

# DISTRIBUTION AND PREVALENCE OF PBDEs, ORGANOPHOSPHORUS AND NEW BROMINATED FLAME RETARDANTS IN ENVIRONMENTAL SAMPLES

Lacorte S<sup>1</sup>, Cristale J<sup>1</sup>, Hurtado A<sup>1</sup>, Bertolero A<sup>2</sup>, Ramos D<sup>1</sup>, van Drooge B<sup>1</sup>

<sup>1</sup> Department of Environmental Chemistry, IDAEA-CSIC, Jordi Girona 18-26, 08034 Barcelona, Spain; <sup>2</sup> IRTA Aquatic Ecosystems, Ctra. Poble Nou km 5.5, 43540 Sant Carles de la Ràpita, Spain

## Introduction

Since the last century, technology advances changed human life. Nowadays, a huge variety of materials are manufactured and applied to different products to facilitate modern life or make it more comfortable. As a result, people are surrounded by a wide diversity of polymers in clothing, furniture, electronics, vehicles and computers. Most of these polymers are petroleum-based and flammable, and some applications can promote fire ignition. For example, miniature components in high-powered computers generate a high concentration of heat that can lead to fast overheating of internal components. Therefore, safety regulations have been adopted to prevent accidental fires and to protect human beings<sup>1</sup>. In this context, flame retardants (FRs) are used in diverse types of materials to reach fire standards requirements. FRs are substances incorporated to materials to inhibit or slow down the spread of a fire. The term “flame retardant” does not refer to a specific class of chemicals but to a function, and different chemicals, with different properties and structures, are included in this group. They consist mainly of inorganic and organic compounds based on bromine (e.g. high brominated aromatic and cyclo-aliphatic compounds), chlorine (e.g. chloroparaffins, dechlorane plus), phosphorus (e.g. phosphate-esters, phosphonates and phosphinates, ammonium phosphate), nitrogen (e.g. melamina and melamina derivatives), boron (e.g. sodium borate, borax and zinc borates), and metallic hydroxides (e.g. aluminum and magnesium hydroxides). FRs are either additive or reactive. Reactive FRs are added during the polymerisation process, modifying the polymer structure, and giving FR properties. Additive FRs are monomer molecules, not chemically bound to the polymer, incorporated mainly after polymerization<sup>2</sup>. Nowadays, the worldwide consumption of FRs is about 2 Million tons/year, and an annual consumption grow of 4-5% is estimated. Approximately 85% of FRs are used in plastics, with textiles and rubber products accounting for most of the rest. Aluminium hydroxide is the most consumed FRs (40.4 %), followed by brominated FRs (19.7 %), organophosphorus flame retardants (OPFRs) (14.6 %), chlorinated flame retardants (11.3 %), antimony oxide (8.7 %), and other (4 %).

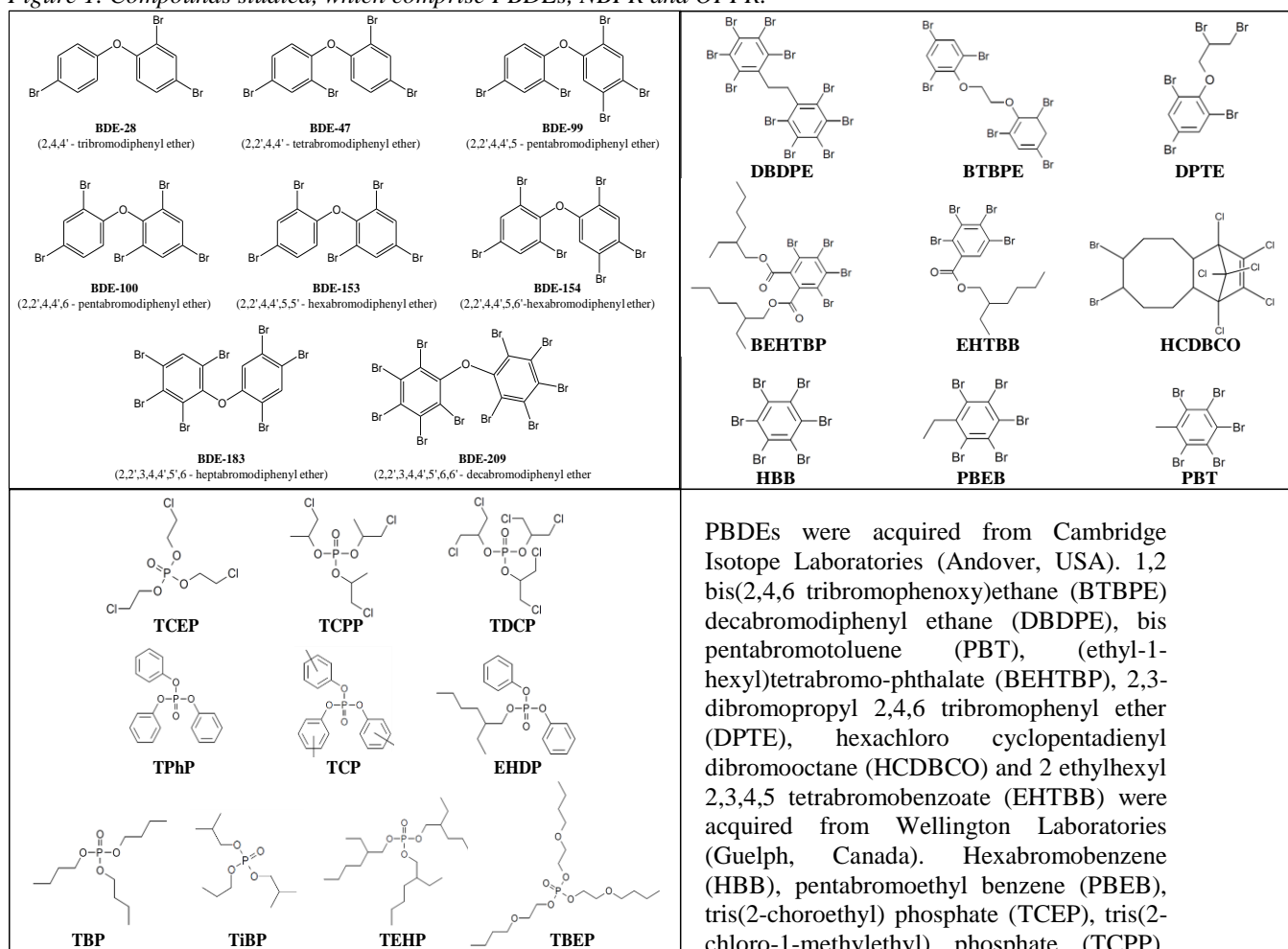
Despite the benefits associated to the use of FRs in terms of decreasing number of deaths and injuries related to fires, some of these compounds deserve environmental concern due to their toxicity and bioaccumulation potential. Halogenated FRs (especially brominated FRs), and more recently organophosphorus flame retardants (OPFRs), have been considered as a potential threat to the environment. Since these FRs are high production and persistent chemicals, they have been detected in all environmental compartments<sup>3-5</sup>. The fate of organic FRs in the environment is complex, and depends on their physicochemical properties (e.g. water solubility, log Kow, vapour pressure, etc.) and their degradability potential (e.g. biodegradation, photodegradation, etc). Once released, the most volatile compounds will be detected in atmosphere, whereas soluble ones will be found in water and the most lipophilic will be detected in sediments, sludge and accumulated in biota.

The objective of the present study is to determine the presence of 8 Polybromodiphenyl Ethers (PBDEs), 9 New Brominated Flame Retardants (NBFR) and 10 Organophosphorus Flame Retardants (OPFR) in various environmental matrices in order to determine their occurrence, partitioning and compound distribution. Matrices involved in this study are river water, sediments, wastewaters, sludge, dust, air and gull eggs.

## Materials and methods

A multiresidue method based on selective extraction and GC-EI-MS/MS was developed for the simultaneous extraction, clean-up and analysis of 27 priority and (re-)emerging flame retardants (PBDEs, NBFRs and OPFRs), as indicated in Figure 1, in river water, sediments, wastewater, sludge, dust, air and gull eggs. The accuracy of the method was evaluated by using a certified reference material and by participating in an interlaboratory study<sup>6</sup>.

Figure 1. Compounds studied, which comprise PBDEs, NBFR and OPFR.



PBDEs were acquired from Cambridge Isotope Laboratories (Andover, USA). 1,2 bis(2,4,6 tribromophenoxy)ethane (BTBPE) decabromodiphenyl ethane (DBDPE), bis pentabromotoluene (PBT), (ethyl-1-hexyl)tetrabromo-phthalate (BEHTBP), 2,3-dibromopropyl 2,4,6 tribromophenyl ether (DPTE), hexachloro cyclopentadienyl dibromooctane (HCDBCO) and 2 ethylhexyl 2,3,4,5 tetrabromobenzoate (EHTBB) were acquired from Wellington Laboratories (Guelph, Canada). Hexabromobenzene (HBB), pentabromoethyl benzene (PBEB), tris(2-chloroethyl) phosphate (TCEP), tris(2-chloro-1-methylethyl) phosphate (TCPP),

tris[2-chloro-1-(chloromethyl)ethyl] phosphate (TDCP), triphenyl phosphate (TPhP), 2-ethylhexyl diphenyl phosphate (EHDP) and tributyl phosphate (TBP) were acquired from Sigma Aldrich (Germany). TCPP was acquired as a mixture of isomers (tris(2-chloro-1-methylethyl) phosphate, bis(1-chloro-2-propyl)-2-chloropropyl phosphate, and bis(2-chloropropyl)-1-chloro-2-propyl phosphate). Tris(2-butoxyethyl) phosphate (TBEP), tris(2-ethylhexyl) phosphate (TEHP) and tricresyl phosphate (TCP) were acquired as pure standard from Dr. Ehrenstorfer (Augsburg, Germany). Tri-isobutyl phosphate (TiBP) at 1000  $\mu\text{g mL}^{-1}$  was acquired from Chiron (Trondheim, Norway). The surrogates used were [ $^{13}\text{C}_6$ ]hexabromobenzene (MHBB), 3,3',4,4'-tetrabromo[ $^{13}\text{C}_{12}$ ]diphenyl ether (MBDE-77) and decabromo[ $^{13}\text{C}_{12}$ ]diphenyl ether (MBDE-209), triphenyl phosphate-D15 (TPhP-D15), tributyl phosphate-D27 (TBP-D27). Internal standards were 2,3,5,6-tetrachlorobiphenyl (PCB-65) and decachlorobiphenyl (PCB-209). Acetone, hexane, methanol, dichloromethane, ethyl acetate and toluene as were acquired from Merck (Darmstadt, Germany). Cyclohexane was acquired from Scharlau (Sentmenat, Spain). Copper (particle size < 63  $\mu\text{m}$ ) was acquired from Merck (Darmstadt, Germany). Oasis HLB 200 mg solid phase extraction cartridges (SPE) were from Waters (USA). Florisil cartridges were acquired from Phenomenex (10 g, 60 cc) and from Waters (5 g, 20 cc). GC-EI-MS/MS analysis was performed in a GC Agilent 7890A equipped with a 7000A GC-MS Triple Quadrupole. The column used was a DB-5MS with 15 m (length) x 0.250 mm (I.D.) x 0.10  $\mu\text{m}$  (film) (J&W Scientific, USA). The oven program was set at 60 to 220  $^{\circ}\text{C}$  at 10  $^{\circ}\text{C}/\text{min}$  and to 315  $^{\circ}\text{C}$  at 15  $^{\circ}\text{C}/\text{min}$  (8 min). Helium (purity 99,999%) was employed as carrier gas with a constant flow of 1.5 mL  $\text{min}^{-1}$ . The injection volume was 2  $\mu\text{L}$  by splitless, with a splitless time of 1.5 min.

Samples studied were 12 surface water (particulate and soluble fractions) and sediment collected from the Besos river (Catalonia); influent and effluent waters and sludge collected from 5 WWTP around Barcelona; dust collected from 5 houses in Barcelona, outdoor air collected daily during one week in Barcelona and gull eggs (*Larus michahellis*) collected from the Ebro delta colony.

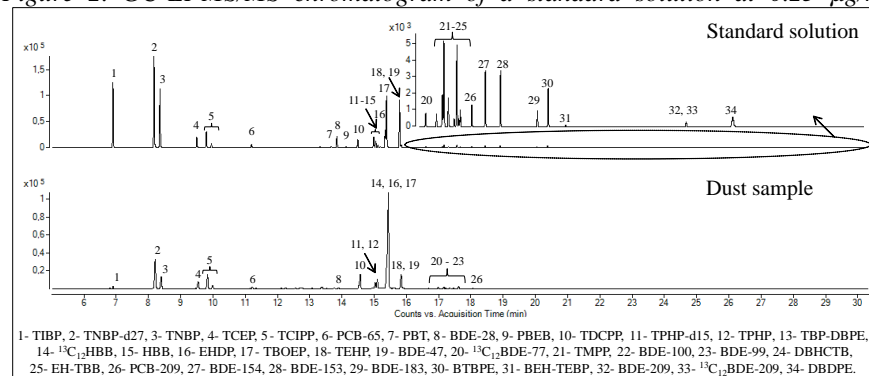
## Results and discussion

PBDEs have low vapour pressure and low water solubility, consequently it is estimated that once they are released to the environment they preferably will be associated to particles and to the organic matter of sediments. On the other hand, OPFRs present different chemical structures (substituent bound to oxygen) and physicochemical properties, which affect their fate on water environment. The chloroalkyl-phosphates are more soluble than the aryl-phosphates, while solubility and lipophilicity of alkyl-phosphates vary and thus affect the partitioning in the environmental compartments. Few studies are available concerning the partition and fate of NBFRs in the aquatic environment. Finally, based on their solubility, Kow and Koc coefficients, it can be expected that NBFRs present a partition behaviour similar to PBDEs, tending to be associated to suspended particles and sediments, whereas different chemical and biological transformations should be expected due to differences in their chemical structure.

In river waters, OPFR were the compounds detected at the highest concentration, with  $\sum$ OPFR up to 4.2  $\mu\text{g/L}$ . In sediments,  $\sum$ OPFR of 824  $\mu\text{g/kg-dw}$  were detected, being TCPP the most ubiquitous compound. Contrarily, PBDEs were only detected in sediments at concentrations up to 807  $\mu\text{g/kg-dw}$  and BDE-209 was the main congener detected. Regarding NBFR, only DBDPE was detected. This same pattern was observed in influent and effluent waters, where by far OPFR were the most ubiquitous compounds detected and for TCPP, TCEP, TDCP and TBP, their concentration in influents were the same as effluents, indicating that these compounds are not degraded during activated sludge treatment. However, both OPFR and PBDEs were accumulated in sludge at concentrations up to 2,000  $\mu\text{g/kg-dw}$  for TiBP, TCEP, TEHP and TCP and between 20 and 1,000  $\mu\text{g/kg-dw}$  for BDEs 47 and 209, being the latter the most ubiquitous. Regarding the occurrence of NBFR, only PBT, BEHTBP, BTBPE and DBDPE were detected in sludge at concentrations up to 900  $\mu\text{g/kg-dw}$ . This indicates that in river waters-sediment and in wastewater-sludge systems, the patterns of occurrence of flame retardants is very similar, being OPFRs the most ubiquitous compounds, followed by BDE 209 as main PBDE detected and only few NBFR are present in these systems. Therefore, it is likely that NBFR are not being used in the study area or still have not reached the environment.

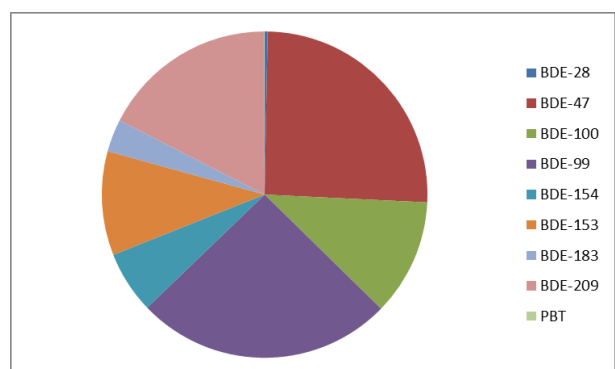
Regarding the analysis of dust and air, OPFRs were also the main compounds detected, although the range of concentrations greatly varied. Whereas  $\text{pg/m}^3$  levels were detected in air, house dust contained levels up to 5,000  $\mu\text{g/kg-dw}$ . Figure 2 indicates a chromatogram with the contribution of each compound, compared to a standard solution. In dust, penta-BDEs were detected at a mean concentration of 10  $\mu\text{g/kg-dw}$ , while BDE 209 was detected at levels between 1,000 and 10,000  $\mu\text{g/kg-dw}$ . For this type of sample, NBFR were detected at levels between 50 and 500  $\mu\text{g/kg-dw}$ , being BEHTBP, BTBPE and DBDPE the most ubiquitous compounds detected. Differences were observed in the patterns of flame retardants detected in the different house dust, with prevalence of PBDEs in older houses and the presence of NBFR in the most modern houses.

Figure 2. GC-EI-MS/MS chromatogram of a standard solution at 0.25  $\mu\text{g/mL}$  and a house dust sample.



Finally, flame retardants were determined in *Larus michahellis* gull eggs which are used as indicators of environmental pollution<sup>7</sup>. OPFR were not determined with the method used due to peak interferences. Figure 3 shows the profile of flame retardants detected, with main contribution of BDEs 47, 99 and 209, and traces of PBT, which was the only NBFR detected. Mean PBDE levels over the period of 2009-2013 were between 0.03 and 2.82 µg/kg-dw whereas PBT was detected at a mean concentration of 0.08 µg/kg-dw. Therefore, gulls have the ability to accumulate both penta and deca BDE formulations and transfer these compounds to the eggs. The incidence of flame retardants in gull eggs provide information on the pollution impact of these compounds in marine ecosystems.

Figure 3. PBDE congener specific distribution in gull eggs collected from the Ebro delta.



Overall, among the 3 different families of flame retardants available in the market and used in different applications, this study clearly demonstrates that OPFR are the most ubiquitous compounds in all abiotic samples analyzed. PBDEs follow in a 10 fold lower concentrations than OPFR, with BDE 209 being the most ubiquitous congener detected in sludge and sediment samples. Finally, the incidence of NBFR is low in both abiotic and biotic samples collected in Spain over the period 2009-2013. Considering water matrices, OPFR are the only compounds detected at high concentration, whereas

PBDEs and NBFR are seldom detected or at very low concentration, indicating that even both the dissolved and particulate fraction of water was analysed, they tend to be accumulated in sediments or sludge. Therefore, these latter compounds should be preferably analyzed in sediments and sludge. Because flame retardants are present in many household items, dust has been identified as the matrix with the highest levels of all flame retardants, and this finding has high health implications due uptake by humans. Finally, outdoor air from Barcelona only contained OPFR at very low concentration and neither PBDEs nor NBFR were detected after preconcentrating 300 m<sup>3</sup> of air.

### Acknowledgements

This study has been financed by the projects 2012/768 "Control de Contaminantes Orgánicos Persistentes según Convenio de Estocolmo y mercurio en huevos de láridos: bases de datos, series históricas y gestión ambiental" from the Organismo Autónomo de Parques Nacionales, Ministerio de Agricultura, Alimentación y Medio Ambiente (Spain) and by the Ministry of Education and Innovation of Spain, project CTM2008-03263/TECNO. Joyce Cristale acknowledges a FPI grant from the same Ministry (BES-2009-016460).

### References

1. SpecialChem - Flame Retardants Center. In: <<http://www.specialchem4polymers.com/tc/flame-retardants/index.aspx>>. Accessed 06/05/2014.
2. EHC - Environmental Health Criteria 192. Flame Retardants: A General Introduction. In: <<http://www.inchem.org/documents/ehc/ehc/ehc192.htm>>. Accessed 05/05/2014
3. Vonderheide AP, Mueller KE, Meija J, Welsh GL, (2008). *Sci Total Environ* 400:425-436
4. Covaci A, Harrad S, Abdallah MAE, Ali N, Law RJ, Herzke D, de Wit CA, (2011); *Environ Internat* 37:532-556.
5. Van der Veen I, de Boer J. (2012). *Chemosphere* 88:1119-1153.
6. Cristale J, Lacorte S. (2013); *J. Chromatogr. A* 1305, 267-275.
7. Morales L, Martrat MG, Olmos J, Parera J, Vicente J, Bertolero A, Ábalos M, Lacorte S, Santos J, Abad E. (2012); *Chemosphere* 88(11): 1306-1316.