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ORGANOCHLORINE PESTICIDES RESIDUES AND PCBs IN BENTHIC ORGANISMS OF THE INNER SHELF OF THE SÃO SEBASTIÃO CHANNEL, SÃO PAULO, BRAZIL

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ABSTRACT

Thirty seven benthic samples of the inner shelf area of São Sebastião, Brazil, were collected between April 1994 and August 1998 and analysed for seventeen chlorinated pesticide residues and PCBs congeners. Pesticide residues and PCBs congeners levels were low (ng/g) and predominantly found in the crustacean samples. DDE was the most frequently residue with a maximum of 9,7 ng/g followed by HCHs with maximum of 17,1ng/g. As for the PCBs, the heavier congeners predominate: CB 138,153,170, 180 and 183. Maximum total PCBs was 17,4 ug/g in a crab sample. Higher levels of PCBs are related to feeding habits and local inputs of raw sewage or land runoff. Although EPA and FDA (U.S.A) below the guidelines for human consumption propose these levels, they do show that even in marine areas without intense agricultural or industrial activities these compounds are present at detectable levels.

RESUMO

Trinta e sete amostras de bentos da área interna do Canal de São Sebastião, Brasil, foram coletadas entre Abril de 1994 e Agosto de 1998 e analisadas quanto aos níveis de resíduos de 17 pesticidas organoclorados os congêneres dos PCBs. Os níveis de resíduos de organoclorados e PCBs foram baixos(ng/g) e encontrados com maior freqüência nas amostras de crustáceos. DDE foi o resíduo de pesticida encontrado com mais freqüência apresentado um máximo de 9,7 ng/g seguido dos isômeros de HCHs com um máximo de 17,1 ng/g. No caso dos PCBs os congêneres mais pesados foram os predominantes: CB 138, 153, 170, 180 e 183. O valor máximo de PCBs totais foi de 17,4 ug/g numa amostra de crustáceo. Níveis maiores de PCBs estão associados aos hábitos alimentares e introduções pontuais de esgotos e água de drenagem urbana. Apesar dos níveis observados estarem abaixo dos recomendados para consumo humano pela EPA e da FDA(U.S.A) ,eles demonstram que mesmo em área marinhas costeiras sem agricultura intensiva ou atividades industriais de porte , estes compostos orgânicos persistentes sintéticos (POPS) estão presentes em níveis mensuráveis.

Descriptors: Benthic Biota, PCBs, OCs Residues, São Sebastião Channel, São Paulo, Brazil
Descritores **:** Biota Bêntica, PCBs, Resíduos de OCs, Canal de São Sebastião, Brasil.

INTRODUCTION

Residues of organochlorine pesticides (OCs) and polychlorinated biphenyls (PCBs) are ubiquitous organic contaminants due to their widespread use and their physico-chemical properties. They belong to the group of persistent organic pollutants (POPs) in the environment. Because of and due to their strong cumulative capacities, these classes of compounds are the top priority list of environmental contaminants (UNEP, 1990, 1995).

Although their use is basically on land in agricultural or public health programs in the case of the pesticides, or industrial applications in the case of PCBs, they rapidly reach the marine environment. Land runoff, sewage discharges, river and atmospheric transport rapidly carry these substances to the coastal zones reaching even the polar zones and the deep open ocean. Pesticides residues and PCBs were already found in the Antarctic biota in the mid-seventies by Risebrough *et al.* (1976) and also in the

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deep open ocean (Tanabe, 1988). The lack of sources of pesticides and PCBs in these remote areas has led to conclude that atmospheric transport is the primary pathway for organic pollutants to remote areas like the Antarctic continent (Weber & Montone, 1990) and the open ocean (Tanabe, 1988). Due to their resistance to chemical and microbiological degradation and their strong affinity for lipid tissues, they are biomagnified on the trophic web. Although the use of organochlorine pesticides and PCBs is now practically banned on a global basis, penguins and seals of the Antarctic still show measurable levels of OCs in blood, lipid, muscle tissue etc. (Lara *et al.,* 1990; Inomata *et al.*, 1996).

Although data on residues of organochlorine pesticides and PCBs in marine biota are abundant, few studies are concerned with bottom dwellers benthic organisms. The majority of studies were carried out in mussels, fishes birds or sediments. For the Brazilian coast, in particular, there are few published studies on residues of organochlorine pesticides and PCBs occurrence in benthic animals. Earlier works of Ferreira *et al.* (1980) and Lara *et al*. (1980), done with packed GC columns, provided data on oysters of the locations of Cananéia and Santos, in São Paulo State. Tavares *et al.* (1988) presented OCs data of bivalves and oysters of Todos os Santos Bay in Salvador, Bahia. More recently, the International Mussel Watch Program (IMW) has furnished data along the Brazilian coast (Sericano *et al.* 1995, Taniguchi *et al.,* 1999), as part of the IMW (1994) for Latin and Central America.

Benthic organisms are good indicators of environmental contaminants, because they are bottom dwellers as well as scavengers, so their feeding habits will reflect well the local contamination. As part of a thematic project for the study of oceanographic characteristics of the inner shelf of the São Sebastião area (OPISS) funded by FAPESP – São Paulo State Funding Agency for Research, the residues of OCs pesticides and PCBs were measured in a variety of benthic animals collected between 1994-1998.

The main objectives of the present work are:

1- to assess the occurrence of residues of organochorine pesticides and PCBs in the benthic fauna of the inner part of the São Sebastião Channel and on the continental shelf between the 50 and 100 m isobaths;

2 - to investigate their possible sources;

3 - to verify what species are more prone to accumulate OCs and PCBsStudy Area.

Study Area

The São Sebastião Channel, São Paulo, Brazil (Fig. 1) is an important tourist resorts and oil port located within 23º41' and 23º53,5S and the 45º19' and 45º30' longitude. The channel is 25 km long, with its width varying from 1.9 up to 7.4 km. The narrowest part of the channel is located on its central part. Depths can reach 45 meters but normally vary between 20 -25 meters on the SW and 10-20 meters in the northern part. Furtado (1995) studied the geology of the Channel area as well as the sedimentation patterns and distribution. The benthic fauna and its distribution was described by Pires-Vanin *et al.* (1997).

In addition to the largest oil terminal of the Atlantic Coast of Latin America (DTCS, Petrobrás), the São Sebastião Harbour has other commercial activities as fisheries and tourism. Raw discharges of sewage from the city and residential condominiums and the effluents of the Oil Terminal are released in the Channel in many points.

The main submarine outlet is located at the Araçá Beach, point 10 on Figure 1, with a diffusion point at 8 meters depth in a spot where the currents of the Channel are of low intensity.

The rapid expansion of tourism condominiums in the last ten years has also contributed to intensify the sewage discharges to the Channel Area.

MATERIALS AND METHODS

Sampling

Sampling points are shown on Figure 1. The collection of the marine organisms was done between 1994 and 1998 using different vessels and sampling strategies. The first two samplings were done in April and October 1994.

Points 1-7. An otter trawl net was used making two sweeps of 15 minutes duration on board the R.V. Veliger II of the Oceanographic Institute of University of São Paulo. Samples from point 8 were composed only of *Xiphopenaeus kroyeri* and *Litopenaeus schimitti* bought in February 1998 from a local fisherman operating in the area of the São Francisco Bight on the Channel. For Point 9 a small commercial shrimp-fishing vessel was rented in August of 1998 for taking samples between Cigarras and Enseada Beaches. Fishing net was mesh 2-4, 20 minutes of sweep. Only *Callinectes ornatus* and *Hepatus pudibundus* were selected from this catch. At point 10 on the Araçá Beach only *Callinectes ornatus* were caught manually in 1.5

meter deep water using fish baits on a line (February 1998). At point 11 the sampling area was the rocky bottom surrounding a light house, Farol dos Moleques, on the margin of São Sebastião Channel. Sampling was done in October 1995 by divers of the Centre of the Marine Biology Centre of São Paulo University.

Our sampling criteria was to analyse only adult animals (bigger size), no sex discrimination or sexual maturity assessment was made.

After sampling all organisms were wrapped in hexane pre-cleaned aluminium foil and stored on board in iceboxes or in a refrigerator. On land they were frozen to –15º C before analyses.

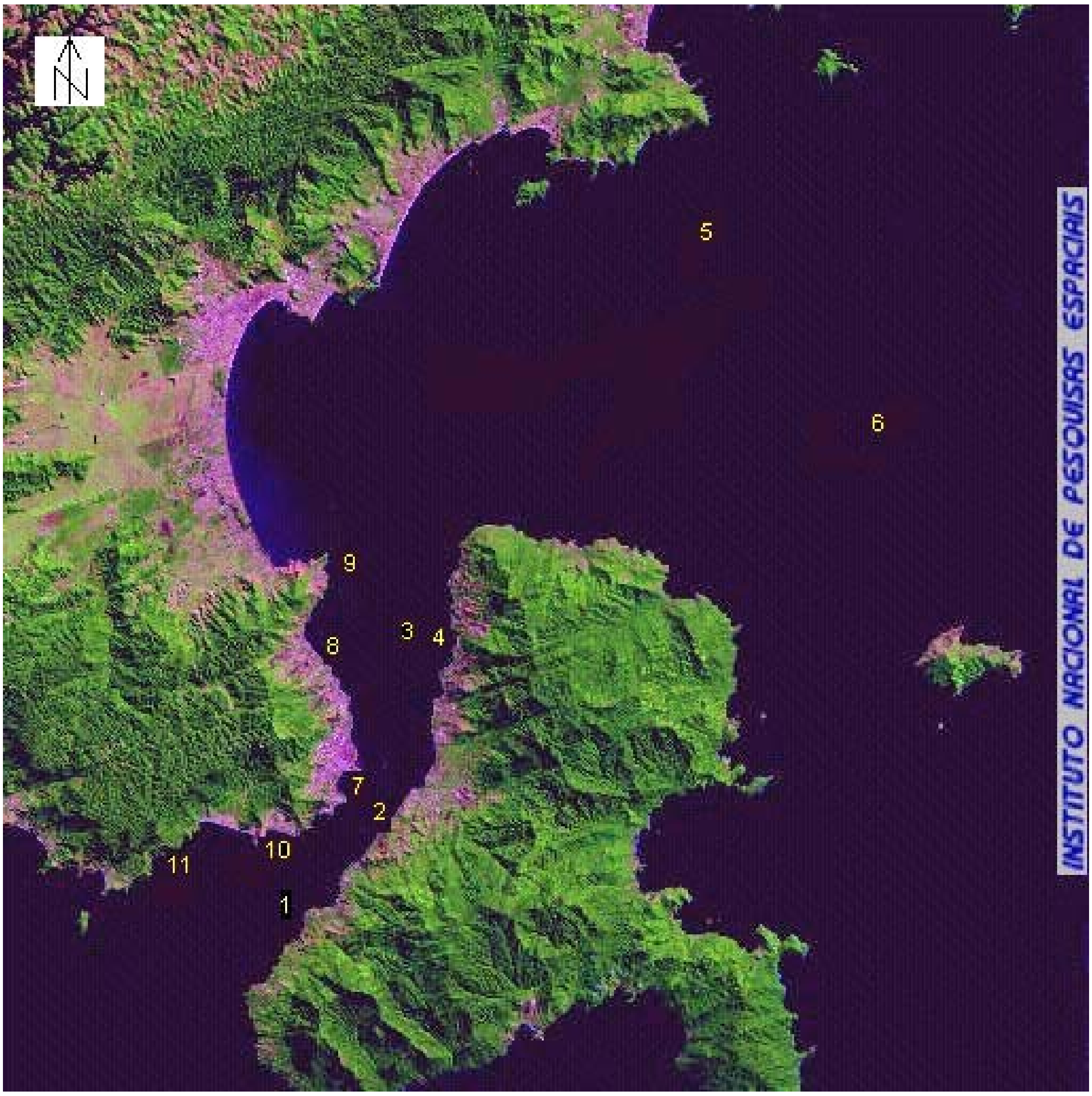

Fig. 1. Sampling stations on the São Sebastião Channel Inner Shelf Area, São Paulo, Brazil.

Sedimentological Description of the Sampling Points

Furtado (1995) and Barcellos & Furtado (1999) give a general description of the sediments of the Channel Area and its surroundings. The sedimentological description of the bottom on our sampling points is given on Table 5.

Analytical Procedures

Analytical protocol followed AOAC (1975)

In order to obtain representative results, 25 organisms from each sample to be analysed were cut in small pieces and well homogenised in a blender. Approximately 10g of sample was mixed with 100 ml acetonitrile, shaked during 2 minutes and was kept still overnight. An aliquot of 50ml was taken and transferred to a separatory funnel contained distilled water, 20 g of sodium chloride and 100 ml of a mixture of petrol ether and methylene chloride (4:1). The separatory funnel was shaked during 2 minutes and after phase separation, the aqueous phase was discarded. The organic phase was dried with sodium sulphate and concentrated to 2-3 ml, using a rotary evaporator at 42ºC. The clean-up was performed by Florisil column (6g) deactivated at 3%. The components of interest, organochlorine pesticides and PCBs were eluted using 100 ml of petroleum ether and methylene chlorine (4:1). Sample extracts were concentrated to 5 ml in n-hexane or isoctane and analysed by gas chromatography equipped with a 25 m, 0.32 mm i.d, 0.32 μm fused-silica column – Ultra 2 and electron capture detector.

The chromatographic conditions were:
Oven: 70ºC, increasing at 40ºC/min to 150ºC and increasing at 2ºC/min to 250ºC with final hold of 15min.
Injector: splitless – 60 ml/min, open after 0.75 min.
Injector temperature: 200ºC
ECD detector temperature: 300ºC
Nitrogen make-up flux: 60ml/min
Helium gas carrier: 2ml/min

The instrument was calibrated by injection of the standard component mixtures at four differents levels.

Validation process

The method was validated using Reference Material of Monaco – IAEA #351 – Fish Homogenate and samples artificially contaminated with organochlorine pesticides as well as PCBs.The results can be appreciated at Table 1 and Table 2 respectively.

Results and Discussion

Organochlorine Pesticides Residues(OCs)

Residues of organochlorine pesticides are given in Table 3. Of the 37 samples analysed for 17 pesticides only 38 % presented detectable levels of these compounds.

Table 1. Accuracy and Precision – Reference Material of MONACO-IAEA # 351 (Fish homogenate).

	Mean N=6 ng/g	Standard deviation	Coefficient variation %	Reference value acceptable ng/g
HCB	0,6	0,13	22	0,5±0,2
γ-HCH	1,5	0,33	22	1,8±0,5
pp-DDE	175	17,23	10	150±40
pp-DDD	21	1,63	8	27±7
pp-DDT	24	1,51	6	33±8
PCB 138	100	6,65	7	110±28
PCB 153	115	5,64	5	130±33
PCB 52	5	1,07	21	5±1
PCB 180	74	6,62	9	88±22

Table 2- Recovery study / quantitation and detection limits.

PCB's N	LOD ng/g	LOQ ng/g	recovery (%) n=6	OC's	LOD ng/g	LOQ ng/g	recovery (%) n=6
18	0,1	0,5	96	α-HCH	0,1	0,3	89
44	0,2	0,7	102	HCB	0,07	0,2	65
52	0,2	0,6	101	β-HCH	0,1	0,5	90
101	0,2	0,5	102	γ-HCH	0,1	0,3	90
118	0,2	0,7	102	δ-HCH	0,1	0,4	82
153	0,1	0,5	104	Heptachlor	0,1	0,3	96
138	0,1	0,5	107	Aldrin	0,1	0,4	91
187	0,1	0,4	102	H.epoxide	0,1	0,4	93
128	0,1	0,5	101	γ-clordane	0,1	0,4	114
180	0,1	0,5	103	α-clordane	0,1	0,3	102
170	0,1	0,5	103	Dieldrin	0,1	0,5	89
				pp-DDE	0,2	0,6	104
				Op-DDD	0,2	0,6	93
				Endrin	0,1	0,4	92
				pp-DDD	0,2	0,7	108
				Op-DDT	0,2	0,6	93
				pp-DDT	0,2	0,6	90
				Mirex	0,1	0,3	92

Among thirteen samples done in April 1994 and October 1995 only *Xiphopeneaus kroyeri* and *Strombus pugilis* showed traces of HCHs (17,1 ng/g as equal levels of α-HCH and γ-HCH and 5,6 ng/g also as equal levels of α-HCH and γ-HCH respectively). Regarding these levels, it is very difficult to suggest which product was accumulated in this region: technical HCH´s where high levels of α-HCH is found or pure HCH´s, richer in γ-HCH.The fact that samples of *Encope emarginata, Luidia senegalensis, Litechinus variegatus, Holothuria* sp and *Nereis nereis* did not show contamination could be related to their feeding habits. One could expect to find residues of OCs pesticides in the blue crab *Callinectes ornatus* which is carnivorous detrivorous and on the other two shrimp species *Litopeaneus schimitti* and *Farfantepenaeus brasiliensis,* which are detrivorous, but those residues were not detected.

The main reason for having found only residues of HCHs in the first sampling trip? is that these isomers are really more ubiquitous in the environment due to their relatively higher volatility compared to the other OCs pesticides (Simonich & Hites, 1995)? Another possibility for the unique presence of HCHs in this area is the small grain size (sandy silt) of the sediments, which also contributed to the retention of organochlorine pesticides. In the samples of July 1997, only *Callinectes ornatus* and *Hepatus pudibundus* showed traces of OCs pesticides in the form of pp'-DDE, with 1,5ng/g and 8.0 ng/g respectively. The fact that only pp'-DDE was found and not DDTs or DDDs is consistent with the metabolism of DDT to DDE by the biota in well-oxygenated waters. According to Brown *et al* (1986 in Lee & Kruse, 1996), DDT is metabolised to DDD and DDE by bacteria. DDT is transformed to DDE in aerobic conditions and to DDD in anaerobic conditions. Lee & Kruse (1996), in a study of the OCs residues in Baltic mussels found that DDT was mainly transformed to DDD near Flensburg, Germany, where the waters are very poor in oxygen. In the São Sebastião Channel, the waters are well flushed and normally the dissolved oxygen levels are close to the saturation values on the surface dropping only 30 % in the bottom (Pires-Vanin *et al.,* 1997). In the sampling of February 1998, measurable levels of pp'-DDE (3.2ng/g and 1.8ng/g) were detected in the two *Callinectes ornatus* samples. In contrast with the samplings of October 1995 and July 1997, at this time the white shrimp (*Litopenaeus schimitti*) sample also presented traces of pp'-DDE (1.4ng/g).

Table 3. Organochlorine Pesticides distribution in marine organisms- ng/g (dry weight).

Sample	Name	Point	Sampling date	HCH total (a)	Aldrin + Dieldrin	Heptachlor/ H. epóxido	α+ γ clordane	pp-DDE	DDT total (b)	Mirex
1. *Xiphopenaeus kroyer* (d)	Seabob	7	April/94	17,1	nd	nd	nd	nd	nd	nd
2. *Loligo* sp(c)	Squid	1	April/94	nd	nd	nd	nd	nd	nd	nd
3. *Strombus pugilis* (d)	Fighting conch	3	April/94	5,6	nd	nd	nd	nd	nd	nd
4. *Nereis virens* (d)	Polychaeta	2	April/94	nd	nd	nd	nd	nd	nd	nd
5. *Litechinus variegatus* (d)	Sea Urchin	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
6. *Callinectes ornatus* (c)	Blue Crab	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
7. *Perna perna* (d)	Mussel	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
8. *Encope emarginata* (d)	Sandollar	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
9. *Luidia senegalensis* (d)	Seastar	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
10. *Litopenaeus schimitti* (d)	White Shrimp	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
11. *Farfantepenaeus brasiliensis* (d)	Pink Shrimp	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
12. *Xiphopenaeus kroyeri* (d)	Seabob	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
13. *Holluturia* sp (d)	Sea cucumber	11	Oct./95	nd	nd	nd	nd	nd	nd	nd
14. *Xiphopenaeus kroyeri* (d)	Seabob	5	July/97	nd	nd	nd	nd	nd	nd	nd
15. *Litopenaeus schimitti* (d)	White Shrimp	5	July/97	nd	nd	nd	nd	nd	nd	nd
16. *Farfantepenaeus brasiliensis* (d)	Pink Shrimp	6	July/97	nd	nd	nd	nd	nd	nd	nd
17. *Hepatus pudibundus* (c)	Box Crab	5	July/97	nd	nd	nd	nd	nd	nd	nd
18. *Callinectes ornatus* (c)	Blue Crab	6	July/97	nd	nd	nd	nd	nd	nd	nd
19. *Portumus spinimanus* (c)	Blotched Swimming Crab	5	July/97	nd	nd	nd	nd	nd	nd	nd
20. *Libinia spinosa* (c)	Spider Crab	6	July/97	nd	nd	nd	nd	nd	nd	nd
21. *Hepatus pudibundus* (c)	Box Crab	6	July/97	nd	nd	nd	nd	nd	nd	nd
22. *Libinia spinosa* (c)	Spider Crab	5	July/97	nd	nd	nd	nd	nd	nd	nd
23. *Callinectes ornatus* (c)	Blue Crab	5	July/97	nd	nd	nd	nd	nd	nd	nd
24. *Hepatus pudibundus* (c)	Box Crab	1	July/97	nd	nd	nd	nd	1,5	1,5	nd
25. *Callinectes ornatus* (c)	Blue Crab	4	July/97	nd	nd	nd	nd	8,0	8,0	nd
26. *Litopenaeus schimitti* (d)	White Shrimp	1	July/97	nd	nd	nd	nd	nd	nd	nd
27. *Xiphopenaeus kroyeri* (d)	Seabob	8	Feb/98	nd	nd	nd	nd	nd	nd	nd
28. *Litopenaeus schimitti* (d)	White Shrimp	8	Feb/98	nd	nd	nd	nd	1,4	1,4	nd
29. *Callinectes ornatus* (c)	Blue Crab	10	Feb/98	nd	nd	nd	nd	1,8	1,8	nd
30. *Callinectes ornatus* (c)	Blue Crab	10	Feb/98	nd	1,5	nd	nd	3,2	3,2	nd
31. *Callinectes ornatus* (c)	Blue Crab	10	Aug/98	nd	nd	nd	nd	2,1	2,1	nd
32. *Callinectes ornatus* (c)	Blue Crab	9	Aug/98	nd	nd	nd	nd	7,7	7,7	nd
33. *Hepatus pudibundus* (c)	Box Crab	9	Aug/98	nd	1,0	nd	nd	3,5	3,5	nd
34. *Hepatus pudibundus* (c)	Box Crab	9	Aug/98	nd	nd	nd	nd	5,9	5,9	nd
35. *Callinectes ornatus* (c)	Blue Crab	9	Aug/98	nd	nd	nd	nd	9,7	9,7	nd
36. *Callinectes ornatus* (c)	Blue Crab	9	Aug/98	nd	nd	nd	nd	3,1	3,1	nd
37. *Hepatus pudibundus* (c)	Box Crab	9	Aug/98	nd	nd	nd	nd	7,7	7,7	nd
Detection limit				0,1	0,1	0,1	0,1	0,2	0,2	0,1

(a) Total HCH (α+β +γ +δ HCH)
(b) Total DDT (op`DDD+pp`DDD+op`DDT+pp`DDT+ pp`DDE)
(c) Carnivorous
(d) Detrivorous

Finally, in the last sampling carried-out in August 1998, the *Callinectes ornatus* and *Hepatus pudibundus* were specifically examined because they had presented residues more frequently than the other species, being pp'-DDE found in all specimens. The *Callinectes ornatus* were all from Araçá Beach (Point 10 on Fig. 1) where there is continuous sewage discharge from the municipal sewage outlet located at 8 meters depth in a position where currents are not very intense. At Point 9, the region between Cigarras and Ensued Beach, only *Hepatus pudibundus* were sampled. This area is also impacted by sewage discharge (Zanardi *et al.,* 1999).

In a study done with DDT levels in samples of fishes and crustaceans from New Jersey,USA, Kenish *et al*. (1996) also found the highest levels of total DDT in the blue crab samples. Crabs have a mixed diet composed of detritus, phyto and zooplankton (suspended material) and benthic species as polychaetes. They can be carnivores as well and in the case of the blue crabs, also cannibals. The feeding habits of the Brazilian brachyuran crabs of the northeastern coast of São Paulo were described by Petti *et al.* (1996). After these authors, *Callinectes ornatus* was found to feed on carnivores and subsurface deposit-feeders, Hepatus pudibundus also feed on carnivores and deposit-feeders both from surface and subsurface.

In general our data agrees with the results of the macrobenthic fauna of the eastern coast of Mauritania, Africa found by Everaarts *et al.* (1993).

Polychlorinated Biphenyl's (PCBs)

The PCB data is shown on Table 4 and the majority of species analysed presented levels below the detection limit of the method. The exceptions, as in the case of the OCs pesticides, are the crustacean samples.

Callinectes ornatus, Hepatus pudibundus, Libinia spinosa and *Portunus spinimanus* presented detectable PCBs congeners. The highest level was found in Callinectes ornatus from sample number 35, where the total PCBs were 17,4 ng/g. Although *Libinia spinosa* and *Portunus spinimanus* have different feeding habits than *Callinectes ornatus* and *Hepatus pudibundus*, feeding mostly on surface animals such as sessile and mobile deposit feeders, and not appearing to forage in the sediments (Petti *et al.,*1996), all species presented PCBs residues in their tissues. The levels in São Sebastião are typical of not heavily PCBs polluted zones. Porte and Albaigés (1993) presented data for the crab Macropipus tuberculatus from a polluted industrialised zone (Barcelona) and a clean zone (St Carlos). The total PCBs were 90.5ng/g in Barcelona and 23ng/g in St Carlos. The highest levels of PCBs contamination in marine biota and sediments are always associated with heavy industrial and shipping activities as well as sewage outlets (IMW, 1994).

In our study the highest levels of PCBs where found at the Araçá (Point 10, Fig 1) and Cigarras Beach (Point 09). Both spots receive sewage discharges or small streams, which carry sewage and debris. The granulometric distribution of the sediments, with predominance of sandy silt, also contributes to the accumulation of organic compounds on these areas. Among the species analysed, the crabs *Callinectes ornatus* and *Hepatus pudibundus* presented the higher incidence of both residues of organochlorine pesticide and PCBs. The feeding habits and also the type of bottom sediment influences the distribution of these species. In general they have a very mixed diet which can contribute to the higher level of organic contaminants found.

The bottom area of the Channel is a mixed environment: sediments are heterogeneous, varying from very fine clay up to coarse sand, and present highly variable percentages of biodetritus and organic matter (Furtado, 1995). Sandy sediments with low clay predominate but muddy sediments can also be found in some areas as well. (Barcellos & Furtado, 1999).

The *Calinectes ornatus* (blue crab) for instance is found in all types of sediments of the Channel area being one of the dominant species on the whole area . On the other hand *Hepatus pudibundus* (box crab) is restricted to softer sediments with higher clay content (Pires-Vanin, personal communication)*.

Although these two crab's species presented the highest levels of organic contaminants, the PCBs levels are far from an alarming environmental pattern for human consumption. The value of 17.3ng/g for total PCBs is low when compared to the guideline value of 500ng/g proposed by the National Academy of Sciences (USA) and to the 2000ng/g of the Food and Drug Administration for total PCBs in fish muscle. All the others species showed very low contamination by residues of organochlorine pesticides or PCBs.

At Point 4, in the North-eastern part OT São Sebastião Island (Sample 25), relatively high levels of total PCBs (11,8ng/g) were found in the blue crab sample, *Callinectes ornatus*, were also found. Even though there is no intense industrial or human activities on this spot there are four small streams flowing into the area, which can carry domestic sewage and other debris with PCBs.

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(*) Pires-Vanin, A. M. S. 2000. Instituto Oceanográfico da Universidade de São Paulo.

Table 4. PCBs distribution in marine organisms - ng/g (dry weight).

Sample	Name	Point	Sampling Date	**CB-118**	CB-153	CB-138	CB-187	CB-128	CB-180	CB-170
1. Xiphopenaeus kroyer (d)	Seabob	7	April/94	nd	nd	nd	nd	nd	nd	nd
2. Loligo sp(c)	Squid	1	April/94	nd	nd	nd	nd	nd	nd	nd
3. Strombus pugilis (d)	Fighting conch	3	April/94	nd	nd	nd	nd	nd	nd	nd
4. Nereis virens (d)	Polychaeta	2	April/94	nd	nd	nd	nd	nd	nd	nd
5. Litechinus variegatus (d)	Sea Urchin	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
6. Callinectes ornatus (c)	Blue Crab	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
7. Perna perna (d)	Mussel	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
8. Encope emarginata (d)	Sandollar	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
9. Luidia senegalensis (d)	Seastar	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
10. Litopenaeus schimitti (d)	White Shrimp	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
11. Farfantepenaeus brasiliensis (d)	Pink Shrimp	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
12. Xiphopenaeus kroyeri (d)	Seabob	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
13. Holluturia sp (d)	Sea cucumber	11	Oct/95	nd	nd	nd	nd	nd	nd	nd
14. Xiphopenaeus kroyeri (d)	Seabob	5	July/97	nd	nd	nd	nd	nd	nd	nd
15. Litopenaeus schimitti (d)	White Shrimp	5	July/97	nd	nd	nd	nd	nd	nd	nd
16. Farfantepenaeus brasiliensis (d)	Pink Shrimp	6	July/97	nd	nd	nd	nd	nd	nd	nd
17. Hepatus pudibundus (c)	Box Crab	5	July/97	nd	5,4	3,2	2,0	nd	1,7	nd
18. Callinectes ornatus (c)	Blue Crab	6	July/97	nd	nd	nd	nd	nd	nd	nd
19. Portumus spinimanus (c)	Blotched Swimming crab	5	July/97	nd	1,0	nd	nd	nd	nd	nd
20. Libinia spinosa (c)	Spider Crab	6	July/97	nd	2,5	1,5	nd	nd	nd	nd
21. Hepatus pudibundus (c)	Box Crab	6	July/97	nd	3,6	1,4	nd	nd	nd	nd
22. Libinia spinosa (c)	Spider Crab	5	July/97	nd	5,8	1,6	nd	nd	nd	nd
23. Callinectes ornatus (c)	Blue Crab	5	July/97	nd	nd	nd	nd	nd	nd	nd
24. Hepatus pudibundus (c)	Box Crab	1	July/97	nd	1,3	nd	nd	nd	nd	nd
25. Callinectes ornatus (c)	Blue Crab	4	July/97	nd	5,5	3,3	1,3	nd	1,7	nd
26. Litopenaeus schimitti (d)	White Shrimp	1	July/97	nd	nd	nd	nd	nd	nd	nd
27. Xiphopenaeus kroyeri (d)	Seabob	8	Feb/98	nd	nd	nd	nd	nd	nd	nd
28. Litopenaeus schimitti (d)	White Shrimp	8	Feb/98	nd	nd	nd	nd	nd	nd	nd
29. Callinectes ornatus (c)	Blue Crab	10	Feb/98	nd	nd	nd	nd	nd	nd	nd
30. Callinectes ornatus (c)	Blue Crab	10	Feb/98	3,1	3,1	3,6	3,2	nd	nd	0,7
31. Callinectes ornatus (c)	Blue Crab	10	Aug/98	nd	4,1	4,5	nd	nd	nd	nd
32. Callinectes ornatus (c)	Blue Crab	9	Aug/98	nd	5,1	3,2	1,1	nd	nd	nd
33. Hepatus pudibundus (c)	Box Crab	9	Aug/98	nd	3,2	2,4	0,8	nd	0,8	nd
34. Hepatus pudibundus (c)	Box Crab	9	Aug/98	nd	3,3	2,4	0,9	nd	nd	nd
35. Callinectes ornatus (c)	Blue Crab	9	Aug/98	nd	7,7	5,4	1,6	nd	2,7	nd
36. Callinectes ornatus (c)	Blue Crab	9	Aug/98	nd	5,1	3,21	1,1	nd	1,4	nd
37. Hepatus pudibundus (c)	Box Crab	9	Aug/98	nd	5,6	4,3	1,3	nd	1,9	nd
Detection limit				0,2	0,1	0,1	0,1	0,1	0,1	0,1

(c) Carnivorous

(d) Detrivorous

As the sediments at point 5 and 6 are predominantly sandy, which do not allow the organic material accumulation, the samples from these points presented low levels of PCBs in *Hepatus pudibundus* and *Libinia spinosa*. At both points, PCBs were below the detection level in the *Callinectes ornatus* samples.

As important as the total PCBs levels is their relative distribution by congeners. . The toxicity of each congener and its resistance to degradation vary widely. The PCB congeners profile in the marine biota can vary widely depending on the trophic level and feeding strategies. The lighter congeners with 3 to 4 chlorine atoms, such as CB-18, 52 and 44, tend to remain in the water column, due to their higher solubility, whereas the heavier congeners with 4 to 5 chlorine atoms tend to bind to particulate material and the biota. Consequently mussels, which are basically filter feeders, present lighter congeners as tetrachlorobiphenyls (PCBs 44,49,52) and the pentachlorobiphenyl (PCB 118) in their tissues.

The heavier congeners of PCBs, which contain more chlorine atoms, are less soluble in seawater; therefore they tend to have a preferential association with particles of sediments or detritus. PCBs are associated with all sizes of particles but their concentration decreases as the particle size increases (Holsen et al., 1991)

Figure 2 shows the relative distribution of PCBs congeners of our samples. The lighter congeners CBs: 18,44,52,101 are virtually absent. Only the heavier CBs: 118,138,153,170,180, 183, and 138 were detected. PCB-153 is the main component followed by 138 and 187. Only heavier PCBs congeners were found in all crustacean samples and none of the lighter congeners were observed in the mussel samples. This kind of distribution suggests a source contribution of commercial mixtures similar to Arochlor 1254 and 1260.

It is also worth mentioning that the samples of *Libinia spinosa* (samples 21 and 22) presented lower total PCBs levels (4.0 and 7.4ng.g) than those of Hepatus pudibundus (17.4ng/gmax). In *Callinectes ornatus* (10,8ng/gmax) only CB138 and 153 were present. In a similar way, *Portumus spinimanus* presented only traces of PCBs (1ng/g) represented by a single congener, CB 153.Our PCB profiles for the crustaceans agrees very well with the results of Porte and Albaigés (1993) for crustaceans on the Alicante Coast of Spain. The hexa (PCB-153/138) and pentachlorobiphenyls (PCB-170/180/187) represent 47% and 30 % respectively of the total PCBs present in the crab *Macropipus tuberculatus*. Knickmeyer and Steinhardt (1990) in the German Bight also reported a similar pattern of heavy congeners for the eremite crab (*Pagurus bernhardus*).

This is also consistent with the feeding pattern of crustaceans which are detrivorous and carnivorous. The feeding habits of crustaceans depends on the availability of local food sources and on the size of the organisms. According to Iannuzzi *et al.* (1996) blue crabs smaller than 31 mm feed on algae, detritus and bivalves. The bigger ones, between 31 and 60 mm prefer mussels like bivalves and gastropods. Those bigger than 60 mm feed on mussels and other crustaceans. Our samples of *Callinectes ornatus* were around 30 mm, and the *Hepatus pudibundus* and *Libinia spinosa* crabs were all greater than 50 mm. As the feeding strategy changes to higher trophic levels, the biomagnification of PCBs also increases. Nevertheless, the levels of PCBs found in *Callinectes ornatus* and *Hepatus pudibundus* were not significantly different, even with the organisms having quite different sizes. It is worth mentioning that *C. ornatus* is more abundant in São Sebastião Channel, especially at the coastal zone, than *H. pudibundus*. Both species are more adapted to living in clay sediments. According to (Amâncio, personal communication)*, Tararam *et al.* (1993) and Petti (1997), who studied feeding habits of different crustaceans from the São Sebastião and Ubatuba region, the diet of the 25 mm-long *C. ornatus* is more diversified than that of *H. pudibundus*, and includes fish, crustaceans, polychaetes and shell fragments. Considering that the specimen of *H pudibundus* studied had a size of 50 mm, its diet is composed mostly of crustaceans, followed by fish in minor amounts. Indeed, *C. ornatus* is considered more a opportunistic a predator than *H. pudibundus*, which is more selective (Pires-Vanin, personal communication)**.

When comparing levels of PCBs and pesticide residues in different organisms, one has to take into account a series of factors such as lipid content, depuration taxes through metabolism, enzymatic activities and differences in congener assimilation due to diet or interaction with the sediments. In the case of benthic animals there is always an additional factor due to a strong interaction with the bottom sediments. Tracey & Hansen (1996) made a statistical study using the Biota Sediment Accumulation Factor (BASF's). It was observed that there is a substantial difference in the accumulation of organic substances in benthic organisms from different types of bottom and feeding habits. For PCBs, for instance, bivalve molluscs have the higher accumulation factors, followed by polychaetes and crabs.

(*) Amâncio, I. M. 2000. Instituto Oceanográfico da Universidade de São Paulo.

(**) Pires-Vanin, A. M. S. 2000. Instituto Oceanográfico da Universidade de São Paulo.

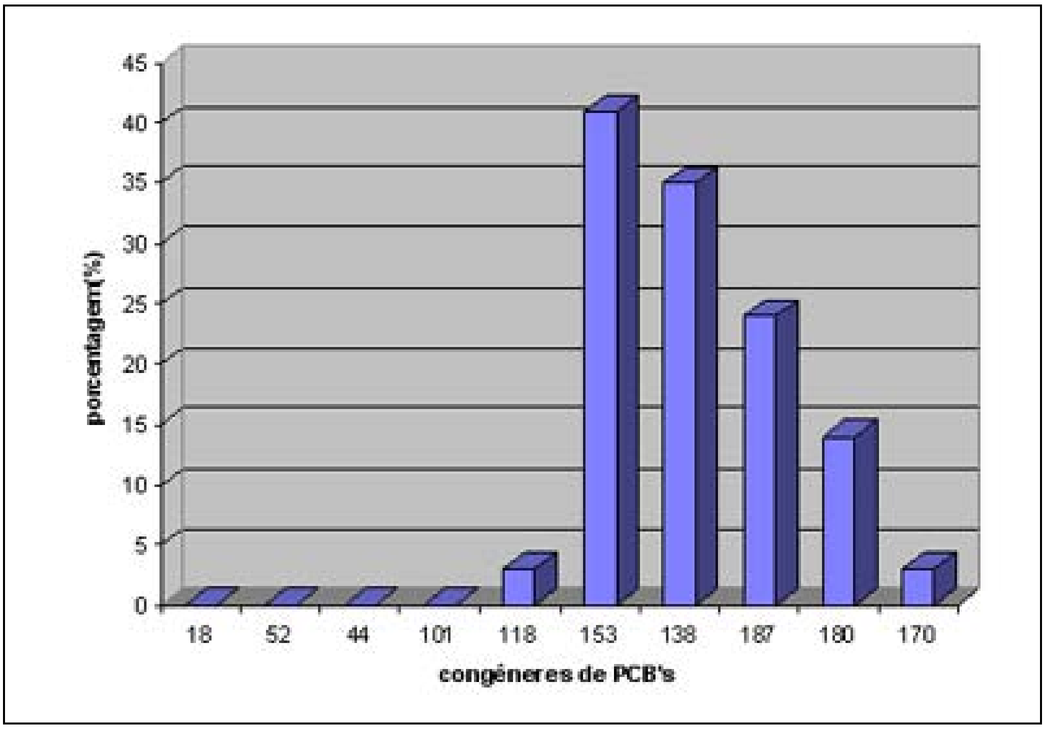

Fig. 2. Relative Distribution of PCBs Congeners in São Sebastião Benthic Samples.

Another important fact is that the metabolism of PCBs in crabs leads to the complete degradation of the lighter congeners and the bioaccumulation of the heavier ones (Porte & Albaigés, 1993). Particularly, the heavier congeners with chlorine atoms on the 2,3 and positions in one or both rings present a very low metabolic degradation. In contrasts the other congeners, specially the ones with a hydrogen atom close to meta and para are completely metabolised.

Seasonal variation of PCBs content in female crabs were also observed by Porte & Albaigés (1993) due to reproduction cycles where there is considerable variation in the frequency of feeding and the lipid content.

Conclusions

Of the organochlorine pesticide residues, DDE was the compound more frequently found in our benthic samples. This is consistent with the pattern found in well-oxygenated waters all over the world, as is the case of the São Sebastião area. DDE was found mainly in the crabs and shrimps of the area due to their diet.

The highest concentrations were found on the Araça and Cigarras Beaches because of a systematic introduction of pesticide residues and PCBs from domestic and port sewage and pluvial waters. PCBs residues were found mostly in the crab samples and the congener distribution showed a predominance of the heavier CBs as 138, 153, 170, 180 and 183. This kind of distribution indicates mixed source contributions of Arochlor 1254 and 1260.

Differences in PCBs distribution in different species such as *C. ornatus* and *H. pudibundus* are associated to different type of bottom sediments as well as differences in their feeding habits and probably metabolic differences in PCBs bio-transformations.

The levels of both pesticide residues and PCBs are not alarming being well below the guidelines for fish ingestion by human recommended by the National Academy of Sciences of USA (500 ng/g) and the Food and Drug Administration of USA (2000ng/g).

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REFERENCES

AOAC - Official Methods of Analysis .1975; 12^{th} ed. 29001 - 29011 - 29014 - 29015 - 29018 – 28027.

Barcellos, R. L. &, Furtado,V. V. 1999. Processo sedimentar atual e a distribuição de carbono e nitrogênio orgânicos no Canal de São Sebastião (SP) e plataforma interna adjacente Rev. bras. oceanogr., 47(2):207-221

Everaarts, J. M.; Heersters, R.; Fischer, C. V. & Hildebrand, M. T. J. 1993. Baseline levels of cyclic pesticides and PCB's in benthic invertebrates from the continental slope of the Banc d'Arguin (Mauritania). Mar. Pollut. Bull., 26(9):515-521.

Ferreira, J. R.; Prado Filho, L. C. & Castro, L. B. A. 1980. Alguns dados sobre poluição por pesticidas clorados na região lagunar estuária de Cananéia. Bolm Inst. Pesca, S Paulo, 7:103-109.

Furtado, V. V. 1995. Sedimentação quaternária no Canal de São Sebastião. Publção esp. Inst. oceanogr. S Paulo, 11:27-35.

Furtado, V. V.; Bonetti, J. F.; Rodrigues, M. & Barcellos, R. L. 1998. Aspectos da sedimentação no Canal de São Sebastião. Relat. téc. inst. Oceanogr., 43:15-41.

Holsen, T. M.; Noll, K.; Liu, S. P. & Lee, W. J. 1991. Dry deposition of polychlorinated-biphenyls in urban areas. Environ Sci. technol., 25(6):1075-1081.

Iannuzzi, T. J.; Harrington, N. W.; Shear, N. M.; Curry, C. L.; Carlson-Lynch, H.; Henning, M. H.; Su, S. H. & Rabbe, D. E. 1996. Distributions of key exposure factors controlling the uptake of xenobiotic chemicals in an estuarine food web. Environ. Toxicol. Chem. 15(11):1979-1992.

Inomata, O. N. K.; Montone, R. C.; Lara, W. H.; Weber, R. R & Toledo, H. H. B. 1996. Tissue distribution of PCBs and organochlorine pesticides in antarctic penguins. Antarctic. Sci., 8(3):253-255.

IMW. International Mussel Watch Project – Initial Implementation Phase - Final Report. 1994. Woods Hole Oceanographic Institution Coastal Research Center. 63 p.

Kennish, M. J. & Ruppel, B. 1996. E.DDT contamination in selected estuarine and coastal marine finfish amd shellfish of New Jersey. Archs environ. Contamin. Toxicol, 31(2):256-262.

Knickmeyer, R. & Steinhardt, H. 1990. Concentrations of organochlorine compounds in the hermit crab *Pagurus bernhardus* from the German Bight, December 1988 - May 1989. Neth. J. Sea Res., 25(3):365-376.

Lara, W. H.; Barreto, H. H. & Inomata, O. N. K. 1980. Níveis de BHC e DDT em peixes, camarões e ostras do litoral de Santos, Estado de São Paulo. Rev. Inst. Adolpho Lutz, 40(1):29-33.

Lara,W. H.; Barreto, H. H.; Inomata, O. N. K.; Montone, R. C. & Weber, R. R. 1990. Organochorine residues in antarctic penguins. Pesq. antárt. bras., 2(1):1-6.

Lee, K. M. & Kruse, O. W. 1996. The pattern of organochlorines in mussels *Mytillus edulis* L. from the South West Baltic Sea. Archs. Envirion. Contamin. Toxicol. 31:68-76.

Petti, M. A.; Nonato, E. F. & Paiva, P. C. 1996. Trophic relationships between polychaetes and brachyuran crabs on the southeastern Brazilian coast. Rev. bras. oceanogr., 44(1):61-67.

Petti, M. A. 1997. Papel dos crustáceos braquiúros na rede trófica da plataforma interna de Ubatuba, São Paulo (Brasil). Nerítica, (11):123-137.

Pires-Vanin, A. M. S. P.; Corbisier, T. N.; Arasaki, E. & Moellmann, A. M. 1996. Composição e distribuição espaço temporal da fauna bêntica no Canal de São Sebastião. Relat. téc. inst. oceanogr., 41:29-46.

Porte, C. & Albaigés, J. 1993. Bioaccumullation patterns of hydrocarbons and polychlorinated biphenyls in bivalves, crustaceans and fishes. Archs environ. Contamin., Toxicol., 26(3): 273-281.

Risebrough, R. W.; Walker, I. W.; Schmidt, T. T.; De Lappe, B. W. & Connors, C. W. 1976. Transfer of chlorinated biphenyls to Antarctica. Nature (London). 264:738-739.

Sericano, J. L.; Wade, T. L.; Jackson, T. J.; Brooks, J. M.; Tripp, B. W.; Farrington, J. W.; Mee, L. D.; Readmann, J. W.; Villeneuve, J. P. & Goldberg, E. D. 1995. Trace organic contamination in the Americas: An overview of the U.S. National Status & Trends and the International Mussel Watch Programmes. Mar. Pollut. Bull., 31(4):214-225.

Simonich, S. L. & Hites, R. A. 1995. Global distribution of persistent organochlorine compounds. Science, 269:1851-1854.

Tanabe, S. 1988. PCBs problems in the future: foresight from current knowledge. Environ. Pollut., 50:5-28.

Taniguchi, S.; Montone, R. C.; Weber, R. R.; Lara, W. H. & Sericano, J. L. 1999. The International "Mussel Watch" Program in Brazil: assessment of coastal marine pollution. Mar. Pollut. Bull.,

Tararam, A. S.; Y Wakabara, Y. & Equi, M. 1993. Hábitos alimentares de onze espécies da megafauna bêntica da plataforma continental de Ubatuba, SP. Publção esp. Inst. oceanogr., S Paulo, (10):159-167.

Tavares, T. M.; Rocha, V. C.; Porte, C.; Barcelo, D. & Albaigés, J. 1988. Application of the mussel watch concept in studies of hydrocarbons, PCBs and DDT in the Brazilian Bay of Todos os Santos (Bahia). Mar. Pollut. Bull., 19(11):575-578.

Tracey, G. A. & Hansen, D. J. 1996. Use of Biota-Sediment accumulation factors to assess similarity of nonionic organic chemical exposure to benthically-coupled organisms of differing trophic mode. Archs environ. Contamin. Toxicol., 30:467-475.

UNEP/GESAMP. 1990. The State of the Marine Environment. Quênia, UNEP/Nairobi. 156p.

UNEP/OCA/LBA/IG.2/7 Programa de ação global para proteção do meio ambiente marinho frente às atividades baseadas em Terra. 46p.

Weber, R. R. & Montone, R. C. 1990. Distribution of organochlorides in the atmosphere of the South Atlantic Oceans. In: Kurtz, D.A. ed. Long range transport of pesticides. Chelsea, Lewis Publishers. p.185-197.

Zanardi, E.; Bícego, M. C.; Miranda, L. B. & Weber, R. R. 1999. Distribution of petroleum aromatic hydrocarbons in seawater and sediments of the São Sebastião Channel, São Paulo, Brazil. Mar. Pollut. Bull., 38(4):262-267.

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