PBDE LEVELS IN SEDIMENT SAMPLES FROM SÃO PAULO STATE, BRAZIL

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Introduction

Persistent Organic Pollutants (POPs) are recognized as global environmental pollutants. The use of these compounds is of great concern worldwide because of their toxicological effects and the bioaccumulative potential to fish and sediment-dwelling organisms. Sediments are the sink for particle-sorbed contaminants, as well a source of pollutants in aquatic environments.
The State of São Paulo is the most industrialized region in the country, has a population of more than 40 million people and accounts for about 33% of Brazilian Gross Domestic Product. As an impact of the State´s heavy industrialization, disposal of undesirable toxic wastes and discharge of sewage and industrial effluent constitutes major sources of surface water pollution.
Since the 1970s, São Paulo State Environmental Company (CETESB) evaluates the quality of surface waters in the 22 Watershed Management Units (WMU) of the State. CETESB's monitoring network program evaluates the water quality in terms of physicochemical, ecotoxicological and biological parameters. Since 2002, this Program was extended to Sediment Quality Monitoring, including POPs like organochlorinated pesticides and PCBs and in 2014, dioxin like POPs were included in this monitoring network. In 2017 and 2018, new studies indicates the need to include polybrominated diphenyl ethers (PBDE) in future monitoring programs.

PBDE are members of a large class of chemicals containing bromine used as flame retardants. These products are often added to plastics, upholstery, foams, computers, television sets, furniture, carpets and cushioning. According to the inventory from the Brazilian National Implementation Plan for the Stockholm Convention[1], these substances were not produced in Brazil and it was not possible to verify if these POPs were imported as a substance. However, data from the inventory indicated that these products are present in electrical and electronic equipment and in imported vehicles, and that recycling parts of these products contain PBDEs.

There is a lack of information about the use and environmental levels of PBDE in Brazil and this study was performed in order to evaluate the PBDE presence in the sediments of São Paulo State water bodies during the period of 2017 and 2018.

Materials and methods

A total of 47 sediment samples were collected from rivers and reservoirs located at 11 different Watershed Management Units (WMU) within the São Paulo State. Figure 1 shows the location of sampling sites and the predominant activity in each region. The WMU 2, 5, 6, 7 and 10, located in the eastern region of the State, concentrate most of the population (73%) and have the largest number of heavy industry. The WMU 4, 8, 9 and 13 are located in undergoing industrial development areas and WMU 1 and 14 are located in the eastern and south coast region, respectively, and are both considered mainly areas of conservation.

Composite sediment samples (triplicate) were collected using van Veen grab sampler, air dried at ambient temperature, grinded and sieved (1mm). Composite samples were utilized in order to obtain more homogeneous sample as well as a better spatial coverage at each sampling site.

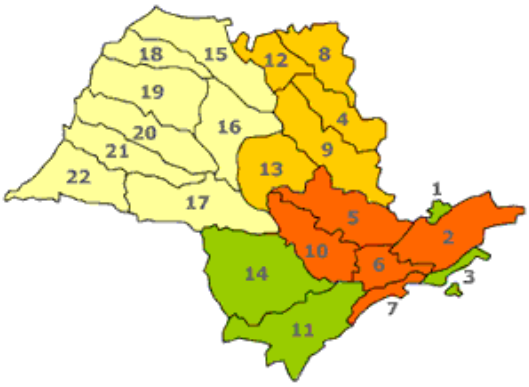
The sediment samples were spiked with $^{13}C_{12}$-PBDE surrogate standards and extracted in a microwave extractor with toluene: acetone (8:2). Spherical copper was added to the extract in order to remove sulfur, then other clean-up steps were performed using three different columns: first, a multilayer silica column (40% H_2SO_4 and

10% $AgNO_3$) was connected in series with an alumina column. n-Hexane, dichloromethane and toluene/n-hexane (2:1) were used as eluent. A third carbon column clean-up was performed using dichloromethane/n-hexane (1:1) as eluent to collect PBDE congeners. The final extracts were concentrated to dryness, the PBDE internal standards were added and then were analyzed by high resolution gas chromatography (GC6890, Agilent Technologies, USA) coupled in a high resolution magnetic sector mass spectrometer (AutoSpec Ultima, Micromass, UK), operating with a 35eV electron impact ionization at mass resolution of 5000. The GC was fitted with a DB5-ms UI capillary column (15m x 0.25mm id x 0.25µm) and for BDE-209 congener analysis was used a RTX-1614 capillary column (15m x 0.25mm x 0.10µm) additional column.

The laboratory participates in international interlaboratory studies, including PBDE analysis in sediment samples, and for this study, a standard reference material (SRM NIST 1944 - New York/New Jersey waterway sediment) analysis for the PBDE congeners #47, #99, #100, #153, #154, #183 and #209, was included, in order to certify the quality of the results obtained.

Figure 1 – São Paulo State Watershed Management Units (WMU) and sampling sites according to land occupation

Main Land Use	WMU selected	Nº Sampling sites	Nº Samples
Industrial	2, 5, 6, 7, 10	27	34
In industrial development	4, 8, 9, 13	10	10
Agriculture	--	--	--
Conservation	1, 14	2	3
Total		**39**	**47**



Results and discussion

The recovery rates for the $^{13}C_{12}$-PBDE surrogate standards added in the samples are between 53.2 and 98.4% and these results met the acceptance criteria specified in the US EPA method 1614A[2] (25-150%) for PBDE analysis by isotopic dilution and HRMS. The results of the SRM analyzed with the sediment samples during 2017 and 2018 are in accordance with the certified values.

The results of PBDE analysis are summarized in Table 1. A total of 19 PBDE congeners were analyzed in all 47 samples collected in 2017 and 2018, and the BDE-209 was analyzed in 22 samples collected in 2018.

The BDE#209 was quantified in 100% of the samples collected and is present in the highest concentrations among the PBDE congeners (302 – 673,774 pg/g d.w). The BDE#47 was quantified in 100% of the samples analyzed (17.4 – 1,243 pg/g dw), followed by the BDE#99 that was quantified in 91.5% of the samples (11.3 – 1,676pg/g dw), and BDE#100 quantified in 66.0% of the samples (10.1 – 396 ng/g dw).

Compared to other regions in the world, the PBDE results in sediments from São Paulo State are similar to the sediments from some regions in the United States (12-650ng/g dw, BDE#209) and lower than some regions in Europe (ND-16,000 ng/g dw, BD#209)[3].

There are no regulations or quality standard values for PBDE in Brazil to evaluate environmental quality monitoring and the results were compared to Canadian Environmental Quality Guidelines[4]. A total of 40.9% of the BDE-209 results (63,533 – 673,774pg/g dw) were above the Canadian Guideline (19,000pg/g) all in sampling sites located in industrial land use areas, except one sample that was located in an industrial development area. The BDE-209 concentrations at the WMU 1 and 14 (conservation area) were below the Canadian Guideline value.

A total of 6.4% of the samples presented BDE#99 concentrations (591-1,676pg/g) that exceeded the Canadian Guideline, all of them located in an Industrial region. All the samples analyzed presented BDE#100 concentrations below the Canadian Guideline.

The results of the study indicate that the PBDE are present in almost all the samples, especially BDE#47 and BDE#209, most of them located in Industrial areas that are the most populated regions in the State. Cristale et al.[5] have found similar profile for the PBDE congeners (#209, #47, #99, #100) in indoor dusts from apartments, houses, primary schools, offices and cars in Araraquara city, São Paulo. It suggest that the gradient of PBDE concentration in sediment samples reflects a transition from more to less urban developed sites.

Despite the lack of information about the use of these substances in Brazil, these results indicate that they have been introduced to the environment, probably from products containing such substances, such as flame retardants, that may be manufactured in Brazil, or from imported products.

For better understanding the PBDE presence in the environment, the São Paulo State Environment Company (CETESB) will include the PBDE monitoring in the sediment annual monitoring network and the results will contribute for the debate of environmental quality and pollutants monitoring in the State.

Acknowledgements
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References:
1. [MMA] *National Implementation Plan Brazil – Stockholm Convention*, (2015). Brasília, MMA
2. [US EPA] United States Environmental Protection Agency, (2010). Method 1614A. Washington, DC., USA
3. [ATSDR] – Toxicological Profile for PBDEs (2017) - https://www.atsdr.cdc.gov/toxprofiles/tp207-c6.pdf
4. [EC] *Canadian Federal Environmental Quality Guidelines - PBDEs* (2013).
5. Cristale J, et al. (2017), *Environmental Pollution*, https://doi.org/10.1016/j.envpol.2017.10.110

Table 1 – Levels of PBDE in sediment samples from São Paulo State (pg/g dry weight) – 2017/2018.

PBDE	Reference Value (pg/g d.w.)	WMUs										
		1	2	4	5	6	7	8	9	10	13	14
#17		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ-91.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ-13.5	< LOQ
#28		<LOQ	11.3	<LOQ	<LOQ-17.9	<LOQ -438	<LOQ	<LOQ-11.2	<LOQ	<LOQ	<LOQ-16.0	< LOQ
#49		<LOQ	26.4	<LOQ-12.1	<LOQ-227	<LOQ-665	<LOQ	<LOQ	<LOQ	22.1	<LOQ-52.7	< LOQ
#71		<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#47		21.5-30.2	110	25.9-60.0	17.4-265	47.9-1243	67.2-70.8	32.1-119	51.4-52.8	45.2	45.9-142	42.1
#66		<LOQ	<LOQ	<LOQ	<LOQ-18.9	<LOQ-92.2	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#77		<LOQ	<LOQ	<LOQ-13.3	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#100	400	<LOQ	31.4	<LOQ	< LOQ-109	<LOQ-396	<LOQ	<LOQ	<LOQ	21.5	<LOQ-21.5	< LOQ
#119		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#99	400	16.7-30.7	92.1	<LOQ-43.1	11.3-385	11.3-1676	<LOQ-33.6	17.1-17.8	<LOQ-17.8	<LOQ	28.1-75.4	14.0
#85		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ-64	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#126		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#154		<LOQ	20.7	<LOQ	<LOQ-56.2	<LOQ-254	<LOQ	<LOQ	<LOQ	18.8	<LOQ-27.6	< LOQ
#153		<LOQ	22.7	<LOQ-11.3	<LQ -94.9	<LOQ-282	<LOQ	<LOQ	<LOQ	15.7	<LOQ-16.3	< LOQ
#138		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#156		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ	< LOQ
#184		<LOQ	<LOQ	<LOQ	<LOQ-19.3	<LOQ-107	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ-46.2	< LOQ
#183		<LOQ	63.7	<LOQ-16.8	<LOQ -166	16.8-294	<LOQ	<LOQ	<LOQ	22.1	<LOQ-183	< LOQ
#191		<LOQ	<LOQ	<LOQ	< LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	< LOQ
#209*	19000	302	--	3409	214906-309862	964-673774	793	--	315-1674	--	1608-355826	1373
Samples (n)		2	1	2	9	21	2	2	2	1	4	1
Samples (n)*#209		1	-	1	2	12	1	--	2	--	2	1
TOC(%)		<1.0-1.1	2.6	<1.0-2.81	1.37-3.2	<1.0-14.0	<1.0	<1.0	-<1.0	1.31	2.21-12.1	4.88

Reference Value: according to EC, 2013. Limit of Quantitation (LOQ): 10 – 150pg/g dw depending on the BDE congener/sample