PERSISTENT ORGANIC POLLUTANTS CONCENTRATION LEVELS IN SEDIMENTS IN THE INLAND WATER MONITORING PROGRAM OF SÃO PAULO STATE, BRAZIL – A SIX YEAR SURVEY

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Introduction

Persistent organic pollutants (POPs) are a group of organic compounds which tend to resist degradation and remain intact for long periods in the environment [1]. The usage of POPs is a great concern worldwide because of their toxicological effects, bioaccumulative potential to fishes and sediment-dwelling organisms (benthic invertebrates) [2,3]. In relation to Brazilian scenario, Sao Paulo State is the most industrialized area in the country. In terms of regulation of POPs, Brazil signed the Stockholm convention and issued a law that regulates the use and production of POPs in its territory[4]. 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 (São Paulo State Environmental Protection Agency) conducts since the 70s an Inland Water Quality Program, including the 22 Watershed Management Units (WMUs) [5] 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 six year survey of the PCBs (polychlorinated biphenyls) and organochlorinated pesticides in sediments from rivers and reservoir located in 17 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)[6] 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].

Materials and Methods

A total of 116 sediment samples were collected in 76 different sites located in 17 WMUs (Fig 1) during the period of 2002 to 2007. 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 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, 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 and transported to the laboratory in glass bottles, protected from light at 4 ± 2 ºC. Samples were air dried at room temperature, grinded and sieved (1mm) and then extracted in a microwave oven (U.S EPA method 3546)[8]. The solvent used for extraction was hexane:acetone(1:1), organic residue analysis grade. The extracts were cleaned up by gel permeation and then by silica gel (U.S EPA methods 3640A and 3630C)[8]. The final extracts (in n-hexane, organic residue analysis grade) were analysed in a Hewlett Packard 5890 model gas chromatography/electron capture detector (GC/ECD). The GC was fitted with a J&W DB-5 fused capillary column (30m x 0,25mm id. coated with 0.25 µm film tickness of 5% phenyl-substituted methylpolysiloxane phase). The results were confirmed in a GC 5890 fitted with a J&W DB-1701 capillary column (30m x 0.25mm id. coated with 0,25µm film tickness of 14% cyanopropyl-phenyl methylpolysiloxane phase). The compounds determined were PCBs (congeners 28, 52, 101, 118, 138, 153 and 180), aldrin, endrin, dieldrin, chlordane, heptachlor, hexachlorobenzene(HCB), DDT (4,4´-DDT, 4,4´-DDD, 4,4´-DDE), dodecachlor, toxaphene and lindane.

Results and discussion

The results of POPs detected, are shown in Table 1. Among 76 sampling sites, 22 sites (28.9%) presented positive results. From these 22 sites, 17 sites (77.3%) are located in the industrial region, one site (4.54%) in the region undergoing industrial development and four sites (18.2%) in the agricultural region. None of the conservation regions presented POPs at detection level. The POPs detected in industrial and in industrial development areas were PCBs, HCB, DDD, DDE, heptachlor and lindane, while DDD and DDE where the only POPs detected in agricultural areas . The prohibition of using chlorinated pesticides in Brazil (aldrin, BHC, toxaphene, DDT, dodecachlor, endrin, heptachlor, lindane, endosulfan, metoxiclor, nonachlor, PCP, dicofol and chlorobenzilate) was signed in 1985, according to the law nº329 (02/09/1985)[9], 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 (lindane, heptachlor and sodium pentachlorophenate). 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 indicates that the contamination of heptachlor may be recent. The presence of DDD and DDE may indicate the past use of DDT, mainly in agricultural and cattle bleeding areas. Total PCBs were detected at 13.2% of 76 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)[10], Ministry of Interior, there is obsolete equipment and used oil that may constitute significant sources of PCBs. HCB were detected at 14.5% of 76 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[11].

The POPs detected that exceeded PEL values were PCBs (01 site), lindane (03 sites), DDE (05 sites) and DDD (01 site) and total PCBs was above TEL values in 07 sites. PEL and TEL values established at the CONAMA 344 resolution[6] were used as a guide to evaluate the results and if there is evidence of contamination that may cause any impact on biota. However, the calculated quantification limits for DDE, DDT, chlordane, toxaphene and lindane are higher than established TEL values. Due to the complexity of the sediment matrices, even after cleanup steps, it was not possible to achieve lower values. In this case, to avoid inappropriate results because of matrix interferences, those high quantification limits were kept. 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 organochlorinated pesticides (past or recent) in these places, indicating the need for further investigation. The determination of POPs in muscle tissue, bones and blood of fish samples could be useful to evaluate the availability of those compounds in the environment as well as the potential risk to the biota and could differentiate between recent and past exposures. Certainly, further studies are necessary for the improvement of analytical methodologies, including different environmental matrices 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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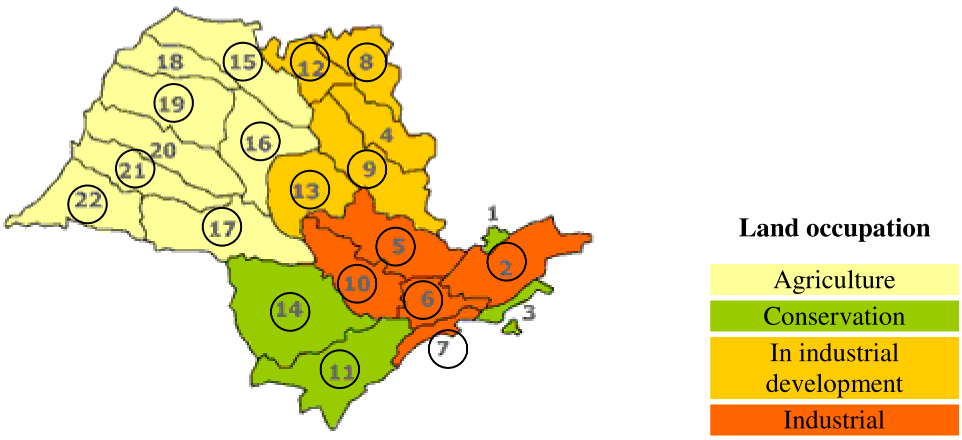
Figure 1 – São Paulo State Watershed Management Units (WMUs).



Land Occupation	WMUs selected	Nº Sampling sites	Nº Samples	Nº Positive sites
Industrial	2, 5, 6, 7, 10	48	83	17
In industrial development	08, 09, 12, 13	07	10	1
Agriculture	15, 16, 17, 19, 21, 22	12	14	4
Conservation	11, 14	09	09	0
Total	17	76	116	22

Table 1: Concentration ranges of POPs (µg/kg-dry weight) detected in sediments of Watershed Management Units (WMUs), São Paulo State, Brazil, from 2002 to 2007.

WMU	POPs detected	2002	2003	2004	2005	2006	2007
2	HCB	--	--	<0.50	<0.50	1,03	<0.50
	Lindane	--	--	1.46**	<1.25	<1.25	<1.25
Nº sites		0	0	01	01	01	01
5	PCBs	--	<20.0	<20.0-32.6	<20.0 - 33,4	<20.0	<20.0
	HCB	--	<0.50	<0.50-1.09	<0.50	<0.50	<0.50
	Heptachlor	--	<1.25	<1.25	<1.25	<1.25-85.6	<1.25
Nº Sites		0	03	04	03	06	05
6	PCBs	<20,0 – 125*	<20,0 – 116*	<20.0-179*	<20.0-55.9*	<20.0-20.0	<20.0-484**
	DDE	<2.50	<2.50-28,4**	<2.50	<2.50-2.7*	<2.50	<2.50-5.97*
	HCB	<0.50	<0.50-2.03	<0.50-26.0	<0.50	<0.50-6.63	<0.50-3.91
	Lindane	<1.25	<1.25	<1.25-10.9**	<1.25	<1.25	<1.25
Nº sites		06	08	09	05	06	06
7	HCB	<0.50	<0.50-7.61	<0.50-12.8	37.2	1.03	5.28
Nº Sites		01	02	02	01	01	01
9	HCB	<0.50	<0.50	0.95	--	--	--
Nº Sites		01	01	01	0	0	0
10	HCB	--	<0.50	2.46	<0.50	<0.50	<0.50
	Lindane	--	<1.25	3.38**	<1.25	<1.25	<1.25
Nº Sites		0	02	01	02	01	01
15	DDD	--	12.4**	--	<2.50	<2.50	--
	DDE	--	10.2**	--	<2.50	<2.50	--
Nº Sites		0	01	0	01	01	0
19	DDE	--	--	--	<2.50	11.2**	16.0**-20.8**
Nº Sites		0	0	0	01	01	02
22	DDE	--	--	--	--	--	<5.71-30.3**
Nº Sites		0	0	0	0	0	03

* concentration level above TEL values.
**concentration level above PEL values.