PERSISTENT ORGANIC POLLUTANTS ASSESSMENT IN THE WATER QUALITY MONITORING PROGRAM OF SÃO PAULO STATE, BRAZIL

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Introduction

Persistent Organic Pollutants (POPs) are recognized as global environmental pollutants and the usage of these compounds is a great concern worldwide because of their toxicological effects and the bioaccumulative potential to fishes and sediment-dwelling organisms (benthic invertebrates)[1] In relation to Brazilian scenario, Sao Paulo State is the most industrialized area in the country, has a population of more than 40 million people and accounts for about 33% of Brazil Gross Domestic Product. The São Paulo State Environmental Agency (CETESB) is responsible for controlling, inspecting, monitoring and licensing all the activities that are potentially generators of any kind of pollution within the whole of the state of São Paulo. In terms of regulation of POPs, Brazil has signed the Stockholm convention and issued a law that regulates the use and production of POPs in its territory[2]. The previous use of POPs in Brazil and the possibility of the unofficial use of some compounds these days indicate the need of their inclusion in monitoring programs. CETESB conducts since the 70s an Inland Water Quality Program in the 22 Watershed Management Units (WMUs)[3] of the State, which evaluates the quality of surface water through physical-chemical, ecotoxicological and biological analyses in water and more recently in sediment. This study reflects a nine year survey of the PCBs (polychlorinated biphenyls) and organochlorinated pesticides in sediments from rivers and reservoir located in 19 different WMU, with different land occupation activities (industrial, agriculture and conservation areas). The Sediment Quality in terms of chemical contamination grade was evaluated according to the Brazilian specific law for dredged material(CONAMA 344 resolution)[4] that is based on PEL (probable effect level) and TEL (threshold effect level) values established by Canadian Sediment Quality Guidelines for the Protection of Aquatic Life (CSeQGs)[5]. There is no specific regulation in Brazil for dioxins and furans evaluation in sediment matrix and the results were compared to CSeQGs values.

Materials and Methods

A total of 51 sediment samples were collected in 30 different sites located in 14 WMUs during the period of 2008 to 2010. Considering the previous study data (2002-2007)[11], a total of 167 sediment samples were collected in 86 different sites located in 19 WMUs (Fig 1) during the period of 2002 to 2010. Figure 1 shows the collection and the predominant activity in each region: WMUs 2, 5, 6, 7 and 10 are located at eastern São Paulo State and contain the largest concentration of people (73%) and heavy industries in the state; WMUs 8, 9, 12 and 13 are located in areas undergoing industrial development; WMUs 3, 11 and 14 are on the south coast and southeast region of Sao Paulo State and are considered areas of conservation; WMU 15, 16, 17, 18, 19, 21 and 22 are located at western State where the land occupation concerns mainly agricultural activities and cattle breeding. Sediment samples were collected using Van Veen grab sampler, air dried at room temperature, grinded and sieved (1mm). For PCB and organochlorinated pesticides analysis the samples were extracted in a microwave oven (U.S EPA method 3546)[6] with hexane:acetone(1:1). The extracts were cleaned up by gel permeation and then by silica gel (U.S EPA methods 3640A and 3630C)[6]. The final extracts were analysed in a Agilent 7890 model gas chromatography/electron capture detector (GC/ECD/ECD). The GC was fitted with a CPSil 8CB (60m x 0,25mm id. x 0.25 μm film thickness) and a VF-Xms (60m x 0,25mm id. x 0.25 μm film thickness) fused silica column. The compounds determined were PCBs (congeners 28, 52, 101, 118, 138, 153 and 180), aldrin, endrin, dieldrin, chlordane, endosulfan, heptachlor, heptachlor epoxide, hexachlorobenzene(HCB), DDT (4,4´-DDT, 4,4´-DDD, 4,4´-DDE), mirex, toxaphene, α, β and δ – hexachlorocyclohexane (HCH) and lindane.

Dioxins and furans were analysed according to the method U.S. EPA 8290A[6]. Sediment samples were extracted in a *Soxhlet* extractor with toluene:acetone (9:1). The sample was spiked with $^{13}C_{12}$-PCDD/F internal standards before extraction, and extracted for 25 hours. The extracts were purified in an acid silica column (40% H_2SO_4 and 10% $AgNO_3$) using n-hexane as eluent, and after in an Alumin column using dichloromethane to elute the fraction containing PCDD/Fs. The final extracts were concentrated to dryness and ressuspended with 25µL of internal standards ($^{13}C_{12}$-1,2,3,4-TCDD and $^{13}C_{12}$-1,2,3,7,8,9-HxCDD) before analysis. The final extracts were analyzed in a Agilent 6890 model high resolution gas chromatographic coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS). The equipment was operating with electron impact ionization of 35eV at a mass resolution of 10.000. The GC was fitted with a VF-Xms capillary column (60m x 0.25mm id x 0.25 µm film thickness).

Results and discussion

The results of POPs detected, are shown in Figure 1 and Table 1. Among 86 sampling sites, 36 sites (41.9%) presented positive results. From these 36 sites, 27 sites (75%) are located in the industrial region, two sites (5.56%) in the region undergoing industrial development, six sites (16.67%) in the agricultural region and one site (2.78%) in the conservation region. The POPs detected in industrial and in industrial development areas were PCBs, Aldrin, HCB, DDD, DDE, DDT, heptachlor and lindane, while in agricultural region were detected DDD, DDE and lindane. In the conservation region were detected DDE in only one sampling site at concentration near quantitation limit. The prohibition of using chlorinated pesticides in Brazil was signed in 1985, according to the law nº329 (02/09/1985)[7], Ministry of Agriculture, but allowed restricted use to some of these compounds as wood preservatives, or when applied under the responsibility of public institution in the benefits of the public health. This legal aspect may be acting as a gate for the use of some POPs as lindane and heptaclor, that were detected in industrial areas or it may reflect the past use of these compounds. The absence of heptachlor epoxide and the presence of DDT in some sampling sites indicate that the contamination of heptachlor and DDT may be recent. Total PCBs were detected at 16.3% of 86 sites surveyed. PCBs have been extensively used mainly in electrical equipment and although Brazil has signed the prohibition of use and commercialization of PCBs in 1981 according to the law nº19 (29/01/81)[8], Ministry of Interior, there is obsolete equipment and used oil that may constitute significant sources of PCBs. HCB were detected at 13.95% of 86 sites surveyed. There are well known highly contaminated sites and stockpiles of HCB in São Paulo, e.g. Cubatão (WMU#7), that may be a significant environmental contamination source.

The POPs detected that exceeded PEL values were PCBs (01 site), DDD (02 sites), DDE (11 sites), DDT (1 site) lindane (06 sites), and the POPs that exceeded TEL values were PCBs (08 sites), DDD (06 sites), DDE (08 sites) and DDT (02 sites). PEL and TEL values established at the CONAMA 344 resolution[5] were used as a guide to evaluate the results and if there is evidence of contamination that may cause any impact on biota. The concentration of POPs above TEL and PEL values especially at WMU #6, a highly industrialized area, indicates the possibility of active sources of PCBs, HCB and use of organochlorine pesticides (past or recent) in these places, indicating the need for further investigation. CETESB has conducted soil quality monitoring programs[9,10], and has detected aldrin, dieldrin, DDD, DDE, DDT, HCB and lindane in soil along WMU#6 that agree with sediment results for that region, indicating that contaminated soil can be one of source of sediment contamination. Dioxin and furans monitoring has just started in 2010 including only WMU#7 (3 sampling sites) in estuarine region and the results were below PEL values. Certainly, further studies are necessary for the improvement of this evaluation, including more WMU sites for soil monitoring, other WMU sites for dioxins and furans monitoring, other environmental matrices and improvement of analytical method to establish practicable limits for TEL and PEL values based on field conditions for a better understanding of the extent of the contamination.

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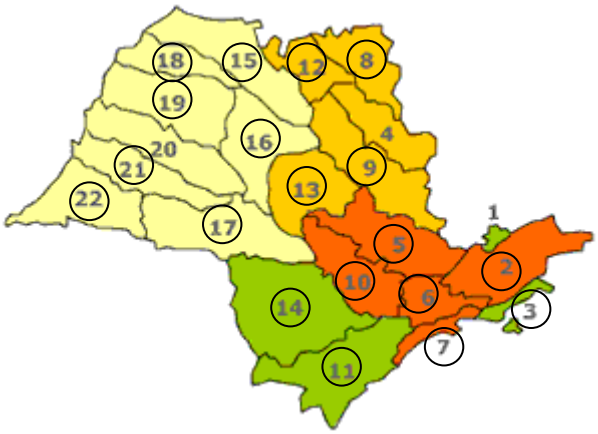
Figure 1 – São Paulo State Watershed Management Units (WMUs) and POPs detected in sediment samples during 2002 to 2010.



Land Occupation	WMUs selected	Nº Sampling sites	Nº Samples	Nº Positive sites	Compounds detected (2002 – 2010)
Industrial	2, 5, 6, 7, 10	51	115	27	Aldrin, DDD, DDE, DDT, HCB, Heptachlor, Lindane, PCBs, Dioxins*, Furans*
In industrial development	08, 09, 12, 13	10	13	2	HCB, DDE
Agriculture	15, 16, 17, 18, 19, 21, 22	13	24	6	DDD, DDE, Lindane
Conservation	3, 11, 14	12	15	1	DDE
Total	**19**	**86**	**167**	**36**	

*Dioxins and furans were evaluated only at WMU#7 in 2010 (3 sampling sites)

Table 1 – Concentration ranges of POPs detected in sediments (µg/kg-dry weight) – São Paulo State, 2002-2010

WMU	POPs detected	2002 – 2007 [11]	2008-2010
2	HCB	<0,50 - 1,03	<0,50
	Lindane	<1.25 - 1.46**	<1.25
5	PCBs	<20.0 - 33.4	<20.0
	DDE	<2.50	<0.58 - 2.05*
	DDT	<2.50	<1.73 - 3.25*
	HCB	<0.50 - 1.09	<0.50
	Heptachlor	<1.25 - 85.6	<1.25
6	PCBs	<20,0 - 484**	<20 - 74.2*
	Aldrin	<1.25	<1.25 - 4.17
	DDD	<2.50	<2.29 - 15.0**
	DDE	<2.50 - 28.4**	<0.58 - 26.7**
	DDT	<2.50	<1.73 - 7.52**
	HCB	<0.50 - 26.0	<0.86 – 134
	Lindane	<1.25 - 10.9**	<1.44 - 4.04**
7	DDE	<2.50	0.9
	HCB	<0.50 - 37.2	4.21
	Dioxins/Furans*** (total TEQ)	--	0.76 – 6.90 ng/kg (TEQ)
9	HCB	<0.50 - 0.95	--
10	DDE	<2.50	3.29-7.53**
	HCB	<0.50 - 2.46	<0.50
	Lindane	<1.25 - 3.38**	<1.25
11	DDE	<2.50	1.56*
12	DDE	<2.50	3.67*
15	DDD	<2.50 - 12.4**	--
	DDE	<2.50 - 10.2**	--
16	DDE	<2.50	4.23*
17	DDE	<2.50	1.36 - 1.80*
19	DDD	<2.50	<0.57 - 3.66*
	DDE	<2.50 - 20.8**	11.7 - 32.2**
	Lindane	<2.50	<1.25 – 2.46**
22	DDD	<2.50	6.39*
	DDE	<5.71 - 30.3**	56.0**

*concentration level above TEL value **concentration level above PEL value ***TEQ total - WHO 1998 TEF for fish