

UNIVERSIDADE FEDERAL DO PARANÁ

AMANDA CÂMARA DE SOUZA

**BIFENILAS POLICLORADAS EM SEDIMENTOS DO ESTUÁRIO DE SANTOS,
BRASIL: DISTRIBUIÇÃO, HISTÓRICO E POSSÍVEIS FONTES**

PONTAL DO PARANÁ

2018

AMANDA CÂMARA DE SOUZA

**BIFENILAS POLICLORADAS EM SEDIMENTOS DO ESTUÁRIO DE SANTOS,
BRASIL: DISTRIBUIÇÃO, HISTÓRICO E POSSÍVEIS FONTES**

Dissertação apresentada como requisito parcial à obtenção do grau de Mestre em Sistemas Costeiros e Oceânicos, no Curso de Pós-Graduação em Sistemas e Costeiros e Oceânicos, Setor de Ciências da Terra, da Universidade Federal do Paraná.

Orientador: Prof. Dr. César de Castro Martins

PONTAL DO PARANÁ

2018

CATALOGAÇÃO NA FONTE:
UFPR / SiBi - Biblioteca do Centro de Estudos do Mar
Caroline Felema dos Santos Rocha – CRB 9/1880

S719b Souza, Amanda Câmara de
Bifenilas policloradas em sedimentos do estuário de Santos, Brasil: distribuição, histórico e possíveis fontes. / Amanda Câmara de Souza. – Pontal do Paraná, 2018. 51 f.: il.; 29 cm.

Orientador: Prof. Dr. César de Castro Martins.

Dissertação (Mestrado) – Programa de Pós-Graduação em Sistemas Costeiros e Oceânicos, Centro de Estudos do Mar, Setor de Ciências da Terra, Universidade Federal do Paraná.

1. Bifenilas policloradas (PCBs). 2. Inventário de bifenilas policloradas. 3. Consumo de bifenilas policloradas. 4. Avaliação de risco. 5. Testemunhos de sedimentos. 6. Análise estatística multivariada. 7. Atlântico Sul. I. Título. II. Martins, César de Castro. III. Universidade Federal do Paraná.

CDD 615.9512



MINISTÉRIO DA EDUCAÇÃO
SETOR CIÊNCIAS DA TERRA
UNIVERSIDADE FEDERAL DO PARANÁ
PRÓ-REITORIA DE PESQUISA E PÓS-GRADUAÇÃO
PROGRAMA DE PÓS-GRADUAÇÃO SISTEMAS COSTEIROS
E OCEÂNICOS

TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação em SISTEMAS COSTEIROS E OCEÂNICOS da Universidade Federal do Paraná foram convocados para realizar a arguição da dissertação de Mestrado de **AMANDA CÂMARA DE SOUZA** intitulada: **Bifenilas policloradas em sedimentos do estuário de Santos, Brasil: distribuição, histórico e possíveis fontes**, após terem inquirido a aluna e realizado a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.

A outorga do título de mestre está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

Pontal do Paraná, 22 de Março de 2018.



CÉSAR DE CASTRO MARTINS

Presidente da Banca Examinadora (UFPR)



JULIANA LEONEL

Avaliador Externo (UFSC)



DENIS MOLEDO DE SOUZA ABESSA

Avaliador Externo (UNESP)

AGRADECIMENTOS

À Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior (CAPES) pela bolsa de mestrado, ao CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) e à FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo - 01/10704-8) pelo auxílio financeiro.

Ao meu orientador, o Prof. Dr. César de Castro Martins, que mesmo com todas as dificuldades e falta de tempo sempre esteve presente e disposto a resolver os problemas. Sem dúvida, nesses vários anos de orientação foi fundamental para o meu crescimento pessoal e profissional.

Às LaGPoM *girls*, Ana Carol, Ana Lúcia, Fer, Helo, Marina, Marininha e Marines por toda a parceria e socorro dentro e fora do laboratório. Um agradecimento especial à Tati que tantas vezes corrigiu meus trabalhos e me ajudou a discutir os dados.

Ao pessoal da USP, Dra. Satie Taniguchi, Dra. Márcia Bicego, Dra. Rosalinda Montone e Dr. Rubens Figueira por ceder as amostras superficiais, pela datação dos testemunhos, ajuda com as quantificações e todas as contribuições para o trabalho escrito.

A todos os funcionários e professores do CEM que direta e indiretamente contribuíram para a minha formação e para a realização deste trabalho.

Aos amigos da PGSISCO, em especial à turma de 2016, sempre presente desde os momentos mais felizes de festas e comidas, os mais constrangedores de karaokês, até os mais difíceis de entrega de trabalhos. Agradeço pelo companheirismo e por tornarem esses dois anos muito mais leves.

A todos os amigos da graduação. Em especial à Lai, Moa, Ilara, Thaise, Mariel e, principalmente, a minha “roommi” Fernanda, que são minha família de Pontal, as “muito migas” que tiveram tanta paciência e me apoiaram simplesmente em tudo.

Por fim, agradeço aos meus pais, Solange e Reginaldo, ao meu irmão, Rodrigo, e aos meus queridos avós, Neusa e Manuel, pela compreensão e por toda a estrutura que sempre me deram.

RESUMO

A deposição histórica das bifenilas policloradas (PCBs) foi estudada em dez amostras de sedimentos superficiais e três testemunhos sedimentares do Estuário de Santos, um importante centro industrial e urbano da América do Sul. A concentração ($190,7 \text{ ng g}^{-1}$) e o inventário de PCBs ($295,50 \text{ ng cm}^{-2}$) máximos foram detectados nos sedimentos referentes aos anos de 1980, dez anos depois do pico de emissão de PCBs no Brasil. O consumo de PCBs, o padrão de congêneres e as análises estatísticas multivariadas indicaram que os níveis começaram a aumentar a partir do desenvolvimento industrial e urbano da região, interferindo na magnitude dos aportes durante os últimos 50 anos. A avaliação de risco indicou que os níveis observados na maioria das amostras estão em uma faixa capaz de produzir riscos ecológicos para a biota marinha. Este estudo fornece as primeiras estimativas do inventário histórico de PCBs em sedimentos do Estuário de Santos, Atlântico Sudoeste, contribuindo com dados para gerenciamento regional e global e destacando o papel dos sedimentos para o armazenamento permanente de poluentes orgânicos persistentes e os riscos envolvidos em sua ressuspensão, especialmente em regiões que são constantemente dragadas como o Estuário de Santos.

Palavras-chave: Inventário de PCBs. Avaliação de risco. Consumo de PCBs. Testemunhos de sedimentos. Análise estatística multivariada. Atlântico Sul.

ABSTRACT

The depositional history of polychlorinated biphenyls (PCBs) was studied from ten surficial sediments and three sediment cores sampled in the Santos Estuary, an important industrial and urban centre in South America. The maximum concentration (190.7 ng g^{-1}) and inventory ($295.50 \text{ ng cm}^{-2}$) were detected in sediments related to the 1980s, representing a ten year delay of the emission peak in Brazil. PCB consumption, the congener patterns and multivariate statistical analyses indicated that the levels started to increase with the intensification of regional urban and industrial development that continued to interfere in the magnitude of input during the past 50 years. In addition, the risk assessment indicates that levels observed in most of the samples are in a range capable of producing ecological risks to the marine biota. This study provides the first estimates of historic sediments PCB inventories in the Southwestern Atlantic, contributing data for regional and global management and highlighting the role of sediment as a compartment for permanently storing persistent organic pollutants and the risks involved in their resuspension, especially in regions that are constantly dredged such as the Santos Estuary.

Key-words: PCBs inventories. Risk assessment. PCBs consumption. Sediments cores. Multivariate statistical analysis. South Atlantic.

SUMÁRIO

High hazard depositional and global correlation history of PCBs in sediments around a South American industrial coastal area (Santos Estuary, Southwestern Atlantic)	7
Highlights	8
1 Introduction	9
2 Material and methods	10
2.1 <i>Study area and sediments sampling</i>	10
2.2 <i>PCB determination</i>	11
2.3 <i>Quantification and quality assurance procedures</i>	12
2.4 <i>Data analyses</i>	13
3 Results and discussion	13
3.1 <i>PCBs levels, trends and risk assessment</i>	13
3.2 <i>Correlation between PCBs, bulk sediment parameters and hydrocarbons</i>	15
3.3 <i>Congeners distribution and sources of PCBs</i>	18
3.4 <i>Historical record of PCBs input in the Santos Estuary</i>	20
4 Conclusion.....	24
Acknowledgments.....	25
Appendix A. Supplementary Data	25
Figure captions	25
Table and figure captions (supplementary material).....	26
References	27
Supplementary material	32
ANEXO – DADOS BRUTOS	38

High hazard depositional and global correlation history of PCBs in sediments around a South American industrial coastal area (Santos Estuary, Southwestern Atlantic)

Deposição de alto risco e correlação com a história global de PCBs em sedimentos do entorno de uma área costeira industrial sul-americana (Estuário de Santos, Atlântico Sudoeste)

Revista pretendida: Journal of Hazardous Materials (*J. Hazard. Mater.*), ISSN (0304-3894), Fator de Impacto (JCR, 2016) = 6.065, Qualis CAPES = Estrato A1.

* Amanda Câmara de Souza ¹, Satie Taniguchi ², Rubens C. L. Figueira ², Rosalinda Carmela Montone ², Marcia Caruso Bicego ², [§] César C. Martins ^{2,3}

¹ Programa de Pós-Graduação em Sistemas Costeiros e Oceânicos (PGSISCO), Universidade Federal do Paraná, Caixa Postal 61, 83255-976, Pontal do Paraná, PR, Brazil.

² Instituto Oceanográfico da Universidade de São Paulo, Praça do Oceanográfico, 191, 05508-900, São Paulo, SP, Brazil.

³ Centro de Estudos do Mar, Universidade Federal do Paraná, Caixa Postal 61, 83255-976, Pontal do Paraná, PR, Brazil.

Corresponding authors

E-mail addresses: * amandacamaradesouza@gmail.com (A.C. Souza)

[§] ccmart@ufpr.br (C.C. Martins)

Highlights

- PCBs in dated sediments provide evidence of high hazard historic contamination;
- Levels started to increase in 1960 following emissions in Brazil and worldwide;
- Concentrations in sediments showed a faster response to PCB consumption in Brazil;
- High concentrations and inventories were detected in sediments after the PCB ban;
- 50 years of increased industrial activity changed the magnitude of PCB input.

1 Introduction

Persistent organic pollutants (POPs) are characterized by chemical stability, toxicity potential, persistence, long-range transport and bioaccumulation capacity [1,2]. Additionally, they were widely produced and used, and thus, they are a significant threat to human health and the environment, which led to their being banned at the Stockholm Convention in Sweden in 2001 [3]. Polychlorinated biphenyls (PCBs) are among the most important groups of POPs, mostly associated with urbanized and industrial areas, and they have been extensively used in capacitors, transformers, hydraulic tools, heat exchange liquid, cutting oils, lubricants, plasticizers, surface coatings, adhesives, carbon-less copy paper, ink, dyes, and waxes [4,5].

These compounds can be introduced into the marine environment via atmospheric precipitation, industrial and urban effluent, river discharge and continental runoff [6]. Once they reach the ocean, their hydrophobic property and the high partition coefficients generate a tendency for POPs to adsorb in the suspended particulate matter and consequently to accumulate in the sediments, an important reservoir and secondary source of these compounds in the marine environment [7]. Therefore, the analysis of surface sediments and sediment cores can provide data on the recent and historical contamination, respectively [8].

The determining factors for the adsorption of organic pollutants and their concentrations in dated sediments primarily depend on the sources related to anthropic activities around the studied area, the physicochemical properties such as the lipophilicity and solubility of each contaminant, and the geochemical sediment features, including grain size and organic matter content [6]. Therefore, these factors can support the understanding of the PCB depositional history in aquatic ecosystems for environmental impact studies.

The Santos Estuary is one of the most important industrial, urban and economic centres in South America. Industrialization and urbanization were intensified as a result of the Cubatão Industrial Complex, which has more than 1100 industries, and the expansion of the Port of Santos. These are the main sources of contaminants for the estuarine system, besides municipal solid waste and industrial and domestic effluent [9–12].

To reconstruct a first full history of PCB contamination in the Santos Estuary sediments, this study (i) evaluates the concentration profiles in sediment cores and compares them with the history of PCB emissions and consumption; (ii) evaluates the concentrations in superficial sediments to establish the current spatial distribution patterns; (iii) assesses a preliminary environmental risk, comparing international and local threshold levels, and (iv) uses multivariate statistics in order to assess whether these POPs levels are being more

influenced by the intensification of urban and industrial development of the region or whether it is related to favorable natural accumulation conditions, by checking the relationship between the concentrations of PCBs, geochemical sedimentary parameters (total organic carbon - TOC, C/N ratio, grain size), magnetic susceptibility (MS) and hydrocarbon concentrations, in this case representing the anthropogenic activities in the region. This approach would improve the knowledge of the past and current contamination sources and improve our understanding of the depositional trends of POPs.

2 Material and methods

2.1 Study area and sediments sampling

Located on the South-eastern coast of Brazil ($23^{\circ}30' - 24^{\circ}00'S$; $46^{\circ}05' - 46^{\circ}30'W$), the Santos Estuary (Fig. 1) receives a high load of organic and inorganic contaminants from the diversity of local human activity [10–15]. The port of Santos activities, such as constant ship traffic, cleaning operations of tanks and basements, and garbage and sewage production from docks and ships release of a large number of pollutants. Additionally, there are the dredging of the historically contaminated sediments of the Santos and Piaçaguera channels, domestic sewage, garbage dumps and landfills from a permanent population of over 1,200,000 settled in the cities of Santos and São Vicente, as well as the activities of numerous chemical, petrochemical and metallurgical industries installed in the region.

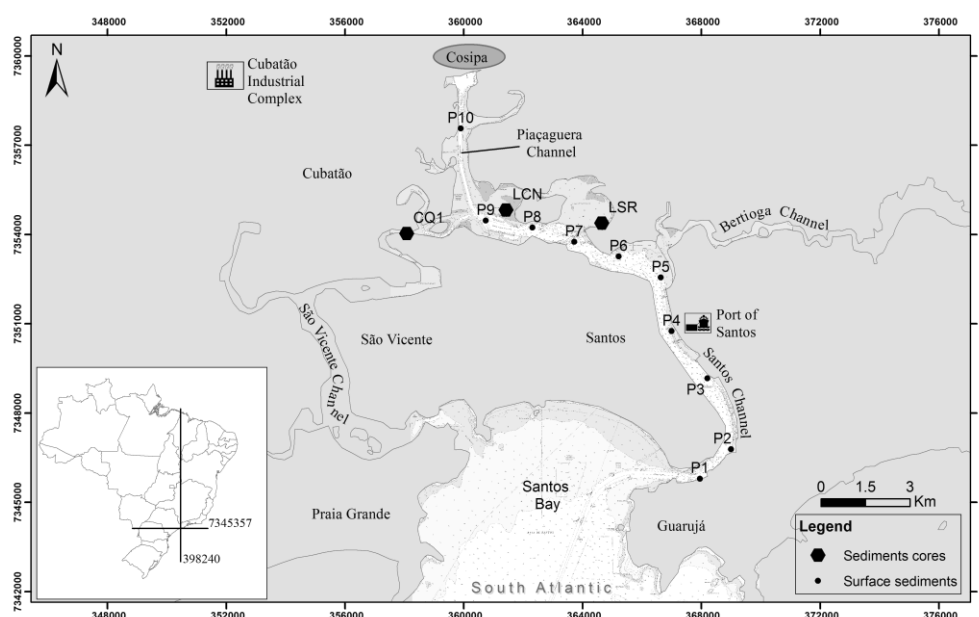


Fig. 1: Map of the study area showing the sampling stations in superficial and core sediments of the Santos Estuary, South Atlantic.

Three vibracores (3 m long, 0.75 m wide aluminium barrels, 10 cm i.d.) sampled at the Casqueiro River (CQ1), the Largo de Santa Rita (LSR) and the Largo do Canéu (LCN) (Table S1, Supplementary Material) were collected in a shallow water column (below 1.0 m) of the Santos Estuary, São Paulo, Brazil (Fig. 1) in 2002. They were sectioned in 2-cm intervals (0–40 cm for CQ1; 0–60 cm for LSR; 0–90 cm for LCN) and then in one sub-sample in each 20 cm section to the core bottom, and they had been previously analysed for organic geochemical proxies (e.g., TOC, TN, linear alkyl benzenes-LABs, and hydrocarbons) by Martins et al. [11,12,15]. The detailed dating method (calibration, detector counting efficiency and errors) was also fully described in Martins et al. [11,12], and the average sedimentation rates obtained from each core were 1.47 ± 0.13 (CQ1), 1.24 ± 0.11 (LSR) and 1.29 ± 0.12 (LCN) cm y⁻¹. The depth and estimated years are presented in Table S2.

Additionally, in order to cover the time lapse between sediment core sampling and recent times, 10 surficial sediments (0 – 2 cm) were collected with a stainless-steel grab sampler in the Santos Channel in 2012. TOC analyzed in superficial sediments were performed using the method based on the oxidation of the organic carbon using potassium dichromate, H₂SO₄ and titration of excess of dichromate with ammoniacal ferrous sulphate [15]. All the samples were placed in pre-cleaned aluminium containers and stored at -20 °C, oven-dried at less than 40 °C, and finally stored in clean glass bottles until subsequent analysis.

2.2 PCB determination

The analytical procedure (extraction, fractioning and purification) was based on the United Nations Environmental Programme [16]. Organic extracts archived in the laboratory, previously analysed for hydrocarbons and described in Martins et al. [11,12], were used for PCB determination. Briefly, approximately 25 g of dry sediment was Soxhlet-extracted with hexanes (95% n-hexane) and dichloromethane (both from J. Baker) (1:1) for a period of 8 h. The solvent extract was concentrated in a rotary evaporator to approximately 2 mL. The extract was fractionated by adsorption liquid chromatography into aliphatic and aromatic hydrocarbons using a column of alumina (1.8 g) and silica gel (3.2 g) with hexane and 3:1 dichloromethane/hexane for the aliphatic (F1) and aromatic (F2) fractions as eluent, respectively. The fractions were concentrated once more in a rotary evaporator and transferred to a vial, and then, the volume was adjusted to precisely 1 mL using a stream of N₂ gas. To determine the PCB concentration, 100 µL of fraction 1 (F1; aliphatic hydrocarbons-AHs) and

fraction 2 (F2; polycyclic aromatic hydrocarbons-PAHs), 25 μL of internal standard (PCB 103, 1 $\text{ng } \mu\text{L}^{-1}$; C-103N, from AccuStandard, New Haven, CT, USA) and 25 μL of *n*-hexane were added to injection vials, resulting in a 250 μL extract.

The concentration and identification of PCBs were determined through the injection of sample extracts into an Agilent GC 7890A gas chromatograph coupled with a mass spectrometer (GC/MS) (Agilent 5975C inert MSD with Triple-Axis Detector) equipped with an Agilent 19091J-433 capillary fused-silica column coated with 5% Phenyl Methyl Siloxan (30 m length, 0.25 mm ID, and 0.25 μm film thickness) in SIM (System Ion Monitoring) mode. Helium was used as the carrier gas. The oven temperature was programmed to begin at 75 $^{\circ}\text{C}$ for 3 min, increasing at 15 $^{\circ}\text{C } \text{min}^{-1}$ up to 150 $^{\circ}\text{C}$, then at 2 $^{\circ}\text{C } \text{min}^{-1}$ up to 260 $^{\circ}\text{C}$, and finally at 20 $^{\circ}\text{C } \text{min}^{-1}$ to up to 300 $^{\circ}\text{C}$ (holding for 10 min), in a total time of 75 min.

The following compounds were analysed: (i) low-chlorinated PCBs: 8, 18, 28, 31, 33, 44, 49, 52, 56/60, 66, 70, and 74; (ii) high-chlorinated PCBs: 87, 95, 97, 99, 101, 105, 110, 114, 118, 123, 128, 132, 138, 141, 149, 151, 153, 156, 157, 158, 167, 170, 174, 177, 180, 183, 187, 189, 194, 195, 201, 203, 206, and 209.

2.3 *Quantification and quality assurance procedures*

The PCBs were individually identified by matching their retention time and the mass/charge of ion fragments with those obtained from a mixture of external standards (C-WNN and C-WCFS from AccuStandard, New Haven, CT, USA) using an HP Enhanced Chemstation G1701CA. The concentration of individual compounds was obtained through the internal standard peak area method and an 8-point analytical curve for individual components (1, 5, 10, 20, 80, 100, 150, and 200 $\text{pg } \mu\text{L}^{-1}$, $r^2 = 0.995$).

The quality assurance included analyses of procedural blanks, precision tests, and certified reference material [17]. The measured peaks found in the blanks did not interfere with the analyses of the target compounds. The detection limits (DL) were 0.5 $\text{ng } \text{g}^{-1}$ for individual PCBs. These data are based on the lowest sensitive PCB concentration (0.004 $\text{ng } \mu\text{L}^{-1}$) multiplied by the final extracted volume (250 μL) and divided by the weight sediment (20 g) before extraction. The results from the standard reference sediment IAEA-383 analysis were within the upper and lower 95% confidence interval reference values for 100% of PCBs, confirming the validation of the PCBs results obtained from the archived organic extracts.

2.4 Data analyses

ArcGIS version 9.3 software was used to create maps with the spatial distribution of PCBs in the study area. Statistical analyses were performed using R 3.0.3 software [18]. The correlation between variables was estimated by the Pearson correlation coefficient (r). A simple linear regression analysis was applied between the TOC and PCB concentrations. A multivariate approach was also adopted, using principal component analysis (PCA) to verify the interactions of PCB with other previously analysed parameters (TOC, C/N ratio, grain size, MS and hydrocarbon concentrations) and their influence on the sample distribution in each core.

3 Results and discussion

3.1 PCBs levels, trends and risk assessment

The PCB totals in the sediment cores are presented in Table S2. The CQ1 core presented the highest total PCB concentration of the three analysed cores, ranging from <DL to 190.7 ng g⁻¹ (mean value \pm SD = 93.3 \pm 64.8 ng g⁻¹). The concentrations of total PCBs in LSR were slightly lower than CQ1 and varied from <DL to 128.1 ng g⁻¹ (mean value \pm SD = 62.1 \pm 38.6 ng g⁻¹). Finally, the LCN core values varied from <DL to 96.3 ng g⁻¹ (mean value \pm SD = 30.5 \pm 29.4 ng g⁻¹) and presented the lowest concentrations. The higher concentrations of PCBs in CQ1 are probably due to its proximity to the Cubatão Industrial Complex, the solid waste disposal at Alemoa hill, and the freshwater discharge from several small- or moderate-flow rivers that cut off potentially contaminated areas [11,12]. A previous study in the Santos Estuary also detected the Cubatão Industrial Complex as one of the main sources of PCBs, with the highest concentrations (254.0 ng g⁻¹; sampling in 2000) [10] comparable to values obtained in sediments from 2001 in core CQ1 (153.8 ng g⁻¹).

The levels in superficial recent sediments varied between 0.36 and 9.80 ng g⁻¹ (mean value \pm SD = 3.19 \pm 2.77 ng g⁻¹; Fig. 2) and were significantly lower than the top of all cores. This decrease in concentrations over the years is expected as a result of the PCB ban in Brazil, which began in 1981. In addition, the core sampling sites are located in more sheltered areas surrounded by mangrove vegetation and where the low local hydrodynamics and depth favour the sedimentation of fine sediments [19] and support an accumulation of contaminants. Sites P9 and P10 are under the direct influence of the Cubatão Industrial Complex, and they

presented the highest PCB concentrations of the superficial sediments. Sites P8 to P1 are located in the constantly dredged Santos Channel, which may have contributed to the lower concentrations, despite the proximity to the city and the port of Santos. Site P1 is located furthest from the main pollutant sources of the estuary and presented the lowest concentrations. This is due to the low estuary circulation influencing the deposition of substances near their input sources [20].

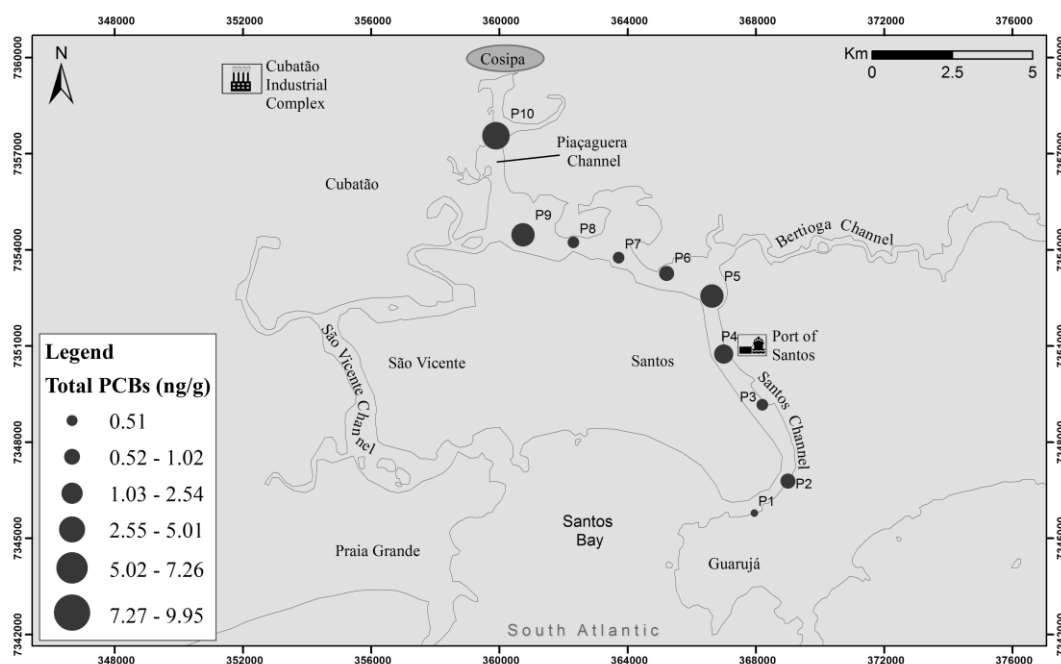


Fig. 2: Map of the study area showing the concentrations of total PCBs (ng g⁻¹) in superficial sediments of the Santos Estuary, South Atlantic.

To accomplish a preliminary risk assessment, we calculated the hazard quotient (HQ) by dividing the measured concentration (MEC) of PCBs by the predicted no-effect concentration (PNEC). The maximum and minimum concentrations of the superficial and core sediments were used as MEC (the values <DL of the bottom cores were excluded from the calculation), whereas the PNEC was based on sediment-quality guidelines (SQG) based on parameters established by National Oceanic and Atmospheric Administration (US-NOAA) [21], and a second SQG (SQG') specifically for the Santos estuary was based on available data from Choueri et al. [22]. The SQG' values were derived from few data and should be carefully analysed, and it was used only in order to compare local and international data. These acute toxicity values were divided by a factor of 1000 (Table S3). For interpretation, an HQ < 0.1 indicates no hazard, 0.1 – 1.0 a low hazard, 1 – 10 a moderate hazard, and >10 a high hazard [23,24].

All calculated HQs were above 1.0. Separately, HQs calculated by the site-specific SQG', which is more restrictive than the classic SQG established by the US-NOAA, were always above 10 and ranged between 137.4 to 3,740 and between 324.4 to 72,782 in superficial and core sediments, respectively. The HQ values calculated for the classic SQG ranged from 2.0 to 54.4 and from 4.72 to 1,059 in superficial and core sediments, respectively. The results between 1 and 10 only appeared when the minimum MEC was calculated with the PNEC from SQG. Therefore, the results indicate a moderate to high hazard, which is a concern through the exposure of estuarine organisms and for a constantly dredged area. This activity generates the resuspension of contaminated sediments representing a high risk to aquatic organisms due to the possibility of these toxic contaminants becoming bioavailable in the water column [25]. Finally, the process of dredging may generate permanent contamination of the marine biota from remobilization of previously immobilized compounds in the sediments.

3.2 Correlation between PCBs, bulk sediment parameters, and hydrocarbons

The sediment grain sizes and organic matter amounts may influence the vertical distribution of PCBs, since large percentages of fine sediments and TOC increase the accumulation and deposition of organic compounds [26]. The TOC for surficial sediments varied between 0.18 in P6 and 2.46% in P10 (mean value \pm SD = $1.09 \pm 0.63\%$; Fig. 3). Total PCB concentrations were strongly correlated to TOC ($r^2 = 0.82$, $p < 0.05$), suggesting that it was a determining factor for PCB accumulation in superficial sediments.

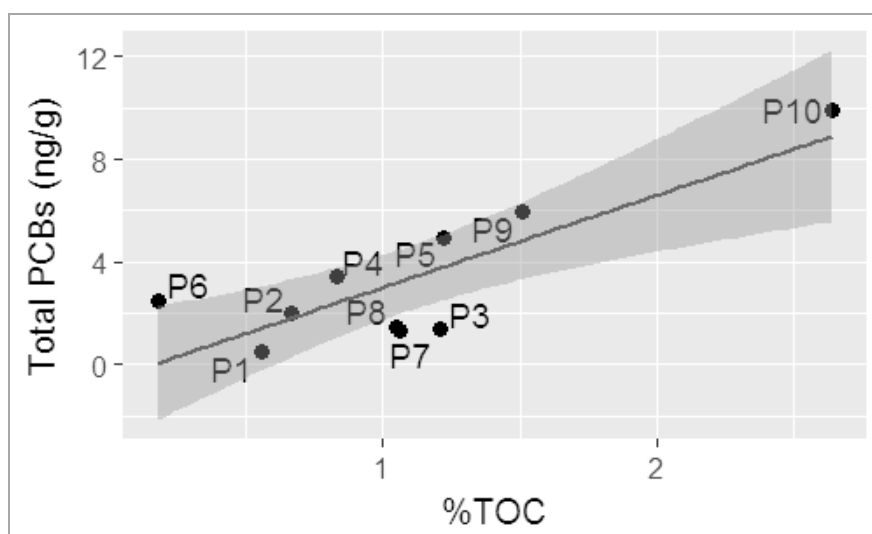


Fig. 3: Plot of the measured total PCB concentrations versus predicted TOC values. Linear regressions have been fitted for each sampling date shown as lines. The graph shows a good correlation between the PCB and TOC values ($r = 0.83$, $p < 0.5$).

Summary results regarding grain size distribution, TOC, the C/N atomic ratio, PAHs, MS and AHs for sedimentary cores (Table S2 and Fig. S1, Supplementary Material) were previously presented and discussed by Martins et al. [10,11,14]. In this study, a PCA was performed to evaluate the influence of these parameters on PCB distribution (Fig. 4 and Fig. S2, S3 and S4, Supplementary Material) in each of the analysed cores.

In CQ1, the principal component (PC) 1 explained approximately 65% of the data and was related to PCBs, PAHs, AHs and the C/N ratio (inversely correlated), whereas PC 2 explained approximately 17% of the variability and was associated with TOC values. Similarly, in LSR, PC 1 explained approximately 65% of the data and was related to the same variables listed for CQ1, whereas PC 2 explained approximately 18% of the variability and was associated with the percentage of fine sediments. In both cores, the PCA scores discriminated among samples from (A) years 1980 to 2000, dominated by the presence of high concentrations of PCBs, HAs and PAHs; (B) intermediary years (represented by the 1970s), marking a transition from natural to anthropogenic sources, and; (C) past years, associated with high values of the C/N ratio with a predominant origin from terrestrial organic matter. The association between PAHs, AHs, and PCBs indicates that concentrations of these compounds may have increased in the same years and are probably influenced by the local intensification of industrialization and urbanization.

Finally, in LCN, PC 1 explained approximately 48% of the data and was related to PCBs, AHs, and MS, whereas PC 2 explained approximately 28% of the variability and was associated with the percentage of TOC and the C/N ratio. No groups could be assumed. However, PCBs were also associated with other contaminants due to apparent correlation based on positive PC1 values.

Therefore, in this study, superficial PCB concentrations were strongly associated with TOC, indicating an accumulation influenced by sediment characteristics. In contrast, sediments related to periods of greater production and consumption, with significant input of PCBs to the environment, do not correlate with TOC and fine sediments and suggest that in the Santos Estuary, the influence of these parameters on the concentration of PCBs possibly depends on the magnitude of the input.

3.3 Congeners distribution and sources of PCBs

The PCB homolog distribution shows that the relative composition of the PCB congeners was dominated by Hexa-PCBs > Penta-PCBs > Tetra-PCBs with these three homologs representing 73 - 100% of the total PCBs in surficial sediments (Fig. 5). A similar homologue distribution pattern was detected by Bicego et al. [9] in the Santos Estuary, suggesting a continuous input of these compounds in the region, besides the resuspension of PCBs deposited in the past due the dredging activities carried out close to the studied area.

High-chlorinated congeners (from penta- to deca-CBs) were dominant in the superficial sediments of the Santos Estuary. These congeners are less volatile than low-chlorinated PCBs (di-, tri- and tetra congeners). Consequently, they mainly originate from the local emissions from anthropogenic activity and are deposited close to their sources [5,27]. Therefore, Santos Estuary contamination is probably from local sources, mainly from the Cubatão Industrial Complex, since the highest concentrations with the highest levels of high-chlorinated congeners were found near this region. Site P1, the farthest site from the industrial complex, is the only superficial sample dominated by low-chlorinated congeners, and the low concentrations of total PCBs probably influenced in this inversion.

In addition, this contrast was also in evidence when we calculated the following ratio:

$$R = ([PCB28] + [PCB52])/([PCB28] + [PCB52] + [PCB138] + [PCB153] + [PCB180])$$

PCB 28 and 52 are more volatile and slightly more hydrophilic than PCB 138, 153, and 180, which are less volatile but sorb stronger on solid phases [27]. Therefore, when analysed carefully, since PCBs have different resistance degradation and the commercial products have varying amounts of these congeners, the ratio between these compounds is considered an indicator of the distance/pathway of contamination. A high R-value might be related to atmospheric deposition of the PCB air pollution since a low R-value could be consistent with a local source of PCB [27]. In the superficial sediments of the Santos Estuary, the R-value ranged from 0.14 to 1.00 (Fig. 5), with low levels in most analysed samples, except for sample P1.

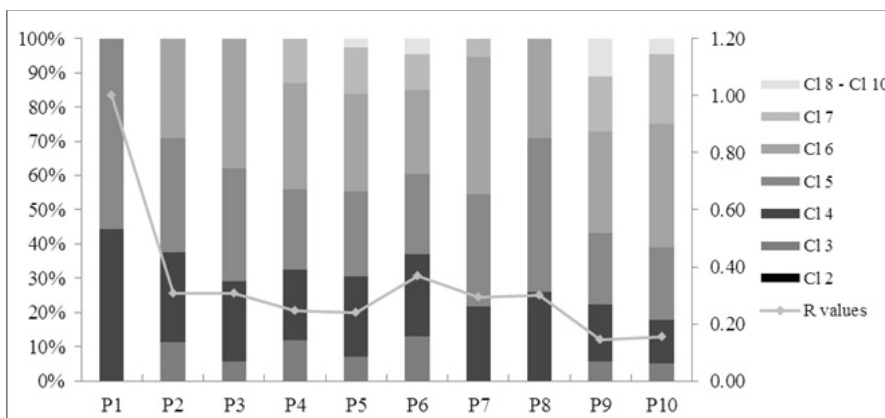


Fig. 5: The relative distribution of PCB homologs and R values in superficial sediments from the Santos Estuary.

Analogous to superficial sediments, the same PCB homologues were predominant (Hexa-PCBs > Penta-PCBs > Tetra-PCBs) and represented 69 - 77%, 67 - 76%, and 63 - 74% of the total PCBs for the CQ1, LSR, and LCN sediment cores, respectively (Fig. 6). This slight variation may indicate that the sources did not differ spatially and over time.

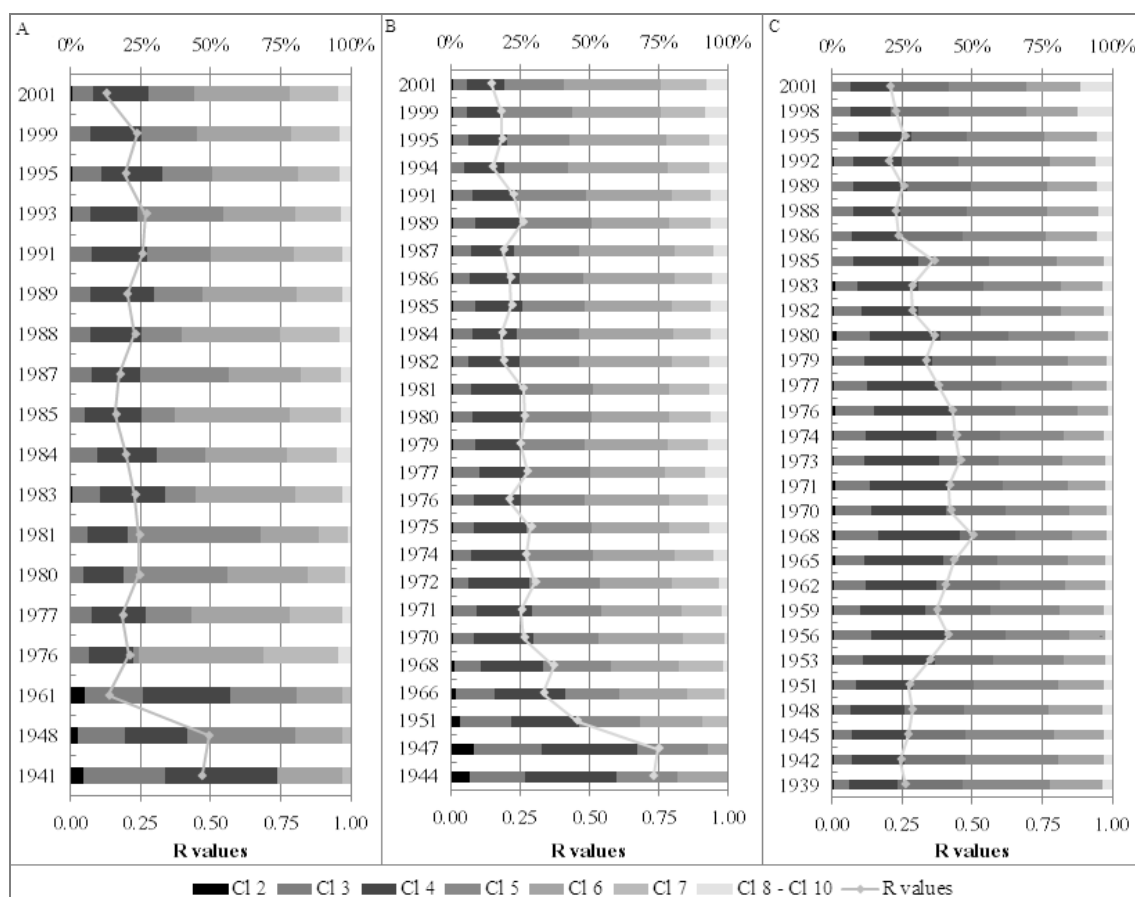


Fig. 6: The relative distribution of PCB homologs and R values in the CQ1 (A), LSR (B) and LCN (C) cores from the Santos Estuary.

In cores CQ1 and LSR, the downcore congener distributions were rather constant, except for a change of concentrations in the bottom core layers. In these samples, the concentrations of low-chlorinated PCBs exceeded the levels of high-chlorinated PCBs. After that, the concentrations of low-chlorinated PCBs remained constant. The R-value for both cores respected the same patterns and ranged between 0.14 to 0.52 and 0.15 to 0.75, respectively (Fig. 6), for cores CQ1 and LSR. The bottoms of these cores were marked by sediment deposited prior to the industrial activity intensification in the region. Therefore, the low-chlorinated contaminants are probably related to atmospheric deposition. However, it is important to emphasize that the CQ1 and LSR bottoms presented low levels for all the analysed PCBs, which may have influenced this inversion of sources.

The distribution of PCB congeners along sediment core LCN was rather constant. A high contribution of high-chlorinated PCBs was also detected in the bottom of the sediment core, and the R-value indicated the same PCB pattern with the smallest variation of all the cores sampled, ranging from 0.20 to 0.50 (Fig. 6). It is unlikely that these values in the bottom are related to local sources, especially because these results indicate a local contribution in years with minimal anthropic activities in the region and, in some samples, even before the beginning of the worldwide production of PCBs. Most likely, they occurred by factors such as physical mixing of sediments, bioturbation, and/or downward migration of PCB congeners in the sediment column [28,29].

3.4 Historical record of PCBs input in the Santos Estuary

The dates estimated from the ^{137}Cs model and concentrations of total PCBs are presented in Fig. 7.

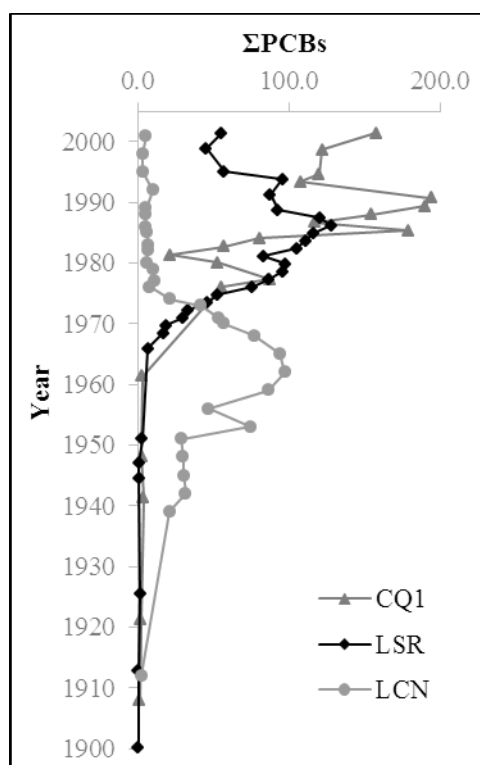


Fig. 7: Total PCB concentration (ng g^{-1}) in different sediment cores from the Santos Estuary.

The history of PCBs, PAHs and LABs is similar in the Santos Estuary. PCB levels in the CQ1 core began to increase in 1975 at the same time that Martins et al. [11,12] detected an increase in concentrations in LABs and PAHs. The authors identified the implementation of solid waste disposal at Alemoa hill as the main source of this significant input of organic compounds. Since 1970, solid waste has been disposed of and burned close to the banks of the Casqueiro River [15] and could have contributed to this increase in PCBs. A small decrease in total PCBs also coincided with a decrease in PAHs from 1978 to 1982, and it probably occurred via a decline in industrial activity in the Santos Estuary in reaction to the world oil crisis that contributed to a global industrial production decline during this period [12]. Additionally, these low values could be a rapid response to the prohibition of PCBs in Brazil in 1981 [30].

Subsequently, the concentrations increased again and reached a peak in the late 1980s and early 1990s. The high levels of PAHs and LABs in the same layers [11,12] suggests a significant anthropogenic input in this period. Especially for PCBs in Brazil, despite the existing resolution n° 1075/2011, which provides for the controlled disposal of PCBs and their wastes, decontamination and disposal of transformers, capacitors and other electrical equipment containing PCBs, the current legislation permit equipment

containing PCBs to remain in use until the end of its lifespan, so the electric sector is an active source of PCBs for the environment [30], and the increase in concentrations even after PCBs were banned could be a result of the leakage of these products. It is estimated that a much larger volume of 2,665 m³ of oil contaminated with PCBs is found in the Brazilian power industry, and since approximately 80% of the PCBs existing in Brazil are found in this sector [31], one can assume that these contaminants still represent a threat due to the possibility of leaks. This threat poderia ser controlada se o for aprovado.

The vertical distribution of total PCBs in LSR is similar to the distribution in the CQ1 core. Concentrations started to increase between the mid-1960s and late-1970s, a period of industrial development in the Santos Estuary marked by expansion and elevated production in oil refineries, metallurgical complexes and several industries considered potential sources of PCBs, such as paper, cement, chlorine, fertilizers, polyethylene, chlorinated fungicides and solvents [31]. Two periods of decline in PCB concentrations were detected in the LSR core. The first is the same as in the CQ1 core and occurred before the maximum concentration in 1986. The second occurred in late 1980 and could be a reflection of the prohibition of PCBs and the pollution controls adopted by most industries in the Santos Estuary, since 1984, and it also coincided with a decline in the LAB and PAH concentrations [11,12].

In particular, the LCN core presented a different vertical PCB distribution (Fig. 6). An early increase in levels was detected in sediments relative to 1930, despite the low industrialization in the Santos Estuary in this period and the beginning of the worldwide production of PCBs. In addition, the maximum concentrations occurred early, in the mid-1950s and 1970s, compared to the other sediment cores. This variation also occurred for previously analysed PAHs [12].

The Santos Estuary has been dredged often since 1940 for deepening and maintenance of the navigation channel. In addition, the access channel to the most important metallurgical complex in Latin America (COSIPA), adjacent to the LCN core, has been dredged since 1966 [32]. These activities easily interfere with the bottom topography and modify the sediment composition surrounding the dredging site [33]. All the core sampling sites were outside the dredging areas. However, the LCN core site may have received dredging material due to its greater proximity to the COSIPA access channel, which may have modified the historical rate of sedimentation and interfered in the dating model and consequently the PCB vertical profile.

To complement the history of PCBs in the Santos Estuary, we calculated the PCB inventories according to the following equation adapted from [28,34] based only on the CQ1 and LSR cores due to uncertainty in the LCN date estimation:

$$(1) \text{ Total inventory} = \sum C_i * \rho * h_i$$

where: C_i is the concentration of PCBs in the sediment layers (ng g^{-1}) of seven selected PCBs (PCBs 28, 52, 101, 118, 138, 153 and 180), h_i is the thickness of the sediment layer (cm), and ρ is the average density of the dry sediment particles calculated for the Santos Estuary (2.3 g cm^{-3} ; [35]). The PCB concentrations for unanalysed intervals were estimated by linear interpolation of the adjacent measured intervals.

The total inventories in CQ1 and LSR were 6,493 and 3,998 ng cm^{-2} , respectively. In agreement with other data in this study, the maximum inventory values were related to sediments of the 1990s and 1980s representing the years of higher PCB deposition that constitute 55% and 62% of the total PCB inventories estimated from 1940 and 2012 in CQ1 and LSR, respectively. Furthermore, the calculated inventories of superficial sediments (mean value \pm SD = $0.68 \pm 0.68 \text{ ng cm}^{-2}$) are actually currently decreasing.

The total inventory is significantly higher than that detected in regions such as open sea sediments from the Adriatic Sea (2.5 ng cm^{-2}) [29] and Admiralty Bay, Antarctica (47 ng cm^{-2}) [36], with the minor influence of anthropic impacts. In addition, the values are also high when compared to densely urbanized areas such as the Pearl River Delta, China ($1,310 \text{ ng cm}^{-2}$) [28] and the St. Lawrence Estuary, Canada (488 ng cm^{-2}) [37]. However, they were low compared to enclosed areas such as Lake Harding, USA ($28,000 \text{ ng cm}^{-2}$) [38].

The predicted trends in PCB emissions in Brazil followed the temporal trend of estimated global emissions, except for a small delay [39] (Fig. 8). The maximum emissions in Brazil occurred later than in the Northern Hemisphere, and this difference was expected for a country that has no production history and was late to issue a ban of these compounds. In addition, the maximum emission estimated for Brazil coincided with the industrial development in Santos Estuary, and similarly, the inventories in this study also followed the pattern in PCB emissions, with a ten-year delay (Fig. 8). Therefore, PCB concentrations in coastal impacted sediments take time to respond to changing emissions. The inventory patterns showed a faster response to consumption in

Brazil [40]. In general, the values started to increase from the industrialization process in the Santos Estuary and decreased with the banning of PCBs, followed by the total interruption of consumption and the gradual decrease in inventories. An inventory peak after the consumption interruption also indicates a probable leakage of products containing PCBs.

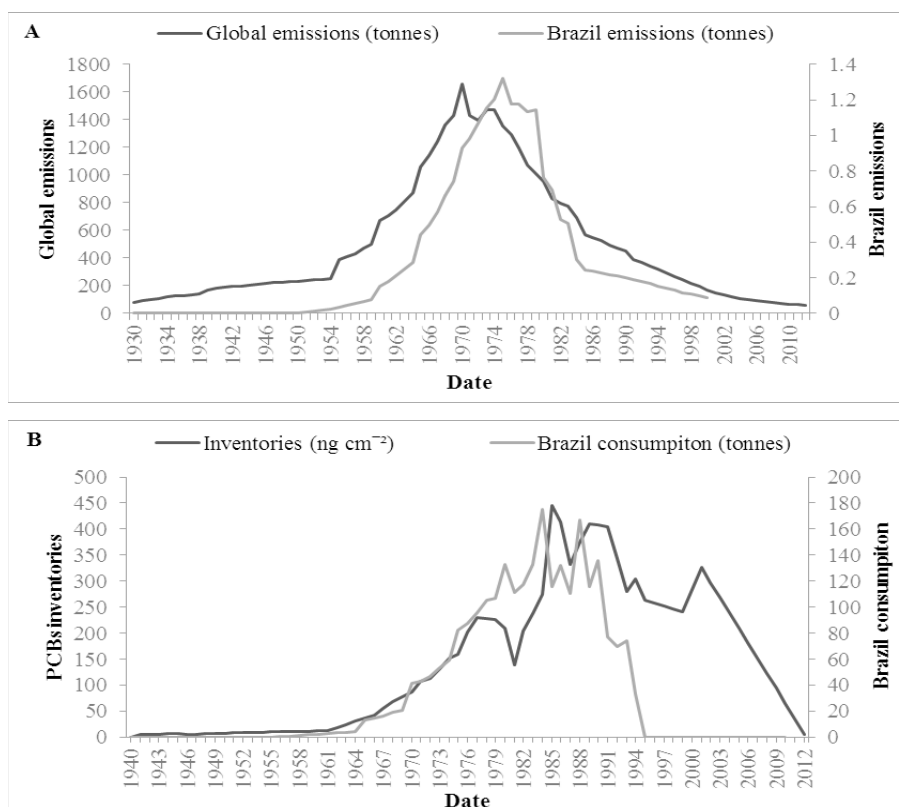


Fig. 8: Comparison of global and Brazilian annual PCB emissions (according to data provided by Breivik et al., [39]) (A). Comparison of Brazilian consumption (tonnes) (according to data provided by Breivik et al., [40]) and inventories (ng cm⁻²) of 7 PCBs (28, 52, 101, 118, 138, 153 and 180) in the CQ1 and LSR sediment cores from the Santos Estuary, Brazil (B).

4 Conclusion

The present study produced unpublished data regarding the history of PCBs and integrated several environmental parameters in the Santos Estuary. Our results allow a comprehensive view of PCB contamination in the region and indicate a decreasing pattern in concentration and inventories, correlating to international emissions and consumption.

PCB consumption, the congener patterns and statistical analyses indicate local sources of contamination, influenced by the regional intensification in urban and industrial development that changed the input magnitude during the past 50 years, including PCBs and other organic pollutants, such as PAHs, LABs, and AHs. In particular, equipment containing PCBs from a power sector could be a current source of

contamination for the Santos Estuary. It is probably responsible for the increase in sediment concentrations of the late 1990s and represents a significant threat from the amount of equipment that remains currently in use.

Finally, most of the sediments analyzed presented a moderate to high hazard and highlighted the important role of sediments as a compartment for storing POPs as well as the risks involved in their resuspension, especially in regions that are constantly dredged such as the Santos Estuary.

Acknowledgments

A.C. Souza wishes to thank CAPES (Coordenação de Aperfeiçoamento de Pessoal de Ensino Superior) for an MSc Scholarship. C.C. Martins thank CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico) and FAPESP (Fundação de Amparo a Pesquisa do Estado de São Paulo - 01/10704-8) for a research grant. This study was developed as part of a post-graduate course on estuarine and ocean systems at the Federal University of Paraná (PGSISCO-UFPR).

Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.jhazmat.2018.XX.XXX>.

Figure captions

Fig. 1: Map of the study area showing the sampling stations in superficial and core sediments of the Santos Estuary, South Atlantic.

Fig. 2: Map of the study area showing the concentrations of total PCBs (ng g^{-1}) in superficial sediments of the Santos Estuary, South Atlantic.

Fig. 3: Plot of the measured total PCB concentrations versus predicted TOC values. Linear regressions have been fitted for each sampling date shown as lines. The graph shows a good correlation between the PCB and TOC values ($r = 0.83$, $p < 0.5$).

Fig. 4: The principal component analysis score and loading plots of the PCBs, bulk sediment parameters and hydrocarbons in the CQ1 (A), LSR (B) and LCN (C) sediment cores from the Santos Estuary.

Fig. 5: The relative distribution of PCB homologs and R values in superficial sediments from the Santos Estuary.

Fig. 6: The relative distribution of PCB homologs and R values in the CQ1 (A), LSR (B) and LCN (C) cores from the Santos Estuary.

Fig. 7: Total PCB concentration (ng g^{-1}) in different sediment cores from the Santos Estuary.

Fig. 8: Comparison of global and Brazilian annual PCB emissions (according to data provided by Breivik et al., 2007) (A). Comparison of Brazilian consumption (tonnes) (according to data provided by Breivik et al., 2007) and inventories (ng cm^{-2}) of 7 PCBs (28, 52, 101, 118, 138, 153 and 180) in the CQ1 and LSR sediment cores from the Santos Estuary, Brazil (B).

Table and figure captions (supplementary material)

Fig. S1: PCBs, AHs, PAHs, MS concentrations, total organic carbon (TOC), grain size (silt + clay) and C/N atomic ratio in sediment cores collected in the Santos Estuary, South Atlantic.

Table S1: Location of studied sites in the Santos Estuary, South Atlantic.

Table S2: Total organic carbon (TOC), grain size (silt + clay), C/N atomic ratio and concentrations of total PCBs in sediment cores collected in the Santos Estuary.

Table S3. Data used to perform the environmental risk assessment.

References

- [1] K.C. Jones, P. Voogt, Persistent organic pollutants (POPs): state of the science, *Environ. Pollut.* 100 (1999) 209–221. doi:10.1016/S0269-7491(99)00098-6.
- [2] A. Pariatamby, Y.L. Kee, Persistent Organic Pollutants Management and Remediation, *Procedia Environ. Sci.* 31 (2016) 842–848. doi:10.1016/j.proenv.2016.02.093.
- [3] UNEP (United Nations Environment Programme), 2001. The Stockholm Convention on persistent organic pollutants (POPs). Available at: http://chm.pops.int/Portals/0/Repository/convention_text/UNEP-POPS-COP CONVTEXT-FULL.English.PDF
- [4] G. Wang, J. Peng, D. Yang, D. Zhang, X. Li, Current levels, composition profiles, source identification and potentially ecological risks of polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs) in the surface sediments from Bohai Sea, *Mar. Pollut. Bull.* 101 (2015) 834–844. doi:10.1016/j.marpolbul.2015.11.028.
- [5] J. Borja, D.M. Taleon, J. Auresenia, S. Gallardo, Polychlorinated biphenyls and their biodegradation, *Process Biochem.* 40 (2005) 1999–2013. doi:10.1016/j.procbio.2004.08.006.
- [6] P. Bigus, M. Tobiszewski, J. Namieśnik, Historical records of organic pollutants in sediment cores, *Mar. Pollut. Bull.* 78 (2014) 26–42. doi:10.1016/j.marpolbul.2013.11.008.
- [7] P. Montuori, S. Aurino, F. Garzonio, M. Triassi, Polychlorinated biphenyls and organochlorine pesticides in Tiber River and Estuary: Occurrence, distribution and ecological risk, *Sci. Total Environ.* 571 (2016) 1001–1016. doi:10.1016/j.scitotenv.2016.07.089.
- [8] H. Yang, S. Zhuo, B. Xue, C. Zhang, W. Liu, Distribution, historical trends and inventories of polychlorinated biphenyls in sediments from Yangtze River Estuary and adjacent East China Sea, *Environ. Pollut.* 169 (2012) 20–26. doi:10.1016/j.envpol.2012.05.003.
- [9] M.C. Bicego, S. Taniguchi, G.T. Yogui, R.C. Montone, D.A.M. Silva, R.A. Lourenço, C. de C. Martins, S.T. Sasaki, V.H. Pellizari, R.R. Weber, Assessment of contamination by polychlorinated biphenyls and aliphatic and aromatic hydrocarbons in sediments of the Santos and São Vicente Estuary System, São

- Paulo, Brazil, *Mar. Pollut. Bull.* 52 (2006) 1784–1804. doi:10.1016/j.marpolbul.2006.09.010.
- [10] C.C. Martins, M.C. Bicego, M.M. Mahiques, R.C.L. Figueira, M.G. Tessler, R.C. Montone, Depositional history of sedimentary linear alkylbenzenes (LABs) in a large South American industrial coastal area (Santos Estuary, Southeastern Brazil), *Environ. Pollut.* 158 (2010) 3355–3364. doi:10.1016/j.envpol.2010.07.040.
- [11] C.C. Martins, M.C. Bicego, M.M. Mahiques, R.C.L. Figueira, M.G. Tessler, R.C. Montone, Polycyclic aromatic hydrocarbons (PAHs) in a large South American industrial coastal area (Santos Estuary, Southeastern Brazil): Sources and depositional history, *Mar. Pollut. Bull.* 63 (2011) 452–458. doi:10.1016/j.marpolbul.2011.03.017.
- [12] C.A. Magalhães, S. Taniguchi, M.J. Cascaes, R.C. Montone, PCBs, PBDEs and organochlorine pesticides in crabs *Hepatus pudibundus* and *Callinectes danae* from Santos Bay, State of São Paulo, Brazil, *Mar. Pollut. Bull.* 64 (2012) 662–667. doi:10.1016/j.marpolbul.2011.12.020.
- [13] I.C.A.C. Bordon, J.E.S. Sarkis, G.M. Gobbato, M.A. Hortellani, C.M. Peixoto, Metal concentration in sediments from the Santos Estuarine system: A recent assessment, *J. Braz. Chem. Soc.* 22 (2011) 1858–1865. doi:10.1590/S0103-50532011001000005.
- [14] C.C. Martins, M.M. Mahiques, M.C. Bicego, M.M. Fukumoto, R.C. Montone, Comparison between anthropogenic hydrocarbons and magnetic susceptibility in sediment cores from the Santos Estuary, Brazil, *Mar. Pollut. Bull.* 54 (2007) 240–246. doi:10.1016/j.marpolbul.2006.11.006.
- [15] H.E. Gaudette, W.R. Flight, L. Toner, D.W. Folger, An inexpensive titration method for the determination of organic carbon in recent sediments. *J. Sedim. Petrology*, 44, (1974), 249-253.
- [16] UNEP, Determination of petroleum hydrocarbons in sediments, *Ref. Methods Mar. Pollut. Stud.* (1992) 75.
- [17] T.L. Wade, A.Y. Cantillo, Use of standards and reference materials in the measurement of chlorinated hydrocarbon residues – chemistry workbook. In: NOAA Technical Memo NOS ORCA 77 (National Status and Trends Program 612 for Marine Environmental Quality). NOAA, Silver Spring, MD 77 (1994).
- [18] R Core Team. R: A Language and Environment for Statistical Computing; R

- Foundation for Statistical Computing:Vienna, Austria, (2016).
- [19] F. Aprile, G.W. Siqueira, Seasonal and spatial variations of dissolved carbon and nitrogen in the Santos estuarine system, Southeastern Brazil., *J. Oceanogr. Mar. Sci.* 3 (2012) 8–18.
- [20] P.M. Medeiros, M. Caruso Bicego, Investigation of natural and anthropogenic hydrocarbon inputs in sediments using geochemical markers. I. Santos, SP - Brazil, *Mar. Pollut. Bull.* 49 (2004) 761–769. doi:10.1016/j.marpolbul.2004.06.001.
- [21] E.R. Long, D.D. Macdonald, S.L. Smith, F.D. Calder, Incidence of Adverse Biological Effects Within Ranges of Chemical Concentrations in Marine and Estuarine Sediments, *Environ. Manage.* 19 (1995) 81–97. doi:10.1007/bf02472006.
- [22] R.B. Choueri, A. Cesar, D.M.S. Abessa, R.J. Torres, R.D. Morais, I. Riba, C.D.S. Pereira, M.R.L. Nascimento, A.A. Mozeto, T.A. DelValls, Development of site-specific sediment quality guidelines for North and South Atlantic littoral zones: Comparison against national and international sediment quality benchmarks, *J. Hazard. Mater.* 170 (2009) 320–331. doi:10.1016/j.jhazmat.2009.04.093.
- [23] A.D. Lemly, Evaluation of the hazard quotient method for risk assessment of selenium., *Ecotoxicol. Environ. Saf.* 35 (1996) 156–162. doi:10.1006/eesa.1996.0095.
- [24] T. Combi, M.G. Pintado-Herrera, P.A. Lara-Martin, S. Miserocchi, L. Langone, R. Guerra, Distribution and fate of legacy and emerging contaminants along the Adriatic Sea: A comparative study, *Environ. Pollut.* 218 (2016) 1055–1064. doi:10.1016/j.envpol.2016.08.057.
- [25] R.J. Torres, D.M.S. Abessa, F.C. Santos, L.A. Maranhão, M.B. Davanzo, M.R.L. do Nascimento, A.A. Mozeto, Effects of dredging operations on sediment quality: Contaminant mobilization in dredged sediments from the Port of Santos, SP, Brazil, *J. Soils Sediments.* 9 (2009) 420–432. doi:10.1007/s11368-009-0121-x.
- [26] Z.Z.A. Kuzyk, R.W. MacDonald, S.C. Johannessen, G.A. Stern, Biogeochemical controls on PCB deposition in Hudson Bay, *Environ. Sci. Technol.* 44 (2010) 3280–3285. doi:10.1021/es903832t.
- [27] E. Naffrechoux, N. Cottin, C. Pignol, F. Arnaud, J.P. Jenny, M.E. Perga, Historical profiles of PCB in dated sediment cores suggest recent lake

- contamination through the “halo effect,” *Environ. Sci. Technol.* 49 (2015) 1303–1310. doi:10.1021/es5043996.
- [28] B. Mai, E.Y. Zeng, X. Luo, Q. Yang, G. Zhang, X. Li, G. Sheng, J. Fu, Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China., *Environ. Sci. Technol.* 39 (2005) 49–56. doi:10.1021/es049015d.
- [29] T. Combi, S. Miserocchi, L. Langone, R. Guerra, Polychlorinated biphenyls (PCBs) in sediments from the western Adriatic Sea: Sources, historical trends and inventories, *Sci. Total Environ.* 562 (2016) 580–587. doi:10.1016/j.scitotenv.2016.04.086.
- [30] F.V. Almeida, A.J. Centeno, M.C. Bisinoti, W.F. Jardim, [in Portuguese] Substâncias tóxicas persistentes (STP) no Brasil, *Quim. Nova.* 30 (2007) 1976–1985. doi:10.1590/S0100-40422007000800033.
- [31] Ministry of the Environment, National Implementation Plan – Brazil: Stockholm Convention, (2015) 180.
- [32] CODESP (Companhia das Docas do Estado de São Paulo), [in Portuguese] Estudo de impacto ambiental, dragagem de aprofundamento do canal de navegação, bacias de evolução e berços de atracação do Porto Organizado de Santos - São Paulo (2007).
- [33] OSPAR Commission, Assessment of the environmental impact of dredging for navigational purposes. OSPAR Commission, New Court, (2009) 48.
- [34] D. Kaiser, D.E. Schulz-Bull, J.J. Waniek, Profiles and inventories of organic pollutants in sediments from the central Beibu Gulf and its coastal mangroves, *Chemosphere.* 153 (2016) 39–47. doi:10.1016/j.chemosphere.2016.03.041.
- [35] C.C. Martins, [in Portuguese] Marcadores Orgânicos Geoquímicos em testemunhos de sedimento do Sistema Estuarino de Santos e São Vicente, SP: um registro histórico da introdução de hidrocarbonetos no ambiente marinho, Tese. (2005) 215.
- [36] T. Combi, C.C. Martins, S. Taniguchi, J. Leonel, R.A. Lourenço, R.C. Montone, Depositional history and inventories of polychlorinated biphenyls (PCBs) in sediment cores from an Antarctic Specially Managed Area (Admiralty Bay, King George Island), *Mar. Pollut. Bull.* 118 (2017) 447–451. doi:10.1016/j.marpolbul.2017.03.031.
- [37] M. Lebeuf, T. Nunes, PCBs and OCPs in sediment cores from the Lower St.

- Lawrence Estuary, Canada: Evidence of fluvial inputs and time lag in delivery to coring sites. *Environ. Sci. Technol.* 39, (2005) 1470-1478.
- [38] P.C. Van Metre, E. Callender, C.C. Fuller, Historical trends in organochlorine compounds in river basins identified using sediment cores from reservoirs. *Environ. Sci. Technol.* 31, (1997) 2339-2344.
- [39] K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 2. Emissions. *Sci. Total Environ.* Vol. 290, (2002) 199-224.
- [40] K. Breivik, A. Sweetman, J.M. Pacyna, K.C. Jones, Towards a global historical emission inventory for selected PCB congeners - a mass balance approach. 1. Global production and consumption. *Sci. Total Environ.* 290, (2002) 181-198.

Supplementary material

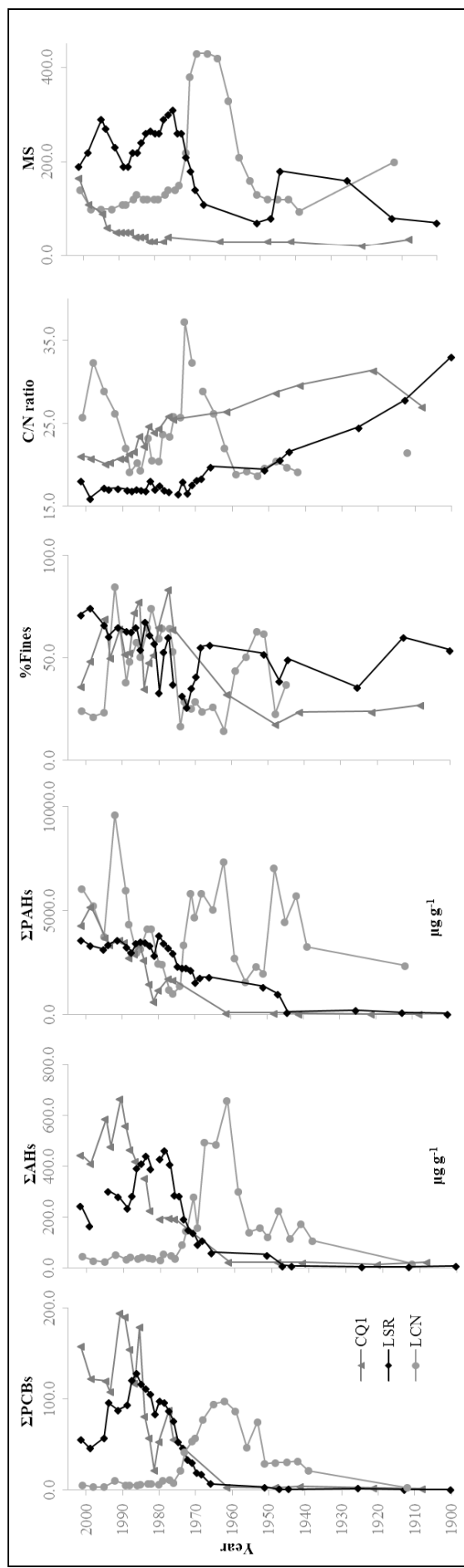


Fig S1: PCBs, AHs, PAHs, and MS concentrations, total organic carbon (TOC), grain size (silt + clay) and C/N atomic ratio in sediments cores collected in the Santos Estuary, South Atlantic.

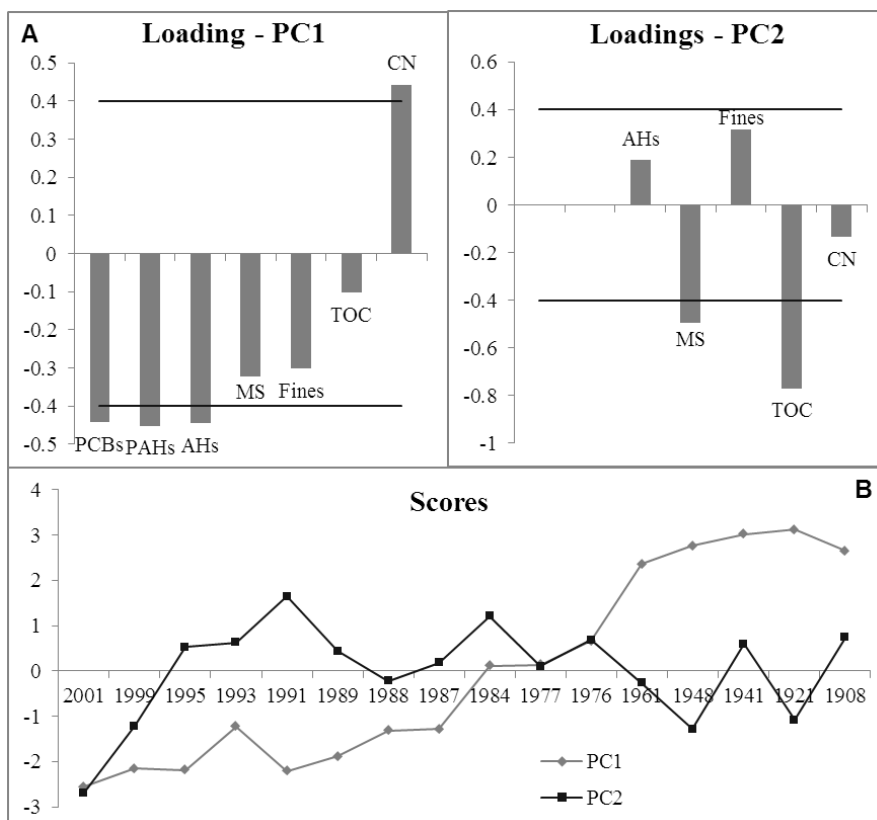


Fig S2: Loadings of PC1 and PC2 and the black lines indicating the cutting factor (0.4) (A) and scored (B) of the PCA analysis of CQ1 core.

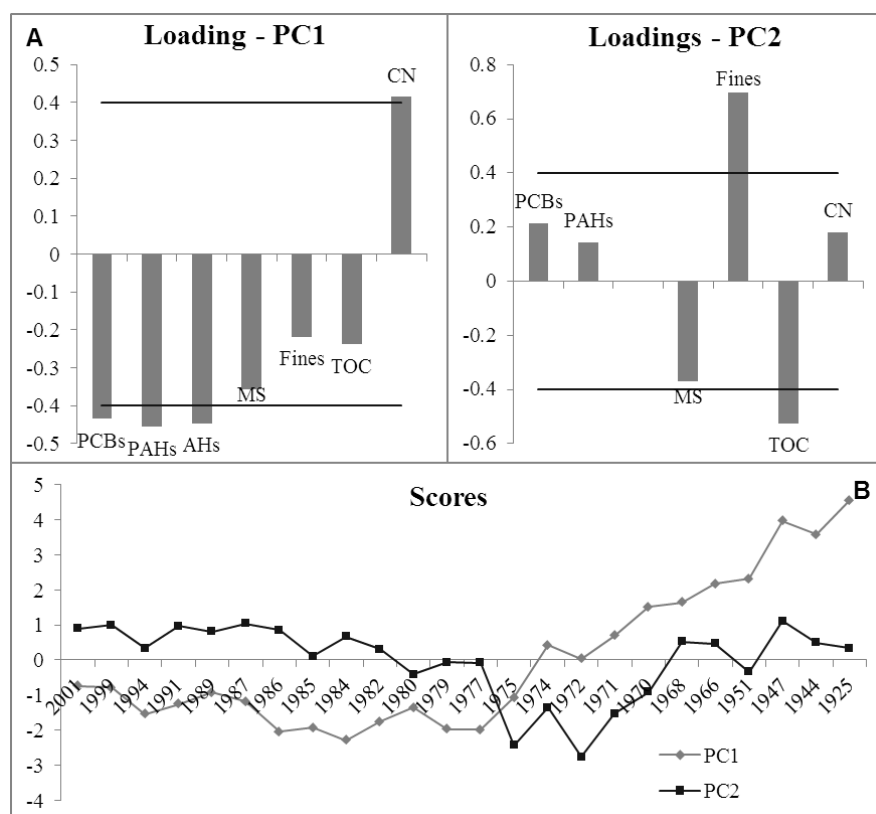


Fig S3: Loadings of PC1 and PC2 and the black lines indicating the cutting factor (0.4) (A) and scored (B) of the PCA analysis of LSR core.

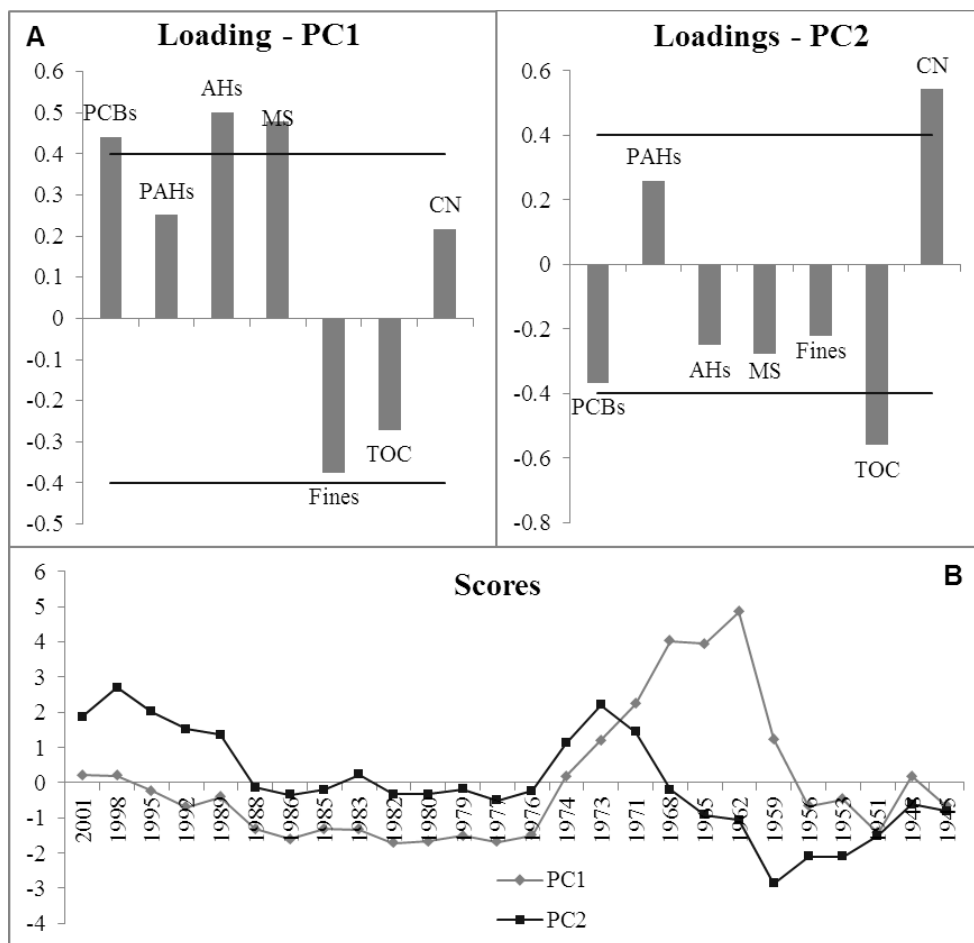


Fig S4: Loadings of PC1 and PC2 and the black lines indicating the cutting factor (0.4) (A) and scored (B) of the PCA analysis of LCN core.

Table S1

Location of studied sites in the Santos Estuary, South Atlantic.

Superficial sediments			
Site	Local	Latitude	Longitude
P1	Rio do Meio/CING	23°59,655'S	46°17,887'O
P2	Foz do Rio Santo Amaro	23°59,123'S	46°17,264'O
P3	Terminal de Veículos	23°57,831 S	46°17,720'O
P4	Vicente de Carvalho - Torre Grande	23°56,964'S	46°18,421'O
P5	Vicente de Carvalho - Paquetá (Ponte Férrea)	23°55,984'S	46°18,625'O
P6	Ilha Barnabé – Embraport	23°55,595'S	46°19,458'O
P7	Alemoa - BTP (Brasil Terminais Portuários)	23°55,322'S	46°20,335'O
P8	Alemoa - Ilha dos Bagres	23°55,056'S	46°21,164'O
P9	Casqueiro	23°54,920'S	46°22,089'O
P10	Canal Piaçaguera - Foz do Rio Quilombo	23°53,238'S	46°22,569'O
Sediments cores			
CQ1	Casqueiro River	23°55,142'S	46°23,663'O
LSR	Largo de Santa Rita	23°54,987'S	46°19,786'O
LCN	Largo do Canéu	23°54,735'S	46°21,686'O

Table S2

Total organic carbon (TOC), grain size (silt + clay), C/N atomic ratio and concentrations of total PCBs in sediments cores collected in the Santos Estuary.

Depth (cm)	Age	TOC (%)	silt + clay (%)	C/N ratio	Total PCBs (ng g⁻¹)
CQ1					
1	2001	6.3	36.4	21.1	157.4
5	1999	5.5	48.8	20.8	122.2
11	1995	4.5	69.5	20.1	119.9
13	1993	4.3	50.0	20.3	107.8
17	1991	3.8	64.5	20.8	193.8
19	1989	4.9	51.9	20.8	189.9
21	1988	5.6	52.6	21.3	154.3
23	1987	5.3	72.3	21.6	117.0
25	1985	5.1	77.6	23.5	179.3
27	1984	3.5	35.2	22.3	80.7
29	1983	3.9	47.9	24.7	56.7
31	1981	5.0	51.8	23.9	21.7
33	1980	6.3	65.3	24.4	53.2
37	1977	5.6	83.5	25.9	87.2
39	1976	4.4	64.2	25.5	55.7
61	1961	4.8	32.3	26.4	3.12
81	1948	5.7	17.8	28.7	2.55
91	1941	3.6	23.6	29.6	3.79
121	1921	5.6	23.9	31.4	2.43
141	1908	3.5	27.1	27.0	1.46
LSR					
1	2001	3.4	71.3	18.1	55.6
5	1999	3.1	74.5	16.0	45.6
11	1995	3.2	66.2	17.3	57.2
13	1994	3.2	60.7	17.1	95.8
17	1991	3.0	65.2	17.2	87.8
21	1989	3.2	63.2	17.0	93.0
23	1987	3.1	63.0	16.9	120.2
25	1986	3.3	65.3	17.1	128.1
27	1985	3.4	54.3	17.0	116.6
29	1984	3.4	67.9	16.9	111.1
31	1982	3.4	61.3	18.1	105.3
33	1981	3.0	57.4	17.1	83.0
35	1980	2.9	33.1	17.5	97.7
37	1979	3.3	53.0	17.0	95.7
39	1977	3.3	60.3	16.8	86.8
41	1976	n.a	n.a	n.a	75.8
43	1975	3.9	37.2	16.5	52.9
45	1974	3.2	31.6	18.0	46.3

47	1972	3.9	26.2	16.6	33.5
49	1971	3.5	35.5	17.6	30.0
51	1970	3.4	41.1	18.2	18.9
53	1968	3.0	55.4	18.4	17.2
57	1966	3.3	56.5	19.8	6.72
81	1951	3.8	52.0	19.4	3.20
87	1947	2.20	38.9	20.6	0.95
91	1944	2.6	49.5	21.6	1.09
121	1925	2.5	35.7	24.5	1.62
141	1913	1.6	60.1	27.8	0.69
161	1900	1.7	54.0	33.0	0.70
LCN					
1	2001	0.5	24	25.7	5.52
5	1998	0.5	21.2	32.3	3.49
9	1995	0.7	23.2	28.9	3.35
13	1992	0.9	84.8	26.2	10.1
17	1989	0.5	38.0	22.0	5.75
19	1988	2.1	48.1	19.1	5.77
21	1986	2.2	57.7	20.2	5.42
23	1985	1.8	50.4	19.3	6.1
25	1983	1.8	65.0	23.2	7.22
27	1982	2.1	74.1	20.5	7.06
29	1980	2.0	59.7	20.4	6.05
31	1979	2.2	64.2	23.7	10.8
33	1977	2.4	64.3	23.4	11.2
35	1976	2.7	53.3	25.8	8.07
37	1974	0.5	16.5	25.7	21.8
39	1973	0.4	28.6	37.2	42.0
41	1971	0.5	25.3	32.3	53.7
43	1970	n.a	28.5	n.a	57.1
45	1968	0.7	23.9	28.9	77.2
49	1965	0.9	26.0	26.2	94.3
53	1962	0.5	14.6	22	97.6
57	1959	3.2	43.8	18.8	86.5
61	1956	3.4	50.6	19.2	47.2
65	1953	2.8	62.9	18.7	74.8
69	1951	3.1	61.6	19.6	28.9
73	1948	3.4	22.8	20.4	30.4
77	1945	3.0	37.1	19.7	30.6
81	1942	3.2	n.a	19.1	31.8
85	1939	n.a	n.a	n.a	21.4
121	1912	2.8	n.a	21.4	2.80

n.a: not analyzed

Table S3.

Data used to perform the environmental risk assessment.

Compound	Species	Toxic value (ng g⁻¹)	Acute/chronic	PNEC (ng g⁻¹)	References	Study area
∑PCBs	Several organisms	EC50: 180	A	0.18	Long et al. (1995)	Estuarine sediments
∑PCBs	<i>Tiburonella viscana</i>	2.62	A	0.00262	Choeuri et al. (2009)	Estuarine sediments

ANEXO – DADOS BRUTOS

Tabela 1: Concentrações (em ng g⁻¹) de bifenilas policloradas (PCBs) do testemunho CQ1, Estuário de Santos, Brasil.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Profundidade (cm)	0-2	04-06	10-12	12-14	16-18	18-20	20-22	22-24	24-26	26-28	28-30	30-32	32-34	36-38	38-40	60-62	80-82	100-102	120-122	140-142
Data estimada	2001	1999	1995	1993	1991	1989	1988	1987	1985	1984	1983	1981	1980	1977	1976	1961	1948	1941	1921	1908
PCB 8	1,32	0,6	1,03	0,74	0,51	0,56	0,53	0,47	0,69	0,36	0,33	0,13	0,28	0,27	0,15	0,15	0,07	0,12	<LD	<LD
PCB 18	2,46	2,03	2,73	1,98	5,99	4,54	2,52	2,69	3,02	1,84	1,33	0,46	0,89	1,77	0,76	0,15	0,10	0,18	<LD	<LD
PCB 28	3,68	2,02	3,08	2,21	2,73	2,96	1,98	2,10	3,36	1,85	1,33	0,37	0,62	1,25	0,63	0,15	0,11	0,18	<LD	<LD
PCB 31	1,42	1,99	2,85	1,77	2,22	1,77	2,32	2,40	1,12	1,44	0,95	0,44	0,48	0,97	0,62	0,18	0,13	0,21	<LD	<LD
PCB 33	2,75	2,11	2,85	2,18	3,61	2,41	2,71	2,86	<LD	1,77	1,26	0,43	0,62	1,62	0,67	0,13	0,10	0,16	<LD	<LD
PCB 44	2,21	1,78	2,91	1,99	4,82	4,28	2,22	2,66	3,66	1,20	1,74	0,53	0,93	1,67	0,66	0,14	0,10	0,15	<LD	<LD
PCB 49	5,76	4,59	5,46	4,48	10,2	8,81	5,31	5,24	5,59	4,96	1,94	0,65	1,42	2,91	1,36	0,13	0,09	0,12	<LD	<LD
PCB 52	6,20	4,02	5,03	4,23	7,12	8,10	4,94	2,37	5,87	2,74	2,23	0,90	1,90	3,31	1,58	0,24	0,20	0,29	<LD	<LD
PCB 56/60	2,82	1,74	1,97	1,59	3,15	3,16	2,03	2,09	2,71	1,18	0,95	0,33	0,74	1,27	0,65	0,06	<LD	0,07	<LD	<LD
PCB 66	4,22	3,29	3,69	2,78	4,32	5,34	3,50	3,90	4,51	1,95	1,60	0,61	1,29	2,31	0,87	0,11	0,09	0,11	<LD	<LD
PCB 70	2,42	1,92	2,12	1,65	2,75	3,99	2,45	1,77	3,31	1,69	1,31	0,52	1,11	1,53	0,70	0,16	0,12	0,17	<LD	<LD
PCB 74	4,85	3,83	3,54	3,45	6,07	4,02	5,02	4,87	4,54	2,46	1,71	0,40	1,23	2,13	1,23	0,08	<LD	0,08	<LD	<LD
PCB 77	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 81	0,42	0,56	0,39	0,33	1,05	1,12	0,54	0,76	<LD	<LD	<LD	0,06	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 87	2,28	1,85	1,84	1,73	3,10	3,68	2,42	1,78	3,71	1,42	1,06	0,41	1,01	1,46	0,83	0,08	0,09	0,09	<LD	<LD
PCB 95	5,28	3,98	4,29	3,61	6,22	7,47	4,67	3,40	6,26	2,80	2,13	0,86	1,91	3,34	1,69	0,16	0,12	0,19	<LD	<LD
PCB 97	1,99	1,58	1,67	1,76	3,22	3,78	2,24	1,62	3,63	1,01	1,02	0,37	0,97	1,26	0,69	0,07	<LD	0,07	<LD	<LD
PCB 99	3,19	2,32	1,93	1,87	3,06	3,75	3,12	1,85	3,73	1,42	1,06	0,44	1,14	1,65	0,81	0,07	0,08	0,09	<LD	<LD
PCB 101	7,09	5,2	5,07	4,08	7,84	8,76	5,86	3,77	8,19	3,34	2,58	0,95	2,55	3,79	2,18	0,18	0,16	0,22	<LD	<LD
PCB 105	<LD	<LD	<LD	0,36	0,62	<LD	<LD	0,41	2,08	1,50	0,37	0,29	0,94	0,39	0,40	<LD	<LD	<LD	<LD	<LD
PCB 110	6,89	5,05	5,36	4,39	7,76	10,1	6,35	4,62	8,60	3,78	2,80	1,09	2,72	4,22	2,15	0,16	0,16	0,21	<LD	<LD
PCB 114	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	3,04	2,08	<LD	<LD	<LD	<LD	<LD

PCB 118	4,87	3,57	3,46	2,72	5,04	7,75	4,86	3,17	7,55	2,53	1,80	0,84	2,24	2,77	1,69	0,10	0,09	0,14	<LD	<LD
PCB 123	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 126	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 128	0,14	1,26	0,94	1,04	1,51	2,40	1,92	0,78	<LD	0,22	0,06	0,07	0,10	0,23	0,12	<LD	<LD	<LD	<LD	<LD
PCB 132	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 138	14,7	10,9	9,89	9,28	15,7	16,8	13,8	8,65	18,0	6,72	4,37	1,77	4,99	7,17	4,71	0,18	0,16	0,21	<LD	<LD
PCB 141	2,56	2,18	1,89	2,25	3,36	3,39	2,94	1,93	3,58	1,38	0,80	0,31	0,80	1,31	0,88	<LD	<LD	<LD	<LD	<LD
PCB 149	9,09	7,34	6,29	6,31	10,8	11,5	9,66	5,89	10,8	4,60	2,98	1,13	2,77	5,05	3,41	0,11	0,12	0,15	<LD	<LD
PCB 151	2,74	2,06	2,00	1,77	3,17	3,11	2,52	1,71	3,16	1,41	0,87	0,30	0,77	1,46	0,97	<LD	<LD	<LD	<LD	<LD
PCB 153	7,95	6,43	5,93	3,21	12,2	5,96	5,19	8,11	10,7	2,46	4,13	0,68	3,48	5,43	5,25	0,06	0,06	0,07	<LD	<LD
PCB 156	1,23	1,02	0,25	0,73	<LD	1,89	1,56	0,87	1,62	<LD	0,44	0,10	0,54	0,52	0,38	<LD	<LD	<LD	<LD	<LD
PCB 157	<LD	0,21	<LD	0,14	<LD	0,32	0,26	0,20	0,31	<LD	<LD	<LD	0,10	<LD	0,12	<LD	<LD	<LD	<LD	<LD
PCB 158	1,15	0,88	0,76	0,71	0,88	1,24	1,15	0,64	1,43	0,46	0,39	0,13	0,35	0,60	0,33	<LD	<LD	<LD	<LD	<LD
PCB 167	0,98	0,20	<LD	<LD	0,26	0,29	0,65	0,20	1,69	0,62	0,31	0,17	0,53	0,50	0,39	<LD	<LD	<LD	<LD	<LD
PCB 169	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 170	5,28	4,28	3,49	4,22	6,43	4,69	6,43	3,74	4,14	2,85	1,69	0,57	1,49	2,72	2,18	<LD	<LD	<LD	<LD	<LD
PCB 174	3,69	3,10	2,56	3,06	5,18	4,12	4,86	2,79	4,68	1,90	1,21	0,43	1,18	2,13	1,64	<LD	<LD	<LD	<LD	<LD
PCB 177	2,38	1,98	1,59	1,69	3,30	2,53	2,59	1,66	2,67	1,11	0,78	0,28	0,72	1,32	1,02	<LD	<LD	<LD	<LD	<LD
PCB 180	7,72	6,28	4,91	5,95	10,9	8,77	8,87	6,54	8,82	4,14	2,49	0,85	2,51	4,50	3,84	0,09	0,08	0,08	<LD	<LD
PCB 183	2,02	1,84	1,38	1,63	3,03	2,47	2,38	1,81	2,47	1,10	0,70	0,24	0,67	1,21	0,95	<LD	<LD	<LD	<LD	<LD
PCB 187	4,33	3,40	2,66	3,29	6,07	4,95	4,76	3,57	4,76	2,20	1,46	0,50	1,32	2,51	2,00	<LD	<LD	<LD	<LD	<LD
PCB 189	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 194	1,29	1,11	0,96	1,17	2,12	1,90	1,98	1,41	1,75	0,93	0,43	0,14	0,53	1,03	0,87	<LD	<LD	<LD	<LD	<LD
PCB 195	0,53	0,46	0,46	0,62	1,03	0,81	0,77	0,51	0,78	0,48	0,13	<LD	0,12	0,40	0,24	<LD	<LD	<LD	<LD	<LD
PCB 201	1,22	0,83	0,85	0,81	1,92	1,48	1,61	1,11	1,02	0,72	0,42	0,15	0,36	0,66	0,60	<LD	<LD	<LD	<LD	<LD
PCB 203	<LD	2,07	1,72	1,85	3,13	2,31	<LD	1,95	2,35	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 206	0,65	0,52	0,51	0,50	0,70	0,57	0,57	0,50	0,61	0,37	0,14	<LD	0,08	0,23	0,13	<LD	<LD	<LD	<LD	<LD
PCB 209	2,72	1,98	2,07	1,08	0,33	0,94	1,06	1,44	1,62	1,37	0,32	0,08	0,19	0,28	0,08	<LD	<LD	<LD	<LD	<LD
PCBs Totais	144,49	114,36	110,79	101,21	183,42	178,79	141,12	110,81	169,09	76,28	53,62	18,98	48,59	82,28	52,63	2,94	2,23	3,36	<LD	<LD

<LD = abaixo do limite de detecção (0,05 ng g⁻¹)

PCB 128	0,09	0,08	0,10	0,20	<LD	0,10	0,13	0,26	0,23	0,14	0,15	<LD	0,17	0,23	0,24
PCB 132	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 138	4,15	3,56	4,32	6,32	5,85	6,26	7,62	7,90	6,74	6,79	6,43	5,88	7,09	6,18	5,73
PCB 141	0,48	0,41	0,49	0,65	0,65	0,53	0,70	0,86	0,66	0,66	0,67	0,60	0,81	0,72	0,60
PCB 149	3,83	3,63	3,95	7,49	7,20	7,20	9,74	9,95	7,99	7,84	7,17	6,36	7,31	5,91	4,96
PCB 151	0,81	0,68	0,90	1,44	1,26	1,51	1,78	1,99	1,63	1,47	1,44	1,30	1,48	1,34	1,22
PCB 153	4,54	1,76	4,82	9,44	5,32	2,38	10,4	11,8	8,92	10,0	9,39	2,36	2,60	5,48	2,19
PCB 156	0,28	0,23	0,25	0,32	0,39	0,36	0,42	0,45	0,40	0,46	0,43	0,31	0,35	0,46	0,37
PCB 157	<LD	<LD	<LD	0,08	0,09	0,09	<LD	0,11	0,11	0,10	0,16	0,11	0,12	0,08	0,14
PCB 158	0,35	0,25	0,26	0,45	0,42	0,43	0,53	0,60	0,43	0,46	0,49	0,43	0,55	0,45	0,46
PCB 167	0,42	0,29	0,28	0,55	0,46	0,42	0,59	0,66	0,53	0,60	0,58	0,58	0,55	0,58	0,52
PCB 169	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 170	1,66	1,34	1,36	2,56	2,01	2,46	3,21	3,11	2,86	2,82	2,40	2,10	2,76	2,65	2,15
PCB 174	0,99	0,86	1,06	1,70	1,55	1,63	1,89	2,11	1,75	1,61	1,65	1,50	1,87	1,66	1,51
PCB 177	0,92	0,69	0,85	1,40	1,19	1,35	1,56	1,68	1,35	1,37	1,27	1,21	1,45	1,18	1,00
PCB 180	2,54	2,03	2,47	3,99	3,54	3,87	4,46	4,90	4,31	4,06	3,81	3,58	4,27	3,85	3,35
PCB 183	0,77	0,64	0,78	1,32	1,11	1,29	1,57	1,58	1,45	1,32	1,22	1,07	1,34	1,18	1,03
PCB 187	1,79	1,44	1,76	2,84	2,55	2,85	3,47	3,64	3,35	3,04	2,86	2,44	2,90	2,63	2,33
PCB 189	0,14	0,08	0,11	0,19	0,10	0,14	0,11	0,11	0,21	0,34	0,11	0,10	<LD	<LD	<LD
PCB 194	0,69	0,58	0,66	1,00	0,91	0,86	1,34	1,30	1,15	1,07	1,03	0,89	0,98	0,98	0,93
PCB 195	0,31	0,15	0,19	0,36	0,29	0,32	0,44	0,41	0,53	0,37	0,33	0,38	0,41	0,41	0,45
PCB 201	0,60	0,34	0,48	0,82	0,72	0,85	0,82	0,99	0,87	0,80	0,85	0,69	0,71	0,73	0,65
PCB 203	<LD	0,75	0,11	<LD	1,00	1,11	0,79	1,57	1,40	1,12	1,07	<LD	1,13	1,19	1,19
PCB 206	0,53	0,31	0,41	0,52	0,51	0,48	0,56	0,58	0,53	0,62	0,61	0,51	0,56	0,63	0,63
PCB 209	1,99	1,41	1,93	2,27	1,84	2,06	2,42	2,68	2,66	2,51	2,72	2,20	2,36	2,7	2,74
PCBs Totais	49,55	40,54	51,3	85,44	80,61	84,84	108,59	120,33	103,31	98,27	93,03	77,4	91,22	85,02	73,84

<LD = abaixo do limite de detecção (0,05 ng g⁻¹)

PCB 194	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0,06	0,17
PCB 195	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 201	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0,10
PCB 203	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD
PCB 206	<LD	<LD	<LD	<LD	<LD	<LD	<LD	<LD	0,08	<LD
PCB 209	<LD	<LD	<LD	<LD	0,12	0,11	<LD	<LD	0,51	0,18
PCBs totais	0,36	1,78	1,06	3,24	4,87	2,38	1,10	1,38	5,89	9,80

<LD = abaixo do limite de detecção (0,05 ng g⁻¹)