Bull. Environ. Contam. Toxicol. (2003) 70:1151–1157

DOI: 10.1007/s00128-003-0102-5

Bulletin of Environmental Contamination and Toxicology

Polychlorinated Biphenyls and Organochlorine Pesticides in Edible Fish Species and Dolphins from Guanabara Bay, Rio de Janeiro, Brazil

A. M. F. da Silva,[1] V. R. R. Lemes,[2] H. H. C. Barretto,[2] E. S. Oliveira,[3] I. B. de Alleluia,[3] F. J. R. Paumgartten[1]

[1] Laboratory of Environmental Toxicology, National School of Public Health, FIOCRUZ, Rua Leopoldo Bulhões 1480, Rio de Janeiro, RJ 21041-210, Brazil
[2] Adolfo Lutz Institute, São Paulo, SP 01246-000, Brazil
[3] National Institute of Technology, Rio de Janeiro, RJ 20081-310, Brazil

Received: 27 August 2002/Accepted: 8 March 2003

Guanabara Bay is located in southeastern Brazilian coast, between the Sea Mountain range ('Serra do Mar') and the Atlantic Ocean. It is surrounded by a densely populated urban area including three big cities: Rio de Janeiro, the second largest city in the country, Niteroi and São Gonçalo. Pollution of Guanabara Bay waters by organic matter discharges and industrial effluents has become a matter of great concern in the last decades. It has been estimated that more than 470 tons of organic matter from domestic sewage discharges, 90% of which is untreated, are daily released into bay waters (Lavrado et al., 1991, Paranhos, 1995). Dump landfills receiving about 7,000 tons of garbage per day are also located on the shores of Guanabara Bay. Furthermore, 10,000 industries, 2 harbors, 2 oil refineries, 16 oil terminals and 12 shipyards are responsible for a daily discharge of 6.9 tons of pollutants, including oil and metals, in the bay. Despite the substantial amount of organic and industrial discharges, data on the levels of chemical pollutants in Guanabara Bay waters, sediments and biota are still scarce. A few studies on the contamination of Guanabara Bay mollusks by heavy metals and chlorinated pesticides have been performed on the mussel *Perna perna* (Brito et al., 2002, Costa et al., 2000). The occurrence of imposex in *Thais haemastoma*, a possible indication of contamination by organotin compounds, was also reported (Fernandez et al., 2002). As far as the authors are aware, no study has been published on the levels of polychlorinated biphenyls (PCBs) and organochlorine pesticide residues (OCPs) in fish collected at Guanabara Bay.
The objective of this study was to determine PCBs and OCPs levels in eight species of fish caught at Guanabara Bay. Since all these species are edible and consumed by the local population, data provided by the present study also add to the evaluation of fish as a source of human contamination by PCBs and OCPs in Rio de Janeiro. Additionally, samples of blubber of two dolphins (*Sotalia fluviatilis*) found dead on Guanabara Bay beaches were also analyzed for the presence of PCBs congeners.

Correspondence to: F. J. R. Paumgartten

MATERIALS AND METHODS

All fish were collected by commercial fishermen from different sites in Guanabara bay, Rio de Janeiro, Brazil, between January and March 1999. The captured fish species (Brazilian popular names in brackets) were as follows: family Centropomidae: *Centropomus parallelus* and *Centropomus undecimalis* ('robalo'); family Mugilidae: *Mugil liza* and *Mugil curema* ('tainha', 'parati'); family Sciaenidae: *Micropogonias furnieri* ('corvina'); family Pomatomidae: *Pomatomus saltatrix* ('anchova'); family Clupeidae: *Sardinella brasiliensis* ('sardinha') and family Trichiuridae: *Trichiurus lepturus* ('peixe-espada'). Fish species were identified by Prof. Dr. Gustavo W. Nunan, from the Department of Ichthyology of the Federal University of Rio de Janeiro, and at least one fish of each species was deposited in the Ichthyologic Collection of the National Museum in Rio de Janeiro. The average weight, length and lipid content of all fish collected for the present study are shown in Table 1.

Table 1. Average weight (g), length (cm) and lipid content (%) of edible fish species caught at Guanabara Bay.

Fish species	Samples x N^{+}	Weight (g)	Length (cm)	Lipid (%)
Pomatomus saltatrix	3x10	216±56	22.7±3.6	0.4
Micropogonias furnieri	3x4	642±91	34.7±1.1	3.0
Trichiurus lepturus	3x4	795±11	90.8±3.4	1.6
Mugil curema	4x10	286±190	24.5±4.8	2.0
Mugil liza	3x4	1056±112	40.9±2.9	1.9
Sardinella brasiliensis	4x10	50±6	14.8±0.4	0.6
Centropomus parallelus	1x4	1230±207	42.0±2.2	3.1
*Centropomus undecimalis**	4x1	713±111	33.5±1.3	1.0

$^{+}$ Samples x (N) = (number of pooled samples) x (number of individual fish per pool); * four individual samples, in this case each sample comprises only one specimen. Values are shown as means ± SD. Each sample was a pool from a number (N) of individuals collected at the same place in the same day.

After being homogenized with a blender, 10 g of each sample of muscle tissue was ground in a mortar and pestle with 15 g of anhydrous sodium sulfate. The dried tissue was Soxhlet-extracted for 8 hours with 200 mL of n-hexane (residue grade).

The lipid extract was then transferred to a graduated flask and the solvent was evaporated to dryness by using a rotavapor. Purification was carried out by loading extracts onto an activated silica column and eluting with n-hexane: dichloromethane (4:1 v/v). Recoveries, determined in spiked samples, were all higher than 81.4 ± 1.6%. PCBs and organochlorine pesticides were analyzed by using a gas chromatograph (GC HP6890 with an auto-sampler) equipped with a ^{63}Ni electron capture detector (ECD). Nitrogen (high purity grade) was the carrier gas at 1 mL/min. Chromatographic parameters were as follows: column temperature: 60 to 190 °C, 25 °C / min, 190 to 280 °C, 5 °C / min, 280 °C (2 min); injector temperature: 250 °C and detector temperature: 320 °C. A capillary column (30 m x 0.32 mm x 0.25 μm) with 5 % phenyl methyl siloxane was used. The limits for residue quantification which were validated for the present method were as follows: PCBs (congeners 28, 52, 101, 138, 153, 180) = 5 ng/g; Hexachlorocyclohexane (HCH), α-HCH and γ-HCH = 5 ng/g, β-HCH = 20 ng/g; hexachlorobenzene (HCB) = 5 ng/g; dieldrin = 5 ng/g; hept-epoxide = 10 ng/g; Dichloro-diphenyl-trichloroethane (DDT), pp`DDD, op`DDT and pp`DDT = 20 ng/g, pp`DDE = 10 ng/g. For statistical computations (mean) a value of one half the limit of quantification of the method was used for concentrations below this limit as suggested by Kushner (1976). Samples (100 g) of blubber of one female and one male dolphin (*Sotalia fluviatilis*) stranded on Guanabara Bay beaches in September 1996 were also analyzed for PCBs levels. PCBs were also extracted with n-hexane and analyzed by CG-ECD. The limit of quantification in this case was 0.06 μg/g for all PCBs congeners. All fish and dolphin samples were stored frozen (-20 °C) until analysis.

RESULTS AND DISCUSSION

Hexachlorocyclohexane isomers (α-, β- and γ-HCH), aldrin, endrin, hexachlorobenzene, heptachlor, heptachlor-epoxide and the DDT derivatives *op'*DDT, *pp'*DDT and *pp'*DDD were not found in any sample analyzed. Dieldrin was detected at a rather low level (10.6 ppb) only in one of the three samples of *M. liza* analyzed. *pp'*DDE was not found in *S. brasiliensis*, *M. curema*, *M. liza*, *T. lepturus*, *C. undecimalis* and *P. saltatrix* (Table 2). Low levels of *pp'*DDE (below 20 ppb), however, were detected in *M. furnieri* and in the only pooled sample of *C. parallelus* analyzed (Table 2).

Concentrations of OCPs in fish collected at Guanabara Bay were rather low and only two long lived residues (dieldrin in one species and *pp'*DDE in two species) were found above the limit of detection of the method. Findings from the present study thus seem to indicate that Guanabara Bay and nearby continental platform waters have not been markedly polluted by these environmentally persistent compounds. Reports that *pp*`DDE, at very low levels, was the only OCP residue found in the blood serum of people living in Rio de Janeiro apparently support this conclusion (Delgado et al., 2002). Low concentrations of several OCPs residues, with a predominance of DDE, have been recently detected in the mussel *P. perna* collected at six sampling places located between the Rio de Janeiro-

Niteroi bridge and the mouth of Guanabara Bay (Brito et al., 2002). It is of note that, in Brazil, DDT and other persistent organochlorine pesticides were banned for agricultural use in 1985, but they remained allowed for use in public health campaigns until 1998 (Brazil, 1985, 1998). In Rio de Janeiro, however, there has been no report on the use of OCPs to control insect-borne diseases for decades (Brazil, 1985). On the other hand, in the Brazilian Amazon region, where DDT was employed to control malaria until mid 1990s, levels of total DDT as high as 500 ppb (wet weight) have been recently found in edible parts of freshwater fish (Torres et al., 2002).

Table 2. Concentrations (mean and range) of *pp*'DDE and polychlorinated biphenyls (PCBs) (ppb or ng/g wet weight) in the muscle tissue of edible fish species caught at Guanabara bay, Rio de Janeiro, Brazil in January-February 1999.

Fish species	**N**	***pp*'DDE**	**PCB congeners** 28	52	101	138	153	180	**Σ PCBs**
P. saltatrix	3	<10.0	**6.3** <5.0-10.6	<5.0	**5.3** <5.0-7.0	**7.2** <5.0-12.5	**5.8** <5.0-9.6	<5.0	**32.5** 3.0-41.2
M. furnieri	3	**14.0** <10-19.7	<5.0	**6.0** <5.0-13.1	**8.6** <5.0-17.2	**18.7** 10.2-34.6	**15.5** 8.0-25.9	**11.1** 5.6-21.6	**72.9** 31.2-115
T. lepturus	3	<10.0	<5.0	<5.0	**6.0** <5.0-13.2	**9.3** <5.0-22.9	**7.2** 5.0-16.8	**5.5** <5.0-11.6	**35.1** 15.0-75.2
M. curema	4	<10.0	<5.0	**7.7** <5.0-13.6	<5.0	<5.0	<5.0	<5.0	**25.1** 15.0-39.5
M. liza	3	<10.0	**8.0** <5.0-17.0	**5.1** <5.0-18.9	<5.0	<5.0	<5.0	<5.0	**27.6** 15.0-49.8
S brasiliensis	4	<10.0	<5.0	**5.2** <5.0-13.2	<5.0	<5.0	<5.0	<5.0	**19.2** 15.0-25.7
C. parallelus	1	**16.2**	**21.8**	**9.0**	**18.7**	**25.2**	**27.4**	**13.6**	**115.8**
C. undecimalis	4	<10.0	**7.7** <5.0-13.6	**5.3** <5.0-13.0	**5.1** <5.0-17.0	**6.1** <5.0-33.3	**11.2** 5.0-22.5	**6.8** <5.0-16.6	**42.1** 15-115.9

Limit of detection: 5 ng/g for PCBs and 10 ng/g for *pp*'DDE. Means and Σ PCBs were calculated by using a value of one half the detection limit of the method for concentrations below this limit. Except for *C. undecimalis* (individual samples), each sample (N) is a pool of 3 (*M. furnieri*, *T. lepturus*), 4 (*M. liza*, *C. parallelus*) or 10 (*P. saltatrix*; *M. curema*, *S. brasiliensis*) individuals collected at the same place in the same day.

PCBs were found at levels somewhat higher than those of OCP residues. As shown in Table 2, PCB congeners were detected in all fish species and in 17 out of 24 samples analyzed. The highest levels of total-PCBs (Σ PCBs), above 50 ppb, were found in the only (pooled) sample of muscle tissue of *C. parallelus* (115.8 ppb), and in *M. furnieri* (72.9 ppb). In both instances, the heaviest congeners, *i.e.* PCBs 138, 153, 180, accounted for a major part of total-PCBs content (Table 2). Intermediate levels of total-PCBs, between 30 and 50 ppb, were found in *P. saltatrix* (32.5 ppb), *T. lepturus* (35.1 ppb) and *C. undecimalis* (42.1 ppb) (Table 2). A major contribution of heavier congeners (PCBs 138, 153, 180) to total-PCBs content was also found in these samples. The lowest levels of total-PCBs, *i.e.* levels below 30 ppb, were found in *M. liza* (27.6 ppb), *M. curema* (25.1 ppb) and *S. brasiliensis* (19.2 ppb). It is of note that only light congeners (PCBs 28 and 52) were found in *S. brasiliensis* (Table 2).

The levels of *pp*`DDE and PCB congeners in fish muscle tissue depend on the contamination of the aquatic environment and also on the mode of feeding of the fish, as well as on the size (weight and length) and reproductive status of the individual (WHO, 1993). Fish take up OCPs and PCBs rapidly from water, and depending on the species and habitat, also from the sediment or food to different degrees (WHO, 1993). Owing to their extremely high lipid:water partition coefficients, and slow rates of biotransformation, *pp*`DDE and PCBs accumulate in fish lipid-rich tissues and have long elimination half-lives. In the case of PCBs, lighter congeners are eliminated more rapidly than those with greater degrees of chlorination. PCBs are also known to accumulate along sea trophic chains and higher ranking predators usually present greater body burdens with an increased proportion of heavier or higher chlorinated congeners (WHO, 1993).

In the present survey, the highest levels of PCBs, including the heaviest congeners, were found in carnivorous fish species (*M. furnieri, C. parallelus T. lepturus, C. undecimalis* and *P. saltatrix*). As shown in Table 2, concentrations of total-PCBs as well as those of PCB153 were particularly high in *M. furnieri* and *C. parallelus*. *M. furnieri* ('anchova') is a benthic fish and a voracious predator that feeds mainly on bottom fauna including macro and microcrustacea, polychaeta, mollusks and fish (Vazzoler, 1975). *C. parallelus* and *C. undecimalis* ('robalo') are both carnivorous fish and higher levels of PCBs in the former species were probably due to its bigger size and higher lipid content (Table 1). On the other hand, much lower levels of PCBs, and only less chlorinated congeners, were found in *S. brasiliensis,* a small fish species with a filtering mode of feeding. In *M. liza* and *M. curema*, which are rather herbivorous species, lighter congeners also accounted for a major part of total-PCBs content. Interspecies variability with regard to PCBs and *pp*`DDE levels may in part be explained by the rank of the fish in the food chain, its habitat and mode of feeding but it may also reflect differences in the size or age of individuals as well as in lipid content of muscle tissue samples (Table 1).

As far as the authors are aware, no study on PCBs levels in biota and sediments from Guanabara Bay has been published. Concentrations of PCB congeners found in this study were much lower than those reported for marine fish from highly polluted regions such as Baltic sea in the 1970s (WHO, 1993). Levels found in fish from Guanabara Bay are still lower than those measured in some fishes (herring and eel) from Baltic sea in 1992/3 (Atuma et al., 1996) and are far below the maximum limit of 0.1 mg/kg fresh weight established for PCB153 by the Swedish National Food Administration (Atuma et al., 1996).

Table 3. Concentrations PCBs congeners (ppm or μg/g wet weight) in the adipose tissue (blubber) of two dolphins (*Sotalia fluviatilis*) found dead on beaches of Guanabara Bay, Rio de Janeiro, Brazil in September 1996.

Sex	**Length (cm)**	**PCB congeners**						
		28	**52**	**101**	**138**	**153**	**180**	**∑ PCBs**
F	84.0	0.07	<0.06	0.08	1.87	0.39	0.21	2.62
M	147.5	0.15	0.11	0.14	6.73	1.08	0.78	8.99

M; male; F: female.

As shown in Table 3, PCBs with a predominance of heavier congeners (PCBs 138, 153 and 180) were also found in the blubber of two dolphins (*S.fluviatilis*) stranded on Guanabara Bay beaches. Levels of PCBs measured in these two dolphins were comparable to or even lower than those generally found in the blubber of small cetaceans from different regions of the world (O`Shea et al., 1980, WHO, 1993, Corsolini et al., 1995).

Our data indicated that concentrations of organochlorine pesticides in edible fish collected at Guanabara Bay are low. PCBs were detected in all fish species analyzed at levels higher than those of *pp*`DDE, the most abundant OCP residue in Guanabara Bay fish. It seems unlikely, however, that PCBs at levels found in the present survey pose any health risk to fish consumers in Rio de Janeiro. The levels of PCBs reported in this paper are 17 to100 times lower than the FDA tolerance (action) levels for total PCBs in fish (2 ppm), and also far below the maximum limit of 0.1 ppm established for PCB153 in fish by the Swedish National Food Administration (Atuma et al, 1996). Since there are no previous data, we cannot know whether PCBs levels are decreasing or increasing in Guanabara Bay biota. Further monitoring should be performed to evaluate temporal trends in concentrations of PCBs in fish from Guanabara Bay.

Acknowledgments. We thank Prof. Dr. Gustavo W. Nunan from the Federal University of Rio de Janeiro for having identified the fish species analysed in this survey. FJRP is the recipient of a research fellowship from CNPq (Brazilian National Research Council).

REFERENCES

Atuma SS, Linder C-E, Wicklund-Glynn A, Anderson O, Larsson L (1996) Survey of consumption fish from Swedish waters for chlorinated pesticides and polychlorinated biphenyls. Chemosphere 33: 791-799.

Brazil (1985) Ministry of Agriculture Directive 329. Diário Oficial da União, Brasília, Section 1, p 12941.

Brazil (1998) Ministry of Health Directive 11. Diário Oficial da União, Brasília, Section 1, p 2.

Brito APX, Brüning IMRA, Moreira I (2002) Chlorinated pesticides in mussels from Guanabara Bay, Rio de Janeiro, Brazil. Mar Pollut Bull 44: 71-81.

Corsolini S, Focardi S, Kannan K, Tanabe S, Borrell A, Tatsukawa R (1995) Congener profile and toxicity assessment of polychlorinated biphenyls in dolphins, sharks and tuna collected from Italian coastal waters. Mar Environ Res 40: 33-53.

Costa M, Paiva E, Moreira I (2000) Total mercury in Perna perna mussels from Guanabara Bay – 10 years later. Sci Total Environ 261: 69-73.

Delgado IF, Barretto HH, Kussumi TA , Alleluia IB, Baggio CA, Paumgartten FJR (2002) Serum levels of organochlorine pesticides and polychlorinated biphenyls among inhabitants of Greater Metropolitan Rio de Janeiro, Brazil. Cad Saúde Pública, 18: 519-524

Fernandez MA, Limaverde AM, Castro IB, Almeida AC, Wagener ALR (2002) Occurrence of imposex in Thais haemastoma: possible evidence of environmental contamination derived from organotin compounds in Rio de Janeiro and Fortaleza, Brazil. Cad Saúde Pública 18: 463-476.

Kushner EJ (1976) On determining the statistical parameters for pollution concentration from a truncated data set. Atmos Environ 10: 975-979.

Lavrado HP, Mayr LM, Carvalho V, Paranhos R. Evolution (1980-1990) of ammonia and dissolved oxygen in Guanabara bay, RJ, Brazil. Proceedings of the Seventh Symposium on Coastal and Ocean Management, Long Beach, California July 8-12, 1991, Volume 4, p. 3234-3245.

O'Shea TJ, Brownell RL, Clark DR, Walker WA, Gray ML, Lamont TG (1980) Organochlorine pollutants in small cetaceans from the Pacific and South Atlanic Oceans, November 1968-June 1976. Pest Monit J 14: 35-46.

Paranhos R, Nascimento S M, Mayr LM (1995) On the faecal pollution in Guanabara bay, Brazil. Fresenius Environ Bull 4, 352-357.

Torres JPM, Pfeiffer WC, Markowitz S, Pause R, Malm O, Japenga J (2002) Dichlorodiphenyltrichloroethane in soil, river sediment, and fish in the Amazon in Brazil. Environ Res 88: 134-139.

Vazzoler G. (1975) Distribuição da fauna de peixes demersais e ecologia dos Sciaenidae da plataforma continental brasileira entre as latitudes 29° 21′ S (Torres) e 33° 41′S (Chuí). Bol Inst Oceanográfico São Paulo, 24: 85-169.

WHO - World Health Organization (1993) Polychlorinated biphenyls and terphenyls (Second Edition). Environmental Health Criteria 140. 682 pp. Geneva.