

Occurrence of Organochlorines Contaminants in Coastal Fish from Sepetiba Bay: Levels and Human Health Repercussions

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(Received: 20 July 2013)

Accepted: 15 August 2013)

Abstract: The aim of this study was to survey levels of polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-*p*-dioxins (PCDDs) in white mullet (*Mugil curema*), common snook (*Centropomus undecimalis*), and acoupa weakfish (*Cynoscion acoupa*), collected at Sepetiba bay, Rio de Janeiro, Brazil, March-August 2013. PCBs and PCDD/Fs were determined by High Resolution Gas Chromatography/High Resolution Mass Spectrometry (HRGC/HRMS) as stated by the US EPA 1613B, 1668B, and 8290A methods. The concentration of total PCBs ranged from 0.589688 ~ 0.6981629 pg-WHO-TEQ/g ww and PCDDs/PCDFs ranged from 0.134037 ~ 0.242573 pg-WHO-TEQ/g ww. The concentrations of these contaminants on fish species currently appear to fall below critical values, and the dietary consumption of these species did not represent a risk for human health. However, seeking to avoid future problems, systematic monitoring can prevent complications to the environment, marine wildlife and public health impacts.

Keywords: organochlorine contaminants, fish, Sepetiba bay

INTRODUCTION

Persistent Organic Pollutants (POPs) are a class of organic compounds regularly used in the industry as chemical conductors, for electrical insulator systems, in the production carbonless copy paper, and for pesticides [1,2]. Many POPs are used in industrial processes and in the production of a of products such as solvents, polyvinyl chloride, and pharmaceutical [3, 4]. Due to their persistency, the distribution and recirculation in the environment frequently lasts for a long period of time [5]. They are chemically stable, have low solubility in water, and have been shown to be accumulated in food web [6, 7].

As highlighted within the POPs, polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs), and polychlorinated dibenzo-*p*-dioxins (PCDDs) are greatly lipophilic persistent

organochlorines contaminants proficient to hold out degradation and with the capability to bioaccumulate through the food chain [8], and constitute groups of relevant persistent organic pollutants with chronic toxicity to humans and biota [9-11]. It has been reported recently that PCDD/F owns the toxicity of endocrine disrupting [12]. Those isomers with chlorines substituted in the 2,3,7,8 positions are thought to pose a risk to human health due to their toxicity, carcinogenic potency and potential effects on animal reproductive and immunological systems [11, 13,14].

In relation to PCDD/Fs, the literature points the quantitative of 75 different PCDDs and 135 PCDFs, that fact diverge from each other in the number and positions for the chlorine atoms [15].

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chlorine replacement in the (2, 3,7,8-) positions are regarded to be toxicologically important [10]. Concerning to PCBs, there are 209 possible congeners, but even the technical mixtures of have just a fraction of the total potential number. Some PCBs are called dioxin-like (co-planar/non-ortho) PCBs. These congeners don't have any or have only one chlorine atom (mono-ortho-PCBs) in the ortho-position to the

carbon-carbon bond between the two benzene rings. Nearly 120 of PCBs are present in products such as Aroclor 1254, Aroclor 1260 and Chlophen A60 [16]. Ballschmiter and Zell [17] suggested a simple numbering structure of the PCB congeners, providing each congener a number since one to Thus, PCBs have two benzene rings involved to each other, through 1-10 chlorine atoms as substituents (Figure 1).

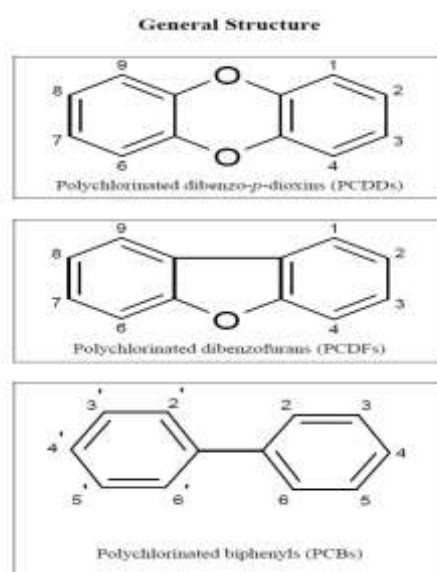


Figure 1. Generalised structure of dioxins (PCDDs), furans (PCDFs) and PCBs

Human chronic exposition to those exceedingly lipophilic and persistent compounds via food chain has induced the accumulation of both parent compounds and its metabolites in lipid rich tissues such as adipose tissues and human breast milk [18-20]. One possible exposure pathway by which humans and other upper trophic level species can be exposed to PCDD/Fs and PCBs is through consumption of dietary fish [21-24], due to its accumulation in the tissues of humans and animals [25, 26]. These chemicals consist of pesticides or industrial chemicals, and by-products of industrial processes [2].

Fish accumulate chemical substances either from the surrounding environment or from their diet [11, 22,24,27-29]. Humans are consumers of

fish, and exposure valuations now routinely consider fish ingestion as a potential route of human exposure to chemicals in the environment [6, 10,30,31]. To assess the risk of dioxins in the general population and to determine the time trends, regular testing of levels of these in environmental food chain is very important for evaluating dioxins concentrations that pose a potential health hazard [7, 14]. The immediate objective of monitoring studies is to obtain information about the levels of contaminants and congener profiles actively identifying potential for reducing human exposure [6,10].

The evaluation of the impact of pollution on fish has therefore to be undertaken on a holistic perspective, considering, likewise, the potential of

pollutants to interfere with their ability to recuperate from stress caused by other environmental forces [32, 33]. The ingestion of dioxin-contaminated foods contributes to more 90% of the total human exposure, with fish and seafood being recognized amongst the main contributors [21]. On the other hand, saltwater fish are a significant component of a healthy diet, containing low levels of saturated fats and high levels of polyunsaturated fatty acids beneficial to the prevention of coronary heart disease and also providing other dietary benefits like being a source of valuable protein, vitamins, and minerals (including magnesium, calcium, fluorine, iodine, selenium). However, fish reservoir harvested from polluted waters may also contain harmful chemicals in concentrations that pose a potential health hazard [34].

The white mullet, *Mugil curema* (Valenciennes, 1836) is a pelagic schooling fish in the family *Mugilidae* [35]. It is a commercially important fish throughout the world, also representing a substantial recreational fishery [36]. The common snook, *Centropomus undecimalis* (Bloch 1792) is a demersal species that spends much of its life in estuaries, but migrates to ocean inlets or just offshore to spawn. It predaceous and occupies high levels in the trophic web [37]. *Centropomid* fishes are commercially important and widely used in aquaculture as a food fish and also as recreational fish [38]. The acoupa weakfish, *Cynoscion acoupa* (Lacepède 1801), is a large, ecologically and economically important genus of marine fishes in the family *Sciaenidae* found throughout tropical and subtropical coastal waters of the New World.

Cynoscion are important predators in coastal ecosystems and have relatively streamlined, elongate bodies, large mouths and sharp teeth, including well-developed canines. The genus is highly valued as a human food source and is actively exploited throughout its range [39].

The aim of this study was to determine the concentration levels of PCDD/Fs and PCBs in tissue samples of *Mugil curema* (Valenciennes 1836), *Centropomus undecimalis* (Bloch 1792) and *Cynoscion acoupa* (Lacepède 1801), collected March to August 2013 at Sepetiba Bay situated in the southern Atlantic Coast of Rio de Janeiro Brazil.

MATERIALS AND METHODS

Study site

Sepetiba Bay is located in the State of Rio de Janeiro, Brazil, (22° 55' and 23° 05'S / 43° 40' and 44° 40'W) is a body of brackish and saline waters, with a 520 km² area housing a wide range of habitats including mangroves, sandbanks, and small estuarine areas (Figure 2). Depth overall is below 5 m, and waters are rich in organic nutrients from continental drainage; bottom is muddy. This region presents its northern and eastern area limited by the continent, a sandbank vegetation on southern limit, and Ilha Grande Bay on the west. Its greatest length is 42.5 kilometres from east to west and its greatest width is 17.2 kilometres from north to south, with a perimeter of 122 km. The bay plays an important role in aquatic ecology, mainly for juvenile fishes that use the area as a rearing ground.

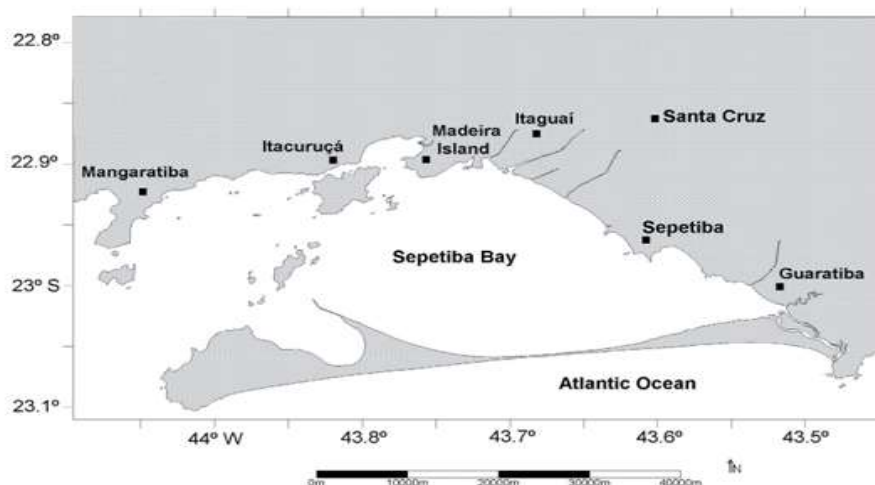


Figure 2. Study site: Map of Sepetiba Bay, Atlantic Coast of Rio de Janeiro State, Brazil

Sampling

A total of 33 fishes (*Mugil curema*, n= 12, *Centropomus undecimalis*, n=11, and *Cynoscion acoupa*, n=10) were caught at Sepetiba Bay from March to August 2013.

Sample preparation procedure

Prior to analysis, each sample was categorized upon its sample number, fish species, length (cm), weight (g) and gender. The gender was determined macroscopically by gonad observation after dissection; gonad stage was determined according to Vazzoler (1996). The head, tail fin and viscera were removed from the fish, before analysis. The samples were sealed in polyethylene bags and stored at -20 °C for subsequent analysis.

Chemical extraction method

About 10 g of freeze-dried combined pooled tissue samples from each species were weighed and lyophilised. Dry tissues were introduced in a steel extraction cell and placed in the Accelerated Solvent Extractor (ASE 200, Dionex). Subsequently being extracted, the samples were concentrated using Kuderna-Danish, the extract evaporated down to 1 ml, and the solvent was transported to 10 ml of n-hexane. Seventeen 2,3,7,8-substituted ¹³C-labeled tetra- through octa-CDD and CDF congeners and 12 dioxin-like PCBs (IUPAC - 81, 77, 126, 169, 105, 114, 118,

123, 156, 157, 167, 189) were spiked. Moreover, aliquots were treated with sulphuric acid in a separation funnel. Then the hexane layer with and PCDDs/Fs was rinsed with hexane-washed water and dried by passing through anhydrous sodium sulphate in a glass funnel. The solution concentrated to 2 ml and sequentially subjected to silica gel, alumina, and silica gel-impregnated activated carbon column chromatography. In sequence, extracts were passed through a silica gel-packed glass column (Wakogel, silica gel 60; 2g) and eluted with 130 ml of hexane. The hexane extract was Kuderna-Danish concentrated and passed through alumina column, and eluted with ml of 2% dichloromethane in hexane as a first fraction, which contained multi-ortho-substituted PCBs. The second fraction eluted with 30 ml of 50% dichloromethane in hexane, containing non- and mono-ortho-PCBs and PCDDs/Fs, was Kuderna-Danish concentrated and passed through silica gel-impregnated activated carbon column (0.5g). The first fraction eluted with 25% dichloromethane in hexane contained mono- and di-ortho-PCBs. The second fraction eluted with ml of toluene containing PCDDs/Fs was concentrated and analyzed on HRGC/HRMS.

Instrumentation and method of analysis

PCBs and PCDD/Fs were analysed by high-resolution mass spectrometer (HRGC/HRMS) according to USEPA methods: 1613B [40], 8290A [41], and 1668B [42]. Identification and quantification of 2,3,7,8-substituted congeners of PCDDs/Fs and dioxin-like PCBs (non- and mono-ortho-substituted congeners) were performed by use of a (i) Shimadzu GC-14B gas chromatograph with AOC-1400 auto-sampler. Columns: CBP-1 (SE-30) and CBP-5 (SE-52/54 confirmatory column). Injection: Split less (30 seconds) 300°C. Temperature program of the oven: 110°C (1 min.); 15°C/min up 170°C; 7.5°C/min up to 290°C, hold for 10 minutes. Total run time: 25 minutes. Electron Capture Detector (⁶³Ni) temperature: 310°C; (ii) HPLC: Shimadzu LC-10AS; Mobile phase: acetonitrile: water 80%, isocratic run. Column: Shimadzu STR-ODS-II (C-18 reverse phase) 25cm, L: 4mm ID. UV/VIS detector model: Shimadzu SPD-10A.

The results of chemical analysis for the compounds were analyzed and the initial data are expressed as (pg/g, w.w.) and (pg TEQ/g, w.w.). Where the

concentration of a specific compound remains below the detection limits (nd), this was treated as a zero value. Toxic equivalent factors (TEQ), recommended by WHO, were used for the further analysis of the data. TEQ of the analyzed PCDD/Fs and dioxin-like PCBs (DL-PCBs) were calculated using the WHO-TEF values [16]. TEQ is the product of the concentration of an individual dioxin-like compound in an environmental mixture and the corresponding TCDD-TEF for that compound.

Statistical analysis

The statistical analysis was carried out using the Origin 7.5 statistical software. The data obtained were described and qualitatively used descriptive statistics Basic (mean and standard deviation) with a significant level of $p < 0.05$.

RESULTS

Morphometric data

The average of morphometric data of fishes captured at Sepetiba Bay from March to August 2013, are presented in Table 1.

Table 1. Morphometric data of fish species (Average total - length and weight), gender, collect from Sepetiba Bay, Rio de Janeiro State, Brazil, March-August 2013.

Species	n	Average total Length (cm)	Average total Weight (g)	Gender	
				male	female
Common snook (<i>Centropomus undecimalis</i>)	11	20.09 ± 0.75	59.80 ± 6.37	10	1
White mullet (<i>Mugil curema</i>)	12	27.81 ± 2.37	214.49 ± 51.64	7	5
Acoupa weakfish (<i>Cynoscion acoupa</i>)	10	732.7 ± 47.4	1221.93 ± 61.59	8	2

PCB and PCDD/F concentrations

A total of 33 composite fish samples were evaluated. The European legislation quoted earlier sets limits for PCBs and PCDD/Fs in fish muscle for human consumption, and these levels were used as base in this study.

Outlines of PCBs and PCDD/Fs concentrations are showed in Tables 2 and 3, presenting the average concentrations (min ~ max concentration) for each fish species. The column headed WHO-TEQ refers

to the total toxicity from all PCBs and 17 2,3,7,8-substituted PCDDs/Fs congeners based on the World Health Organization Toxic Equivalents' method [16]. For calculating WHO-TEQ for PCDDs/Fs and PCBs, a concentration of 1/2 of the detection limit was used for each no detect. The concentration of total PCBs ranged from 0.589688 ~ 0.6981629 pg-WHO-TEQ/g ww and PCDDs/PCDFs ranged from 0.134037 ~ 0.242573 pg-WHO-TEQ/g ww.

The European Union established maximum permissible levels for human consumption of 4.0 pg WHO-TEQ/g fresh weight and 8.0 pg WHO-TEQ/g fresh weight of toxic equivalents (WHO-TEQ), for PCDD/Fs and for PCDD/Fs plus dioxin-like compounds, respectively, in the muscle meat of fish and fishery products [43]. All fish species analyzed in the current survey showed PCDD/F plus DL-PCB concentrations under the EU maximum permissible level. The sum of PCDD/PCDFs concentration found was 0.222424 pg WHO-TEQ/g in white mullet, 0.134037 pg WHO-TEQ/g in acoupa weakfish, and 0.242573 pg WHO-TEQ/g in common snook. The sum of PCDD/PCDF/PCBs was 0.920586 pg WHO-TEQ/g in white mullet, 0.737325 pg WHO-TEQ/g in acoupa weakfish, and 0.832261 pg WHO-TEQ/g in common snook.

By means of the toxicity factors WHO-TEF, the contribution to the toxicity found was caused by PCB 77 (acoupa weakfish), PCB 126 (common snook, white mullet, and acoupa weakfish), and PCB 169 (white mullet). For analysis of the toxicity factors WHO-TEF, related to PCDD/Fs, the toxicity found was found by 2378-TCDD, 12378-PeCDD, and 23478-PeCDF in common snook, white mullet, and acoupa weakfish.

DISCUSSION

Coastal areas incorporate an extensive range of saltwater ecosystems, with coral reefs, rocky shores, gravel shores, sandy shores, mudflats, sea grasses, marshes and mangrove forests. Urban and industrial actions situated in these regions produce large volumes of wastewater that are finally discharged into marine ecosystems, causing damage on water and sediment quality. Sepetiba Bay becomes a model of a marine environment that has been harshly impacted by industrial activities and human occupation in its basin. Around 420

industries including metallurgical, pyrometallurgical smelters and petrochemical, which emitted pollutants to soil, water and air, were established in Sepetiba Basin during the past 40 years.

Though a countless number of datasets recording total concentrations of persistent organic chemicals in an assortment of marine biota are available, the toxicity, bioaccumulative nature, biomagnification, and the fate of these compounds in the marine ecosystem is yet poorly realized. Reported adverse outcomes of PCBs and PCDD/Fs in wildlife include population decays, rises in cancers, reduced reproductive function, disrupted development of immune and nervous systems, and also elicit toxic responses which might result in the disturbance of the endocrine system [1, 6,14].

The crucial reasons for the lack of evidence of the effect of contamination on fishes are the difficulty or impossibility of experimenting in laboratory circumstances with them, and the frequent happening of confounding factors that hamper the establishing of cause-effect relationships. Examples of these causes are the fact that contamination continuously occurs as a mix of a great number of chemical compounds, the lack of data on biological variables influencing tissue levels, quality of samples usually analyzed, the limited information on pathology and manifestation of disease in the specimens studied, the absence of reliable population data, and the lack of information on the influence of other damaging factors such as the impact of fisheries and of other human related sources of disturbance.

Described adverse effects of PCBs and PCDD/Fs on public health mention cases of disrupted development of immune and nervous systems, elicit toxic responses which could result in the disruption of the endocrine system, reduced reproductive function, and increases in cancers [12,44]. According to Quinete and his colleagues [24]

concentrations of organochlorine compounds are been detected in some fish species along the Brazilian coast, suggesting the presence of a highly polluted source, which may be related to the industrial growth in recent years, furthermore potential impacts perceived in others developed nations.

Lavandier and his colleagues [33] analysing PCBs in three fish species from Sepetiba Bay, founded concentrations varying from 3.97 ± 1.32 to 11.04 ± 3.74 ng g⁻¹ ww (mean \pm SD) in *scabbard fish* muscle and 4.54 ± 2.41 to 22.71 ± 8.69 ng g⁻¹ ww in *scabbard fish* liver. For *croaker*, PCBs levels ranged from 2.29 ± 1.07 to 25.88 ± 5.69 ng g⁻¹ ww in muscle and from 3.41 ± 2.14 to 34.22 ± 11.19 ng g⁻¹ ww in liver. For *mullet*, PCBs ranged from 2.37 ± 1.85 to 27.60 ± 12.06 ng g⁻¹ ww in muscle and from 3.70 ± 1.92 to 24.53 ± 4.82 ng g⁻¹ ww in liver.

Table 2. Medians (range) of concentrations (pg/g, w.w.) of PCDD/Fs and toxic equivalents of PCDD/Fs (pg TEQ/g, w.w.) in common snook, white mullet, and acoupa weakfish.

Elements	Common snook		White mullet		Acoupa weakfish	
	Concentration	WHO TEQ (fish)	Concentration	WHO TEQ (fish)	Concentration	WHO TEQ (fish)
<i>Non-ortho PCBs</i>						
3,3',4,4'-TCB (77)	198 (119 – 334)	0.099	196 (133 – 288)	0.098	210 (123 – 276)	0.105
3,4,4',5-TCB (81)	442 (345 – 622)	0.0442	513 (244 – 688)	0.0513	629 (236 – 937)	0.0629
3,3',4,4',5-PeCB (126)	38 (14 – 55)	0.19	43 (14 – 68)	0.215	27 (11 – 40)	0.135
3,3',4,4',5,5'-HxCB (169)	1998 (1126 – 2681)	0.0999	3409 (1987 – 5625)	0.17045	2662 (2008 – 3112)	0.1331
<i>Mono-ortho PCBs</i>						
2,3,3',4,4'-PeCB (105)	778 (560 – 1133)	0.00389	965 (439 – 1340)	0.004825	1020 (608-1241)	0.0051
2,3,4,4',5-PeCB (114)	2675 (1882 – 3124)	0.013375	2780 (1986 – 3533)	0.0139	2329 (1769 – 3222)	0.011645
2,3',4,4',5-PeCB (118)	19 (11 – 34)	0.000095	24 (9.5 – 33.7)	0.00012	31 (17.6 – 44)	0.000155
2',3,4,4',5-PeCB (123)	14479 (8726 – 16744)	0.072395	11665 (7446 – 15722)	0.058325	12733 (9431 – 15223)	0.063665
2,3,3',4,4',5-HxCB (156)	4460 (2356 – 8892)	0.0223	9831 (5231 – 13278)	0.049155	7768 (3688 – 10377)	0.03884
2,3,3',4,4',5'-HxCB (157)	6.6 (1.98 – 13.4)	0.000033	5.4 (3.4 – 11.31)	0.000027	7.6 (2.7 – 15.8)	0.000038
2,3',4,4',5,5'-HxCB (167)	5488 (2877 – 7690)	0.02744	4533 (2437 – 5633)	0.022665	7581 (3255 – 9052)	0.037905
2,3,3',4,4',5,5'-HeCB (189)	3412 (1129 – 6492)	0.01706	2879 (1356 – 3987)	0.014395	1988 (1083 – 2622)	0.00994
	Σ= 33993.6	Σ= 0.589688	Σ= 36843.4	Σ= 0.698162	Σ= 36985.6	Σ= 0.603288

Table 3. Medians (range) of concentrations (pg/g, w.w.) of PCDD/Fs and toxic equivalents of PCDD/Fs (pg TEQ/g, w.w.) in common snook, white mullet, and acoupa weakfish

Elements	Common snook		White mullet		Acoupa weakfish	
	Concentration	WHO TEQ (fish)	Concentration	WHO TEQ (fish)	Concentration	WHO TEQ (fish)
Dibenzo-p-dioxins (PCDD)						
2378-TCDD	0.06 (0.03 – 0.09)	0.06	0.04 (0.02 – 0.06)	0.04	0.03 (0.01 – 0.06)	0.03
12378-PeCDD	0.07 (0.03 – 0.09)	0.07	0.06 (0.02 – 0.09)	0.06	0.03 (0.01 – 0.05)	0.03
123478-HxCDD	0.03 (0.02 – 0.06)	0.0015	0.03 (0.02 – 0.07)	0.0015	0.04 (0.01 – 0.07)	0.002
123678-HxCDD	0.02 (0.01 – 0.05)	0.002	0.04 (0.04 – 0.08)	0.004	0.04 (0.01 – 0.07)	0.004
123789-HxCDD	0.04 (0.02 – 0.07)	0.004	0.05 (0.01 – 0.08)	0.005	0.03 (0.01 – 0.06)	0.003
1234678-HpCDD	0.22 (0.14 – 0.34)	0.0022	0.18 (0.07 – 0.42)	0.0018	0.19 (0.04 – 0.29)	0.0019
OCDD	0.18 (0.05 – 0.26)	0.00018	0.17 (0.10 – 0.26)	0.00017	0.16 (0.07 – 0.30)	0.00016
Dibenzofurans (PCDF)						
2378-TCDF	0.48 (0.25 – 0.77)	0.00048	0.34 (0.13 – 0.56)	0.00034	0.36 (0.14 – 0.54)	0.00036
12378-PeCDF	0.19 (0.08 – 0.32)	0.0095	0.12 (0.04 – 0.26)	0.006	0.11 (0.06 – 0.14)	0.005
23478-PeCDF	0.16 (0.03 – 0.19)	0.08	0.18 (0.10 – 0.26)	0.09	0.16 (0.08 – 0.27)	0.08
123478-HxCDF	0.03 (0.01 – 0.08)	0.003	0.04 (0.02 – 0.06)	0.004	0.02 (0.01 – 0.05)	0.002
123678-HxCDF	0.05 (0.01 – 0.07)	0.005	0.02 (0.01 – 0.07)	0.002	0.03 (0.01 – 0.06)	0.003
1234789-HxCDF	0.02 (0.01 – 0.05)	0.002	0.03 (0.01 – 0.07)	0.003	0.02 (0.01 – 0.05)	0.001
234678-HxCDF	0.02 (0.01 – 0.06)	0.002	0.04 (0.02 – 0.08)	0.004	0.01 (ND – 0.03)	0.001
1234678-HpCDF	0.05 (0.03 – 0.09)	0.0005	0.03 (0.01 – 0.06)	0.0003	0.04 (0.02 – 0.09)	0.0004
1234789-HpCDF	0.02 (ND – 0.04)	0.0002	0.03 (0.01 – 0.09)	0.0003	0.02 (ND – 0.04)	0.0002
OCDF	0.13 (0.05 – 0.22)	0.000013	0.14 (0.09 – 0.26)	0.000014	0.17 (0.08 – 0.25)	0.000017
	Σ= 1.77	Σ= 0.242573	Σ= 1.54	Σ= 0.222424	Σ= 1.43	Σ= 0.134037

ND = concentration below the limit of detection

The incidence of anthropogenic pollutants, such as PCB and PCDD/F congeners, throughout entirely compartments of the marine environment has been of international concern for decades [45], and the data are compatible with ones identified in the species studied in this article. Bayarri and his colleagues [27] studying comestible fish species from Adriatic Sea found levels of PCDD/Fs and PCBs between 0.23 and 1.07 pg I-TEQ/g of wet weight (ww). Kiviranta and his colleagues [30] in research on dietary intake in Finland found PCDD/Fs, where the results indicated 2.0 pg WHO-TEQ/g ww PCBs, and 1.5 pg WHO-TEQ/g ww. In analyses of PCDD/Fs and PCBs in 14 comestible marine species randomly purchased in various cities of Catalonia, Bocio and his colleagues [28] found values of PCDD/F and PCB of 10.28 pg/g ww and 88.10 ng/g ww, respectively. Concentrations and congener-specific profiles of PCDDs, PCDFs, dl-PCBs, and ndl-PCBs were determined by Piskorska-Pliszczynska and his colleagues [34] in five species of comestible fish from the Baltic Sea: salmon (*Salmo salar*), Baltic herring (*Clupea harengus membras*), sprat (*Sprattus sprattus balticus*), sea trout (*Salmo trutta m.trutta*), and cod (*Gadus morhua callarias*). Marker PCBs were the dominant compounds (0.07– 60.84 ng/g w.w.), followed by dl-PCBs (0.64–6.07 pg WHO-TEQ/g w.w.) and PCDD/PCDFs (0.22–5.67 pg WHO-TEQ w.w.). Data from Koenig and his colleagues [32] the levels and profiles of organochlorine contaminants, including PCBs, dichlorodiphenyltrichloroethanes (DDTs), hexachlorocyclohexanes (HCHs) and penta- (PeCB) and HCB, as well as PBDEs were determined in muscle samples of the deep-sea fish *Alepocephalus rostratus*, *Coelorrinchus mediterraneus* and *Lepidion lepidion* from the NW Mediterranean Sea. Mean PCB and DDT levels ranged from the highest concentrations in the fish *A. rostratus* (Σ (7) PCBs 6.93 ± 0.71 ng/gw.w. and

Σ DDTs 8.43 ± 1.10 ng/g w.w.). Ben Ameer and his colleagues [31] analysed thirty one persistent organic pollutants including organochlorine contaminants and its metabolites in *solea solea* muscle from Bizerte Lagoon (northern Tunisia) and from the Mediterranean Sea (northern Mediterranean). Mean levels of organochlorine compounds were 1018 and 380 ng.g⁻¹ lipid weight in fish from Bizerte Lagoon and the Mediterranean Sea, respectively.

CONCLUSION

There is no probability of eliminating dioxin and linked pollutants from the bay, however the level of fish pollution is dependent on the aquatic environment, and human exposure can only be reduced through systematically effective fish control. The success of present societies is, partly, established on extensive accomplishments of chemistry with a systematic development of products in medicine, agriculture, and in almost all manufacturing industry sectors and materials for quotidian use. Even if these chemicals explicitly subsidizes to the quality of life for billions of human beings, however, the negative effects to health and environment are an important issue for systematic monitoring. Environmental and social benefits should not be ignored in spite of the economic forces.

Assuming from the European Union regulation limit levels of PCDD/PCDFs/PCBs and PCDD/PCDFs were lower than the levels found in all samples, and the dietary consumption of fish from Sepetiba region did not represent yet a risk for human health, stays implicit that prevention is the best method to mitigate the risk of diseases to public health.

ACKNOWLEDGMENTS

The author acknowledges the Z-16 Fishing Colony, and Conselho Nacional de Desenvolvimento

Científico e Tecnológico – CNPq (302946/2011-0)
for financial support.

REFERENCES

1. Kumar K. S., Kannan K., Paramasivan O.N., Sundaram V.P.S., Nakanishi J., Masunaga S., 2001. Polychlorinated dibenzo-p-dioxins, dibenzofurans, and polychlorinated biphenyls in human tissues, meat, fish, and wildlife samples from India. *Environ Sci Technol.* 35(17), 3448-3455.
http://www.gcmonitor.org/downloads/Dioxins_India_Study.pdf
2. Weiguang X., Xian W., Zongwei C., 2013. Analytical chemistry of the persistent organic pollutants identified in the Stockholm Convention: A review. *Analytica Chimica Acta* 790, 1-13.
<http://www.sciencedirect.com/science/journal/00032670/790>
3. Muralidharan S., Dhananjayan V., Jayanthi P., 2009. Organochlorine pesticides in commercial marine fishes of Coimbatore, India and their suitability for human consumption. *Environ Res.* 109(1), 15-21.
<http://www.sciencedirect.com/science/journal/00139351/109/1>
4. Reese S.L., Estes J.A., Jarman W.M., 2012. Organochlorine contaminants in coastal marine ecosystems of southern Alaska: inferences from spatial patterns in blue mussels (*Mytilus trossulus*). *Chemosphere* 88(7), 873-880.
<http://www.sciencedirect.com/science/journal/00456535/88/7>
5. Macdonald R., Mackay D., Hickie B., 2002. Contaminant amplification in the environment. *Environ Sci Technol.* 36, 456A-462A.
<http://pubs.acs.org/toc/esthag/36/23>
6. Alcock R.E., Behnisch P.A., Jones K.C., Hagenmaier H., 1998. Dioxin-like PCBs in the environment – human exposure and the significance of sources. *Chemosphere* 37(8), 1457-1472.
<http://www.sciencedirect.com/science/journal/00456535/37/8>
7. Ferreira A.P., 2008. Environmental fate of bioaccumulative and persistent substances: A synopsis of existing and future actions. *Gerenc. Politic. Salud.* 7(15), 14-23.
http://www.scielo.org.co/scielo.php?pid=S1657-70272008000200002&script=sci_abstract&tlng=pt
8. Carlson D.L., Swackhamer D.L., 2006. Results from the U.S. Great Lakes fish monitoring program and effects of lake processes on bioaccumulative contaminant concentrations. *Journal of Great Lakes Research* 32(2), 370-385.
http://www.sciencedirect.com/science?_ob=ArticleListURL&_method=list&_ArticleListID=-425028880&_sort=r&_st=13&view=c&_acct=C000036919&_version=1&_urlVersion=0&_userid=685730&md5=132885b22081f803d2960eb9aab49a2e&se archetype=a
9. Moriarty F., *Ecotoxicology. The study of pollutants in ecosystems.* Third Edition, California: Academic Press, 1999.
10. Pereira M.S., 2004. Polychlorinated Dibenzo-p-Dioxins (PCDD), Dibenzofurans (PCDF) and Polychlorinated Biphenyls (PCB): Main Sources, Environmental fate of bioaccumulative behaviour and risk to man and biota. *Química Nova* 27(6), 934-943.
http://www.scielo.br/scielo.php?pid=S0100-4042004000600018&script=sci_abstract
11. Storelli M.M., Barone G., Perrone V.G., Giacomini-Stuffler R., 2011. Polychlorinated biphenyls (PCBs), dioxins and furans (PCDD/PCDFs): occurrence in fishery products and dietary intake. *Food Chem.* 127, 1648-1652.
<http://www.sciencedirect.com/science/journal/03088146/127/4>
12. An W., Hu J., 2006. Effects of endocrine disrupting chemicals on China's rivers and coastal

- waters. *Frontiers in Ecology and the Environment* 4(7), 378-386.
<http://www.esajournals.org/toc/fron/4/7>
13. Kogevinas M., 2000. Studies of cancer in humans. *Food Additives and Contaminants A* 17(4), 317-324.
<http://www.tandfonline.com/toc/tfac/19/17/4#.Un0Da3BJ6qQ>
 14. Pesatori A.C., Consonni D., Rubagotti M., Grillo P., Bertazzi P.A., 2009. Cancer incidence in the population exposed to dioxin after the Seveso accident: twenty years of follow-up. *Environ Health* 8, 39-48.
<http://www.ehjournal.net/content/8/1/39>
 15. Breivik K., Sweetman A., Pacyna J.M., Jones K.C., 2002. Towards a global historical emission inventory for selected PCB congeners - a mass balance approach 2. Global production and consumption. *Sci Tot Environ.* 290, 181-198.
<http://www.sciencedirect.com/science/article/pii/S0048969701010762>
 16. Van Den Berg M., Birnbaum L.S., Denison M., 2006. The 2005 World Health Organization re-evaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol Sci.* 93(2), 223-241.
<http://toxsci.oxfordjournals.org/content/93/2/223.full>
 17. Ballschmiter K., Zell M., 1980. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius' Journal of Analytical Chemistry* 302, 20-31.
<http://link.springer.com/article/10.1007%2FBF00469758#page-1>
 18. Kitamura K., Kikuchi Y., Watanabe S., Waechter G., Sakurai H., Takada T., 2000. Health effects of chronic exposure to polychlorinated dibenzo-p-dioxins (PCDD), dibenzofurans (PCDF) and coplanar PCB (Co-PCB) of municipal waste incinerator workers. *J. Epidemiol.* 10(4), 262-270.
[http://astp.jst.go.jp/modules/search/index.php?page=DocumentDetail&journalId=0917-5040_10_4_Health+Effects+of+Chronic+Exposure+to+Polychlorinated+Dibenzo-P-Dioxins\(PCDD\)%2CDibenzofurans\(PCDF\)+and+Coplanar+PCB\(Co-PCB\)+of+Municipal+Waste+Incinerator+Workers._N%2FA](http://astp.jst.go.jp/modules/search/index.php?page=DocumentDetail&journalId=0917-5040_10_4_Health+Effects+of+Chronic+Exposure+to+Polychlorinated+Dibenzo-P-Dioxins(PCDD)%2CDibenzofurans(PCDF)+and+Coplanar+PCB(Co-PCB)+of+Municipal+Waste+Incinerator+Workers._N%2FA)
 19. Synnestvedt M., Borgen E., Wist E., Wiedswang G., Weyde K., Risberg T., Kersten C., Mjaaland I., Vindi L., Schirmer C., Nesland J.M., Naume B., 2012. Disseminated tumor cells as selection marker and monitoring tool for secondary adjuvant treatment in early breast cancer. Descriptive results from an intervention study. *BMC Cancer* 12, 616, doi: 10.1186/1471-2407-12-616.
<http://www.biomedcentral.com/1471-2407/12/616>
 20. Ennaceur S., Gandoura N., Ridha Driss M., 2008. Distribution of polychlorinated biphenyls and organochlorine pesticides in human breast milk from various locations in Tunisia: Levels of contamination, influencing factors, and infant risk assessment. *Environ Res.* 108, 86-93.
<http://www.sciencedirect.com/science/article/pii/S001393510800128X>
 21. Binelli A., Provini A., 2004. Risk for human health of some POPs due to fish from Lake Iseo. *Ecotoxicology and Environmental Safety* 58(1), 139-145.
<http://www.sciencedirect.com/science/article/pii/S0147651303001799>
 22. Mazet A., Keck G., Berny P., 2005. Concentrations of PCBs, organochlorine pesticides and heavy metals (lead, cadmium, and copper) in fish from the Drôme river: Potential effects on otters (*Lutra lutra*). *Chemosphere* 61(6), 810-816.
<http://www.sciencedirect.com/science/article/pii/S0045653505005977>
 23. Charnley G., Kimbrough R.D., 2006. Overview of exposure, toxicity, and risks to children from current levels of 2,3,7,8-tetrachlorodibenzo-p-dioxin and related

- compounds in the USA. Food Chem Toxicol. 44, 601-615.
<http://www.healthriskstrategies.com/pdfs/charnley-kimbrough.pdf>
24. Quinete N., Lavandier R., Dias P., Taniguchi S., Montone R., Moreira I., 2011. Specific profiles of polybrominated diphenylethers (PBDEs) and polychlorinated biphenyls (PCBs) in fish and *tucuxi dolphins* from the estuary of Paraíba do Sul River, Southeastern Brazil. Mar Pollut Bull. 62, 440-446.
<http://www.ncbi.nlm.nih.gov/pubmed/21168887>
25. El-Shahawi M.S., Hamza A., Bashammakh A.S., Al-Saggaf W.T., 2010. An overview on the accumulation, distribution, transformations, toxicity and analytical methods for the monitoring of persistent organic pollutants. Talanta 80(5), 1587-1597.
<http://europepmc.org/abstract/MED/20152382>
26. Bjeremo H., Darnerud P.O., Lignell S., Pearson M., Rantakokko P., Nälsén C., Enghardt Barbieri H., Kiviranta H., Lindroos A.K., Glynn A., 2013. Fish intake and breastfeeding time are associated with serum concentrations of organochlorines in a Swedish population. Environ Int. 51, 88-96.
<http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.elsevier-b729c83d-9ea0-3cd1-aa51-b7289cfe8502>
27. Bayarri S., Baldassarri L.T., Iacovella N., Ferrara F., Di Domenico A., 2001. PCDDs, PCDFs, PCBs and DDE in edible marine species from the Adriatic Sea. Chemosphere 43, 601-610.
<http://www.sciencedirect.com/science/article/pii/S0045653500004124>
28. Bocio A., Domingo J.L., Falcó G., Llobet J.M., 2007. Concentrations of PCDD/PCDFs and PCBs in fish and seafood from the Catalan (Spain) market. Environ Int. 33, 170-175.
<http://www.gencat.cat/salut/acsa/html/ca/dir1312/dd16971/pdf5.pdf>
29. Karl H., Bladt A., Rottler H., Ludwigs R., Mathar W., 2010. Temporal trends of PCDD, PCDF and PCB levels in muscle meat of herring from different fishing grounds of the Baltic Sea and actual data of different fish species from the Western Baltic Sea. Chemosphere 78(2), 106-112.
<http://www.sciencedirect.com/science/article/pii/S0045653509012065>
30. Kiviranta H., Ovaskainen M.L., Vartiainen T., 2004. Market basket study on dietary intake of PCDD/Fs, PCBs, and PBDEs in Finland. Environ Int. 30, 923-932.
<http://www.sciencedirect.com/science/article/pii/S0160412004000649>
31. Ben Ameer W., El Megdiche Y., Eljarra T.E., Ben Hassine S., Badreddine B., Souad T., Bèchir H., Barceló D., Ridha Driss M., 2012. Organochlorine and organobromine compounds in a benthic fish (*Solea solea*) from Bizerte Lagoon (northern Tunisia): Implications for human exposure. Ecotoxicol Environ Saf. 88, 55-64.
<http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.elsevier-7c95ce7b-bda6-3a35-9008-dff8503fe0d0>
32. Koenig S., Huertas D., Fernández P., 2012. Legacy and emergent persistent organic pollutants (POPs) in NW Mediterranean deep-sea organisms. Sci Tot Environ. 443C, 358-366.
<http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.elsevier-8385ce4c-349a-3eaf-91ca-94439a1dbc07>
33. Lavandier R., Quinete N., Hauser-Davis R.A., Dias P.S., Taniguchi S., Montone R., Moreira I., 2013. Polychlorinated biphenyls (PCBs) and Polybrominated Diphenyl ethers (PBDEs) in three fish species from an estuary in the southeastern coast of Brazil. Chemosphere 90, 2435-2443.
http://www.unboundmedicine.com/medline/citation/23211324/Polychlorinated_biphenyls_PCBs_and_Polybrominated_Diphenyl_ethers_PBDEs_i

- n_three_fish_species_from_an_estuary_in_the_southeastern_coast_of_Brazil_
34. Piskorska-Pliszczynska J., Maszewski S., Warenik-Bany M., Mikolajczyk S., Goraj L., 2012. Survey of persistent organochlorine contaminants (PCDD, PCDF, and PCB) in fish collected from the Polish Baltic fishing areas. *The Scientific World Journal* 12, 973292. <http://www.readcube.com/articles/10.1100/2012/973292>
 35. Carvalho C.D., Corneta C.M., Uieda V.S., 2007. Schooling behavior in *Mugil curema* in an estuary in Southern Brazil. *Neotrop Ichthyol.* 5(1), 81-83. <http://www.scielo.br/pdf/ni/v5n1/a12v5n1.pdf>
 36. Marin E.B.J, Quintero A., Bussi ere D., Dodson J.J., 2003. Reproduction and recruitment of white mullet (*Mugil curema*) to a tropical lagoon (Margarita Island, Venezuela) as revealed by otolith microstructure. *Fishery Bull.* 101, 809-821. <http://fishbull.noaa.gov/1014/10marinf.pdf>
 37. Perera-Garc a M.A., Mendoza-Carranza M., Contreras-S nchez W.M., Huerta-Ort z M., P rez-S nchez E., 2011. Reproductive biology of common snook *Centropomus undecimalis* (Perciformes: *Centropomidae*) in two tropical habitats. *Rev Biol Trop.* 59(2), 669-681. <http://www.ncbi.nlm.nih.gov/pubmed/21717854>
 38. Begossi A., Salyvonchik S., Nora V., Lopes P.F., Silvano R.A., 2012. The Paraty artisanal fishery (southeastern Brazilian coast): ethnoecology and management of a social-ecological system (SES). *J Ethnobiol Ethnomed.* 8:22, doi:10.1186/1746-4269-8-22. <http://www.ethnobiomed.com/content/8/1/22>
 39. Chao N.L. *Sciaenidae*. FAO Species identification guide for fishery purposes. Rome: FAO. pp. 1583-1653, 2002. <http://www.fao.org/docrep/009/x2400e/x2400e00.HTM>
 40. Usepa. United States Environmental Protection Agency. Method 1613B. Tetra- through Octa-Chlorinated Dioxins and Furans by Isotope Dilution HRGC/HRMS, 1994. <http://water.epa.gov/scitech/methods/cwa/organics/dioxins/index.cfm>
 41. Usepa. United States Environmental Protection Agency. Method 1668, Revision A Chlorinated Biphenyl Congeners in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, 2003. http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2009_01_07_methods_method_1668.pdf
 42. Usepa. United States Environmental Protection Agency. Method 8290 A: revision 1 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) by High-Resolution Gas Chromatography/High-Resolution Mass Spectrometry (HRGC/HRMS), 2007. <http://www.rpc.ca/english/HRMSRefs/8290a.pdf>
 43. European Commission. Commission Regulation No. 199/2006. Setting maximum levels for certain contaminants in foodstuffs as regard to dioxins and dioxin-like PCBs, Official Journal of the European Union, L 32/34, 2006. <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2006:032:0034:0038:EN:PDF>
 44. Scott L.L., Staskal D.F., Williams E.S., Luksemburg W.J., Urban J.D., Nguyen L.M., Haws L.C., Birnbaum L.S., Paustenbach D.J., Harris M.A., 2009. Levels of polychlorinated dibenzo-p-dioxins, dibenzofurans, and biphenyls in southern Mississippi catfish and estimation of potential health risks. *Chemosphere* 74(7), 1002-1010. <http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.elsevier-fc802381-0264-375d-8881-2223013d9246>
 45. Consonni D., Sindaco R., Bertazzi P.A., 2012. Blood levels of dioxins, furans, dioxin-like PCBs, and TEQs in general populations: A review, 1989-2010. *Environ Int.* 44, 151-162. <http://www.ncbi.nlm.nih.gov/pubmed/22364893>