Sources and Temporal Patterns of Polychlorinated Biphenyls Around a Large South American Grain-Shipping Port (Paranaguá Estuarine System, Brazil)

Tatiane Combi · Satie Taniguchi · Paulo Alves de Lima Ferreira ·
Andressa Vianna Mansur · Rubens Cesar Lopes Figueira ·
Michel Michaelovitch de Mahiques · Rosalinda Carmela Montone ·
César C. Martins

Abstract The Paranaguá Estuarine System (PES) is an important estuarine environment on the Brazilian coast. The economic importance of the PES is mainly related to industries, fuel terminals, and the main South American grain-shipping port. The aim of this work was to determine the vertical distribution of polychlorinated biphenyls (PCBs) in three sediment cores from the PES. The methods included Soxhlet extraction, clean-up, and quantification by gas chromatography with electron capture detection. The concentrations of total PCBs ranged from lower than the detection limit to 6.65 ng g^{-1}. Low PCB concentrations were detected in P1 and P3, which were collected far away from direct human activities. In P2, the compositional pattern of PCB congeners showed greater concentrations of tetra- and penta-chlorinated congeners associated with urban and port activities near Paranaguá city. The differences in concentrations between the three sediment cores were attributed to the distance of the sampling points in relation to the possible sources of pollution, which are mostly related to Paranaguá city. The vertical distribution of PCBs in the sediment core P2 was related to historical anthropogenic activities. The highest PCB input was from 1970 to the early 1990s, which coincides with a period of greater use of PCBs in Brazil as well as their greater worldwide production.

Polychlorinated biphenyls (PCBs) are highly persistent in the environment due to their high resistance to degradation processes and chemical stability (Borja et al. 2005). These compounds are hydrophobic, lipophilic, and bioaccumulative, and they are listed as one of the 12 persistent organic pollutants (POPs) restricted or banned globally under the Stockholm Convention on POPs (UNEP 2001).

PCBs were widely used as dielectric fluids in transformers and capacitors, heat-exchange liquids, hydraulic fluids, flame retardants, lubricants, waxes, and carbonless copy paper (Fiedler 1997; Breivik et al. 2004; Erickson and Kaley 2011) because of their high dielectric constants and thermal stability. The use and production of PCBs has been controlled in Brazil since 1981, but equipment containing PCBs can be used until the end of its useful life (Penteado and Vaz 2001). Some present sources of environmental contamination by PCBs are leakage from irregular deposits or contaminated soils, industrial and domestic effluents, and volatilisation (Harrad et al. 1994; Breivik et al. 2002).

The fate of PCBs in the environment is the estuaries, where sediments act as a sink for most pollutants (Sahu et al. 2009; Ruiz-Fernández et al. 2012). Because of their high octanol–water partition coefficient, PCBs tend to adsorb on suspended particulate matter reaching the coastal sediments and accumulating mainly in fine-grained (silt and clay) fractions (Fiedler 1997). This behaviour, combined with characteristics, such as chemical stability and persistence in the environment, allows the study of the concentration of PCBs in marine sediment samples, even

T. Combi (✉) · A. V. Mansur · C. C. Martins (✉)
Centro de Estudos do Mar da Universidade Federal do Paraná,
Caixa Postal 61, 83255-976 Pontal do Paraná, PR, Brazil
e-mail: tatianecombi@gmail.com

C. C. Martins
e-mail: ccmart@ufpr.br

T. Combi
Programa de Pós-Graduação em Sistemas Costeiros e Oceânicos
(PGSISCO) da Universidade Federal do Paraná, Caixa Postal 61,
83255-976 Pontal do Paraná, PR, Brazil

S. Taniguchi · P. A. de Lima Ferreira · R.
C. L. Figueira · M. M. de Mahiques · R. C. Montone
Instituto Oceanográfico da Universidade de São Paulo, Praça do
Oceanográfico, 191, 05508-900 São Paulo, SP, Brazil

those deposited decades ago. Thus, sediment cores represent an important tool for the development of management strategies and for the reconstruction of historical inputs of contaminants (Valette-Silver 1993; Santschi et al. 2001). The historical record of pollution levels is also needed to evaluate the environmental contamination, and understanding pollution trends is helpful to predict future patterns of pollution (Martins et al. 2010a).

The aim of this work was to study the vertical distribution of PCBs in sediment cores from the Paranaguá Estuarine System (PES) in Brazil in an effort to trace the historic evolution of human activities in this economically important area of Latin America, as well as to associate PCB concentration variations with major historical events of human occupation and the use and disposal of these compounds in this environment.

Experimental Methods

Study Area

The PES is located on the northern coast of Paraná state, Brazil, between 25°16′S and 48°17′W (Fig. 1). Cities, such as Antonina, Morretes, Paranaguá, and Pontal do Paraná, are located at the margins of the PES, creating an area of continuous occupation with a total population of approximately 191,700 inhabitants, most of whom (133,600 inhabitants) live in Paranaguá city (Instituto Brasileiro de Geografia e Estatística 2009). This estuary is formed by two main systems: Laranjeiras Bay on the north–south axis and Paranaguá and Antonina Bays on the east–west axis. The latter system has an area of approximately 258 km^2 and an aqueous volume of 1.4×10^9 m^3. The tidal regime in the region is semidiurnal, reaching ≤2 m in spring tide (Lana et al. 2001).

The PES has been influenced by anthropogenic inputs from different sources, including domestic discharges and sewage from the port and industries (Martins et al. 2011a). Human settlement of the area occurred relatively rapidly and in a disorderly manner. Occupation of the region was intensified by the construction of the Paranaguá port, which is currently the largest grain exporter in Latin America (Martins et al. 2010b). Antonina port, despite its smaller capacity, contributes significantly to the transport of iron, timber, fertiliser, and frozen products. Although industrial activities are less developed compared with the rest of the Brazilian coast (Lana et al. 2001), the region has a considerable number of industries, especially fertiliser manufacturing.

The ports and industries, as well as the activities related to them, represent potential sources of contamination by persistent pollutants, such as PCBs (Breivik et al. 2007). These compounds can be found in paints and lubricants for ships and large electrical equipment used in port and industrial sectors (Breivik et al. 2007; Santos et al. 2009). Other potential sources of PES contamination include the inappropriate disposal of solid waste and improper domestic sewage treatment (Kolm et al. 2002; Khairy et al. 2012). In Paranaguá city, waste production was intensified by the increase in population in recent decades, whereas until 1996 all of the waste produced in the region was disposed of in irregular landfills (Cordura 1998). However, even with the recent creation of a sanitary landfill, much of the solid waste produced in the region is still disposed of in inappropriate places or incinerated.

Sampling

Three sediment cores were collected along the PES in August and October of 2008 (P1, P2, and P3). The P1 core was collected close to the city of Antonina in the innermost part of the estuary and close to the mouths of the rivers; the P2 core was collected near the urban and port area of Paranaguá; and the P3 core was collected near Cotinga Island, which has no relevant human occupation or industrial activities.

The sediment cores (diameter = 70 mm; length ≤48 cm) were collected by scuba divers. Two polyvinyl chloride (PVC) cores were used for magnetic susceptibility (MS) measurements, and two aluminium cores were used for organic compound analyses at each sample point. The aluminium sediment cores were sectioned at 2-cm intervals, and the sediment samples were placed in precleaned aluminium pots and stored at −20 °C. The sediments were freeze-dried and stored in glass bottles until laboratory analyses.

MS

MS measurements were performed using a Bartington MS-2C MS (Bartington, Oxford, UK) meter equipped with a 90-mm diameter sensor on the whole and unopened PVC cores of all sampled points. The measurements were taken at 2.5-cm intervals, between 10 and 60 cm, with a resolution of 10^{-5} SI units. The raw data were corrected to account for different sample diameters from the sensor dimensions, and background values were taken to correct for instrumental drift (Martins et al. 2007).

The three sediment cores used showed small variations in MS (Fig. 2). The absence of large variations in MS values may indicate a lack of mixing between the sediment layers (Hanesch and Scholger 2002; Venkatachalapathy et al. 2011) and, consequently, the maintenance of a historical record of PCB input.

Fig. 1 Study area and sampling points of the three sediment cores: P1 (Antonina), P2 (Paranaguá), and P3 (Cotinga Island)
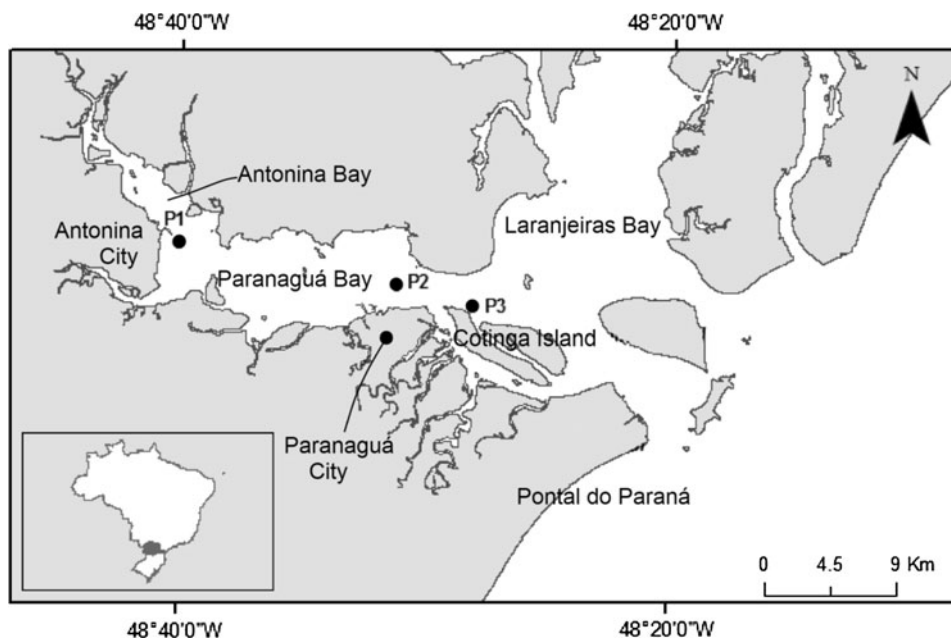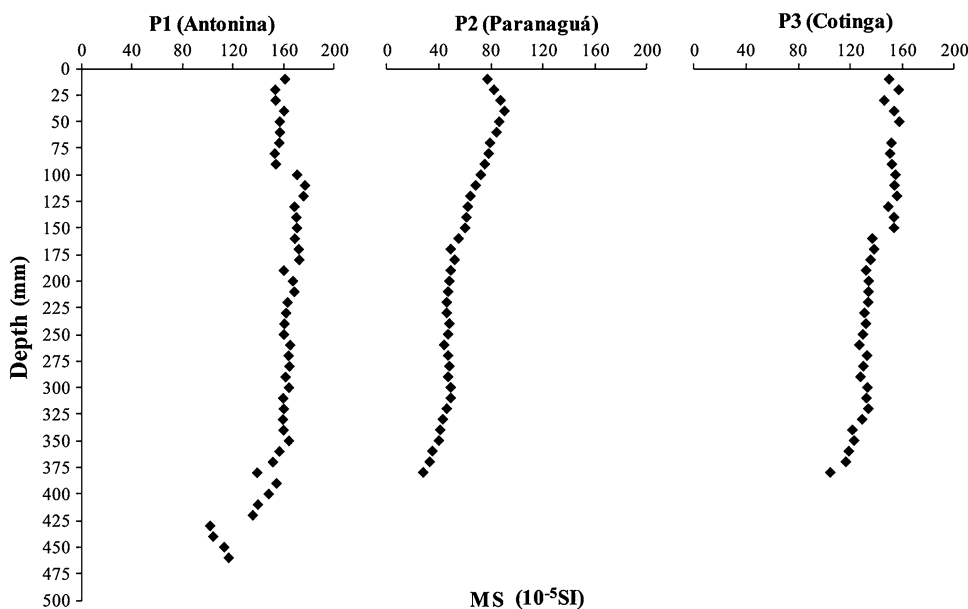

Fig. 2 MS profiles of the P1 (Antonina), P2 (Paranaguá), and P3 (Cotinga Island) sediment cores

Sedimentation Rate and Dating of Sedimentary Core

For the determination of the recent sedimentation rate and core dating, the radiometric approach through instrumental gamma spectrometry, which is a nondestructive and passive method proper for analysis of environmental matrices such as sediments, was chosen.

Sedimentation rates and core dating were determined with the application of two different mathematical models (constant initial concentration [CIC] and vertical migration [VM]) for two radionuclides (lead-210 [^{210}Pb] and cesium [^{137}Cs]) with a series of corrections to account for sediment porosity and dry density (Clifton et al. 1995; Hai et al.

2006; Jweda and Baskaran 2011). Because Pb is a post-transition element and Cs is an alkali metal, the comparison of the data generated with the use of two radionuclides with different geochemical behavior is a way to assert the results of both models.

The CIC (Robbins and Edgington 1975) model of unsupported ^{210}Pb (abbreviated as ^{210}Pb$_{xs}$) considers that there is a continuous input of sediments to the system and an initial activity of ^{210}Pb$_{xs}$ in the core that decays with a time factor dependent solely on ^{210}Pb half-life. The VM model of ^{137}Cs (Ligero et al. 2005; Ajayi and Raji 2010; Ferreira et al. 2013) considers that the temporal evolution of ^{137}Cs activity in a sedimentary column results from its

vertical diffusive flux and vertical convective flux in the sediment porewater as well as natural decay. As contour conditions for the model, it deems that all ^{137}Cs in the location derived from the global fallout of past nuclear tests, which reached a maximum level in approximately 1963. Because this model is based in a tracer that was not present in the environment before the 1950s, it can only be used to calculate sedimentation rates since those years. The VM model is mainly used as a way to confirm the results of the CIC model.

[210]Pb$_{xs}$ and ^{137}Cs activities were determined by gamma-ray spectrometry using a low-background EG&G ORTEC (ORTEC, Oak Ridge, TN, USA) spectrometer with a hyper-pure germanium detector model GXM25190P (ORTEC, Oak Ridge, TN, USA) with mean resolution of 1.92 keV to the 1332.40 keV photopeak of cobalt-60. According to the methodology of analysis and data acquisition described in Figueira et al. (2007) and in Martins et al. (2010c), ^{210}Pb activity was measured at 46.52 keV; [226]Ra (considered to be the supported ^{210}Pb) was measured at 609.31 keV, which is the peak of its daughter [214]Bi (peak assessed after 1 month of sample sealing to allow radioactive equilibrium in the [238]U); and ^{137}Cs activity was measured at 661.66 keV.

Extraction and Clean-Up of PCBs

The analytical procedure for PCB analysis is based on United Nations Environmental Programme (UNEP 1992) with minor modifications (Bícego et al. 2006). Approximately 20 g of sediment was Soxhlet-extracted during 8 h using 80 mL of a mixture of dichloromethane (DCM) and n-hexane (1:1). Activated copper was added to remove sulphur. The extracts obtained were concentrated to 4 mL and divided into two parts: F1 for the analysis of polycyclic aromatic and aliphatic hydrocarbons (not used) and F2 for the analysis of PCBs. Fraction F2 was purified using column chromatography with 3.2 g 5 % deactivated alumina. Elution was performed with 20 mL 3:7 mixture of DCM and n-hexane. The eluate was then concentrated to 0.5 mL under a gentle gas stream of purified nitrogen, and tetrachloro-*m*-xylene (TCMX) (M-8082-SS-10X, AccuStandard, New Haven, CT, USA) was added as internal standard.

Quantification, Instrumental Analyses, and Quality-Assurance Procedures

The determination of PCBs was performed by Agilent 6890 (Agilent Technologies, Palo Alto, CA, USA) gas chromatography (GC) with electron capture detection. The GC column was an HP-5 fused silica column (length 30 m, ID 250 μm, film thickness 0.25 μm). The oven temperature was programmed to begin at 100 °C for 1 min, increasing at 5 °C min^{-1} to 140 °C (holding this temperature for 1 min), increasing at 1.5 °C min^{-1} to 250 °C (holding for 1 min), and finally increasing 10 °C min^{-1} to 300 °C (holding for 10 min).

The quantification of the analytes was based on a mixture of surrogate standards of PCB 103 (C-103N) and PCB 198 (C-198N) (both from AccuStandard, New Haven, CT, USA), which was added before sample extraction. The PCBs were identified by comparison of the retention times of chromatographic peaks of samples with external standard solutions with a known composition (51 congeners: PCB8, PCB18, PCB31, PCB28, PCB33, PCB52, PCB49, PCB44, PCB74, PCB70, PCB66/95, PCB56/60, PCB101, PCB99, PCB97, PCB81/87, PCB110/77, PCB151, PCB123/149, PCB118, PCB114, PCB153, PCB132, PCB105, PCB141, PCB138, PCB158, PCB126, PCB187, PCB183, PCB128, PCB167, PCB174, PCB177, PCB156, PCB157, PCB180, PCB169, PCB170, PCB199, PCB203, PCB189, PCB195, PCB194, PCB206, and PCB209) and concentrations (C-WNN = 10 μg mL^{-1}; C-WCFS = 25 μg mL^{-1}; Accu-Standard, New Haven, CT, USA). For the quantification, calibration curves were prepared at different concentrations: 1, 5, 10, 20, 80, 100, 150, and 200 ng μL^{-1}.

The peaks from the compounds were integrated by determining the response factor of each compound compared with surrogate standard. The coincidence between the retention times of the compounds present in the sample and the standard solutions was used to identify PCBs in the sample. The quantification was made based on the areas obtained for each PCB in the samples, multiplied by the response factor of the calibration curve, in relation to the mass-to-area ratio obtained for the surrogate standard.

The quality-assurance procedures included analyses of procedural blanks, matrix spikes, and precision tests (Wade and Cantillo 1994). Procedural blanks were performed for each group of approximately nine samples using 20 g sodium sulphate anhydride heated to 450 °C before extraction and analysed in the same way as samples. The peaks found showed no external interference. The mean surrogate recoveries, based on the relationship with an internal standard (TCMX) added at the end of laboratory analyses, were 102.8 % ± 23.0 % and 69.3 % ± 11.4 % for PCB 103 and PCB 198, respectively.

The detection limits (DL) (Table 1) and spike tests were performed by analysing seven sediment samples spiked with OCP and PCB standards. The DL was calculated to be three times the SD in the seven replicate analyses. The mean standard recovery in the spike tests was 100.5 % ± 8.6 %.

Results and Discussion

Sedimentation Rate and Dating of Sedimentary Core

Figure 3 presents the logarithmic curve of [210]Pb$_{xs}$. With the coefficients of linear regression of ln([210]Pb$_{xs}$), which is

Table 1 DL of the PCB congeners analysed (in ng g^{-1})

Compound	DL	Compound	DL
PCB 8	0.38	PCB 141	0.30
PCB 18	0.11	PCB 138	0.30
PCB 31	0.21	PCB 158	0.18
PCB 33	0.21	PCB 187	0.17
PCB 52	0.09	PCB 183	0.25
PCB 49	0.10	PCB 128	0.09
PCB 44	0.18	PCB 167	0.15
PCB 74	0.14	PCB 174	0.28
PCB 70	0.14	PCB 177	0.28
PCB 66/95	0.14	PCB 156	0.18
PCB 56/60	0.10	PCB 157	0.18
PCB 101	0.05	PCB 180	0.09
PCB 99	0.05	PCB 170	0.28
PCB 97	0.05	PCB 199	0.17
PCB 81/87	0.12	PCB 203	0.28
PCB 110	0.10	PCB 189	0.17
PCB 151	0.09	PCB 195	0.17
PCB 123/149	0.06	PCB 194	0.15
PCB 118	0.08	PCB 206	0.28
PCB 114	0.08	PCB 209	0.21
PCB 153	0.21		
PCB 132	0.30		
PCB 105	0.37		

Fig. 3 CIC model of ^{210}Pb$_{xs}$. Vertical profile of ln(^{210}Pb$_{xs}$). Linear regression, Pearson correlation coefficient, and respective p value

Fig. 4 VM model of ^{137}Cs. Vertical profile of ^{137}Cs and fitted curve (in mBq cm^{-3}). χ^2 Value of the fit

statistically significant at a confidence level of 0.001, the sedimentation rate obtained was 0.83 ± 0.10 cm y^{-1}. In Fig. 4, which presents the vertical profile of ^{137}Cs and the fitted curve provided by the VM model (with a χ^2 value of 0.41), the sedimentation rate obtained with the VM model was 0.78 ± 0.03 cm y^{-1}.

With the values of sedimentation rate, the core dating (Table 2) was assessed considering these values to be constant in all profile. In addition, the mean core dating and the mean sedimentation rate were calculated because the sedimentation rates are similar (RSD around 4 %). Therefore, the mean sedimentation rate obtained was 0.81 ± 0.06 cm y^{-1}.

Concentrations of PCBs

Concentrations of total PCBs in the P2 core were the highest among the sediment cores analysed, ranging from <DL to 6.65 ng g^{-1}, with the highest concentration in the 12- to 14-cm layer. In the bottom sections (38 to 46 cm), the mean concentration was 0.18 ± 0.14 ng g^{-1}, whereas in the middle sections (36 to 18 cm), the values were greater (mean 0.69 ± 0.17 ng g^{-1}). The top sections (0 to 12 cm) contained the highest concentrations (mean 1.30 ± 0.85 ng g^{-1}).
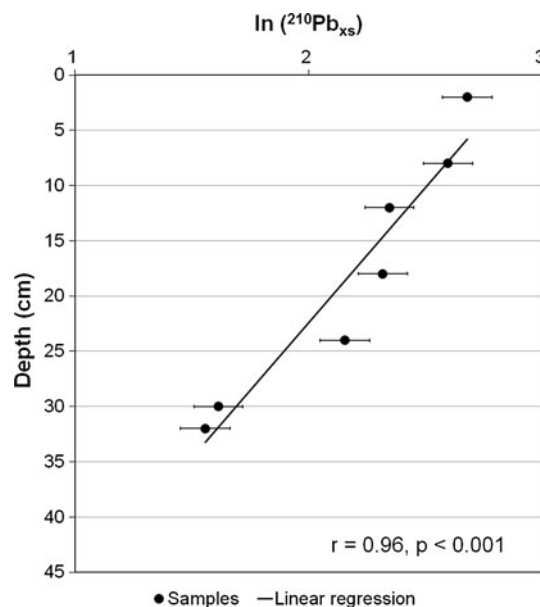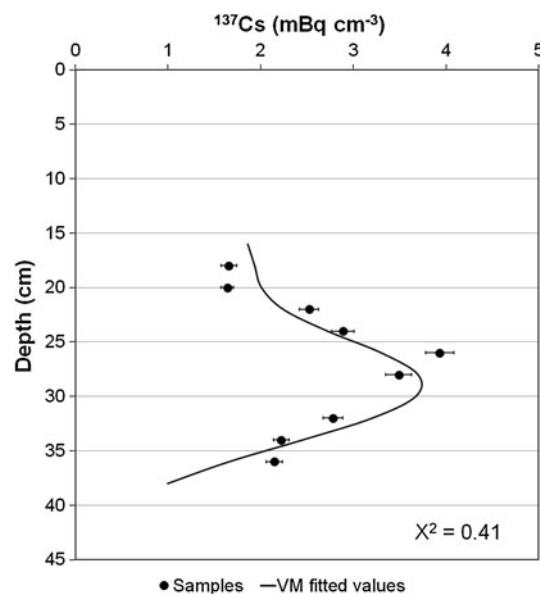
Only four congeners were identified in the P1 core. Total PCBs ranged between <DL and 0.57 ng g^{-1}, with the highest concentration found in the 19- to 21-cm layer, followed by the 8- to 10-cm layer with a concentration of 0.44 ng g^{-1}. In the P3 core, only the 29- to 31-cm section presented a value >DL (0.46 ng g^{-1}).

The data obtained for the three sediment cores was compared with sediment-quality guidelines to assess the sediment potential risk for biota. For this purpose, the effects range-low (ERL), effects range-median (ERM),

Table 2 Core dating of the P2 sediment core

Depth (cm)	Core dating		
	CIC model (^{210}Pb)	VM model (^{137}Cs)	Mean
0–2	2009 ± 0	2009 ± 0	2009 ± 0
2–4	2007 ± 0	2006 ± 0	2007 ± 0
4–6	2004 ± 1	2004 ± 0	2004 ± 0
6–8	2002 ± 1	2001 ± 0	2002 ± 1
8–10	2000 ± 1	1999 ± 0	1999 ± 1
10–12	1998 ± 1	1996 ± 1	1997 ± 1
12–14	1995 ± 2	1994 ± 1	1994 ± 1
14–16	1993 ± 2	1991 ± 1	1992 ± 1
16–18	1991 ± 2	1988 ± 1	1990 ± 2
18–20	1988 ± 2	1986 ± 1	1987 ± 2
20–22	1986 ± 3	1983 ± 1	1985 ± 2
22–24	1984 ± 3	1981 ± 1	1982 ± 2
24–26	1981 ± 3	1978 ± 1	1980 ± 2
26–28	1979 ± 3	1976 ± 1	1977 ± 3
28–30	1977 ± 4	1973 ± 1	1975 ± 3
30–32	1975 ± 4	1971 ± 2	1973 ± 3
32–34	1972 ± 4	1968 ± 2	1970 ± 3
34–36	1970 ± 4	1965 ± 2	1968 ± 3
36–38	1968 ± 5	1963 ± 2	1965 ± 4
38–40	1965 ± 5	1960 ± 2	1963 ± 4
40–42	1956 ± 3	1958 ± 2	1960 ± 4
42–44	1961 ± 5	1955 ± 2	1958 ± 4
44–46	1958 ± 6	1953 ± 2	1956 ± 4

Results for the CIC model, the VM model, and mean dating with both models

Table 3 Comparison between reference levels and maximum PCB concentrations (Σ7 PCBs) detected in the sediment cores (ng g^{-1} dry sediment)

Reference values[a]				This study		
TEL	ERL	ERM	PEL	P1	P2	P3
21.6	22.7	180.0	188.8	0.19	0.35	ND

ND not detected

[a] TEL, ERL, ERM, and PEL

Table 4 Comparison of PCB concentrations (ng g^{-1}) obtained in this study with those of other locations

Location	Σ PCBs	Reference
Paranaguá Bay	ND–6.65	This study
Paranaguá Bay, Brazil	0.20–17.2[a]	Martins et al. (2009)
Santos Estuary, Brazil	0.03–254[b]	Bícego et al. (2006)
Admiralty Bay, Antarctica	0.85–2.47[c]	Montone et al. (2001)
Marseille, France	9.1–226.9[d]	Syakti et al. (2012)
Mumbai, India	<0.01–23.75[e]	Sahu et al. (2009)
Masan Bay, Korea	1.24–41.4[f]	Hong et al. (2003)
East China Sea, China	5.08–19.64[f]	Yang et al. (2012)
Guaratuba Bay, Brazil	ND–5.62[g]	Combi et al. (2013)

ND not detected

[a] Σ44 PCBs

[b] Σ30 PCBs

[c] Σ13 PCBs

[d] Σ7 PCBs

[e] Σ11 PCBs

[f] Σ22 PCBs

[g] Σ51 PCBs

threshold-effects level (TEL), and probable-effects level (PEL) values were adopted. The ERL corresponds to the value below which the probability of adverse effects is rare; the ERM is the value above which biological effects on biota may occur. Above the TEL, adverse effects can be frequent, and above the PEL, adverse effects on biota are expected (Long et al. 1995; MacDonald et al. 1996).

These levels consist of the sum of seven PCB congeners: PCBs 28, 52, 101, 118, 138, 153, and 180. The concentrations in sediment cores did not exceed, at any layer, the levels mentioned (Table 3). Samples from all sections of the P2 core, which had the highest concentrations among the samples, had PCB concentrations lower than the TEL, which is the threshold value above which the concentration may represent a risk to marine organisms.

The regulatory levels for PCBs in marine sediments in Brazil are related to dredged sediments and are based on ERL (level 1 = 22.7 ng g^{-1}) and ERM (level 2 = 180 ng g^{-1}). In this way, the levels of PCBs detected in Paranaguá Bay are lower than allowed by Brazilian legislation (Brazil 2004).

The concentrations obtained in this study are lower than previous results from the region, in which total PCBs (Σ44 congeners) ranged from 0.20 to 17.2 ng g^{-1}; the highest values in that data set were also found in the Paranaguá port area (Martins et al. 2009) (Table 4). PCB concentrations in the samples analysed were far lower than those obtained in more urbanised and industrialised regions of Brazil, such as the Santos estuary (Bícego et al. 2006), as well as worldwide, such as Masan Bay, the coast of South Korea (Hong et al. 2003), the Northwestern Arabian Gulf (Gevao et al. 2012), and Marseille, France (Syakti et al. 2012). The data obtained in this study were similar to those reported in pristine areas as Guaratuba Bay, Brazil (Combi et al. 2013) or the Antarctic continent (Montone et al. 2001), where human activities are limited and the main source of PCBs is atmospheric transport from tropical regions.

Sources of PCBs

Due to few layers having PCBs as well as the low concentrations detected in the P1 and P3 cores, only the P2

core will be discussed hereafter. The distance of the sources of PCBs can be determined by the molecular weight of the congeners analysed, which is directly related to the number of chlorine atoms in the molecules (Fiedler 1997). The low-chlorinated PCBs (fewer than four chlorine atoms) are more soluble in water, are more volatile, and are therefore more mobile in the environment. As a result, we can generally say that they originate from distant sources and may occur in places where they have never used before, *e.g.*, polar regions (Montone et al. 2001). In contrast, congeners with a high degree of chlorination (more than eight chlorine atoms) tend to accumulate closer to the sites where they were generated (Tolosa et al. 1995; Jin et al. 2012). The congeners between these two groups can be considered mid-chlorinated PCBs (Hong et al. 2003).

The mid-chlorinated congeners registered the largest PCB contribution in the P2 core (mean contribution 89.2 % of total PCBs). The predominant congeners in the sediment samples were PCB 66/95 > PCB 110 > PCB 101 > PCB 18 > PCB 132. This congener composition, with greater contribution of penta-chlorinated congeners, suggests a contribution from the commercial mixture Aroclor 1254 (Frame et al. 1996).

The most likely source of PCBs in this environment is Paranaguá city, the urban and industrial activities of which have resulted in the dumping of effluents and the disposal of solid waste in addition to the activities related to Paranaguá port. The nondetection of high-chlorinated PCBs in the P2 core may indicate that these congeners are deposited closer to the margins or at specific points and do not reach the sampled location. However, the low-chlorinated congeners detected may indicate distant sources of PCBs, which would come to the region through marine currents or atmospheric deposition (Iwata et al. 1993; Barra et al. 2006).

Historical Record of Human Occupation in Paranaguá Bay

The integrated analysis of the vertical profile from the P2 core and sedimentation rates determined for the study area can help in the evaluation of the historic contribution of PCBs in Paranaguá Bay by showing the record and the variations of PCB use over time. Because ^{210}Pb- and ^{137}Cs-derived sedimentation rates were similar, the temporal pattern of PCB was estimated using the mean sedimentation rate (0.81 ± 0.06 cm y^{-1}) (Fig. 5).

PCBs were first detected in the P2 core in samples deposited before 1960, with concentrations close to the LD ranging from 0.05 to 0.27 ng g^{-1} (median 0.1 ng g^{-1}). During the 1960s, the concentrations increased slightly, from 0.37 ng g^{-1} in 1962 to 0.79 ng g^{-1}, in 1967 (median = 0.77 ng g^{-1}), probably because this decade was a period of marked increase in the industrial and economic

development of Brazil (Martins et al. 2010a; Martins et al. 2011b). The concentrations remained relatively constant between 1962 until approximately 1985 (mean concentration 0.66 ± 0.15 ng g^{-1}).

From 1987 onward, except for the years 1992 and 1999, the distribution of PCBs was regular and had a tendency to decrease over time. However, the PCB concentrations of the upper layers were greater than those of bottom layers, which ranged from 6.65 to 0.68 ng g^{-1} in 1992 and 2007, respectively (median 1.37 ng g^{-1}). The 1992 and 1999 layers showed concentrations of 6.65 and 2.60 ng g^{-1}, respectively, which are not significantly high concentrations, but they represent the highest concentrations detected in this sediment core.

According to the above description, the profile was divided into time intervals, where interval I refers to the periods before 1960, which presented concentrations close to the DL, indicating a time of minimum input of PCBs into the environment, bioturbation, or PCB migration from greater layers down to the bottom of the core (Peng et al. 2009). Interval II marks the beginning of PCB input, and the subsequent trend in interval III has been a slight decrease in concentrations during the years after the initial contribution.

The highest concentrations were registered in interval III, from 1972 until the mid-1990s, a period described in several worldwide studies as correlating with more intensive use of products containing PCBs. The dissemination and expanded use of products containing these substances and the largest
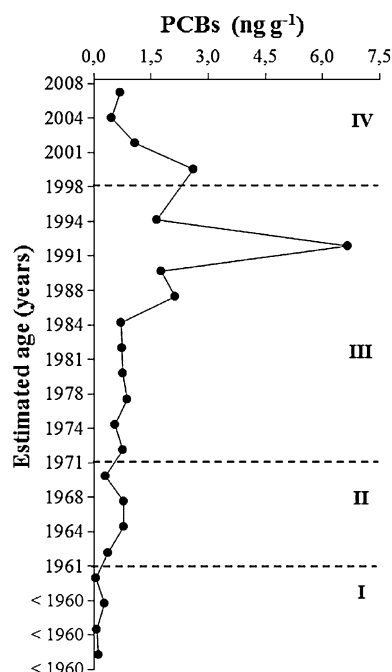

Fig. 5 Vertical distribution of PCBs (ng g^{-1}) in the P2 core according to the mean sedimentation rate divided into four time intervals (I to IV)

area of urban development being in Paranaguá Bay, mainly near the city and port, may explain these variations. The values coincide with the period of maximum production of PCBs in the United States (50,000 tons produced in 1970 (Breivik et al. 2002). The highest value was registered in 1992 (6.65 ng g^{-1}). During this period, an irregular expansion in human occupation in Paranaguá city has been recorded (Costa et al. 1999) that resulted in a greater production of solid wastes and effluents, an effect that was compounded by the lack of sanitary landfills at that time.

Interval IV ranges from 1999 until 2007 and showed a decrease in the concentrations analysed. This decrease is characterised by the prohibition of the use of PCBs in 1981, when new products containing PCB mixtures were not produced or imported into Brazil. The levels obtained even after the ban reflects the use of remaining equipment containing PCBs as has been documented in previous studies (Breivik et al. 2002).

Conclusion

The concentrations found in the PES seem to reflect relatively low local environmental pressures compared with other coastal regions of the world. However, the detection of synthetic compounds, such as PCBs, indicates that the region is subject to the effects of human activities.

The differences in concentrations between the three sediment cores can be mainly attributed to the distance of the sampling sites in relation to possible sources of pollution, which are mostly located near Paranaguá city. The distribution of PCBs in the P2 core (close to Paranaguá city and port) records the beginning of the input of these contaminants into the PES as well as the increasing and decreasing of concentrations related to their high use and subsequent prohibition, respectively. In addition, the maximum concentrations may be related to periods of urban and industrial expansion in the area, and those time periods are coincident with the maximum use and production of PCBs reported for different regions of the world.

The results obtained indicate that PCBs in sediment cores associated with sediment dating can be used as a marker of human activities in the construction of the historic occupation and contaminant inputs into estuarine environments and can contribute information to a global inventory of PCBs.

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