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► **To cite this version:**

Jessica Queron, Adeline Floch-Barneaud, François Lestremau, Caroline Marchand, Marc Durif, et al.. Development of air and dust sampling methods for quantitative measurements of polybromated diphenyl ethers (PBDEs) in offices. 10. International Conference Healthy Buildings (HB2012), Jul 2012, Brisbane, Australia. Queensland University of Technology, pp.NC, 2012. <ineris-00973678>

**HAL Id: ineris-00973678**

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Submitted on 4 Apr 2014

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# Development of air and dust sampling methods for quantitative measurements of polybromated diphenyl ethers (PBDEs) in offices

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## SUMMARY

The PBDEs family consists of 209 congeners widely used in consumer products for improving fire resistance. The global aim of this project was to improve knowledge about the PBDE “source-exposure-intake” continuum for human, by coupling, for the first time in France, PBDEs measurements in air and dust of different offices with PBDEs measurements in the blood of their occupants, all run simultaneously. This paper focuses on the metrological part of the project dedicated to PBDEs measurements in indoor air and dust (development of quantitative sampling methods and field campaign in 24 offices). ΣPBDEs concentrations (corresponding to the sum of the eleven measured congeners) in settled dust ranged between 12-193 or 8-201 pg/cm<sup>2</sup> according to the used method. Indoor air ΣPBDEs concentrations respectively ranged between 2.8-26.9 ng/m<sup>3</sup> and 19.5-100.8 ng, for active and passive air samplings. Weakly and highly brominated PBDEs were respectively mainly found in air fraction and settled dust.

## KEYWORDS

*SVOC, endocrine disruptors, metrological development, field campaign.*

## 1 INTRODUCTION

The family of polybrominated diphenyl ethers (PBDEs) consists of 209 congeners widely used in consumer products for improving fire resistance (computers, polyurethane foams, carpet...). If they are ubiquitous in indoor environments, persistent, bio-accumulated and suspected to be endocrine disruptors, their becoming in the different environmental media and population exposure are not well-known. Moreover, if intake through food consumption is undoubtedly important, several studies highlight the role of indoor dust in PBDE exposure. Lastly, no data is available concerning PBDE concentrations in French offices.

The global aim of this project, supported by the French Agency for Food, Environmental and Occupational Health & Safety (ANSES) and the French Ministry of Environment (MEDDTL), was to improve knowledge about the PBDE “source-exposure-intake” continuum for human, by coupling, for the first time in France, PBDEs measurements in air and dust of different offices with PBDEs measurements in the blood of their occupants.

This paper is focused on the metrological part of the project dedicated to PBDEs measurements in indoor air and dust that consisted of the development of quantitative sampling methods and their use during a field campaign in 24 offices.

## 2 MATERIALS/METHODS

### Targeted congeners

Eleven congeners have been targeted (BDE 1, 12, 28, 47, 99, 100, 153, 154, 183, 206 and 209) in the different investigated media. Most of them are the most frequently congeners found in food and biological media and the quantification of some of them is considered of high priority by the French Food Safety Agency (AFSSA, 2006). Measurement of weakly

brominated PBDEs such as BDE1 and BDE12 is part of the originality of this project as it has never been done in environmental studies.

### **Sampling methods**

A first step in the project was to conduct a feasibility study to assess the performances of different sampling methods for indoor air and dust (analytical blank, recovery rates with static and dynamic doping) in order to choose/optimised the best one for each investigated media. Another goal was to identify methods that would be accepted by offices occupants (noise and space disturbance). Details of this feasibility study are described elsewhere (article in preparation). Based on the obtained results, sampling methods used during the field campaign are the followings. Dust samplings were performed by wiping surfaces of 100 cm<sup>2</sup> according to the ASTM D6661 with commercial electrostatic wipes that were impregnated with 2mL of hexane. Prior to sampling, each wipe was cut in two equal parts, one dedicated to the measurement, the other one to the field blank. Air samplings were performed with passive and active methods. For the first one, a PUF foam disk, conditioned prior to use with a pressurized liquid extraction (mix of hexane/dichloromethane (50/50 v/v)), was placed into a stainless steel passive sampler. For the second one, air was pumped at 3 L.min<sup>-1</sup> with a Microvol® through a quartz fibber filter, baked prior to use, followed by a Supelco® cartridge containing XAD-2 resin sandwiched between two PUF plugs.

### **Field campaign design**

Indoor measurements were performed between the 5<sup>th</sup> of November 2010 and the 3<sup>rd</sup> of December 2010 in 24 offices of a 5 floors building, located in an urban traffic area near Paris and refurbished in 2008.

The first day, a passive air sampler and a 100 cm<sup>2</sup> artificial desk surface, specifically designed for this study to collect "fresh" dust, were installed in each office, respectively at 2 m and 1.80 m height (Figure 1). After 28 days, passive air measurement was stopped and the artificial desk surface was wiped entirely. Another dust sample was performed in each office by wiping a surface of 100 cm<sup>2</sup> over offices cupboards in order to get more dust matter and to observe potential differences between the 2 methods (uncontrolled deposition period for the "cupboards" method). Offices staff was asked not to clean the studied surfaces all over the campaign.



Figure 1. Passive air sampler and artificial desk surface used during the field campaign

Active air samples were collected in 12 offices only. Measurements were performed during the week-end (48h, 3 offices per week-end) to avoid noise disturbance for the occupants.

### **Samples storage and analytical procedures**

After sampling, filters were replaced in their Petri® box before being wrapped with an aluminium foil and put in a polyethylene bag. Wipes, PUF disks and cartridges were directly wrapped with an aluminium foil and then put in a polyethylene bag. All samples were stocked at -20°C before analysis. Prior to extraction, internal standards of BDE 77, 181 and 209C<sup>13</sup> were added to each sample. Quartz filters, PUF foams and XAD-2 resins were extracted with

a pressurised mix of hexane and dichloromethane (50/50 v/v) whereas wipes were dipped in 100 mL of hexane and then extracted for 30 min with ultrasonics. 10  $\mu$ L of keeper (Tridecane) were added to each extract for a better preservation of BDE1 and BDE12 and then solvents were evaporated to dryness under argon flux. Each sample was then diluted in 1 mL of isoctane and analysed by gas chromatography coupled to mass spectrometry (negative chemical ionisation).

### 3 RESULTS

Prior to describe obtained results, it is important to notify that BDE 1 and 12 could have been widely overestimated because of the presence, on chromatograms, of several other brominated compounds near their elution peaks. BDE1 and BDE12 concentrations are then indicative.

#### PBDEs dust concentrations

PBDEs concentrations for each congener are reported in Figure 2. For cupboards, PBDEs congeners profile is mainly covered by BDE209 followed by BDE47 and BDE206. BDE1, BDE100, BDE153, BDE154 and BDE183 have been detected in any sample.  $\Sigma$ PBDEs concentrations ranged between 0.8 and 20.1 ng/100cm<sup>2</sup>. For artificial desk surfaces, PBDEs congeners profile is mainly covered by BDE209, followed by BDE100, BDE99 and BDE206. As for cupboards, BDE1, BDE153 and BDE154 have been detected in any sample.  $\Sigma$ PBDEs concentrations ranged between 1.2 and 19.3 ng/100cm<sup>2</sup>.

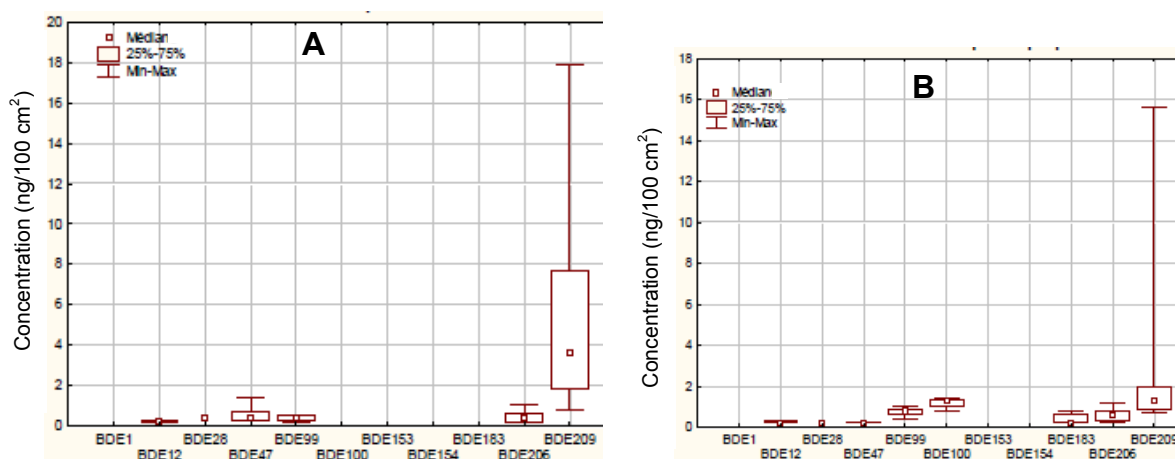


Figure 2. Box plot of PBDEs congeners concentrations (ng/100 cm<sup>2</sup>) for dust samples collected over cupboards (a) and over artificial desk surfaces (b)

#### PBDEs air concentrations (passive sampling)

As passive sampler flow rates are not known precisely (literature reports flow rates ranged between 2.5 to 5 m<sup>3</sup>/day for stainless steel passive samplers (Toms, 2009)), PBDEs concentrations for each congener are expressed in ng and are reported in Figure 3. BDE1 is the most abundant congener (66% of the  $\Sigma$ PBDEs mass on average), followed by BDE209 and BDE12 (respectively 12% and 8% of the  $\Sigma$ PBDEs mass on average). Taking into account congeners medians, PBDEs congeners concentrations can be classified as followed: BDE1 > BDE12 > BDE209 > BDE206 > BDE99 > BDE47 > BDE28 > BDE100. BDE 183, 154 and 153 are detected in very few air samples, respectively in 2, 3 and 7 samples over 24 against 23 to 24 samples for other congeners.  $\Sigma$ PBDEs levels ranged between 19.5 and 100.8 ng.

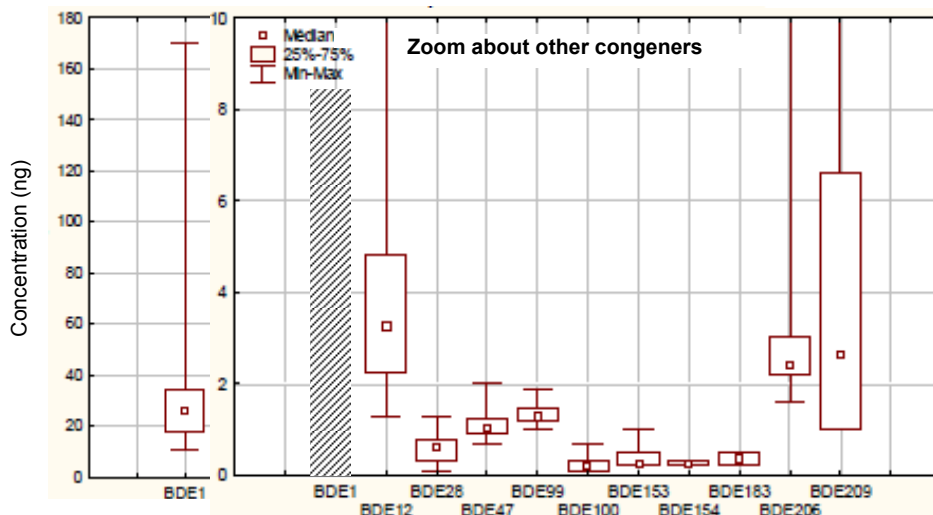


Figure 3. Box plot of PBDEs congeners concentrations (ng) for passive air samplings

### PBDEs air concentrations (active sampling)

PBDEs concentrations for each congener are reported in Figure 4. BDE1 is the most abundant congener (97% of the  $\Sigma$ PBDEs mass on average), followed by BDE12 (only 1.5% of the  $\Sigma$ PBDEs mass on average). Taking into account congeners medians, PBDEs congeners concentrations can be classified as follows: BDE1 > BDE12 > BDE209 > BDE28 > BDE47 > BDE206 = BDE183 > BDE99 > BDE100. BDE 153 and 154 are detected in very few air samples, respectively in 2 and 5 samples over 12 against 10 to 12 samples for other congeners.  $\Sigma$ PBDEs concentrations ranged between 2.8 and 26.9  $\text{ng}/\text{m}^3$ .

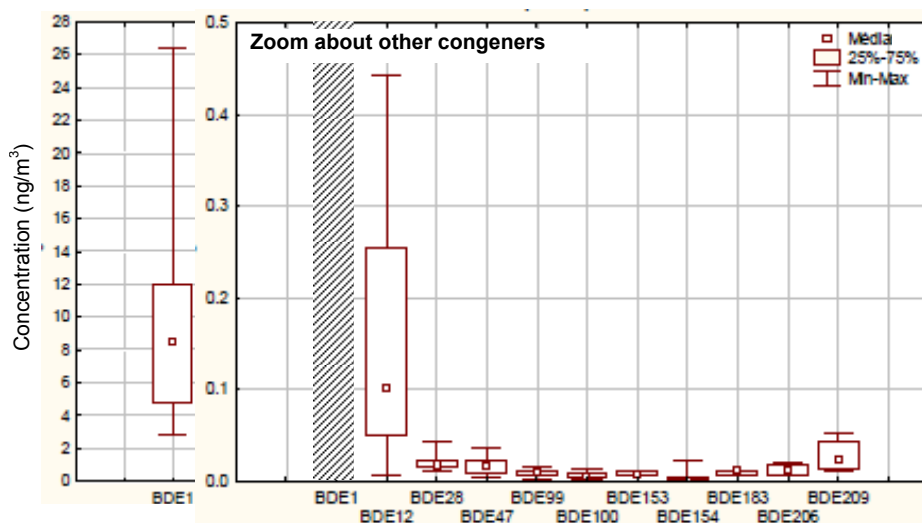


Figure 4. Box plot of PBDEs congeners concentrations ( $\text{ng}/\text{m}^3$ ) for active air samplings

## 4 DISCUSSION

### Comparison of results obtained with different devices for a same environmental media

Concerning settled dust, samplings over cupboards were performed to get more dust matter in case of too small amount of PBDEs collected with artificial desk surfaces. But the deposition period was unknown, implying uncontrolled uncertainties and then a hazardous results interpretation when comparing measured concentrations in each office or with other studies. *In fine*, dust samplings with artificial desk surfaces allowed to collect enough matter, with a

control deposition period. Moreover, this method allowed detecting two more congeners (BDE100 and BDE183) compare to “cupboard samplings”.

About air samples, the three main congeners are the same for passive and active samplings although active samplings are designed to take into account both gaseous and particulate phases whereas passive samplings are designed to collect gaseous phase.

For air concentrations, weakly brominated congeners such as BDE1 and BDE12 are the most abundant whereas BDE209 is the main congener for settled dust concentrations which is consistent with the fact that the most volatile compounds are detected in the airborne phase whereas heavy compounds settled. Whatever the environmental media, BDE209 is relatively abundant, which is probably due to the fact that deca-BDE (formed of 97% of BDE209) is the only authorised commercial formula in Europe since 2004.

### Comparison with literature

As BDE1 and BDE12 have not been measured in any other study, levels registered in our study are not discussed below.

Concerning settled dust, comparison with results of other studies is difficult because wiping-based methods are used in few studies (compare to suction-based methods).settled Moreover, when wiping-based methods are used, the deposition period is often not given.

For passive air samplings, any study in offices is available with expressed concentrations in ng. Table 1 gives PBDEs concentrations measured in dwellings and hostels for a 1 month sampling period. We can observe that PBDEs levels in our study are lower than those registered in Imm study (2009) that is consistent with the different American and European restrictions on the marketing and use of PBDEs. Our concentrations are higher than those registered in Hazrati study (2006) that was also performed in Europe (UK).

Table 1. Comparison of PBDEs levels (ng) for passive air samplings (median (min–max))

Country Source	France This study, 2011	UK Hazrati, 2006	Australia Toms, 2009	Japan Takigami, 2009	USA Imm, 2009
<b>Environment</b>	<b>Offices</b>	<b>Unknown</b>	<b>Dwellings</b>	<b>Hostel</b>	<b>Dwellings</b>
Number	24	2	10	2	38
Sampling period	1 month	1 month	1 month	1 month	1 month
<b>BDE 28</b>	0.6 (0.1 - 1.3)	-	-	-	2.0 *
<b>BDE 47</b>	1.1 (0.7 - 2.0)	(0.1 - 0.6)	1.9 (1.0 - 21.7)	-	15.2 *
<b>BDE 99</b>	1.3 (1 - 1.9)	(0.1 - 0.6)	2,5 (<LQ - 4.1)	-	2.8 *
<b>BDE 100</b>	0.2 (0.1 - 0.7)	-	0.5 (<LQ - 0.6)	-	1.3 *
<b>BDE 153</b>	0.25 (0.25 - 1.0)	-	-	-	3.6*
<b>BDE 154</b>	0.25 (0.25 - 0.3)	-	-	-	ND
<b>BDE 183</b>	0.38 (0.25 - 0.5)	-	-	-	ND
<b>BDE 206</b>	2.4 (1.6 - 11)	-	-	-	ND
<b>BDE 209</b>	2,7 (1 - 49)	-	-	-	5.5 *

\* Geometric mean; LQ = quantification limit; ND = non detected

Concerning active air samplings, an Australian and an American study reports PBDEs concentrations measured in offices with active measurements (Table 2). Our registered concentrations are lower than those of the American study (Batterman, 2010) for congeners with less than 6 bromine atoms (< BDE100). Compare to the Australian study, our registered

concentrations, depending on the congeners, are in the same range are higher.

Table 2. Comparison of PBDEs levels (pg/m<sup>3</sup>) for active air samplings (median (min–max))

Country	France	Australia	USA
Source	This study, 2011	Toms, 2009	Batterman, 2010
Environment	Offices	Offices	Offices
Number	12	8	10
Sampling period	48h	3 days	1 week
<b>BDE 28</b>	19 (10 - 43)	-	60 (<LD - 2600)
<b>BDE 47</b>	17 (3 - 37)	(<LQ - 358)	721 (159 - 12460)
<b>BDE 99</b>	6 (1 - 13)	(<LQ - 20)	154 (<LD - 1663)
<b>BDE 100</b>	9 (2 - 15)	(<LQ - 4.6)	76 (<LD - 443)
<b>BDE 153</b>	1 (1 - 22)	(<LQ - 1.7)	<LD (<LD - 32)
<b>BDE 154</b>	9 (6 - 12)	(<LQ - 1.7)	<LD (<LD - 204)
<b>BDE 183</b>	12 (6 - 12)	(0.9 - 3.7)	<LD (<LD - 21)
<b>BDE 206</b>	12 (6 - 21)	-	<LD
<b>BDE 209</b>	38 (12 - 52)	(5.2 - 12)	<LD

*LQ = quantification limit; LD = detection limit*

## 5 CONCLUSIONS

This study has evaluated for the first time BDE1 and BDE12 concentrations in dust and indoor air of French offices. Moreover, chromatograms showed several peaks of brominated compounds that could be identified and quantified in further projects to improve knowledge about indoor PBDEs exposure. This study also showed that settled dust sampling thanks to an artificial desk surface has several advantages and is sensitive enough.

## ACKNOWLEDGEMENT

The authors would like to thank the ANSES and the French Ministry of Environment for their financial support. We would like also to thank all the volunteers involved in this project.

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