest levels of BDE-209. Compounds sought but not detected included BATE, DBHCTD, OBTMPI, and BEH-TEBP.

### 3.1. Active sampling strategies

Little is known about the day-to-day variability of flame retardant concentrations in indoor air. Differences in BFR concentrations between the active 28-day and snapshot samples from the same office suggest that there is short-term temporal variability in concentrations (Tables 2 and 3, Fig. 3). However, most of the results obtained from the two active sampling methods agreed reasonably well (no significant difference in measured concentrations using a Hotelling's T-square test for all compounds with detection frequency of 50% or higher).

The BFR concentrations measured by the active sampling methods were generally within a factor of 2 of each other (Tables A3 and A4). The largest discrepancies were found for BDE-209 for which the concentration ratio of 28-day to snapshot samples ranged from 0.1 to 100. The largest difference between the two AAS (factor of 100) was from the medium-use office during the last sampling period and that particular 28-day sample concentration of BDE-209 was the highest measured in this study (Fig. 4, Table A4). This suggests short term temporal variation in activities in the offices during sampling, which would affect particle-bound contaminants more than gaseous ones due to re-suspension of settled dust by movement in the room.

In the low-use office (containing the highest BDE-209 levels of the three offices on average), the 28-day sample had consistently lower concentrations (2–10 times) of BDE-209 than in the snapshot sample (Fig. 4). In the other offices however, this relation was the opposite. The mean concentration ratio of 28-day to snapshot samples for all compounds measured above their mLOQ was 1.4 when excluding the anomalously high BDE-209 concentration ratio previously discussed. It is possible that some of these differences

**Table 2**  
Arithmetic mean concentrations (and range) of selected EFRs and HBCDDs as sampled by different air samplers ( $\text{pg m}^{-3}$ ). Compounds not detected are displayed as “< mLOD” and means that fell below the mLOQ are reported as a range from the mLOD to the mLOQ.  $n = 3$  for each mean.  $\Sigma\text{DBE-DBCH} = \alpha\text{-DBE-DBCH} + \beta\text{-DBE-DBCH}$ ,  $\Sigma\text{DDC-CO} = \text{syn-DDC-CO} + \text{anti-DDC-CO}$ ,  $\Sigma\text{HBCDD} = \alpha\text{-HBCDD} + \beta\text{-HBCDD} + \gamma\text{-HBCDD}$ .

		$\Sigma\text{DBE-DBCH}$	PBT	HBB	EHTBB	$\Sigma\text{DDC-CO}$	DBDPE	$\Sigma\text{HBCDD}$
Low-Use Office	Active 28 day	10 (<0.16–18)	2.6 (<1.1–5.6)	4.4 (<5.0–6.3)	12 (4.9–25)	<100	<15	87 (80–90)
	Active 3 day	13 (<0.21–25)	3.4 (<1.4–7.7)	2.3–6.6	12 (<5.5–24)	<140	<20	63–96
	Passive Combo	7.4 (3.1–11)	0.65 (<0.069–1.1)	0.59–1.7	0.76–2.3	25 (13–35)	<2300	<480
Medium-Use Office	Passive PUF only	16 (15–19)	2.7 (1.2–4.1)	1.0–3.0	0.58–1.7	17 (10–30)	<2300	<740
	Active 28 day	<0.15	9.1 (6.7–12)	7.7 (<4.9–10)	1.4–4.1	100–160	29 (<15–61)	160 (54–250)
	Active 3 day	<0.16	7.1 (2.1–11)	6.2 (<5.2–11)	4.3 (<1.4–8.8)	<110	31 (<16–66)	140 (41–200)
High-Use Office	Passive Combo	<2.5	2.8 (2.0–4.0)	1.4 (<1.7–1.9)	0.76–2.3	49 (14–110)	<2300	<480
	Passive PUF only	<4.3	5.0 (3.0–6.9)	10 (<3.0–21)	<0.58	51 (30–90)	<2300	<740
	Active 28 day	46 (10–82)	22 (20–24)	110 (41–200)	1.4–4.1	470 (<160–800)	40 (28–53)	170 (64–250)
High-Use Office	Active 3 day	48 (<0.16–82)	23 (15–28)	70 (42–120)	7.2 (<1.4–19)	240 (<170–630)	16–23	110 (53–180)
	Passive Combo	28 (22–34)	4.0 (1.7–8.5)	20 (7.3–43)	0.76–2.3	100 (93–120)	<21	500 (110–1100)
	Passive PUF only	37 (12–61)	6.1 (2.7–8.2)	37 (21–68)	<0.58	260 (79–450)	<2300	<740

**Table 3**  
Arithmetic mean concentrations (and range) of PBDEs as sampled by different air samplers ( $\text{pg m}^{-3}$ ). Compounds not detected are displayed as “< mLOD” and means that fell below the mLOQ are reported as a range from the mLOD to the mLOQ.  $n = 3$  for each mean.

		BDE-47	BDE-99	BDE-100	BDE-153	BDE-183	BDE-196	BDE-203	BDE-206	BDE-207	BDE-208	BDE-209
Low-Use Office	Active 28 day	<18	<2.5	<1.6	<0.76	<2.1	<1.4	<0.92	100 (12–210)	<0.69	<0.76	1400 (59–2800)
	Active 3 day	<24	<3.4	<2.2	<1.0	2.8–8.6	<1.9	1.2–3.7	150 (61–260)	0.92–1.3	<1.0	5500 (470–11,000)
	Passive Combo	<1.8	0.64–1.9	0.28–0.85	<6.7	<1.1	1.7	<1.1	94 (<4.7–210)	<5.2	<3.3	2800 (81–6800)
	Passive PUF only	4.0 (<1.8–5.7)	0.89–2.7	<0.41	8.4–12	<1.5	<1.7	<1.1	220 (14–470)	<5.2	<3.3	7800 (<260–18,000)
Medium-Use Office	Active 28 day	<18	2.5–4.1	<1.6	<0.75	2.0–6.4	1.4	0.90	<1.3	1.8 (<0.68–4.1)	0.74–1.6	6000 (190–17,000)
	Active 3 day	<19	2.6–4.3	<1.7	<0.79	2.2–6.7	<1.5	<1.0	<1.4	1.5 (1.0–2.1)	<0.79	140 (78–170)
	Passive Combo	2.5 (1.6–3.0)	0.64–1.9	1.0 (<0.28–2.5)	<6.7	<1.1	<1.7	<1.1	<1.6	<5.2	8.0 (<3.3–21)	4200 (1300–8900)
	Passive PUF only	5.6 (4.0–8.0)	3.1 (<2.7–5.5)	<0.41	<8.4	<1.5	<1.7	<1.1	<1.6	<5.2	<3.3	2700 (1500–4800)
High-Use Office	Active 28 day	<18	5.7 (<2.5–10)	7.6 (<1.6–20)	0.75	7.0 (<2.0–15)	1.4	<0.91	25 (<1.3–74)	3.9 (1.1–5.7)	0.75–1.6	450 (160–750)
	Active 3 day	<19	<2.6	<1.7	<0.79	<2.2	<1.5	<1.0	14 (<1.4–35)	1.2 (<1.0–2.6)	<0.79	250 (100–430)
	Passive Combo	4.4 (<0.73–12)	0.64–1.9	0.28–0.85	<7.2	<1.1	<1.7	<1.1	12 (<1.6–28)	2.6 (<0.37–3.7)	0.64–1.9	460 (<23–660)
	Passive PUF only	4.5 (<1.8–8.5)	2.9 (<2.7–4.9)	3.6 (<0.41–10)	<8.4	<1.5	<1.7	<1.1	36 (<1.6–89)	<5.2	<3.3	580 (<380–820)

between the two types of AAS strategies may be caused by passive sampling of the 28-day sample while not in use (21.5 h per day).

### 3.2. Passive samplers

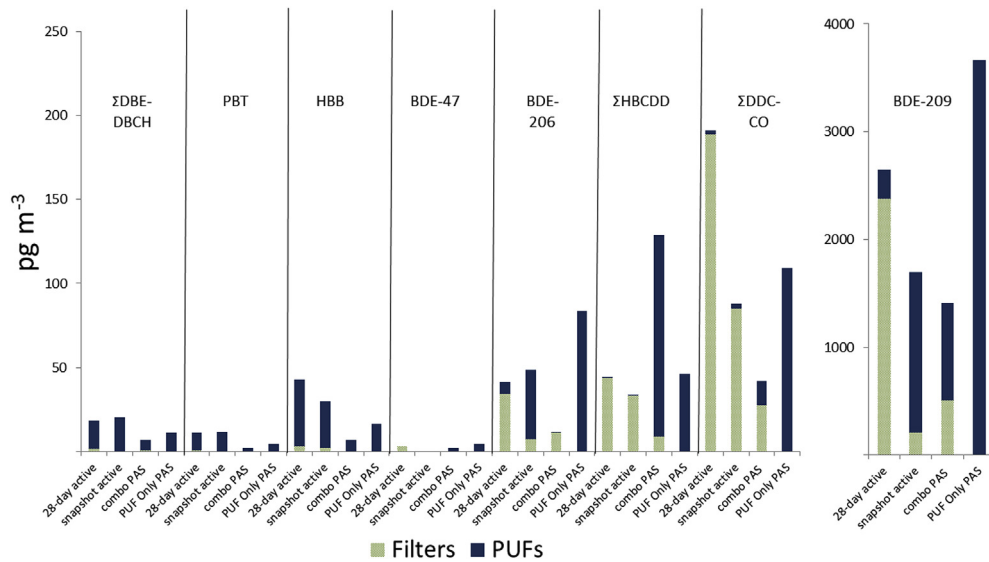
The results from the two passive air samplers were within a factor of 2–3 of each other for the more volatile compounds (DBE-DBCH, PBT, HBB and BDE-47) included in this study (Tables A6 and A7) although a Hotelling's T-square test did not reveal a statistically significant difference between the two. The Combo PAS often resulted in lower amounts accumulated of our target compounds and also resulted in lower concentrations after the sampling rates were applied. The assumed sampling rates for DBE-DBCH, PBT and HBB (Table 1) might be too high for the Combo PAS, which would explain the lower concentrations calculated, but for BDE-47 a calibrated sampling rate was used. The observation that the Combo PAS also accumulated lower amounts of these compounds indicates that the positioning of the PUF inside the sampler influences the uptake of gaseous compounds and that positioning it in the center of the sampler leads to more accumulation which has been observed

previously in another study [32]. This is likely due to there being less exposed PUF surface area in the Combo PAS as half of it is against the upper surface of the housing or it is possible that there is some influence from the filter on the air flow through the sampler.

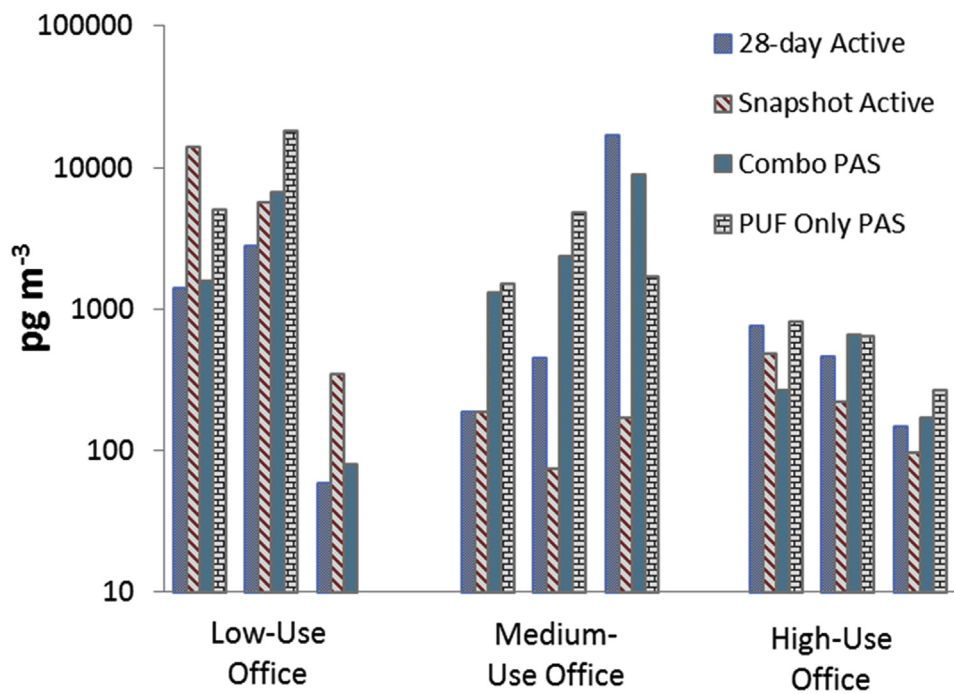
For particle-bound compounds, the ratio between the two passive samplers varied more than for gaseous compounds. For BDE-209 the Combo to the PUF Only PAS concentration ratio ranged from 0.31 to 5.2 with no clear pattern. The GFF in the Combo PAS was placed in the same position as the PUF in the PUF Only PAS but retained less BDE-209 (31–86% by mass) during every sampling period that could be compared (Fig. 4, Table A4). This indicates that PUFs in passive samplers have a retention capacity for air particles similar to (or larger than) GFFs in the indoor environment, but more research is warranted to understand this process.

### 3.3. Active vs passive sampling

Both the active 28-day and snapshot samples measured approximately 2–5 times higher concentrations of volatile EFRs (DBE-DBCH, PBT, and HBB) than the Combo PAS in all three offices



**Fig. 3.** Arithmetic mean concentrations ( $\text{pg m}^{-3}$ ) of selected contaminants in all offices as found on PUFs and filters from different air samplers.  $\Sigma\text{DBE-DBCH}$  = sum ( $\alpha$ - +  $\beta$ -) DBE-DBCH;  $\Sigma\text{HBCDD}$  = sum ( $\alpha$ - +  $\beta$ - +  $\gamma$ -) HBCDD;  $\Sigma\text{DDC-CO}$  = sum (syn- + anti-) DDC-CO.



**Fig. 4.** Concentrations of BDE-209 ( $\text{pg m}^{-3}$ ) as measured by different air samplers in different offices over three sampling periods. Note the logarithmic scale.

(Fig. 3). The two AAS strategies also yielded higher concentrations of these EFRs than the PUF Only PAS, albeit to a lesser extent as concentrations were usually within a factor of two (Fig. 3). Higher sampling rates were used for the Combo PAS for these compounds, which may have led to an underestimation of the concentrations.

The active 28-day samples agreed reasonably well with both passive samples for BDE-209 concentrations, within a factor of 2 for most sampling periods and within an order of magnitude for all (Fig. 4). The results were similar for other particle-bound compounds. For example, the ratio of active 28-day active samples to Combo PAS for  $\Sigma\text{DDC-CO}$  concentrations ranged from 0.5 to 12. Significant differences between the active 28-day and the Combo

PAS air sample concentrations for more volatile compounds were observed. Mean concentrations for DBE-DBCH, PBT, and HBB were 1.5, 4.3, and 4.8 times higher, respectively, for the active 28-day sampler than the Combo PAS. One source of uncertainty is the sampling rates which were derived from calibrated rates of PBDEs in indoor environments. However, the physicochemical properties are similar to the PBDEs included in the calibration, most importantly  $K_{\text{OA}}$ , so the derived rates are not far outside the range of calibrated rates (2.4, 2.3, and 2.1  $\text{m}^3$  per day for DBE-DBCH, PBT, and HBB, respectively, compared to 2.0 for BDE-47). Limited detection of compounds with calibrated rates (other than BDE-209) makes comparison difficult, however.

In order to remove the uncertainty associated with applying the selected sampling rates from Table 1, a fingerprint from each sampler for each office is displayed in Fig. 5. Each bar in this figure represents the total amount of each FR sampled (summed pg) for all three months relative to the other FRs. BDE-209 was excluded from Fig. 5 in order to make other compounds more visible. It comprised 86–97%, 47–96% and 26–53%, of the total for the low-use, medium-use and high-use offices, respectively and a fingerprint figure including BDE-209 can be found in the appendices (Figure A1).

Differences in the fingerprints between offices can be expected because of differing sources of compounds in each office. Differences between samplers in the same office, however, can reveal how samplers accumulate compounds over the sampling period. Qualitatively, all the samplers sampled similar compounds within each office. Very seldom was a compound missing from one sampler type when it was found on the other samplers.

### 3.4. Filter/PUF partitioning

The more volatile EFRs, namely DBE-DBCH, PBT, and HBB, were found almost exclusively in the gas phase (on PUFs) from both active and passive sampling (Fig. 3). This was expected at indoor temperatures (about 25 °C) because of their low  $K_{OA}$  values [33]. The small amounts found on filters (<10%) could be due to either a small proportion of the compounds partitioning to particles or some sorptive capacity of the GFF for gas phase contaminants [34].

BDE-209, with its high  $K_{OA}$  ( $\log K_{OA} = 16.77$ ) [25] would be expected to partition almost entirely to air particles and therefore be trapped on the filter when sampling actively. A significant portion was however detected on PUFs, something that has been observed previously from indoor sampling [9,21]. In the low-use office (having the highest BDE-209 concentrations) as much as 96% from the snapshot and 54% from the 28-day samples was detected in the PUFs. In the other two offices, BDE-209 was almost entirely (more than 97%) detected on the filters. BDE-206 behaved similarly, with 95% and 22% in the PUFs (snapshot and 28-day

samples, respectively), from the low-use office. In active air samples from the high-use office, BDE-206 was only detected on the filters, while in the medium-use office it was below detection limit. The fact that the occupants of the medium- and high-use offices opened their windows for the second two sampling periods while the low-use office occupants did not, is possibly a factor as outdoor air probably contains fewer very small particles that are capable of passing through the GFF into the PUF in the active sampler [35]. However, this phenomenon was not observed for other particle-bound compounds like HBCDD and DDC-CO. Because of the large difference in the contents and use of the offices, there may have been different sources of BDE-209 (e.g. high impact polystyrene vs textile backcoating), which also may have influenced the particle partitioning. Two other FRs with high  $K_{OA}$  values, DDC-CO and HBCDD, were found almost entirely on filters in active samples from all offices (Fig. 3). For the Combo PAS samples, the opposite was observed for BDE-209 as it was detected only on the filter from the low-use office but on the PUFs from the other two offices. The Combo PAS design is not expected to give a meaningful measure of particle-gas partitioning.

### 3.5. Statistical analysis

Three separate one-way multivariate analysis of variance (MANOVA) tests were conducted with data grouped into offices, months, and sampling strategy. Only compounds with more than half of their values above the mLOD were input into these tests and tests were run using only gaseous compounds (DBE-DBCH, PBT, and HBB), only particle-bound compounds (EHTBB, DDC-CO, HBCDD, BDE-209), and using both groups of compounds. For all three compound groupings, Wilks' Lambda tests showed significant differences ( $p < 0.05$ ) between offices but not between months. Significant differences between sampling strategies were observed when using particle-bound and both groups of compounds but not when only gaseous compounds were used. This finding indicates that concentrations measured using the various sampling

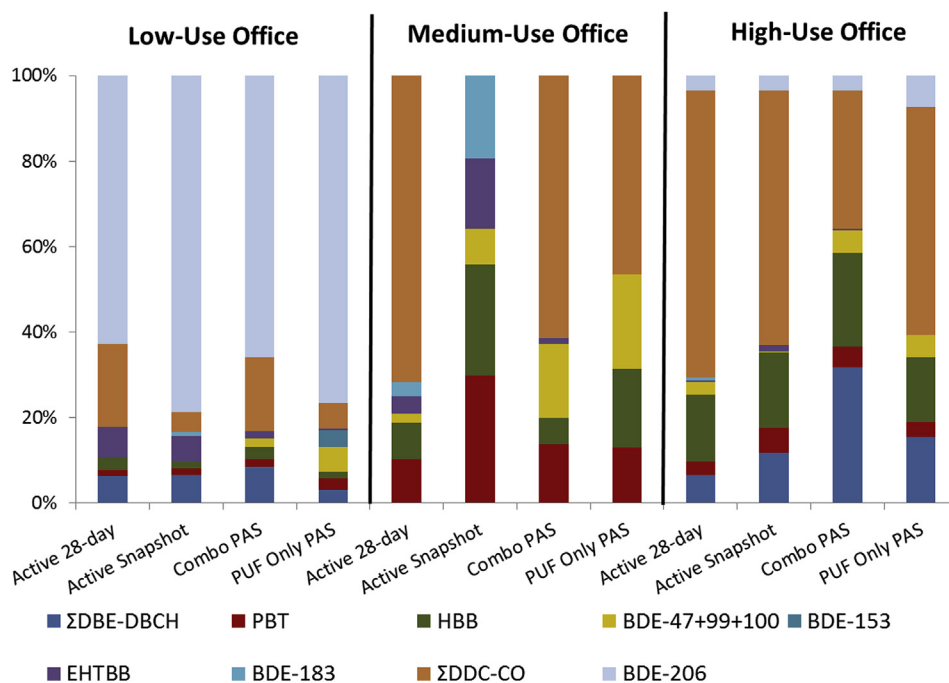


Fig. 5. Percent contribution of each FR to the total amount (pg) of FRs (except BDE-209, HBCDDs, and DBDPE) for each sample type in the three offices. Compounds are arranged by  $K_{OA}$ .  $\Sigma$ DBE-DBCH = sum ( $\alpha$ - +  $\beta$ -) DBE-DBCH.



strategies used in this study are likely more similar for gaseous compounds than for particle-bound compounds. The partial eta squared values for offices and sampling strategies when both groups of compounds were used were 0.678 and 0.693, respectively, meaning that approximately the same amount of variability in the data can be explained by different sampling locations as can be explained by different sampler types when comparing all four sampling strategies.

### 3.6. Measured levels in comparison to other studies

In order to compare our results to other studies, concentrations from the snapshot AAS are compared with other AAS studies and PUF only concentrations from the PAS are compared with PAS studies. Reports of PBDEs in indoor air in China are scarce. Median levels of BDE-209 in this study ( $220 \text{ pg m}^{-3}$ ) as measured by the snapshot AAS were similar to those found in offices and other microenvironments in Guangzhou, China ( $170 \text{ pg m}^{-3}$ ) using high-volume AAS in 2004–2005 [36]. In that study however, BDE-47 and -99 concentrations were found to be similar to those of BDE-209, whereas BDEs-47 and -99 were scarcely detected in this study. A study of outdoor air in Beijing from 2006 to 2007 using PAS also found measurable concentrations of BDEs -47 and -99, along with other congeners in the PentaBDE mix (e.g. BDEs -100, -153, -154), but did not report levels of BDE-209 [37]. DecaBDE has been produced and used in large quantities in Asia, whereas the production and use of the PentaBDE product largely stopped in this region during the 1990s [38]. As of 2012, production of DecaBDE may still have been ongoing in China while its use had already declined or ceased in much of the world [39]. The difference in sampling year between studies may explain why PentaBDE congeners were found in those studies but not in this one.

Reports of DDC-CO in China are many as major production of this compound has occurred in China [40], although most studies focus on outdoor air or contaminated sites such as electronic waste or recycling sites. DDC-CO has been reported in outdoor air in urban and rural locations all across China, including Beijing where it was reported at approximately  $34 \text{ pg m}^{-3}$  using PAS [28]. Indoor air concentrations were much higher in the high-use (mean of  $260 \text{ pg m}^{-3}$ ) but similar in the medium-use and low-use office (means of  $51 \text{ pg m}^{-3}$  and  $16 \text{ pg m}^{-3}$ , respectively). The elevated levels in the high-use office may be attributed to the abundance of electronics in that office as DDC-CO is used in electrical cables [40]. DDC-CO has also been found in indoor air in Norway [6] and Sweden [5], however at low detection frequencies. Levels of DBE-DBCH, PBT, and HBB in this study were comparable to the aforementioned studies in Norway and Sweden.

## 4. Conclusions and summary

Measured concentrations of BDE-209 from the Combo PAS were usually within a factor of 2 of the active 28-day concentrations but sometimes, albeit rarely, ranged up to a factor of 10. Snapshot active samples gave data less comparable than 28-day active samples with those derived from the combo PAS, probably due to daily variability in concentrations. The PUF Only PAS appeared more effective at sampling low-volatility contaminants (mainly BDE-209) than the Combo PAS, but gave more variable results. The retention capacity of PUFs for particles remains one of the largest knowledge gaps for the use of PAS for semi-volatile organic contaminants but that is not the only knowledge gap. Using particle-bound fractions to estimate sampling rates for compounds that have not been calibrated for, likely led to underestimated concentrations of gaseous contaminants. Furthermore, sampling rates for PAS taken from other studies added uncertainty when comparing

to AAS and likely contributed to the differences found in measured concentrations. The placement of the PUF inside the sampler seemed to have influenced the amount of gaseous contaminants sampled, with higher amounts accumulating on the PUF positioned in the center of the sampler rather than the top.

Several emerging flame retardants were identified in Beijing offices including DBE-DBCH, PBT, HBB, DDC-CO, and DBDPE. However, BDE-209 was the most predominant FR, probably due to widespread production and use of DecaBDE in China [38,39]. Levels of PBDE congeners associated with the Penta- and OctaBDE products were very low compared to their more substantial presence in previous studies from China.

Ultimately, our data suggest that the selection of sampler type or strategy should depend on the aim and resources available to conduct the study. Assessment of human exposure may require more precise measurements in which case an active sampling strategy, such as the 28-day active air sampling in this study, may be most appropriate. But this sampling is less convenient and more demanding on researcher time, so a snapshot active air sampling strategy will produce similar results in less time. However, large air sampling campaigns such as the GAPS network [41,42] or studies that require concurrent sampling at multiple sites such as transect studies [43–45] would not be possible without the use of passive samplers. The possibility of a sample being heavily influenced by a spike in concentrations should be considered, which would influence “snapshot” samples more than samples collected over a longer time period. Caution should be taken when comparing studies using different sampling strategies as MANOVAs from this study found that there was approximately the same amount of variability between sampling strategies as there was between different offices.

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## Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.emcon.2016.02.001>.

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