



*Research article*

## **PBDEs versus NBFR in wastewater treatment plants: occurrence and partitioning in water and sludge**

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**Abstract:** This study evaluates the occurrence of flame retardants (FR) in five wastewater treatment plants (WWTPs) located close to Barcelona (NE Spain), an area with high urban and industrial pressures. Compounds studied include eight polybromodiphenyl ethers (PBDEs) and eight New Brominated Flame Retardants (NBFRs), for which little information regarding their presence, partitioning and fate within the WWTPs is available. In unfiltered influent samples, PBDEs were not detected and bis(2-ethyl-1-hexyl)tetrabromophthalate was the only NBFR detected, and all WWTPs were efficient in eliminating this compound as no residues were found in the effluents. However, primary sludge contained from 279 to 2299 ng/g dry weight of  $\Sigma$ FR and the concentration increased in secondary (biological) sludge. NBFRs accounted for the main FR detected in sludge, representing a 63–97% of the total load, and among PBDEs, BDE-209 was the most ubiquitous congener. Considering the amount of sludge generated in each WWTP, it was estimated that 0.34–17.2 kg of FR are released annually through the sludge, which can have negative environmental and health implications if sludge is used as biosolid in agriculture. Overall, this study provides a sampling design and analytical protocol to be used to determine the evolution of FR in WWTPs and compares the levels detected, considering that PBDEs are being phased out to be substituted by other compounds which also have high accumulative and recalcitrant properties.

**Keywords:** polybrominated diphenyl ethers; new brominated flame retardants; wastewater; sludge; WWTP

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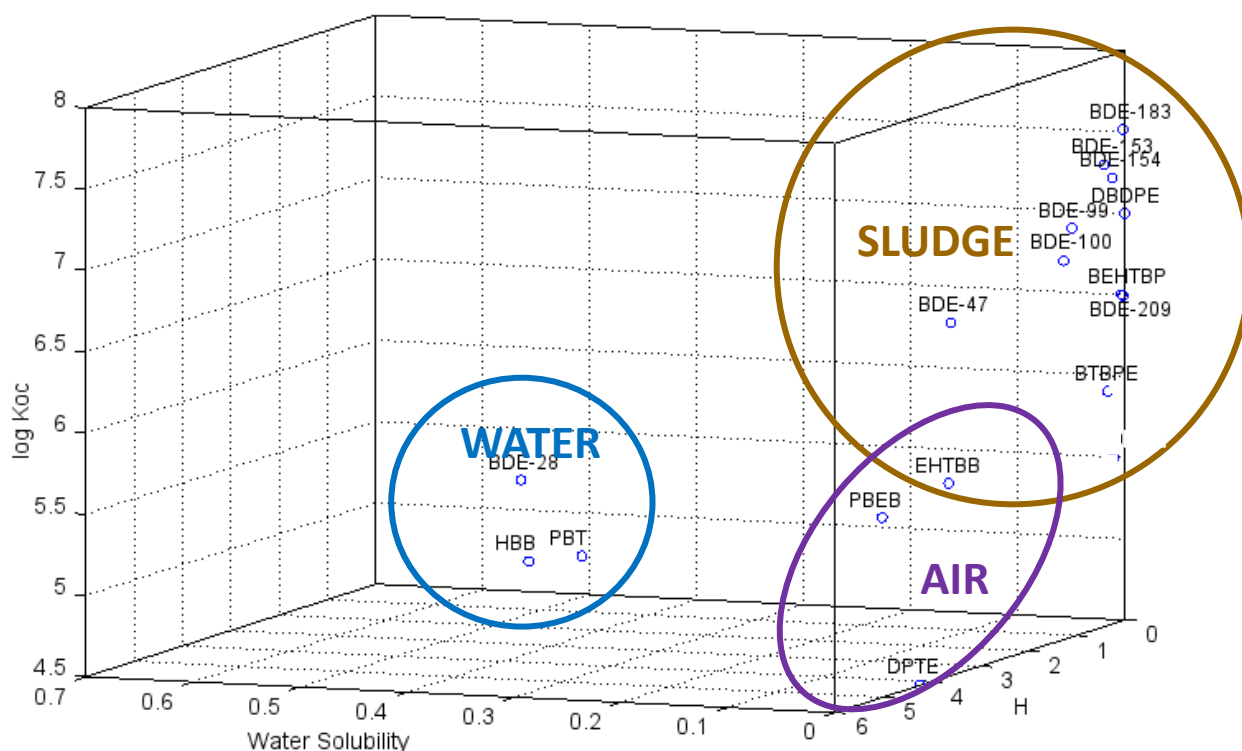
## 1. Introduction

Population growth and the expansion of industrial activities has led to the generation of large amounts of wastewaters which are commonly treated in Wastewater Treatment Plants (WWTPs) prior to discharge to avoid contamination of receiving waters. WWTPs remove approximately 85% of the organic matter in the wastewater, disinfect waters from bacteria and viruses, and then treated water is discharged into the nearest waterway or is being reused [1]. Within a conventional activated sludge WWTP, primary sedimentation and biological treatment are combined sequentially to remove the initial wastewater organic matter. Whilst this treatment is efficient to eliminate many organic contaminants from water, it produces the accumulation of apolar compounds in the sludge which is in many cases used as organic fertilizer. However, some recalcitrant pollutants not eliminated during the treatment are discharged by the effluents and reach receiving waters [2]. Thus, WWTPs effluents represent an important punctual source of contaminants. Innumerable contaminants reach river water through WWTP discharges, including synthetic organic compounds used for diverse applications, such as flame retardants, pharmaceuticals and personal care products, detergents, plasticizers, pesticides, etc. [2,3,4].

Among others, flame retardants are of concern given their toxicity, persistence, accumulative properties and long range transport [5,6]. They have been detected in river waters and sediments [7,8] and in fish [9,10]. Polybrominated diphenyl ethers (PBDEs) have been widely used in a variety of plastics and foams, but after penta-, octa- and decaBDE bans in Europe, US and China, manufactures have phased out the production of these formulations [11] and are being substituted by alternative compounds, the so called New Brominated Flame Retardants (NBFRs). PBDEs and NBFRs co-occur due to the historic but still existing use of PBDEs and the placement into the market of NBFRs. NBFRs refer to brominated FRs other than PBDEs, hexabromocyclododecane (HBCD) or tetrabromobisphenol A (TBBPA) that are new in the market or newly detected in the environment. NBFRs are used in thermoplastic, elastomeric and thermoset polymer systems, unsaturated polyesters, adhesives, coatings, and textiles, in wire and cable insulation, film and sheeting, in polyurethane foam or styrene polymers [12].

Both PBDEs and NBFRs have low water solubilities and a high organic carbon partitioning factors ( $k_{oc}$ ), which imply that they will rapidly sorb to organic and particulate matter. The tendency of a contaminant to accumulate in sludge or undergo treatment depends on their physicochemical properties (e.g. solubility, lipophilicity, vapor pressure, chemical stability) and also on the characteristics of the medium (e.g. pH, temperature, dissolved organic matter, organic carbon content) [14]. Figure 1 illustrates the distribution pattern of studied PBDEs and NBFRs in a WWTP, according to their physicochemical properties. This information provides a theoretical basis of the compounds which will be preferably detected in each matrix (water and sludge) or will be lost due to volatilization.

Because WWTP are a point source of pollutants to the river ecosystems or to land, the aim of this study was to evaluate the presence and partitioning of both PBDEs and NBFR within five WWTPs which receive both urban and industrial effluents from a densely populated area (Barcelona municipality). Sixteen compounds were determined in influent and effluent waters and in primary and secondary (biological) sludge.



**Figure 1. Distribution of FR in a WWTP according to their physicochemical properties, namely, water solubility (S, mg/L at 25 °C), Henry's constant (H, Pa·m<sup>3</sup>/mol at 25 °C) and log K<sub>oc</sub> (Data obtained from [15,16,17]). For some compounds, the parameters were calculated with SciFinder, using the Advanced Chemistry Development Software V11.02 (© 1994–2013 ACD/Labs).**

Acronyms:

PBDEs (BDEs 28, 47, 99, 100, 153, 154, 183 and 209),

BTBPE=1,2-bis(2,4,6-tribromophenoxy)ethane, PBEB= pentabromoethyl benzene,

DBDPE=decabromodiphenyl ethane, BEHTBP=bis(2-ethyl-1-hexyl)tetrabromophthalate,

PBT=pentabromotoluene, DPTE=2,3-dibromopropyl 2,4,6-tribromophenyl ether,

EHTBB=2-ethylhexyl-2,3,4,5-tetrabromobenzoate, HBB=hexabromobenzene.

## 2. Experimental section

### 2.1. Chemicals and reagents

A solution mixture of marker PBDEs (BDEs 28, 47, 99, 100, 153, 154, 183 and 209) in n-nonane at 1 µg/mL was acquired from Cambridge Isotope Laboratories (Andover, USA). Individual solutions of 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE) at 50 µg/mL in 5% toluene in nonane, decabromodiphenyl ethane (DBDPE) at 25 µg/mL in toluene, bis(2-ethyl-1-hexyl)tetrabromophthalate (BEHTBP), pentabromotoluene (PBT), 2,3-dibromopropyl

2,4,6-tribromophenyl ether (DPTE) and 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (EHTBB) (at 50 µg/mL in toluene) were acquired from Wellington Laboratories (Guelph, Canada). Pure standards of hexabromobenzene (HBB), pentabromoethyl benzene (PBEB) were acquired from Sigma–Aldrich (Germany). The surrogates [<sup>13</sup>C<sub>6</sub>]hexabromobenzene (MHBB) at 50 µg/mL in toluene, 3,3',4,4'-tetrabromo[<sup>13</sup>C<sub>12</sub>]diphenyl ether (MBDE-77) at 50 µg/mL in nonane and decabromo[<sup>13</sup>C<sub>12</sub>]diphenyl ether (MBDE-209) at 25 µg/mL in toluene, were acquired from Wellington Laboratories (Guelph, Canada). The internal standards 2, 3, 5, 6-tetrachlorobiphenyl (PCB-65) and decachlorobiphenyl (PCB-209), both at 10 µg/mL in iso-octane, were acquired from Dr. Ehrenstorfer (Augsburg, Germany). Acetone, hexane, methanol, dichloromethane, ethyl acetate and toluene were acquired from Merck (Darmstadt, Germany). Cyclohexane was acquired from Scharlau (Sentmenat, Spain). Florisil cartridges were acquired from Phenomenex (10 g, 60 cc). OASIS HLB 200 mg cartridges were acquired from WATERS (USA).

## 2.2. Sampling

Water and sludge samples were collected at five WWTPs close to Barcelona city, at different stages of the treatment (primary and biological treatment). The WWTP studied had a capacity from 186,666 to 2,843,750 inhabitants' equivalents, a water influent from 33,000 to 525,000 m<sup>3</sup>/d and an annual sludge production from 8428 to 14,442 tons. For water, 24 h composite samples were collected at the influent and effluent of each WWTP. For sludge, 1 kg was collected at the primary tank (primary sludge) and at the biological activated reactor (secondary sludge). Water and sludge were refrigerated for transportation to the main laboratory. Water samples were stored at 5 °C and extracted as soon as possible, within a period no longer than five days to avoid degradation of target compounds. Sludge was freeze-dried, homogenized and sieved (120 µm).

## 2.3. Extraction and analysis

For water samples, 100 mL of unfiltered influent water and 250 mL of unfiltered effluent water were spiked with labelled surrogate standards (100 ng of MBDE-209; 25 ng of MHBB and MBDE-77) and were extracted using OASIS HLB 200 mg cartridges (WATERS, USA). The cartridges were conditioned with 15 mL of hexane followed by 15 mL of dichloromethane, 15 mL of methanol and 15 mL of Milli-Q water. After the preconcentration step, the cartridges were dried using a vacuum manifold, eluted with 15 mL of dichloromethane/hexane (1:1 v/v) followed by 15 mL of dichloromethane/acetone (1:1 v/v), concentrated under N<sub>2</sub> flow to almost dryness and reconstituted in 250 µL of toluene with the internal standards PCB-65 and PCB-209 at 0.05 µg/mL.

For sludge samples, 0.1 g of sludge was placed in a glass centrifuge tube (30 mL), spiked with 100 ng of MHBB and MBDE-77 and 400 ng of MBDE-209 and kept in contact overnight. After that, the samples were extracted with 20 mL of ethyl acetate/cyclohexane (5:2 v/v) by vortex (1 min) followed by ultrasonic extraction (10 min). The extract was centrifuged (10 min at 3000 rpm) and transferred to 40 mL amber vials. This procedure was repeated twice with 10 mL of the solvent mixture. Then, the total extract was concentrated to 1 mL under a N<sub>2</sub> flow in a Turbovap. The clean-up was performed using 10 g Florisil cartridges. The cartridges were conditioned and eluted with 60 mL ethyl acetate/cyclohexane (5:2 v/v). Finally, the extract was concentrated under N<sub>2</sub> flow to almost dryness and reconstituted in 1 mL of toluene containing PCB-65 and PCB-209 at 0.05 µg/mL.

GC-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)  $\times$  0.250 mm (I.D.)  $\times$  0.10  $\mu$ m (film) (J&W Scientific, USA). The oven program was set at 60 to 220  $^{\circ}$ C at 10  $^{\circ}$ C/min and to 315  $^{\circ}$ C at 15  $^{\circ}$ C/min (8 min). Helium (purity 99.999%) was employed as carrier gas with a constant flow of 1.5 mL/min. The injection volume was 2  $\mu$ L, with a splitless time of 1.5 min. The injector, quadrupole, transfer line and ion source were set at 300, 150, 280 and 300  $^{\circ}$ C respectively. Electron ionization (EI) mode was set at 70 eV. The MS/MS acquisition conditions used for PBDEs and NBFs were the ones reported elsewhere [18].

#### 2.4. *Quality control and quality analysis*

The performance of the analytical method for influent, effluent and sludge samples consisted in evaluating the extraction efficiency in samples with high loads of organic matter. Recoveries ( $n = 3$ ) were calculated from influent samples (unfiltered) spiked at 100 ng/L for NBFs and PBDEs (except BDE-209 and DBDPE that were at 1000 ng/L) and from effluent (unfiltered) spiked at 40 ng/L for NBFs and PBDEs (except BDE-209 and DBDPE, that were at 400 ng/L). To obtain good solubilization and to allow the native and surrogate standards reach the partition equilibrium in wastewater, waters were not filtered and the spiking solution was in contact with the water for 1 h previous to extraction. Sludge was spiked with 100 ng of NBFs and PBDEs (except BDE-209 and DBDPE that were 1000 ng). The extraction method for sludge was already reported in a previous study [13] but for clarity, herein we provide the recovery values extracted from that paper. Method detection limits (MDL) were calculated at a signal to noise ratio of 3. Calibration was performed over a concentration range of 0.001 to 1 ng/ $\mu$ L with five concentration levels. Internal standard quantification was performed using the surrogate standards which controlled any losses during sample extraction, clean up and analysis.

### 3. Results and Discussion

#### 3.1. *Method performance*

Table 1 shows the method performance parameters. Good extraction efficiency was obtained for both influent and effluent waters, and MDL were between 4.7 and 550 ng/L in influents and 1.4 and 187 ng/L in effluents, with better repeatability for the latter. In both water matrices, BDE-209 and DBDPE had the highest MDL attributed to the low sensitivity of these compounds under GC-MS/MS. This could be improved by using negative chemical ionization, although the identification criteria could be affected especially for the low brominated compounds [18]. For sludge samples, the extraction efficiency ranged from  $92 \pm 10\%$  to  $126 \pm 13\%$ , and MDL were from 3.7 to 353 ng/g dw, being the highest values for BDE-209 and DBDPE [13]. Altogether, these two families of FR can be extracted and analyzed together by GC-MS/MS, which provides powerful analyte confirmation capabilities (retention time and two transitions), sensitivity at the low ng/L and ng/g level (except for BDE-209 and DBDPE) and high selectivity needed to resolve FR in very complex matrices.

**Table 1. Performance (% Recovery and standard deviation,  $n = 3$ ) and Method Detection Limits (MDL—in ng/L for wastewater and in ng/g dw for sludge) of the analytical method for influent and effluent wastewaters and sludge.**

Compound	Influent wastewater		Effluent wastewater		Sludge <sup>a</sup>	
	% R (SD)	MDL	% R (SD)	MDL	% R (SD)	MDL
BDE-28	145 (8)	4.7	127 (3)	4.3	111 (13)	4.8
BDE-47	113 (6)	6.4	98 (8)	1.4	98 (17)	6.2
BDE-100	88 (3)	18	93 (9)	3.9	100 (1)	15
BDE-99	87 (4)	20	95 (8)	3.7	105 (1)	13
BDE-154	97 (13)	14	107 (12)	1.5	100 (1)	7.1
BDE-153	95 (2)	5.9	109 (10)	2.2	102 (0.3)	17
BDE-183	84 (2)	41	92 (14)	6	105 (2)	25
BDE-209	124 (21)	550	113 (30)	187	98 (1)	300
PBT	100 (17)	12	85 (3)	3.4	108 (7)	14
PBEB	76 (10)	18	80 (5)	2	118 (6)	3.7
HBB	96 (29)	48	89 (6)	13	92 (10)	53
DPTE	136 (24)	7.5	129 (21)	2	120 (12)	9.1
EHTBB	78 (6)	21	99 (3)	3	103 (12)	11
BEHTBP	79 (2)	38	114 (20)	17	99 (4)	43
BTBPE	123 (12)	23	139 (10)	5.7	103 (6)	6.8
DBDPE	128 (15)	230	124 (4)	171	126 (13)	353

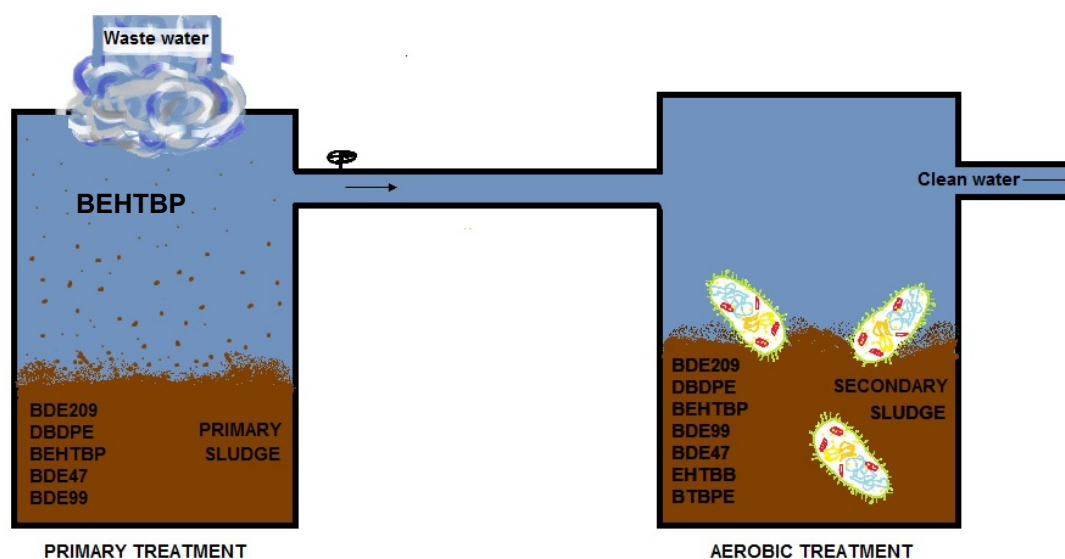
<sup>a</sup> Published values from [13].

### 3.2. Occurrence and fate of FR in water

FRs profiles and concentrations in influent waters are related to their use in consumers' goods (automobiles, electric and electronics, PU foam, plastics, textiles, etc.) and disposal practices. The impact of FR in WWTPs depends on the type of influent waters received (urban, industrial, runoff...) and on the characteristics of the WWTP for eliminating the contaminant loads. The study area represents a worst case scenario due to the high population density of the area and high industrial impact.

In this study, water was not filtered to determine the total concentration of FR as given their  $K_{oc}$  values, it would be expected to detect them in influent waters sorbed to particulate matter. However, the presence of FR in the studied WWTPs was very low. Figure 2 represents a general scheme of the occurrence and partitioning of FR in the studied WWTPs. Contrarily to what was expected, most soluble compounds, such as BDE-28, PBT and HBB (Figure 1), were never detected in water. Compounds with high  $K_{oc}$  (upper right in Figure 1) were neither detected as they rapidly sorbed to the particulate matter and sludge and preconcentrated along the wastewater pathway in the activated sludge process. The exception was BEHTBP, the only compound detected in influent waters at concentrations between  $52 \pm 3$  ng/L and  $130 \pm 10$  ng/L ( $n = 2$ ) in four (out of five) WWTP analyzed. This compound was not identified in any effluent and thus, all WWTP were efficient in its elimination from the aqueous phase. BEHTBP has not been previously reported in influent wastewaters. Actually, the presence of NFRs in wastewaters has not been fully assessed. Kim et al. [19] report similar low

values for other NBFs, with median influent and effluent levels ranging from 0.014 to 3.7 and from 0.001 to 0.180 ng/L, respectively, for DBDPE, BTBPE, PBEB and HBB, with the former being at the highest concentration.



**Figure 2. General scheme representing the occurrence and the water-sludge partitioning of FR (listed by decreasing concentration levels) in the primary and secondary (aerobic) treatment of an activated sludge WWTP.**

Surprisingly, PBDEs were not detected in wastewaters. The relatively high MDL for BDE-209 and DBDPE precluded their trace detection in wastewaters and more sensitive methods would be needed, such as GC with negative chemical ionization. Low brominated PBDEs were neither detected even though MDL were at the low ng/L level. Similar to the present study, PBDEs were neither detected in wastewaters from a municipal WWTP in Catalonia [2]. In other studies, however, PBDEs were detected in influent and effluent wastewaters, albeit at low concentrations. In Shanghai, China,  $\Sigma$ PBDEs in the influent wastewater ranged from 5.31 to 27.9 ng/L and BDE-209 was the most abundant congener, with contributions to the total PBDE levels ranging from 52.9 to 82.6% [20]. In Hong Kong, the concentrations of  $\Sigma$ 8PBDEs in the influents of 4 WWTPs ranged from 1 to 254 ng/L but decreased to 12–27 ng/L in effluents, with removal efficiency ranging from 20 to 53% and the predominant congeners in influent were BDE-47 and 209 but shifted to BDE-47 and 99 in effluents [21]. PBDE levels in influent wastewaters from 20 Canadian WWTP ranged from 21 to 1000 ng/L and final effluent levels ranged between 3 and 270 ng/L, with BDE-209 having the highest contribution [22]. PBDEs were detected in four WWTPs located along the Mexican-USA border at 30.2–342 ng/L in influents and from non-detected to 209 ng/L in effluents, with percentage removals of 84–100% [23].

The phase out of PBDEs might explain the non-detection of PBDEs in WWTP influents, whereas NBFs might not have yet reached the wastewaters as their uses and disposal are quite recent. Besides, the low incidence of FR in influent wastewaters can also be attributed to degradation through the wastewater grid before their entrance to the WWTPs, as has been observed for other contaminants [2]. Overall, these results suggest that despite the studied WWTPs receive urban and

industrial wastes, FR do not represent a serious problem with regards to influent water quality. As no residues were detected in the effluents, WWTPs are not a source of FR to receiving waters in the study area. In addition, combined sewer overflow during rain events or other upsets that might result in periodic releases to surface waters are not expected to happen as the WWTPs studied are over dimensioned and thus, in a rain event, they have the capability to absorb high or excess amounts of water.

### 3.3. Occurrence and fate of FR in sludge

Table 2 indicates the concentration of FRs detected in primary and secondary sludge. Compounds were detected at levels from 8 to 1135 ng/g dw in primary sludge and from 10 to 982 ng/g dw in secondary sludge. Main compounds detected were BDE-209 > DBDPE > BEHTBP, whereas BDE-47 and 99 were detected at one order of magnitude lower concentrations. EHTBB was only detected in secondary sludge of WWTP 3 and 5, and BTBPE in secondary sludge of WWTP 1. All these compounds have a high  $K_{ow}$  and low solubility so they are rapidly sorbed to sludge (Figure 1).

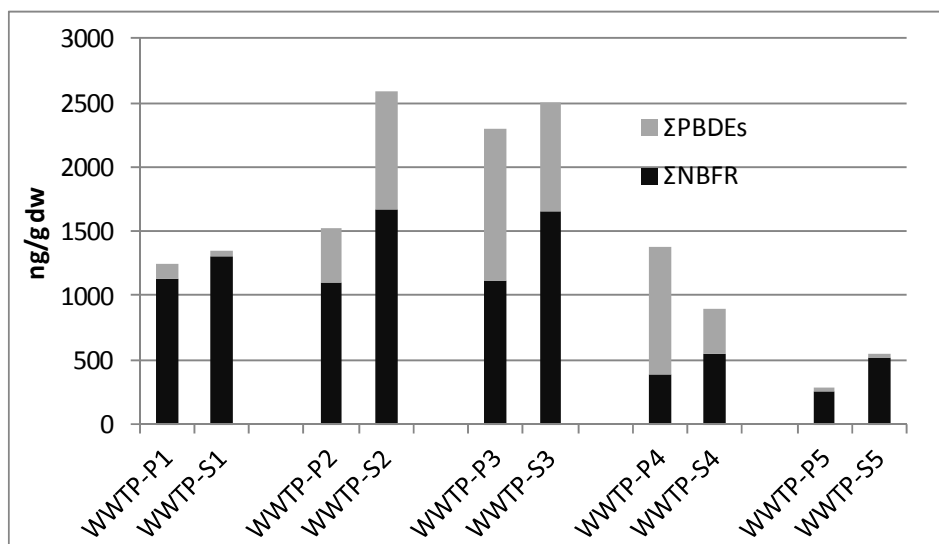
**Table 2. Concentration of FR (ng/g dw) in primary and secondary sludge from five WWTP from Catalonia.**

Compound	Primary sludge					Secondary sludge					
	WWTP	1	2	3	4	5	1	2	3	4	5
BDE-47		90	13	11	11	8	11	18	15	10	11
BDE-99		19	22	29	18	19	30	21	33	22	19
BDE-209		n.d.	396	1135	952	n.d.	n.d.	879	806	325	n.d.
EHTBB		n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	25	n.d.	11
BEHTBP		456	737	394	392	252	487	982	957	547	504
BTBPE		n.d.	n.d.	n.d.	n.d.	n.d.	18	n.d.	n.d.	n.d.	n.d.
DBDPE		681	360	729	n.d.	n.d.	808	689	672	n.d.	n.d.

n.d. = non-detected

NBFR accounted for the 66–97% of  $\Sigma$ FRs, except for primary sludge of WWTP 3 and 4. Figure 3 compares the levels of PBDEs and NBFRs in primary and secondary sludge of each WWTP. Slightly higher values were observed in secondary sludge compared to primary sludge, except for WWTP 4, and this increase was especially significant for NBFRs. Primary sludge contains 30% of the organic matter dissolved in the influent wastewater whereas the secondary sludge contains 60% of the dissolved organic matter. Therefore, the enrichment of FR in the secondary sludge is a result of the concentration of the organic matter during the biological treatment. Taken together, primary and secondary treatments accumulate around 90% of the influent organic matter.





**Figure 3. Concentration of  $\Sigma$ PBDEs and  $\Sigma$ NBFRs in primary (WWTP-P) and secondary sludge (WWTP-S) of each WWTP (1 to 5).**

From the open bibliography, it is well evidenced that PBDEs are always detected in sludge at concentration and distribution patterns that vary according to site or treatment, although all studies coincide that BDE-209 is the predominant congener attributed to its wider use, high accumulation potential and low degradability. Our results follow this pattern and are in the range of previous ones reported in Spain. In Murcia (SE Spain), PBDEs ranged from 57.5 and 2606 ng/g dw in 31 sludge samples, with BDE-209 as the major contributor of  $\Sigma$ PBDEs [24]. In sludge samples from Madrid (central Spain), PBDEs were detected in all of the samples and  $\Sigma$ BDE 28, 47, 99, 153, 154 and 183 ranged between 3.9 and 23.0 ng/g dw while BDE-209 constituted 38.7 to 97.3% of the total concentration and ranged from 8.1 to 717.2 ng/g dw [25].

In other parts of the world, PBDE levels and pattern distribution may vary, but globally it is re-affirmed that BDE-209 is the main congener in sludge, that annually several kg of PBDEs are disposed to land as biosolids but still low risk is observed. Some studies are exemplified to provide insight of the global situation. In Shanghai, China,  $\Sigma$ PBDEs in dewatered sludge ranged from 31.0 to 99.5 ng/g, which produced an annual release of 6.3 kg and BDE-209 contributed to 82.7 to 84.0% of  $\Sigma$ PBDEs levels [20]. Similar pattern was reported in 4 Hong Kong WWTPs, where PBDEs ranged from 9 to 307 ng/g dw in dewatered sludge with BDE-209 as the predominant congener, and every day, 0.17–17 g PBDEs (0.062–0.62 kg annually) were disposed to landfill sites in sludge form [21]. Higher levels were detected in sludge from 3 WWTP from Kuwait, where  $\Sigma$ PBDEs ranged from 5.7 to 1599 ng/g and BDE-209 contributed between 70% and 99% of the total [26]. Similar patterns were detected in the Czech Republic, where BDE-209 was detected as the predominant congener at concentrations between 685 ng/g and 1403 ng/g dw and other lower brominated congeners were detected between 605 and 205 ng/g dw [27]. Sludge from 11 municipal WWTP in Germany collected in 2002–03 contained  $\Sigma$ BDE 28, 47, 99, 153, 154 and 183 from 12.5 to 288 ng/g dw and BDE-209 was the main congener at concentrations from 97.1 to 2217 ng/g dw. Interestingly, in that study no differences in PBDEs profile were observed along the different stages of the wastewater treatment process (primary sludge, secondary excess sludge and dewatered digested sludge), indicating no

degradation or debromination of BDE-209 [28]. Somewhat higher  $\Sigma$ PBDEs levels were observed in eight Italian sewage sludge collected in 2009/10, with concentrations ranging from 158.3 to 9427 ng/g dw, while BDE-209 ranged from 130.6 to 9411 ng/g dw, accounting for 77% to 99.8% of  $\Sigma$ PBDE, and a low risk to soil was predicted [29]. Lee et al. [30] also indicated that the potential risk of soil exposed to industrial, domestic wastewater, and livestock sludge containing 4.01 to 10,400 ng/g dw of  $\Sigma$ 19PBDE (dominated by BDE-209) was relatively low. Similar high levels were detected in a USA sludge inventory of 77 FRs, where  $\Sigma$ PBDE in biosolids composites was  $9400 \pm 960$  ng/g dw, of which BDE-209 constituted 57% followed by nona- and pentaBDE at 18 and 13%, respectively, and represented an annual mean land disposal rate of  $\Sigma$ PBDEs and non-BDE BFRs of 24,000–36,000 and 6400–9700 kg/y, respectively [31]. To evaluate the impact of sludge disposal, Gaylor et al. [32] compared the PBDEs burdens within a soil ecosystem receiving long-term sludge amendments and a reference soil receiving only manure inputs. No PBDEs were detected in reference site samples, but sludge-amended soils contained  $17,600 \pm 2330$  ng/g  $\Sigma$ 3–7PBDEs (total organic carbon (TOC) basis), and these compounds were also detected in soil invertebrates although not in vegetation.

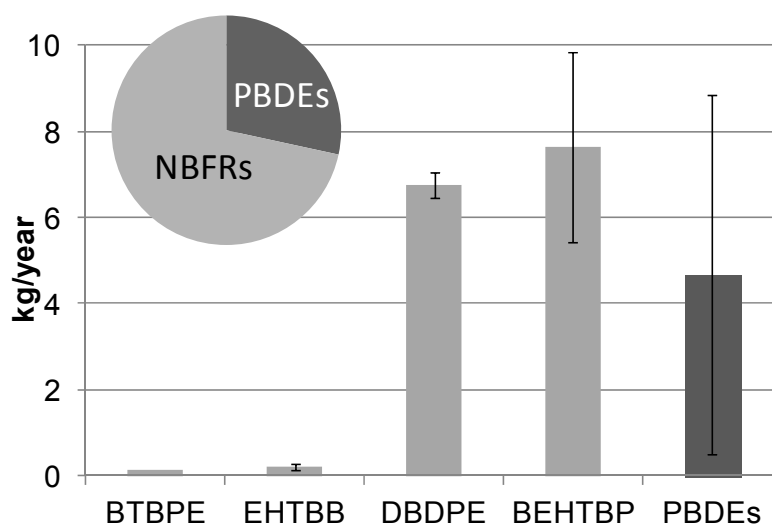
Little information is available regarding the presence and impact of NBFR in sludge. In this study, the sampling was performed in 2013 and we observe an increase of NBFRs with regards to PBDEs. Comparing these results to previous studies from the area, we observe a decrease in the concentration of BDE-209 and a subsequent increase of EHTBB, BEHTBP, BTBPE, DBDPE. Previous studies performed in 2009 report BDE-209 as the main congener in sludge from 17 Catalan WWTPs at levels ranging from nd to 2303 ng/g dw while among NBFRs, DBDPE was detected at nd–257 ng/g dw and in four samples HBB and PBEB were detected at nd–5.71 and nd–2.33 ng/g, respectively [33]. In another study, PBDEs were detected in all four sludge samples analyzed from North Carolina and California (USA) and  $\Sigma$ PBDE concentrations ranged from 1750 to 6358 ng/g dw whereas the PBDE replacement chemicals EHTBB and BEHTBP were detected at concentrations ranging from 120 to 3749 ng/g dw and from 206 to 1631 ng/g dw, respectively [34]. In a Chinese nationwide survey of new halogenated FR in sludge, DBDPE, hexabromocyclododecane and BTBPE were detected in all samples, and the concentrations were in the range of 0.82–215, 0.09–65.8, and 0.10–2.26 ng/g dw, respectively [35]. Therefore, NBFRs are gaining importance due to the growing use and disposal of products containing these compounds.

We found an increase of FRs in secondary sludge compared to primary sludge due to cumulative concentration of organic matter during treatment. Typically, the hydraulic retention time in the biological treatment is of 2–3 h, depending on the WWTP. During the passage of water, FR were basically sorbed in sludge which produced a net accumulation of FR in secondary sludge.

Elimination of PBDEs from sludge needs a specific treatment. Stiborova et al. [27] reported that both lower brominated PBDEs and BDE-209 could be successfully removed from municipally contaminated sludge under aerobic conditions and that BDE-209 followed a first-order kinetic degradation with constants between  $2.77 \times 10^{-3} \text{ d}^{-1}$  and  $3.79 \times 10^{-3} \text{ d}^{-1}$  corresponding to half-lives between 180 and 246 d. Gerecke et al. [36] indicated that BDE-209 exhibited a half-life of 700 d under anaerobic conditions in digested sewage sludge and indicated that full-scale degradation occurred in such system. Also in anaerobic batch cultures, the concentrations of BDE-47, 99, 100 and 209 decreased by 22–40% from their initial concentration whereas BDE-138, 153, 154 and 183 remained stable during a 238 d incubation period. However, in a pilot-scale anaerobic sludge digester, 21–64% loss of BDE 47, 99, 100, 138, 153, 154, 183 and 209 was observed after 30 d incubation [37].

Therefore, the elimination of FR from sludge would require either aerobic or anaerobic treatment for several months, but in real life, sludge is anaerobically digested for one month before disposal, which would mean that FR would not be eliminated.

In the studied plants, sludge is dehydrated prior to disposal. Considering the concentration in secondary sludge, the mean amount of PBDEs in sludge ranged from 0.34 to 8.9 kg/y and from 7.2 to 17.2 kg/y for NBFRs. NBFRs represent 72% of the total FR and the mean annual amount of BTBPE, EHTBB, DBDPE and BEHTBP accumulated in sludge are indicated in Figure 4.



**Figure 4. FR accumulated annually in secondary sludge (kg/year dry weight basis,  $n = 5$ ). PBDEs accounted for 28% and NBFR for 72% of the total FR.**

The amount of FR in sludge from five WWTPs in Catalonia are somewhat lower than those reported in a previous study from Catalonia that indicated 57.8 kg/y, 6.76 kg/y, 13.5 kg/y, 1.56 kg/y, 0.18 kg/y and 0.02 kg/y for PBDEs, DBDPE, TBBPA, HBCDs, HBB and PBEB respectively [33]. In Spain, sludge is dehydrated and then disposed as fertilizer, incinerated or used as construction materials. In Catalonia, 75–100% of the sludge is used in agriculture or as compost, indicating that high amounts of FR are discharged to agricultural soils, according to conventional agronomical practices [38]. The implications this might have on the quality of agricultural products, on human health and indirectly on wildlife are still to be elucidated.

#### 4. Conclusions

In developed countries, effluents of WWTPs are considered one of the main sources of contaminants to surface waters and sludge is an input of contaminants to agricultural land and other outdoor environments. PBDEs and NBFRs were determined in influent, effluent and sludge of five WWTPs situated close to Barcelona, an area receiving urban and industrial pressures. BEHTBP was the only compound detected in influent waters, and all WWTP efficiently removed this compound. No traces of PBDEs nor NBFR were detected in effluents. However, BDE-47, 99 and 209 and BEHTBP, and DBDPE were detected in primary and secondary sludge, being the concentration

slightly higher in the latter sludge due to the higher capacity to concentrate the water organic matter. Secondary sludge also contained EHTBB and BTBPE. NBFRs accounted for 72% of the total FRs detected, suggesting that PBDEs bans have evolved in a higher usage of alternative FRs. Considering that total FRs were detected from 544 to 2589 ng/g dw, the amount discharged through the sludge is of 0.34 to 17.2 kg/year. In Spain, most of the sludge produced is used in agriculture, and this represents that high amounts of FRs are applied to agricultural fields, which can have serious implications for both environmental and human health.

## Acknowledgments

This study was financed 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).

## Conflict of interest

All authors declare no conflicts of interest in this paper.

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