POLYBROMINATED DIPHENYL ETHERS (PBDEs) EMISSION FROM SPANISH URBAN SEWAGE TREATMENT PLANTS.

Alonso E[1], de la Torre A[1], Martínez MA[1],Tarazona JV [2]

[1]Persistent Organic Pollutant Group, Environmental Department. CIEMAT, Avd Complutense 22 Madrid, Spain; [2]Laboratory for ecotoxicology, Department of the Environment. INIA, Ctra de la Coruña, km 7.5, Madrid, Spain.

Abstract

Sewage Treatment Plants (STP) have been described as important source of Polybrominated Diphenyl Ethers (PBDEs) into the environment. Currently, there is a lack of information about the real emission of PBDEs from this source since the products containing PBDEs can act as reservoirs. In this study, a characterization of the specific-congener PBDEs emission to Spanish STPs was performed. For that purpose, a conceptual model was developed for transferring PBDE concentration in sewage sludge into PBDE emissions (mg congener PBDE / inhabitant / year). Eight congeners (IUPAC number BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 206, BDE 207 and BDE 209) were studied and their emissions were characterized. Three emission ranges covering one order of magnitude each one could be established: a) emissions range between 0,01 to 0,1 mg PBDE/eq/year for congeners nº100, 153 and 154; b) range between 0,1 to 1 mg PBDE/eq/year for congeners nº 47, 99, 206 and 207 and c) the highest emission was found for BDE-209 (mean of 6,16 mg BDE-209/eq/year). The model allowed to establish the potential release of PBDE specific-congener from a generic urban scenario due mainly to the usage of articles containing PBDEs. This information could be very useful in the risk management of these compounds.

Introduction

The polybrominated diphenyl ethers (PBDEs) are a group of relatively emergent pollutants presently under review. Due to their potentially hazard characteristics[1], international efforts have been carried out to limit their use and release into the environment. Thus, in the European Union, two groups of the main commercial mixtures were banned on summer 2004, concretely those referred as Penta and Octa-mixtures. Nevertheless, the production and use of DecaBDE still continue.

PBDEs are currently present in many domestic European articles such as electric and electronic equipment, automotive equipment, textiles, furniture and packaging[2]. As PBDEs is a group of “additive” Brominated Flame Retardants (BFR) simply blended with the products, their migration from article surface during their life cycle is relatively easy[3]. That converts the products (such as in-service products, imported products, and new European products manufactured with Deca-BDE formulation) into reservoirs of PBDE.

Hence, Urban Solid Waste (USW) deposited in landfills and Sewage Treatment Plants (STP) through treated effluent discharge and land application of sewage sludge[4]., may be considered as important source of PBDEs into the environment. The urban wastewater reach to STPs comprise PBDEs from different pathways, including from human trophic chain. In the present work, an estimation of the total emission of PBDEs reaching Sewage Treatment Plants from urban area was performed. For such purpose, the PBDE specific-congener concentration in sewage sludge was measured in 25 Spanish urban STPs. These concentrations were transferred into PBDE emissions by using the model developed in this study. Emissions expressed as mg of specific-congener PBDE/ inhabitant / year of eight different congeners (BDE 47, BDE 99, BDE 100, BDE 153, BDE 154, BDE 206, BDE 207 and BDE 209) were characterized. Up to our knowledge, these are the first data of Spanish PBDEs emissions from sewage treatment plants.

Material and Method

The PBDEs emission was derived from PBDEs concentration measured in 25 sewage sludge related to STP at different locations throughout Spain. Sample collection, extraction, clean-up and specific-congener PBDE analysis have been described previously[5]

PBDE Emission model: A conceptual model was design for estimating the emission of specific-congener PBDEs from urban area to STP. Figure 1 shows the picture of this model.

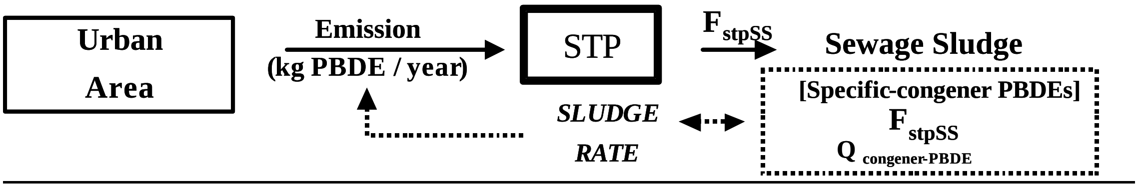


***Figure1**. Scheme of conceptual model designed for estimating the PBDEs emission.*

The Emission of PBDE specific-congener during one year ($E_{PBDE\ congener}$; mg PBDE congener/year), was calculated as follow:

$$E_{PBDE\ congener} = Q_{PBDE\ congener\text{-}} \times 100 / F_{stp\ SS} \quad (1)$$

where

- $F_{stp\ SS}$ is the Emission Fraction of PBDE specific-congener directed to SS (Sewage Sludge) by STP. In order to obtain this fraction, the default values detailed into the Technical Guidance Document (TGD, 2003[6]) were adapted for this study.
- $Q_{PBDE\ congener}$ is the PBDE quantity (kg congener-PBDE/year) present during one year in sewage sludge. Its estimation was derived from the follow equation:

$$Q_{PBDE\ congener\text{-}} = C_{PBDE\ congener} \times \text{Sludge Rate} \quad (2)$$

where

- $C_{PBDE\ congener}$ is the annual concentration of PBDE specific-congener measured in sewage sludge (ng/g dw). Each PBDE specific-congener concentration corresponds to average of four samples (after EU restriction).
- Sludge Rate is the rate of sewage sludge production associated with each STP per year (kg /year). This information was provided by the different municipal STPs.

Emissions were divided by the number of inhabitants (Capacity) that each STP is allowed to treat.

$$E_{PBDE\ congener} / eq = E_{PBDE\ congener} / \text{Capacity} \quad (3)$$

where

- $E_{PBDE\ congener}$ / eq is the emission of PBDE specific-congener per inhabitant (eq.) to STP in one year (kg PBDE congener/year)

Statistical Analysis. The statistical study was performed by STATGRAPHICS®*Plus* Version 5.0. One-variable analysis was implemented in order to a) determine potential outliers in data emission of each congener by detecting those values which lie more than 3 times the inter-quartile range (referred as far outliers) and b) establish 95,0% confidence intervals for the mean of each PBDE congener.

Results and Discussion

Calculation of F_{stp}. In the TGD, values of F_{stp} are detailed in function of chemical biodegradability and for a specific range of log k_{ow} (octanol-water partition coefficient) and log H (Henry's law constant). As the lipophilicity of the majority of PBDEs congeners is higher than those consider in the TGD (log k_{ow} up to 6), new F_{stp} values must be established. Table 1 illustrates the PBDE congener's characteristics and the F_{stp} derived from them, directed to sludge, to water and to air.

In order to estimate Fstp for PBDEs studied, all congeners were considered as not biodegradable (fate of chemicals are not degradable: $kbio_{stp} = 0\ h^{-1}$ in the aqueous phase of activated sludge).

Elimination of non-domestic discharges. PBDE specific-congener concentrations in sewage sludge were converted into emissions (mg PBDE congener / eq / year) by using the model previously explained. The individual congener emission data were analyzed for screening their variability. Figure 2 shows an example of the description performed for each congener. It identifies 25th and 75th percentiles (rectangular part of the plot), the median (centre line) and the mean (plus sign). The minimum and maximum values (whiskers from box) were drawn excluding any outlier and far outlier.

Table 1. *PBDE congener's characteristics and their derived F_{stp} (directed to sludge, to water and to air).*

	BDE-47	BDE-99	BDE-100	BDE-153	BDE-154	BDE-206	BDE-207	BDE-209
Log k_{ow} (-)	6,67 [a]	7,13 [a]	7,00 [a]	7,63 a	7,82 a	8,3 [c]	8,3 [c]	9,97 [d]
Log H (-)	0,18 [b]	-0,64 [b]	-1,16 [b]	-1,17 [b]	-0,62 [b]	-2,16 [e]	-2,16 [e]	-2,16 [e]
F_{stp} sludge (%)	91	92	92	92	92	92	92	92
F_{stp} water (%)	8	8	8	8	8	8	8	8
F_{stp} air (%)	1	0	0	0	0	0	0	0

[a]. Average of data reported by Veltman et al., 2005[7]; Gandhi et al., 2006[8]; Braekevelt et al., 2003[9].
[b]. Data reported by Titlemier et al 2002[10]
[c]. Data reported by Wania and Dugani, 2003[11]
[d]. Data reported by Veltman et al., 2005[8];
[e]. Data reported by EU Risk Assessment 2000[12]

Far outliers were identified and extracted from data emission in order to characterize the PBDE emissions only from municipal residues (mainly from domestic usage) excluding other potential sources (i.e. industrial discharges). The STP referred as nº 28 resulted as far outlier for all studied PBDE congener except for BDE-154 and 207. No emission data could be considered as far outlier for BDE 154. For BDE-207, other STP (referred with number 15) showed high emission value (far outlier). The same STP (nº15) was also found as far outlier for BDE-209. Consequently,, emissions of all studied congeners to STPs nº 28 and 15 were eliminated.

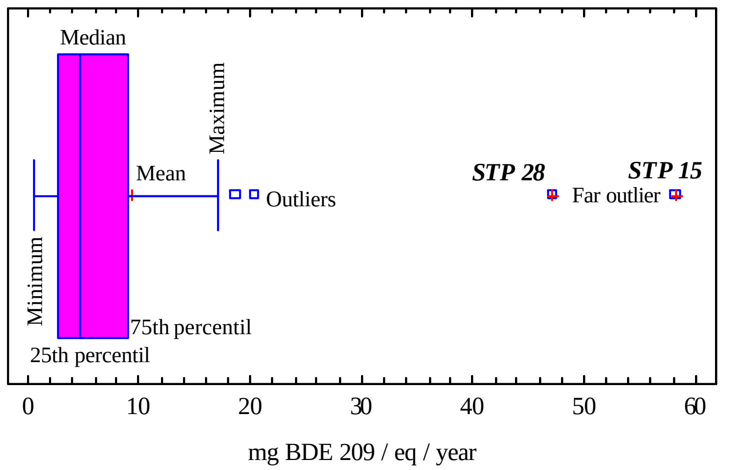
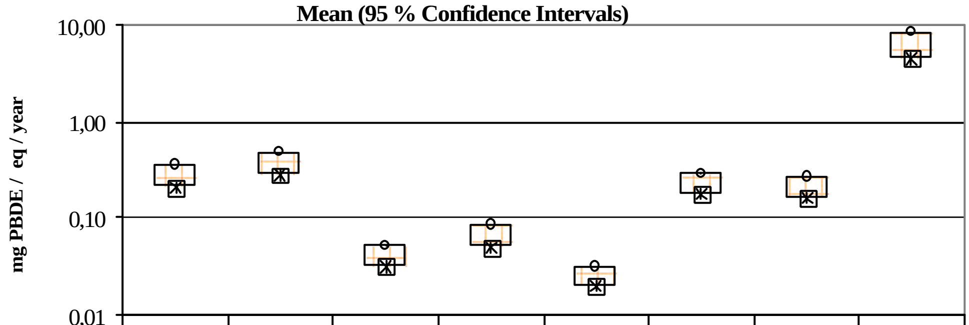


Figure 2. *Example of statistical description carried out with each PBDE congener emission. Concretely, statistical description of BDE 209 emission (mg /eq/year).*

Characterization of PBDE specific-congener emission. After elimination of STP nº 28 and 15, confidence intervals (at 95 %) of the mean emission (estimated for each PBDE congener as mg PBDE / eq/ year) were established. Figure 3 illustrates the results obtained.

Three different emission ranges (covering one order of magnitude each one) could be recognized for studied congeners. For PBDEs nº 100, 153 and 154, the lowest emissions were estimated (mean: 0,04; 0,07 and 0,03 mg of congener /eq/year respectively). Emission between 0,1 and 1 mg PBDE / eq /year were originated for congeners nº 47, 99, 206 and 207 (mean: 0,28; 0,38; 0,23 and 0,21mg of PBDE/ eq /year respectively). Finally, highest emission was found for congener nº 209 (mean: 6,16 mg BDE-209/eq/year).
The emission ranges estimated in this study could be related to congener composition of the three commercial mixtures[13] joint to their global market demand[14]. Future approaches will be performed in subsequently studies regarding to these correlations.



	BDE 47	BDE 99	BDE 100	BDE 153	BDE 154	BDE 206	BDE 207	BDE 209
Bottom Interv	0,20	0,28	0,03	0,05	0,02	0,17	0,16	4,40
Upper Interv.	0,35	0,48	0,05	0,08	0,03	0,29	0,26	8,44

Figure 3. *Confidence intervals of the mean corresponding with estimated PBDE specific-congener emissions (mg PBDE / inhabitant / year).*

The model developed in this study allowed the estimation of PBDE specific-congener emission from a generic urban scenario. This scenario could be considered representative of Europe as Spain is a member state. The estimated emissions could be related to the usage of articles containing PBDEs joint to the rest of potential PBDEs pathways (i.e.the human trophic chain). Hence, potential release of PBDEs from European urban area into the environment through STPs has been quantified after entering into force the EU restriction. This information could be very useful for risk management and could be employed in future restriction and limitation of the use and production of these compounds.

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