PERSISTENT ORGANIC POLLUTANTS 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 area 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 effluents constitutes a major source 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. The 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.

This work evaluated the presence of polychlorinated dibenzo-p-dioxins (PCDD), polychlorinated dibenzofurans (PCDF), polychlorinated biphenyls (PCB) and organochlorinated pesticides (OCP) in sediment samples from São Paulo State water bodies. It compiles the results of a one-year study (2014) of the sediment monitoring network activities towards protection of the São Paulo State's water bodies.

Materials and methods

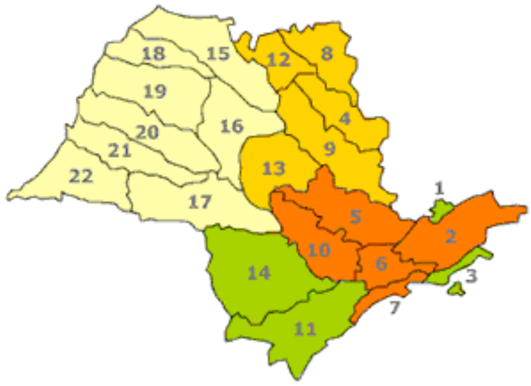
Nineteen sediment samples were collected from eight rivers and eleven reservoirs located in nine different Watershed Management Units (WMU) within the São Paulo State. The Figure 1 shows the location of sampling sites and the predominant activity in each region. The WMU 2, 5, 6, 7 and 10, located in the eastern region of the State, concentrate most of the population (73%) and have the largest number of heavy industry. The WMU 9 is located in undergoing industrial development and the WMU 16 is located at western region of the State where the land occupation is devoted mainly for agricultural activities and cattle breeding. The WMU 11 and 14 are located in the south coast and southeast region, respectively, and are both considered 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.

PCDD/F and PCB were analyzed according to the methods US EPA 8290A[1] and US EPA 1668C[2], respectively. The sediment samples were spiked with $^{13}C_{12}$-PCDD/F and $^{13}C_{12}$-PCB surrogate standards and extracted during 24h in a Soxhlet extractor with toluene: acetone (9:1). The extracts were purified in a multilayer silica column (40% H_2SO_4 and 10% $AgNO_3$) using n-hexane as eluent, and after in an alumina column using dichloromethane to elute the fraction containing PCDD/F and n-hexane/toluene (1:2) to elute PCB fraction. The final extracts were concentrated to dryness and then added PCDD/F/PCB internal standards. PCDD/F and PCB final extract were analyzed in an Agilent 6890 model gas chromatography coupled in an AutoSpec high resolution mass spectrometer (HRGC/HRMS), 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 0.25µm film thickness).

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

Land Occupation	WMU selected	Nº Sampling sites/Samples
Industrial	2, 5, 6, 7, 10	15
In industrial development	09	01
Agriculture	16	01
Conservation	11, 14	02
Total	**09**	**19**



The OCP analysis was performed according to the method US EPA 8081B[3]. The sediment samples were spiked with tetrachloro-m-xylene and decachlorobiphenyl as surrogate standards and extracted with n-hexane: acetone (1:1) in a Soxhlet extractor during 24h. The extract were cleaned up by gel permeation and then by silica gel. The final extracts were analysed in an Agilent 7890 model gas chromatography/dual micro electron capture detector (GC/ECD/ECD). The GC was fitted with a DB-5ms capillary column (60m x 0.25mm id x 0.25 µm film thickness) and a DB-1701 column (60m x 0.25mm id x 0.25 µm film thickness). The compounds determined were aldrin, endrin, dieldrin, chlordane, endosulfan, heptachlor, heptachlor epoxide, hexachlorobenzene (HCB), DDT (and DDE, DDD), mirex, toxaphene, α and β hexachlorocyclohexane (HCH) and lindane. Total organic carbon was analyzed by wet oxidation method according to Gaudette & Fligth[4].

The results of PCDD/PCDF and dl-PCBs were calculated and expressed as WHO_{98} TEQ for fish considering the aquatic life protection[5,6]. Total TEQ was calculated according to the lower and upper bound concept. For lower bound TEQ calculation; all results below limit of detection (LOD) were considered as zero whereas for upper bound TEQ calculation; all results below LOD were considered equal to ½ of the LOD value.

Results and discussion

The results of PCDD/PCDF and dl-PCBs, OCP, sum of indicator PCB and total organic carbon (TOC) are summarized in Table 1.

The octa-chlorinated dioxins (OCDD) and furans (OCDF) congeners were detected at the highest concentrations in almost all samples. However, they represent the congeners with the lowest contributions in terms of toxic equivalent (TEQ) concentration as their toxic equivalent factor (TEF) is very low. Since there is no specific regulation in Brazil for dioxins and furans, the sediment results were compared to the Canadian Sediment Quality Guideline for the protection of aquatic life (CCME, 2001)[6] which is based on PEL (probable effect level) and TEL (threshold effect level) values (21.5 and 0.85 ng TEQ/kg d.w., respectively – $WHO_{98\ fish}$). The PCDD/F TEQ value for Rio Grande reservoir, located at WMU 6 (Industrial), was higher than the PEL value whereas the value for all other samples were below PEL.

Considering the results below LOD as zero, six samples collected from WMU 5, 6, 7 and 10 (industrial) were higher than the TEL value whereas all other samples were below this value. Considering the upper bound values, ten samples collected from WMU 5, 6, 7 and 10 (industrial), one sample from WMU 11 (conservation) and one sample from WMU 16 (agricultural) were higher than the TEL values.

Although the dl-PCB were present in concentrations higher than PCDD/F, the dl-PCB contribution for the total TEQ are very low. The most abundant congener was the congener #118, followed by congener #105 and #156.

According to Eljarrat & Barceló (2009)[7], sediment samples from different background sites (Europe, Asia and North America) have PCDD/F levels ranging from 0.02 to 24 ng TEQ/kg (d.w.). The results of this study showed that only one sample exceeded the upper concentration threshold while the remaining samples results were all below this value, indicating that these sites are not impacted with high levels of PCDD/F. According to the Brazilian Inventory of sources and estimation of emissions of PCDD/F[8], the releases to air represent 52.3% of total emissions whereas releases to water correspond to only 1.0%. Particulate matter deposition can be one of the main sources of PCDD/F present in low concentrations in sediment samples. Nonetheless, some sites with higher PCDD/F levels such as Rio Grande (RGDE02900), Billings (BILL02100) and Guarapiranga (GUAR0900) reservoirs probably have other sources than atmospheric deposition, since they are located in São Paulo Metropolitan Region, a high-density urban area, with industrial activity.

Among the OCP compounds analyzed, only DDE was detected. The detection of this substance was observed in nine samples collected from WMU 5, 6, 7 and 10 (Industrial) and in one sample collected from WMU 9 (undergoing industrial development). When compared to the Brazilian regulation on dredged material quality (Conama 454/2012)[9], one sample from the Billings reservoir (Industrial) exceeded the DDE PEL value (6.75 µg/kg), and two samples from the WMU 6 and 7 (Industrial) exceeded the DDE TEL value (1.42 µg/kg), although below the PEL limit.

Indicator PCB (sum of PCB#28, 52, 101, 118, 138, 153 and 180) was detected in all samples. According to the Brazilian regulation on dredged material quality (Conama 454/2012)[9], only one sample (BILL2100) exceed the TEL value (34.1 µg/kg), but not the PEL value (277 µg/kg).

These results indicate that most of the study areas are not impacted with high levels of POPs analyzed but as these compounds tend to accumulate in sediment as well as in the aquatic biota they can concentrate over a long period. Three reservoirs showed the highest concentrations of PCDD/F, one of them (RGDE02900) with a concentration greater than PEL value, and should be better evaluated, once they are important public water supply reservoirs for the São Paulo Metropolitan Region. The OCP and indicator PCB results were similar to the historical data of the CETESB's monitoring network, showing a slight decrease in the number of contaminants over time. The presence of DDE probably represents the past use of DDT. The results of this study will contribute for the debate of environmental quality and pollutants monitoring in the São Paulo State.

Acknowledgements
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Table 1 – Levels of PCDD/F, dl-PCBs, OCP and indicator PCB in sediment samples (d.w.).

WMU	Sampling site	$TEQ_{\sum PCDD}$ (ng TEQ/kg		$TEQ_{\sum PCDF}$ (ng TEQ/kg)		$TEQ_{\sum PCDD/F}$ (ng TEQ/kg)		$TEQ_{\sum dl\text{-}PCB}$ (ng TEQ/kg)		OCP (DDE) (µg/kg)	∑PCB ind (µg/kg)	TOC (%)	Fine grains = silt+Clay (%)
		LB	UB	LB	UP	LB	UB	LB	UB				
2	SANT0800	0.02	0.28	0.31	0.44	0.33	0.72	0.0002	0.0012	<LOQ	0.26	1.82	69.76
2	PARB2850	0.04	0.24	0.07	0.27	0.11	0.51	0.02	0.02	<LOQ	1.64	2.20	3.85
5	ATIB2800	0.08	1.22	1.14	1.18	1.22	2.40	0.07	0.07	0.53	10.8	2.23	86.08
5	ATSG2800	0.11	1.60	0.41	0.62	0.52	2.21	0.01	0.03	1.29	8.66	1.82	11.75
5	PCAB2195	0.076	0.876	1.00	1.00	1.07	1.88	--	--	0.38	15.1	2.22	78.40
6	BILL2100	7.10	7.10	9.55	9.55	16.7	16.7	--	--	7.31	170	5.36	86.80
6	CLAR2500	0.0005	0.1204	0.0035	0.0915	0.004	0.21	0.000	0.001	<LOQ	<0.03	<1.00	69.10
6	GUAR0900	3.36	3.59	5.75	5.75	9.11	9.34	0.10	0.10	<LOQ	16.0	2.70	14.68
6	NOVA0800	0.057	1.17	0.54	0.76	0.59	1.93	0.001	0.004	1.23	0.72	3.66	96.56
6	RGDE2900	2.9	4.58	21.0	21.0	23.9	25.6	0.15	0.15	2.10	18.2	4.20	95.84
6	TAMT4250	0.004	0.759	0.03	0.13	0.03	0.89	0.001	0.003	NA	0.77	<1.00	99.34
7	MARO2180	2.50	4.44	4.39	4.39	6.89	8.84	0.11	0.11	2.17	15.4	7.12	92.66
7	MOJI2720	0.01	0.48	0.06	0.18	0.07	0.66	0.001	0.003	<LOQ	0.69	<1.00	62.73
9	PEXE2950	0.028	0.531	0.25	0.42	0.27	0.95	0.05	0.05	1.03	5.64	2.20	88.62
10	SOIT2850	0.01	0.91	0.03	0.26	0.04	1.17	0.0001	0.001	1.39	0.08	1.86	93.40
10	TIBB2900	0.12	0.64	1.25	1.29	1.37	1.94	0.004	0.0	0.57	4.49	2.91	96.49
11	CAFR0300	0.08	0.53	0.61	0.81	0.69	1.33	0.001	0.004	<LOQ	0.95	2.64	97.63
14	JURU2600	0.01	0.23	0.01	0.17	0.02	0.40	0.0001	0.001	<LOQ	0.15	1.30	93.60
16	TIPR2800	0.01	1.39	0.02	0.20	0.03	1.58	0.0003	0.001	<LOQ	0.19	1.76	34.80
REFERENCE VALUES													
	TEL	--		--		0.85[5]		--		1.42[9]	34.1[9]	--	--
	PEL	--		--		21.5[5]		--		6.75[9]	277[9]	--	--

* LB: Lower bound TEQ (values <LOD = zero) ** UB: Upper bound TEQ (values <LOD = 1/2LOD value)