ASSESMENT OF PCB CONTAMINATION IN FISH FROM WATER RESERVOIR OF SÃO PAULO STATE, BRAZIL – *BILLINGS AND RIACHO GRANDE RESERVOIR*

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Introduction

Billings reservoir is the largest and most important water body in the São Paulo Metropolitan Region. Its construction begun in 1925 in order to supply the city of São Paulo with electricity. For many years, it presented low environmental quality due to contamination with organic sewage and industrial effluents from the Metropolitan Region. Nowadays, two sites (*Taquacetuba* and *Riacho Grande*) are used for drinking water supply. The reservoir is also used for fishing due to the presence of fish farming and also due to the presence of native and exotic species.

Billings Reservoir

It is well known that the region presents Polychlorinated Biphenyl (PCB) contamination[1]. In spite of its prohibition all around the world, historically PCBs were used in commercial mixtures such as Aroclors 1242, 1248, 1254 and 1260, these were probably the most used in Brazil, since the majority of them were purchased from "Monsanto"[2]. Brazil signed the prohibition of use and commercialization of PCBs in 1981 with law n° 19 (29/01/81)[3].

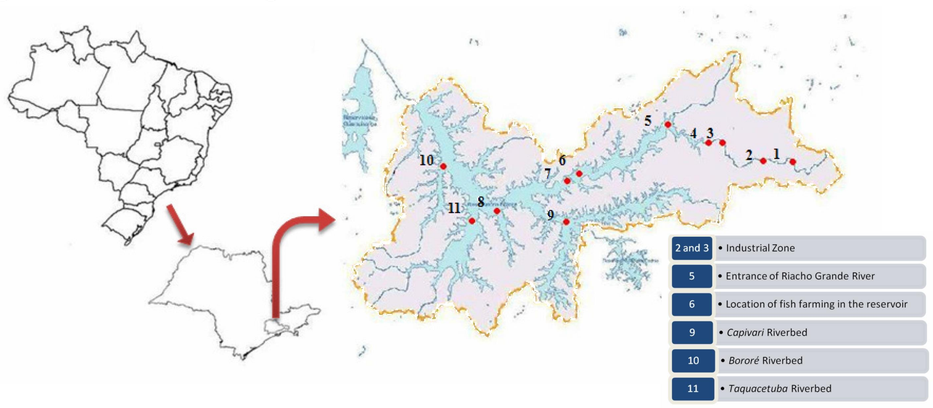
Once these toxic contaminants reach the water surface, they may concentrate in aquatic substratum and bioaccumulate in fish[4]. Thus, fish monitoring serves as an important indicator of contaminated sediments and water quality problems. The previous use of PCBs in these areas (*Billings* and *Riacho Grande*) and the possibility of unofficial use of these compounds coupled with fish consumption, indicated the necessity of chemical analyses to evaluate such contaminant in fish as part of the comprehensive water quality monitoring program of CETESB (São Paulo State Environmental Protection Agency).

As part of the monitoring program, this study is an attempt to evaluate the public health risk related to fish consumption from Billings and Riacho Grande reservoir, since contaminated food is the main intake route for such compounds like PCBs[5].

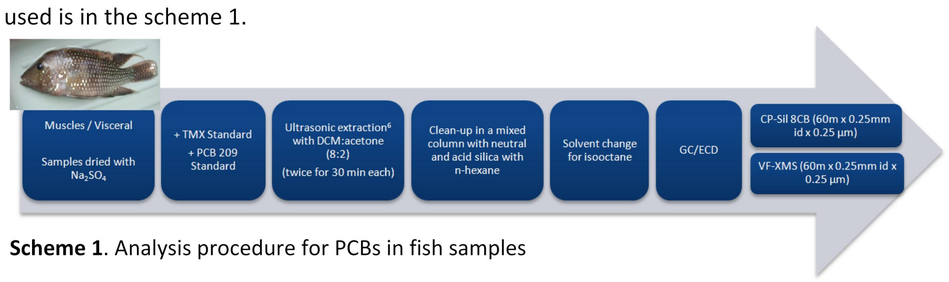
Materials and Methods

A total of 46 fish samples were collected in 7 different sites located in the river *Riacho Grande* and in the *Billings* reservoir during the period between March and April, 2009. At sites 1, 4, 7 and 8 there was no sampling.

Figure 1. Sites located at *Billings* and *Riacho Grande* Reservoir



Different fish species were caught using different types of nets (20; 35; 40 and 60mm). These nets were placed in the sampling sites in the afternoon and at night and were left in position until the next afternoon. The fillets of fish were removed along with the skins. The muscles attached to the skin were removed with the aid of stainless steel scalpels. After removal of the fillets, the fishes were opened in the abdominal region and sometimes the rib bones were removed to facilitate exposure of internal organs and their subsequent removal. Fish muscles and visceral material were separately analyzed. The analysis procedure that was used is in the scheme 1.



Scheme 1. Analysis procedure for PCBs in fish samples

Results and Discussion

Among 46 fish samples, three species were selected to be evaluated in relation to risk consumption: *Astyanax* sp, *Hoplias malabaricus*, *Rhamdia quelen.* The choice was based on the different eating habits of these species. The PCB results measured in the muscles and visceral material are shown in Table 1.

The collected organs were: liver (hepatopancreas in some fishes), kidney and spleen, they reflect not only the latest body metabolism, but also the beginning of the processes of bioaccumulation and biomagnification of contaminants.

Table 1. Concentration of PCB Σ(CB 28, 52, 101, 118, 138, 153 and 180) in fish species (µg/kg)

Fish species		Site2	Site 3	Site 5	Site 6	Site 9	Site 10	Site 11
Astyanax sp	Muscle	25.21	57.82	72.92	NC	NC	NC	NC
	Viscera	89.76	343.96	471.79	NC	NC	NC	NC
R. quelen	Muscle	NC	342.00	275.45	8.16	NC	NC	79.62
	Viscera	NC	350.20	545.70	NA	NC	NC	244.78
H. malabaricus	Muscle	NC	76.43	65.00	1.68	2.24	1.77	NC
	Viscera	NC	2587.00	1065.70	85.92	NA	172.31	NC

Note: NC = Fish specie not caught in this site; NA = Not analyzed

It is possible to observe PCB bioaccumulation in all three species. The fact that concentration found in visceral material was much higher than that found in muscle, except for *R. quelen* in site 3, in which it was detected at almost the same level, indicates a recent contamination. *H. malabaricus,* a carnivorous species, presented proportionally, higher bioaccumulation in the visceral material than in the muscles, the obtained results being, for instance, approximately 15 times higher in the visceral material than in the muscle in Site 5 and 100 times more in Site 10.

Risk evaluation of fish consumption

To evaluate the health risk through consumption of fish, the maximum allowable fish consumption rate (CRlim) were estimated for three groups of population - general population (adults), children from 1 to 4 years old, and children 5 up to 11 years old - considering both carcinogenic and non carcinogenic effects, by equations 1 and 2, respectively. For the calculation, the concentration sum of PCB congeners in the muscles of the sample fish analyzed (C_{PCB}) was used, Table 1. Table 2 presents the daily consumption limits for the three considered groups.

Equation 1

$$CR_{lim}(Kg/d) = \frac{ARL \times BW}{CSF \times C_{PCB}}$$

Equation 2

$$CR_{lim}(Kg/d) = \frac{RfD \times BW}{C_{PCB}} x RSC$$

Equation 3

$$CR_{mm}(meals/month) = \frac{CR_{lim} \times T_{ap}}{MS}$$

Where:
The average body weights are: adult = 70 kg (USEPA, 2000)[7], child between 5 to 11 years of age = 26.4 kg, and children from 1 to 4 years old = 14.4 kg (Health Canada, 2007)[8].
Cancer slope factor (CSF): 2 per mg/kg-d (USEPA, 1997)[9]
Maximum acceptable cancer risk level (ARL): 1 in 100000 (10^{-5})
Reference dose for PCBs (RfD): 2 X 10^{-5} mg/kg-d (USEPA, 1996)[10]
Relative source contribution (RSC): 50% (Voorspoels, 2008)[11]

Table 2. Daily fish consumption limits for three groups of population (kg/d)

Site	Fish species	PCB (µg/kg)	Daily fish consumption limit (kg/d)					
			Limit per Day (kg/d) Carcinogenic effects			Limit per Day (kg/d) Noncarcinogenic effects		
			Gen	Children (1 - 4 yrs)	Children (5 -11 yrs)	Gen	Children (1 - 4 yrs)	Children (5 -11 yrs)
2	*Astyanax* sp	25.21	$1.39x10^{-2}$	$2.86x10^{-3}$	$5.24x10^{-3}$	$2.78x10^{-2}$	$5.71x10^{-3}$	$1.05x10^{-2}$
3	*Astyanax* sp	57.82	$6.05x10^{-3}$	$1.25x10^{-3}$	$2.28x10^{-3}$	$1.21x10^{-2}$	$2.49x10^{-3}$	$4.57x10^{-3}$
	R. quelen	342.00	$1.02x10^{-3}$	$2.11x10^{-4}$	$3.86x10^{-4}$	$2.05x10^{-3}$	$4.21x10^{-4}$	$7.72x10^{-4}$
	H. malabaricus	76.43	$4.58x10^{-3}$	$9.42x10^{-4}$	$1.73x10^{-3}$	$9.16x10^{-3}$	$1.88x10^{-3}$	$3.45x10^{-3}$
5	*Astyanax* sp	72.92	$4.80x10^{-3}$	$9.87x10^{-4}$	$1.81x10^{-3}$	$9.60x10^{-3}$	$1.97x10^{-3}$	$3.62x10^{-3}$
	R. quelen	275.45	$1.27x10^{-3}$	$2.61x10^{-4}$	$4.79x10^{-4}$	$2.54x10^{-3}$	$5.23x10^{-4}$	$9.58x10^{-4}$
	H. malabaricus	65.00	$5.38x10^{-3}$	$1.11x10^{-3}$	$2.03x10^{-3}$	$1.08x10^{-2}$	$2.22x10^{-3}$	$4.06x10^{-3}$
6	*R. quelen*	8.16	$4.29x10^{-2}$	$8.82x10^{-3}$	$1.62x10^{-2}$	$8.58x10^{-2}$	$1.76x10^{-2}$	$3.24x10^{-2}$
	H. malabaricus	1.68	$2.08x10^{-1}$	$4.29x10^{-2}$	$7.86x10^{-2}$	$4.17x10^{-1}$	$8.57x10^{-2}$	$1.57x10^{-1}$
9	*H. malabaricus*	2.24	$1.56x10^{-1}$	$3.21x10^{-2}$	$5.89x10^{-2}$	$3.13x10^{-1}$	$6.43x10^{-2}$	$1.18x10^{-1}$
10	*H. malabaricus*	1.77	$1.98x10^{-1}$	$4.07x10^{-2}$	$7.46x10^{-2}$	$3.95x10^{-1}$	$8.14x10^{-2}$	$1.49x10^{-1}$
11	*R. quelen*	79.62	$4.40x10^{-3}$	$9.04x10^{-4}$	$1.66x10^{-3}$	$8.79x10^{-3}$	$1.81x10^{-3}$	$3.32x10^{-3}$

Note: "Gen" refers to general adult population

The daily consumption limit of fish can be also expressed as number of meals a month (T_{ap} = 30.44 days). Therefore the limits presented in the table 2 were converted into number of meal (CR_{mm}) for the three population groups (Table 3). Assuming that a meal based on fish is equivalent MS (Meal Size) = 0.227 kg, portion adopted by USEPA. The number of meals was obtained by equation 3.

Table 3. Monthly Fish Consumption Limits for the three population groups

Site	Fish species	PCB (µg/kg)	Number of fish meals (meal/month)					
			Carcinogenic effects			Noncarcinogenic effects		
			Gen	Children (1 - 4 yrs)	Children (5 -11 yrs)	Gen	Children (1 - 4 yrs)	Children (5 -11 yrs)
2	*Astyanax* sp	25.21	1.86	0.38	0.70	3.73	0.76	1.40
3	*Astyanax* sp	57.82	0.81	0.17	0.31	1.62	0.33	0.61
	R. quelen	342.00	0.14	0.03	0.05	0.27	0.56	0.10
	H. malabaricus	76.43	0.61	0.13	0.23	1.23	0.25	0.46
5	*Astyanax* sp	72.92	0.64	0.13	0.24	1.29	0.27	0.49
	R. quelen	275.45	0.17	0.03	0.06	0.34	0.07	0.13
	H. malabaricus	65.00	0.72	0.15	0.27	1.44	0.30	0.54
6	*R. quelen*	8.16	5.75	1.18	2.17	11.50	2.36	4.34
	H. malabaricus	1.68	27.89	5.75	10.54	55.91	11.49	21.05
9	*H. malabaricus*	2.24	20.92	4.30	7.90	41.97	8.62	15.82
10	*H. malabaricus*	1.77	26.55	5.46	10.00	52.97	10.91	19.98
11	*R. quelen*	79.62	0.59	0.12	0.22	1.18	0.24	0.45

Note: "Gen" refers to general adult population

Conclusion

According to the results in Table 3, where the monthly number of meals that can be consumed by the three population groups with no risk to the health, is presented, it is possible to recognize that there is a potential risk to the population in all fish species analyzed due to the low number of meal permitted, except for sites 6, 9 and 10. Further studies are necessary to obtain a better understanding of the actual contamination level.

Acknowledgements

We gratefully acknowledge the support and infrastructure provided by CETESB and all the people who worked on this study.

References

1. CETESB. Desenvolvimento de índices biológicos para monitoramento em reservatórios do Estado de São Paulo, 2010. Available on-line: < http://www.cetesb.sp.gov.br/Agua/rios/publicacoes.asp >
2. Almeida F V, Centeno A J, Bisinoti M C, Jardim W F. (2007); *Quim. Nova.* 30(8): 1976-85
3. Brasil. Ministério do Interior. Portaria Nº 19 de 29.01.81. D.O.U., 03.09.85 – pag. 12941, 1985.
4. Schwarzenbach R P, Gschwend P M, Imboden D M. (1995) *Environ Org Chem*. 2nd ed. Wiley-Interscience: USA.
5. WHO. Air quality guidelines 2nd ed. Denmark, 2000.
6. USEPA – SW846. Method 3550C – Ultrasonic Extraction. 2007. Available on-line: < http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/3_series.htm >
7. USEPA. Guidance for Assessing Chemical Contaminant Data for Use In Fish Advisories. Volume 2: Risk Assessment and Fish Consumption Limits. 3rd ed. 2000. Available on-line: < http://www.epa.gov/waterscience/fish/advice/volume2/index.html >
8. Health Canada. Human Health Risk Assessment of Mercury in Fish and Health Benefits of Fish Consumption, 2007. Available on-line: < http://www.hc-sc.gc.ca/fn-an/alt_formats/hpfb-dgpsa/pdf/nutrition/merc_fish_poisson-eng.pdf >
9. USEPA. Integrated Risk Information System. Polychlorinated biphenyls (PCBs) (CASRN 1336-36-3), 1997. Available on-line: < http://www.epa.gov/ncea/iris/subst/0294.htm >
10. USEPA. Integrated Risk Information System. Aroclor 1254 (CASRN 11097-69-1), 1996b Available on-line: < http://www.epa.gov/ncea/iris/subst/0389.htm >
11. Voorspoels S, Covaci A, Neels H. (2008). *Environ Toxicol Pharmacol*. 25(2):179-82.