

UNIVERSIDADE FEDERAL DO PARANÁ

TATIANE COMBI

TENDÊNCIAS HISTÓRICAS E DISTRIBUIÇÃO ESPACIAL DE BIFENILAS
POLICLORADAS (PCBs) E PESTICIDAS ORGANOCLORADOS (POCs) EM
SEDIMENTOS DE UM ESTUÁRIO SUBTROPICAL (BAÍA DE GUARATUBA,
ATLÂNTICO SUL).

PONTAL DO PARANÁ

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Orientador: Prof^o Dr. César de Castro Martins

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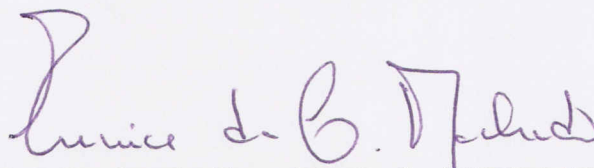
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Tatiane Combi

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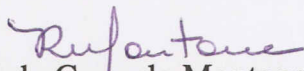
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TERMO DE APROVAÇÃO

Tatiane Combi

Tendências históricas e distribuição espacial de bifenilas policloradas (PCBs) e pesticidas organoclorados (POCs) em sedimentos de um estuário subtropical (Baía de Guaratuba, Atlântico Sul)

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Muito obrigada !!

“Nenhum homem é uma ilha isolada; cada homem é uma partícula do continente, uma parte da terra...”

(John Donne)

Resumo

Os compostos organoclorados (OCs), como as bifenilas policloradas (PCBs) e os pesticidas organoclorados (OCPs) representam um importante grupo de poluentes orgânicos persistentes (POPs), devido a sua toxicidade e elevada persistência no ambiente. A distribuição horizontal e os níveis e base das PCBs e dos OCPs foram investigados em amostras de sedimentos superficiais e de testemunho na Baía de Guaratuba, um estuário bem preservado da costa do Brasil. A distribuição espacial dos OCs sugeriu que as fontes dos OCs estão localizadas fora da baía, relacionadas as atividades humanas ao longo das margens dos dois principais rios da região. A distribuição vertical dos OCs foi utilizada para estimar os níveis de base da Baía. As baixas concentrações de POCs e a não detecção de PCBs no topo do testemunho foram relacionadas às restrições legais ao seu uso. Compostos relacionados à deposição atmosférica também foram detectados, destacando a importância deste estudo para o inventário da distribuição de POPs em diferentes regiões do mundo.

Palavras-chave: pesticidas organoclorados; bifenilas policloradas, níveis de base, Baía de Guaratuba.

Abstract

The organochlorine compounds (OCs), represented by polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs), are an important group of persistent organic pollutants (POPs) due to their toxicity and high persistence in the environment.

The horizontal distribution and background levels of PCBs and OCPs were investigated in surface sediments and sediment core samples from Guaratuba Bay, a large and well preserved estuary of Brazil. The spatial distribution of OCs suggested that the source of OCs is outside the bay, related to the human activities along the margins of two main rivers in the region. The vertical distribution of OCs was used to assess the background levels in the region. The low concentrations of OCPs and the not detection of PCBs at the top of the sediment core may be related to legal restrictions of its use. Compounds related to atmospheric deposition were also detected, highlighting the importance of this study to the inventory of distribution of POPs around the world.

Keywords: organochlorine pesticides; polychlorinated biphenyls; background; Guaratuba Bay.

Resumo geral

Os poluentes orgânicos persistentes (POPs) foram reconhecidos como um dos grupos de produtos químicos antropogênicos mais problemáticos das últimas décadas (HONG *et al.*, 2008). O termo “persistente” deve-se ao fato que, quando introduzidos no ambiente, estão sujeitos a baixa degradação por processos bióticos e abióticos, acarretando em elevada meia-vida no ambiente, que pode chegar a anos ou décadas (JONES & DE VOOGT, 1999).

Sua problemática ambiental deve-se as altas taxas de toxicidade e lipossolubilidade, o que os tornam perigosos para os organismos vivos, devido à tendência a se bioacumularem nos tecidos adiposos dos organismos marinhos (HONG *et al.*, 2003), podendo passar para os níveis mais altos da teia trófica, através da biomagnificação (BORGÅ *et al.*, 2001).

Os compostos organoclorados, entre eles os pesticidas organoclorados (OCPs) e as bifenilas policloradas (PCBs), são uma classe de POPs com elevada relevância dentro dos estudos de contaminação ambiental. Devido a sua relativa volatilidade, chegam à atmosfera na sua fase gasosa e, em menor proporção, adsorvidos às partículas (YEO *et al.*, 2003; WEBER *et al.*, 2009), podendo sofrer transporte e posterior deposição em locais afastados da sua fonte. Desta maneira, estão presentes na maior parte dos ambientes, inclusive em áreas consideradas prístinas, como o continente Antártico (MONTONE *et al.*, 2005).

As PCBs foram amplamente utilizadas no mundo todo como fluidos isolantes de capacitores elétricos e transformadores, borrachas e resinas de poliéster, sistemas de refrigeração, estabilizantes para pesticidas, fluidos hidráulicos em geral, tintas e vernizes, como retardantes de chama e aditivos de lubrificante, em máquinas agrícolas (FIEDLER, 1997; BREIVIK *et al.*, 2004).

A produção de PCBs, em escala industrial, teve início em 1930 nos Estados Unidos, e a produção global foi estimada em mais de 1,3 milhões de toneladas (BREIVIK *et al.*, 2002a). Apesar da proibição do uso de PCBs no

Brasil em 1981, produtos contendo PCBs podem ser utilizados até o final de sua vida útil (PENTEADO & VAZ, 2001). Desta maneira, atualmente as principais fontes de contaminação por PCBs são vazamentos em depósitos, normalmente irregulares, que armazenam os produtos que contem estes compostos, lixões e aterros, lixiviação de solos já contaminados, efluentes domésticos e industriais, além da possível queima de seus produtos (HARRAD *et al.*, 1994; BREIVIK *et al.*, 2002b).

Os POCs foram muito utilizados no controle de pragas agrícolas entre as décadas de 1950 e 1970 (SHEN *et al.*, 2005). Estes compostos também foram utilizados em programas de saúde pública para o controle de vetores de doenças como malária, febre amarela, tifo e leishmaniose (QIU & CAI, 2010; SALDANHA *et al.*, 2010), principalmente em países tropicais e em desenvolvimento, como Brasil, China e Índia (LARA & BATISTA, 1992; ZHANG *et al.*, 2002; KUMAR *et al.*, 2006; ALMEIDA *et al.*, 2007).

Em função das consequências ambientais, o uso de pesticidas organoclorados, desde o início dos anos 70, tem sido progressivamente restringido a aplicações específicas em diversos países do mundo (TORDOIR & VAN SITTERT, 1994). No Brasil, a portaria 329, de 02/09/85, do Ministério da Agricultura proibiu o uso de pesticidas organoclorados, exceto por órgãos governamentais em programas de saúde pública.

Os destinos dos poluentes organoclorados após sua deposição e transporte são, normalmente, regiões portuárias, estuários e sedimentos costeiros (HUNG *et al.*, 2007). Por serem compostos hidrofóbicos com alto valor de partição octanol-água ($\log K_{ow} \approx 4-8$) (PIÉRARD *et al.*, 1996), tendem a se adsorver ao material particulado em suspensão, sendo incorporados aos sedimentos, principalmente na sua fração orgânica (JONKER & KOELMANS, 2002). Desta maneira, as concentrações de OCs nos sedimentos superficiais fornecem informações sobre a contaminação recente, enquanto as concentrações em testemunhos sedimentares proporcionam dados sobre a contaminação através de décadas (HONG *et al.*, 2003).

A Baía de Guaratuba (25° 52'S, 48°34'O) é um dos maiores estuários da costa brasileira. A região abriga umas das maiores reservas preservadas de Mata Atlântica da Serra do Mar e, devido a sua importância ecológica, foi classificada como Área de Proteção Ambiental (APA). A proximidade com a Baía de Paranaguá, que abriga o principal porto exportador de grãos da América do Sul (MARTINS *et al.*, 2010), e com Curitiba e região metropolitana resultam em possíveis impactos antropogênicos. Estudos recentes registraram níveis crescentes de mercúrio (Hg) (SANDERS *et al.*, 2006) e hidrocarbonetos policíclicos aromáticos (HPAs) (PIETZSCH *et al.*, 2010).

O objetivo deste trabalho foi determinar a distribuição espacial e os aportes históricos de PCBs e POCs em sedimentos da Baía de Guaratuba, uma região estuarina ainda considerada prístina, para avaliar possíveis fontes destes compostos e associar os dados obtidos à evolução das atividades antrópicas na região. Este tipo de trabalho é importante para o estabelecimento de níveis de base locais, bem como para o entendimento das tendências históricas de poluição, que pode ser útil para prever tendências futuras em áreas bem preservadas (BOONYATUMANOND *et al.*, 2007; MARTINS *et al.*, 2010).

O somatório das concentrações de PCBs totais ($\Sigma 51$ PCBs) nos sedimentos superficiais variou entre <LQ (limite de quantificação) a 5,62 ng g⁻¹, enquanto os níveis de POCs ficaram entre <LQ a 0,74 ng g⁻¹.

De maneira geral, os OCs foram encontrados principalmente nos pontos localizados no interior da baía. Este comportamento sugere que os maiores rios da região, Cubatão e São João, são os maiores carreadores destes compostos para dentro do estuário. As fontes de PCBs podem ser relacionadas às áreas urbanizadas e industrializadas ao norte da Baía de Guaratuba, enquanto as fontes de POCs foram associadas às áreas agrícolas pelas quais os rios passam desde sua nascente, na Serra do Mar, até desagüarem na baía.

No testemunho T3, os OCs foram encontrados em baixas concentrações e em poucos estratos de sedimentos. O $\Sigma 51$ PCBs variou de <LQ a 0,52 ng g⁻¹ e o $\Sigma 25$ POCs de <LQ a 1,52 ng g⁻¹.

A partir da taxa de sedimentação ($0,36 \pm 0,02 \text{ cm ano}^{-1}$), obteve-se a datação do testemunho, cuja base (30-32 cm) foi estimada em 84 anos. O testemunho datado foi utilizado para estimativa dos níveis de base de organoclorados na Baía de Guaratuba.

Entre os anos de 1926 e 1966 nenhum OC foi detectado. Foram encontradas PCBs em apenas duas camadas de sedimentos, correspondentes aos anos de 1972 e 1989, não sendo obtidas concentrações no topo do testemunho. Esse comportamento pode ser uma consequência da proibição do uso de PCBs no Brasil em 1981, evitando novos aportes para o ambiente.

O primeiro aporte de POCs foi detectado em 1983, e as concentrações mantiveram-se constantes até o topo, com um valor mediano de $0,47 \text{ ng g}^{-1}$. Os POCs foram proibidos no Brasil em 1985, e as concentrações obtidas após esta data podem ser explicadas pelos registros de importações de POCs de aproximadamente 1.500 t de 1989 a 1990 e de aproximadamente 87 t de 200 a 2012 (MDIC, 2012).

A predominância dos pesticidas heptacloro hepoxido-b, *p,p'*-DDD e oxiclordano, que são isômeros do heptacloro, DDT e clordano, respectivamente, confirmaram que o principal aporte de pesticidas na região ocorreu no passado, relacionado ao seu uso histórico. A presença do oxiclordano, que não foi amplamente utilizado no Brasil e na região, sugere a contribuição de fontes relacionadas à deposição atmosférica destes contaminantes.

Devido a persistência destes compostos em áreas remotas e relativamente bem preservadas, como a Baía de Guaratuba, faz-se necessário realizar programas de monitoramento, para que se possa avaliar a eficácia dos esforços regulatórios e medidas restritivas. Além disso, o transporte de POPs é um assunto de preocupação global, e seu estudo é importante para um melhor entendimento do comportamento destes compostos no ambiente, além de fornecer informações para um inventário da distribuição global de POPs.

Tendências históricas e distribuição espacial de bifenilas policloradas (PCBs) e pesticidas organoclorados (POCs) em sedimentos de um estuário subtropical (Baía de Guaratuba, Atlântico Sul).

Historical trends and spatial distribution of polychlorinated biphenyls (PCBs) and organochlorine pesticides (OCPs) in sediments from a subtropical estuary (Guaratuba Bay, SW Atlantic).

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1. Introduction

Organochlorine compounds (OCs), that include organochlorine pesticides (OCPs) and polychlorinated biphenyls (PCBs), have been considered as a concerning group of persistent organic pollutants (POPs) in recent decades because they are hydrophobic, lipophilic, bio-accumulative (VALLACK *et al.*, 1998) and, when introduced into the aquatic environment, can have a half-life of years or decades (JONES & DE VOOGT, 1999). OCs are semi-volatile, reaching the atmosphere mainly in gas phase, where they can be transported for long distances (JONES & DE VOOGT, 1999; YEO, 2003). Thus, these pollutants are present even in pristine areas, as the Antarctic continent (MONTONE *et al.*, 2005), being ubiquitous in the marine environment.

The usage and production of OCs are restricted or banned worldwide since the 1970's and in Brazil since the 1980's. However, there is no information on legal status of PCBs and OCPs in certain South America countries like Paraguay, Uruguay, Bolivia, and Venezuela (UNEP, 2003), which can allow the illegal commerce and usage of these compounds (BARRA *et al.*, 2006; ARREBOLA *et al.*, 2012).

PCBs were world widely used as electric fluids in transformers and capacitors, hydraulic fluids, flame retardants, lubricant, and carbonless copy paper (FIEDLER, 1997; BREIVIK *et al.*, 2004). The industrial-scale production of PCBs began in about 1930 in the USA and the global production is estimated in more than 1.3 million tons (BREIVIK *et al.*, 2002a). Although the PCB usage is restricted in Brazil since 1981, equipment containing PCBs could be used until the end of its useful life (PENTEADO & VAZ, 2001). Therefore, leakages from contaminated landfills and irregular deposits, direct spillages to soils resulting from accidents with electrical equipment, urban runoff, contaminated sewage discharge, and volatilization are currently the main sources of contamination by PCBs (HARRAD *et al.*, 1994; BREIVIK *et al.*, 2002b).

OCPs were extensively used for the control of agricultural pests between the decades of 1950 and 1970 (SHEN *et al.*, 2005). OCPs were also used in public health programs to control disease vector against malaria, yellow fever,

typhus, and leishmaniasis (QIU & CAI, 2010; SALDANHA *et al.*, 2010), mainly in tropical and developing countries as Brazil, China, and India (LARA E BATISTA, 1992; ZHANG *et al.*, 2002; KUMAR *et al.*, 2006; ALMEIDA *et al.*, 2007).

The adverse effects related to their use have been continuously reported (GLADEN *et al.*, 1999; MIRANDA *et al.*, 2008) and, since 1985, the use of OCPs is banned in Brazil. The major problems associated to OCPs use are related to their persistence and volatilization properties. Besides atmospheric transport, leaching of cultivated land is an important way for the input of OCPs to rivers, estuaries and coastal sediments (GÓMEZ-GUTIÉRREZ *et al.*, 2007).

Because they have high octanol–water partition coefficient ($\log K_{ow} \approx 4-8$) (PIÉRARD *et al.*, 1996), OCs tend to adsorb to suspended particulate matter reaching the sediments, the concentrations of these pollutants in sediment cores can provide the reconstruction of historical OCs inputs into coastal areas (VALETTE-SILVER, 1993; SANTSCHI *et al.*, 2001), while the levels in surface sediment provide a report on recent contamination (HONG *et al.*, 2003).

Thereby, the aim of this work is to determine the spatial distribution and the historical inputs of PCBs and OCPs concentrations in sediments from Guaratuba Bay, Brazil, a pristine estuarine region of SW Atlantic to assess possible sources of this compounds and associating the data obtained with the evolution of anthropic activities in the region. The study of OCs is important on the establishment of background levels in an apparent preserved area, as well as on the understanding the historical trends of pollution that may be helpful to predict further tendencies of pollution in pristine regions (BOONYATUMANOND *et al.*, 2007; MARTINS *et al.*, 2010).

2. Study Area

Guaratuba Bay (25° 52'S, 48°34'W), located in the Paraná state, in Southeastern Brazilian coast, is a large estuary of SW Atlantic, with a total area of approximately 50 km² (MARONE *et al.*, 2006) (Figure 1). This area has significant ecological importance, being classified as Environmental Protection Area (EPA). In 2007, this bay was selected by the Conservancy's Coastal and Marine Conservation Program in South America Priority as a site for biodiversity conservation in Brazil (WALKER FOUNDATION, 2012).

Two cities are localized at the margins of the bay: Guaratuba at the south and Matinhos at the north margin, with a total population of about 62,000 inhabitants (IBGE, 2010). In the summer this population reaches almost 400,000 inhabitants, including permanent residents and tourists (IAP, 2006). The proximity with Paranaguá Bay, which shelters the main South American grain shipping port (MARTINS *et al.*, 2010), and with Curitiba, an urban and industrialized Brazilian city with around 2 million inhabitants (IBGE, 2010), results in anthropogenic impacts. Recent studies have pointed out to increasing levels of mercury (Hg) (SANDERS *et al.*, 2006) and polycyclic aromatic hydrocarbons (PAHs) (PIETZSCH *et al.*, 2010) mainly after the 1960s, indicating the increasing human growth and impacts in the region.

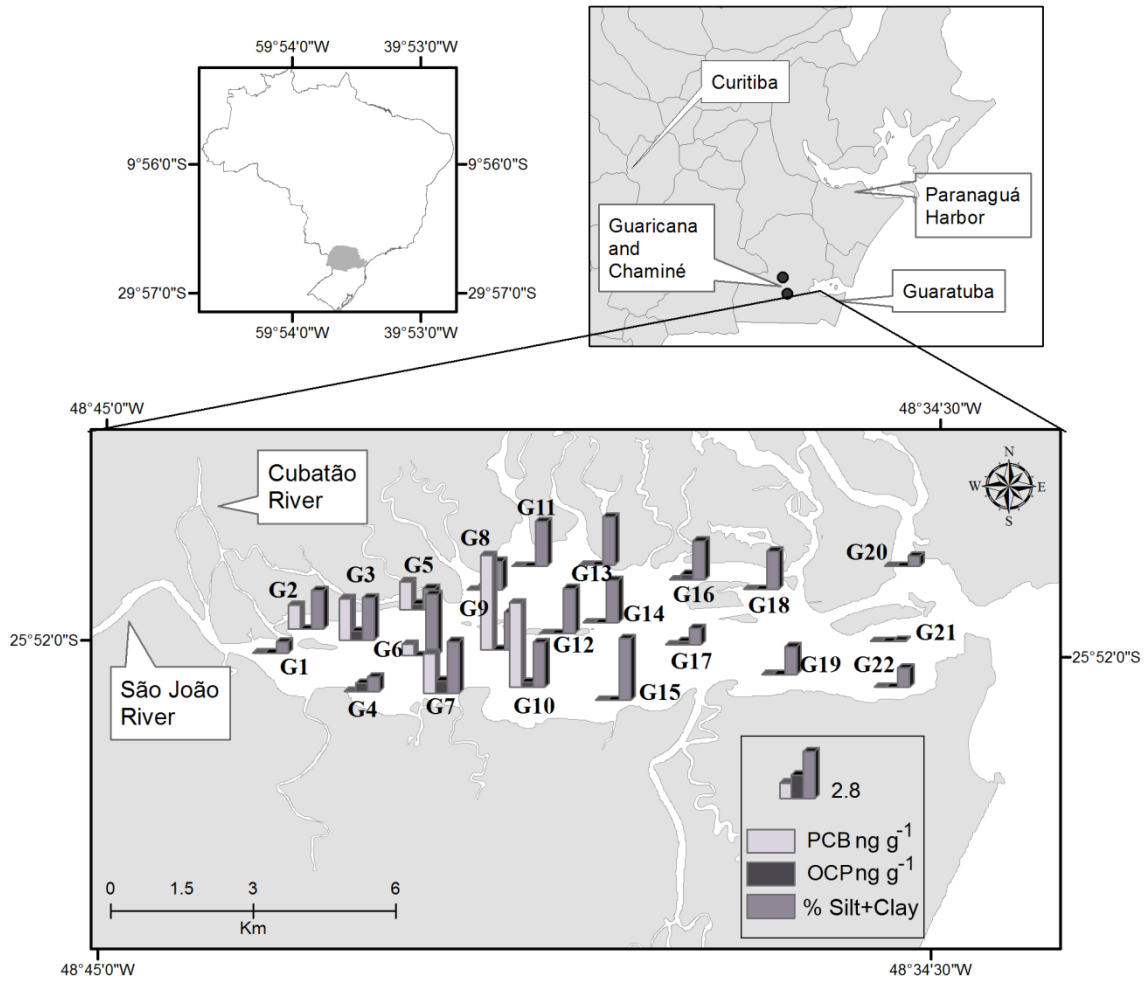


Fig. 1. Map of study area and horizontal distribution of OCPs and PCBs (ng g^{-1}) and sediments fine fraction (silt + clay) (%).

3. Experimental Methods

3.1. Sampling

Twenty-two surface sediment samples (G1 to G22) were collected along the Guaratuba Bay on November 2009 with a stainless steel grab sampler. Sediment cores were manually taken close to the sites G1, G13, G10, G18, and G22 (assigned as cores T1, T2, T3, T4, and T5, respectively). At each site, four cores (diameter: 70 mm; length: up to 50 cm) were collected side-by-side: two aluminum cores for organic compounds analyses, one PVC core for magnetic susceptibility measurements, and one acrylic core for granulometry analyses.

The top 2 cm layer of undisturbed surface sediment was collected to evaluate the recent input of organochlorine compounds. Sediment cores used to describe historical trends were sectioned at 2 cm intervals. The sediment samples were placed into pre-cleaned aluminum foil and stored at -20 °C. The sediments were freeze-dried and stored in glass bottles until laboratory analyses.

3.2. Magnetic susceptibility and particle size

Magnetic susceptibility (MS) measurements were performed using a Bartington MS-2C magnetic susceptibility meter equipped with a 90 mm diameter sensor, on the whole 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 sample diameters different from the sensor dimensions and background values were taken to correct the instrumental drift (MARTINS *et al.*, 2007).

The particle size of the sediments samples were determined by dry sieving method with 8, 14, 42, and 80 mesh sieves. A laser particle size analyzer (CILAS 1064L) was used to measure the particle size distribution of the silt and clay sediments portions.

3.3. Sedimentation rate and core dating

$^{210}\text{Pb}_{\text{xs}}$ activity was determined by gamma-ray spectrometry using a low-background EG&G ORTEC spectrometer, with a hyper-pure Ge detector model GXM25190P with mean resolution of 1.92 keV to the 1332.40 keV photopeak of ^{60}Co . The ^{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 , all according to the methodology of analysis and data acquisition described in FIGUEIRA *et al.* (2007).

The sedimentation rate was determined with the application of CIC (Constant Initial Concentration) (ROBBINS & EDGINGTON, 1975). CIC model of unsupported ^{210}Pb (abbreviated as $^{210}\text{Pb}_{\text{xs}}$) considers that there is a continuous input of sediments to the system and an initial activity of $^{210}\text{Pb}_{\text{xs}}$ in the core that decays with a time factor dependent solely on ^{210}Pb half-life.

3.3. Extraction and clean-up of OCPs and PCBs

The analytical procedure for OCPs and PCBs analyses is based on UNEP (1992) with minor modifications (BÍCEGO *et al.*, 2006). Approximately 20 g of sediment was Soxhlet extracted over 8 h using 80 mL of a mixture of (1:1) dichloromethane (DCM) and n-hexane. Activate copper was added to remove sulphur. A mixture of surrogates of PCB 103 (C-103N) and PCB 198 (C-198N), both from AccuStandard, USA, was added prior to sample extraction. The DCM/n-hexane extract was purified using the column chromatography with 3.2 g of 5% deactivated alumina. Elution was performed with 20 mL of a (3:7) DCM/n-hexane mixture. The eluate was then concentrated up to 0.5 mL under a gentle gas stream of purified nitrogen and the TCMX (tetrachloro-*m*-xylene) (M-8082-SS-10X, AccuStandard, USA) was added as internal standard.

3.4. Instrumental analyses and quality assurance procedures

The determination of PCBs and OCPs was performed by Agilent 7890A gas chromatography (GC) with electron capture detection (ECD) and the results of some samples were confirmed by GC-MS (mass spectrometric) analysis.

The GC-ECD column was an HP-5 fused silica column (length: 30 m, ID: 320 μm , film thickness: 0.25 μm). The oven temperature was programmed from 70 $^{\circ}\text{C}$ for 1 min, increasing at 40 $^{\circ}\text{C min}^{-1}$ to 170 $^{\circ}\text{C}$, increasing at 3 $^{\circ}\text{C min}^{-1}$ to 195 $^{\circ}\text{C}$ (holding this temperature for 3 min), increasing 0.5 $^{\circ}\text{C min}^{-1}$ to 210 $^{\circ}\text{C}$ (holding for 5 min) and increasing 20 $^{\circ}\text{C min}^{-1}$ to 300 $^{\circ}\text{C}$ with a final hold time of 10 min. Injector and detector temperatures were set at 280 and 320 $^{\circ}\text{C}$, respectively. Nitrogen was used as the carrier and make-up gas at constant flow rate of 0.5 mL min^{-1} and 60.0 mL min^{-1} , respectively.

The concentrations and identification of the analytes were determined based on surrogate standards added and analytical curves. Calibration curves were prepared with a mixture of PCBs ($\Sigma 51$ PCBs: 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, PCB 126, PCB187, PCB183, PCB128, PCB167, PCB174, PCB177, PCB156, PCB157, PCB180, PCB 169, PCB170, PCB199, PCB203, PCB189, PCB195, PCB194, PCB206, PCB209) (C-WCFS and C-WNN; AccuStandard, USA) and OCPs ($\Sigma 25$ OCPs: *o,p'*-DDE, *p,p'*-DDE, *o,p'*-DDD, *p,p'*-DDD, *o,p'*-DDT, *p,p'*-DDT, α -HCH, β -HCH, γ -HCH, δ -HCH, HCB, α -Chlordane, γ -Chlordane, Oxychlordane, Heptachlor, Heptachlor Epoxide, Heptachlor Epoxide-a, Aldrin, Isodrin, Dieldrin, Endrin, Endossulfan II, α -Clordana, Endossulfan I, Metoxychlor, Mirex) (AE-00010; AccuStandard, USA) standards at different concentrations (1.0, 2.5, 5.0, 10.0, 25.0, 50.0, 75.0, 100.0, 150.0, 200.0 $\text{pg } \mu\text{L}^{-1}$).

The quality assurance procedures included analyses of procedural blanks, matrix spikes, precision tests and certified reference material (WADE & CANTILLO, 1994). Procedural blanks were performed for each extraction series

of 10 samples and peaks found did not interfere with the analyses of target compounds. Blank samples corresponds a portion of 20 g of sodium sulfate anhydride, heated at 450 °C, prior the extraction procedure. Surrogate recovery, based on the relationship with an internal standard (TCMX), added at the end of laboratory analyses, to PCB 103 and PCB 198, ranged from 66.1 to 106.1 % (82.3 ± 7.0) and 41.6 to 121.8 % (86.9 ± 18.2), respectively.

Sediment samples were spiked with a mixture of PCBs (C-WCFS and C-WNN) and OCPs (AE-00010) and the mean standard recoveries were 100.5 ± 8.6 and $93.6 \pm 16.3\%$, respectively. The recoveries comply with the acceptable matrix spike recovery criteria of 50 – 125% recovery for at least 80% of the analytes (SERICANO *et al.*, 1998).

The limit of quantification (LQ) and repeatability were obtained by analyzing the samples spiked with OCP and PCB standards. The LQ was calculated as ten times the standard deviation in the seven replicates analyzes and it ranged from 0.01 to 0.17 (mean = 0.03 ± 0.01) ng g⁻¹ for PCBs and 0.01 to 0.08 (mean = 0.03 ± 0.01) ng g⁻¹ for OCPs. The precision, expressed as the coefficient of variation between the replicates, ranged from 1.3 to 7.2 (mean = 2.7 ± 0.8) % for PCBs and 1.6 and 9.1 (mean = 4.6 ± 1.8) % for OCPs.

The method accuracy was ensured by the analyses of standard reference material IAEA-417 from the Marine Environment Laboratory, International Atomic Energy Agency. The results were within the upper and lower 95% confidence interval reference values for 90% of PCB congeners and for all the OCPs analyzed, with mean recoveries of $95.6 \pm 24.9\%$ and $86.2 \pm 50\%$, respectively.

3.5. Statistical analyses

Statistical data analyses were performed with R software (R DEVELOPMENT CORE TEAM, 2011). The Pearson's correlation test was used to test the relationship between PCBs, OCPs, and grain size distributions. The grain size statistical parameters were analyzed with Sysgran 3.0 software (CAMARGO, 2005).

4. Results and Discussion

4.1. Magnetic susceptibility

The magnetic materials in marine sediments are derived mainly from continental input into the estuaries and variations on its values may indicate changes in depositional processes. On the other hand, the lack of variations suggests the maintenance of constant sedimentation rates in a study area during in a considered deposition period (HANESCH & SCHOLGER, 2002, VENKATACHALAPATHY *et al.*, 2011).

The values of MS ranged (in 10^{-5} SI) from 42 to 138 (mean = 89 ± 32 ; RSD = 36.2 %) to T1; 25 to 44 (mean = 39 ± 4 ; RSD = 11.3 %) to T2; 15 to 19 (mean value = 17 ± 1 ; RSD = 6.7 %) to T3; 4 to 11 (mean value = 8 ± 4 ; RSD = 47.3 %) to T4, and; 2 to 14 (mean value = 7 ± 5 ; RSD = 61.4 %) to T5 (Table 1). The absence of large variations on MS values may indicate no mixture between the sediment layers. Thus, based on the lower RSD, the T3 sediment core was chosen for OCs analyses.

Table 1 Values of magnetic susceptibility (MS) in 10^{-5} SI, from the five sediment core collected.

Depth (cm)	Sediment core				
	T1	T2	T3	T4	T5
10-12	119.3	42.0	16.9	8.0	12.2
12-14	109.7	40.5	16.8	8.3	12.0
14-16	103.7	40.5	16.7	7.7	10.1
16-18	98.5	43.8	17.5	8.0	2.5
18-20	95.5	42.6	17.9	8.3	7.1
20-22	89.2	41.4	18.9	11.2	6.8
22-24	74.4	36.3	18.9	9.5	5.4
24-26	83.9	37.1	18.1	9.8	5.6
26-28	94.3	37.2	18.2	10.7	4.8
28-30	76.5	38.0	17.4	8.7	3.6
30-32	93.0	24.6	16.9	n.a.	1.8

n.a.: not analysed

The magnetic enrichment of recent sediments may suggest an anthropogenic input of magnetic metals (HANESCH & SCHOLGER, 2002). Further, MS values found at the study sites were, in general, lower those in eastern (mean = 137×10^{-5} SI) and western (mean = 497×10^{-5} SI) Hong Kong Harbor (CHAN *et al.*, 2001) and Santos Estuary, Brazil (maximum value = 470×10^{-5} SI) (MARTINS *et al.*, 2007), where contamination from urban and industrial activities had been reported.

Correlations between OCs and MS have not been reported in literature. However, previous studies have shown the potential for the application of MS in the identification of anthropogenic activities, in particular due the relation of MS signature with polycyclic aromatic hydrocarbons (PAHs) (MORRIS *et al.*, 1994; MARTINS *et al.*, 2007) and heavy metals (STRZYSCZ & MAGIERA, 1998).

No correlations were detected between the MS values and OCs ($r=-0.30$, $p\text{-value}>0.05$ for PCBs and $r=-0.37$, $p\text{-value}>0.05$ for OCPs), suggesting that OCs and magnetic materials can be derived from diffuse sources, like atmospheric transport (SHEN *et al.*, 2005; WEBER *et al.*, 2009). However, it must be considered that the lack of correlations may be a consequence of the low levels of OCs.

4.2. Grain size distribution

The surface sediment samples showed a variable mixture of sand ($78.6 \pm 9.7\%$), silt ($16.2 \pm 8.1\%$), and clay ($3.9 \pm 1.7\%$), with predominance of fine and very fine sand (60 and 32%, respectively) (Figure 2). Medium and coarse sand were detected at stations G1 and G4, respectively, which may be related to fluvial sediments. The fine fraction (silt + clay) were higher at station G6 to G16 (mean value of $27.3 \pm 5.6\%$), which are located in an area with poor circulation and shallow waters (CHAVES, 1998; MARONE *et al.*, 2006), with the highest percentages at stations G6, G7, and G15 (>30%). At the mouth of the estuary (G20, G21, and G22) the higher percentage of sandy fraction was registered ($94.0 \pm 4.4\%$).

The T3 sediment core registered mean value of 70.6 ± 9.2 , 23.7 ± 7.5 , and 5.6 ± 1.7 for sand, silt and clay fractions, respectively (Figure 2). The grain size distribution was more constant than that reported in previous data (SANDERS *et al.*, 2006), with coefficient of variation of 13% for sand fraction and 31% for fine fraction. The sediments varied between coarse silt (18.7%) to medium sand (12.5%), with predominance of very fine sand (56.3%). The fine fraction represents $29.4 \pm 9.2\%$ of the sediments, which complies with the data registered for surface samples in the same region (around G10).

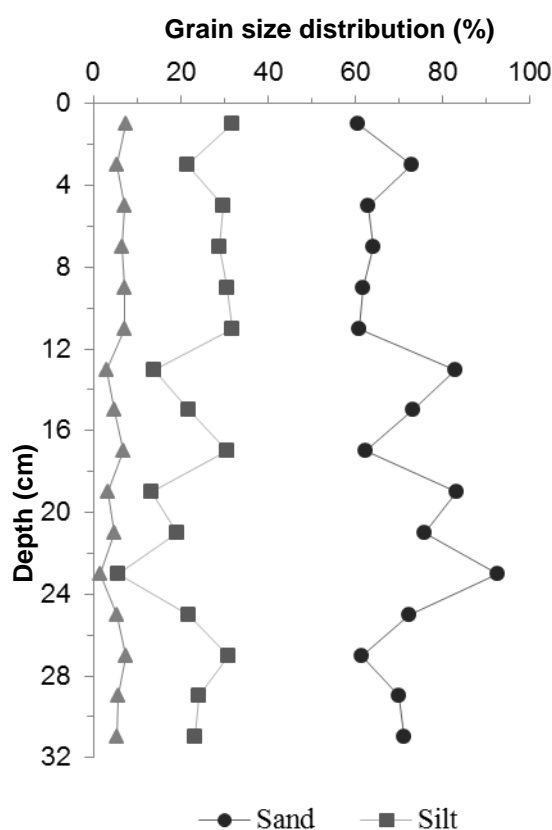


Fig. 2. Grain size distribution (%) in the T3 sediment core according to the depth.

4.3. Sedimentation rate and core dating

The ^{210}Pb activity shows an almost linear decline with depth (Figure 3). The $^{210}\text{Pb}_{\text{xs}}$ was fitted to the least square procedure ($r = -0.98$; $p\text{-value} < 0.001$), and by the slope of the log-linear curve ($y = -10.7 + 39.1$), the average sedimentation rate was $0.36 \pm 0.02 \text{ cm yr}^{-1}$.

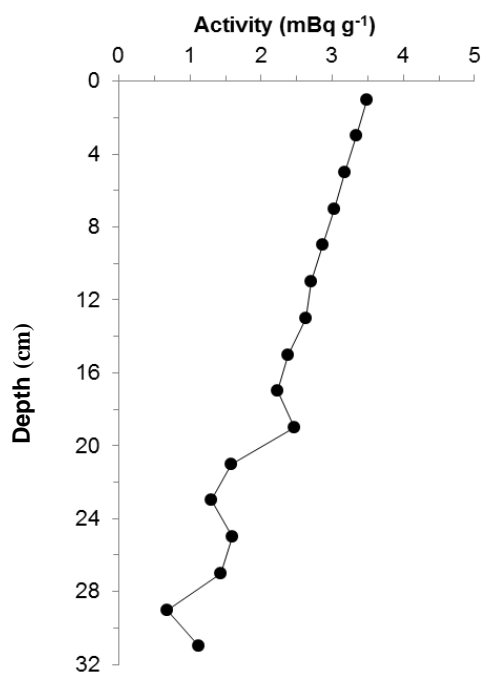


Fig. 3. ^{210}Pb activity in T3 sediment core according to the depth.

With the values of sedimentation rate, the core dating (Table 2) was assessed, considering these values to be constant in all profile. Thus, every 2 cm layer in T3 was deposited for about 5.6 years and, as the sediment core was collected in October 2010, the bottom of the sediment core (30-32 cm) was estimated to be about 84 years old.

Table 2 T3 sediment core estimated dates

Depth (cm)	Estimated age (year)
0-2	2010
2-4	2005
4-6	1999
6-8	1994
8-10	1988
10-12	1982
12-14	1977
14-16	1971
16-18	1966
18-20	1960
20-22	1954
22-24	1949
24-26	1943
26-28	1937
28-30	1932
30-32	1926

4.3. Levels of PCBs and OCPs

Total PCB concentrations ($\Sigma 51$ PCBs) in the surface sediments ranged from <LQ to 5.62 ng g^{-1} (Table 3) and total OCPs concentrations ($\Sigma 25$ OCPs) ranged from <LQ to 0.74 ng g^{-1} (Table 4). OCPs were detected in very low concentrations and PCBs were not detected after the mid-part of the bay (after G10).

Table 3 Concentrations of individual PCB (ng g^{-1}) in the surface sediment samples of Guaratuba Bay. <LQ: Below Limit of Quantification

Compound	Sampling station									
	G1	G2	G3	G4	G5	G6	G7	G8	G9	G10
PCB 52	< LQ	< LQ	0.41	< LQ	< LQ	< LQ	1.26	< LQ	0.80	0.17
PCB 132/105	< LQ	< LQ	0.32	< LQ	0.46	< LQ	< LQ	< LQ	1.29	2.06
PCB 167	< LQ	0.46	0.71	< LQ	< LQ	< LQ	< LQ	< LQ	0.32	< LQ
PCB 174	< LQ	< LQ	0.38	< LQ	< LQ	< LQ	< LQ	< LQ	2.05	< LQ
PCB 177	< LQ	< LQ	< LQ	< LQ	0.11	< LQ	0.21	< LQ	< LQ	0.46
PCB 180	< LQ	0.75	0.66	< LQ	0.22	0.26	0.38	< LQ	0.49	0.63
PCB 194	< LQ	0.20	< LQ	< LQ	0.87	0.42	0.51	< LQ	0.67	1.71
Σ PCB	< LQ	1.41	2.48	< LQ	1.66	0.68	2.36	< LQ	5.62	5.03

Table 4 Concentrations of individual PCB (ng g^{-1}) in the surface sediment samples of Guaratuba Bay. <LQ: Below Limit of Quantification

Compound	Sampling station								
	G1	G2	G3	G4	G5	G6	G7	G8	G9
Oxychlorane	< LQ	< LQ	0.25	< LQ	0.16	< LQ	0.29	0.16	< LQ
<i>p.p'</i> - DDD	< LQ	< LQ	0.29	0.49	< LQ	< LQ	0.23	< LQ	< LQ
Heptachlor Epoxide	< LQ	< LQ	< LQ	< LQ	0.18	< LQ	0.22	0.16	< LQ
Σ OCP	< LQ	< LQ	0.54	0.49	0.34	< LQ	0.74	0.32	< LQ
	G10	G11	G12	G13	G14	G15	G16	G17	
Oxychlorane	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	
<i>p.p'</i> - DDD	0.30	< LQ	< LQ	< LQ	< LQ	< LQ	0.32	0.21	
Heptachlor Epoxide	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	< LQ	
Σ OCP	0.30	< LQ	< LQ	< LQ	< LQ	< LQ	0.32	0.21	

PCBs and OCPs occurred in a few layers and at low concentrations in the sediment core. Regarding PCB, only PCB 174 and PCB 177 were detected at layers 8-10 cm (0.52 ng g^{-1}) and 14-16 (0.19 ng g^{-1}). The OCP were detected at 5 layers, ranging from <QL to 1.52 ng g^{-1} (Table 5). The OCs were not detected below the 14-16 cm sediment layer.

Table 5 Concentrations of individual OCP (ng g^{-1}) in the T3 sediment core samples of Guaratuba Bay. <LQ: Below Limit of Quantification

Compound	Depth							
	0-2	2-4	4-6	6-8	8-10	10-12	12-14	14-16
Oxychlordane	< LQ	< LQ	< LQ	< LQ	< LQ	0.6	< LQ	< LQ
<i>p.p'</i> - DDD	< LQ	0.19	< LQ	<LQ	< LQ	< LQ	< LQ	< LQ
Heptachlor Epoxide	0.20	0.36	< LQ	0.38	0.71	0.92	< LQ	< LQ
Σ OCP	0.20	0.55	< LQ	0.38	0.71	1.52	< LQ	< LQ

To evaluate the ecotoxicological significance of OC contamination in Guaratuba Bay, the data were compared with some of the sediment quality guidelines (SQG) values available. These values are based on the ERL (Effects Range-Low) and ERM (Effects Range-Median) (LONG *et al.*, 1995); and on the TEL (Threshold-Effects Level) and PEL (Probable-Effects Level) (MACDONALD *et al.*, 1996). These values represent the concentrations above which toxicity may be observed (ERL), is expected to occur (ERM), may be frequent (TEL), and is frequently expected (PEL).

The values are related to the Σ 7 PCBs (PCB 28, 52, 101, 118, 138, 153 and 180), total DDTs (sum of DDD, DDE, and DDT concentrations) and total chlordanes (sum of α -chlordane, γ -chlordane, and oxychlordane concentrations). The concentrations obtained in this study did not exceed the levels above mentioned (Table 6).

Table 6 Comparison between the sediment quality guidelines (SQG) values and the mean and maximum concentrations detected in the surface samples and sediment core samples (ng g^{-1} dry weight).

	Surface				Sediment Core	
	TEL	ERL	ERM	PEL	Maximum	Maximum
PCB	21.6	22.7	180	188.8	5.62	0.52
DDT	3.89	1.58	46.1	51.7	0.49	0.19
Chlordane	2.26	0.50	6.00	4.79	0.29	0.60

The concentrations of OCs in the Guaratuba Bay surface sediments were compared to those found in other regions in Brazil and worldwide (Table 7). The ranges detected in this study are far below those of more developed

and populated areas in Brazil, such as Santos Estuary (BÍCEGO *et al.*, 2006), and Guanabara Bay (SOUZA *et al.*, 2008), and in other areas of the world, like Daya Bay in China (ZHOU *et al.*, 2001) and Alexandria Harbour in Egypt (BARAKAT *et al.*, 2002). The PCB and OCP levels are below those found in Paranaguá Bay (MARTINS *et al.*, 2009) and in Florianópolis (SOUZA *et al.*, 2012), respectively, which are nearby coastal areas. Moreover, the values are comparable to those detected in remote and pristine areas, like Antarctica (MONTONE *et al.*, 2001) and the Arctic (JIAO *et al.*, 2009).

Table 7

Comparison of PCB and OCP concentrations (ng g⁻¹) in surface sediments from other locations.

Location	PCBs	OCPs	References
Guaratuba Bay, Brazil	n.d. - 6.06	0.13 - 6.31	This study
Paranaguá Bay, Brazil	0.2 - 17.22 ^a	n.a.	MARTINS <i>et al.</i> (2009)
Florianópolis Bay, Brazil	n.d.	n.d. - 11.86 ^b	SOUZA <i>et al.</i> (2012)
Santos Estuary, Brazil	0.03 - 254 ^c	0.05 - 16 ^d	BÍCEGO <i>et al.</i> (2006)
Guanabara Bay, Brazil	17.83 – 184.16 ^e	28.44 - 216.62 ^f	SOUZA <i>et al.</i> (2008)
Daya Bay, China	0.85- 27.37 ^g	2.43 - 86.25 ^h	ZHOU <i>et al.</i> (2001)
Alexandria Harbour, Egypt	0.9 - 1211 ⁱ	n.d.- 885 ^d	BARAKAT <i>et al.</i> (2002)
Admiralty Bay, King George Island, Antarctica	0.85 – 2.47 ^j	n.a.	MONTONE <i>et al.</i> (2001)
Svalbard, Norwegian Arctic	0.08 - 0.59 ^h	0.07 - 0.28 ^d	JIAO <i>et al.</i> (2009)

n.d.: not detected; n.a.: not analyzed

^a ∑44 PCB; ^b ∑8 OCP; ^c ∑30 PCB; ^d ∑ DDT; ^e ∑7 PCB; ^f ∑14 OCP; ^g ∑12 PCB; ^h ∑15 PCB; ⁱ ∑96 PCB; ^j ∑13 PCB

4.4. Horizontal distribution of OCs in Guaratuba Bay

The PCBs were detected in higher concentrations in surface sediments than OCPs (Figure 1). The concentrations of OCs followed the order PCB 194 > PCB 132/105 > PCB 180 > PCB 174 > *p,p'*-DDD > PCB 167, with median values of 0.59, 0.88, 0.49, 1.22, 0.3, and 0.46 ng g⁻¹, respectively.

No correlations were found between OCs and the distribution of smaller particulates (silt and clay) in sediments ($r=0.24$, $p\text{-value}>0.05$ for OCPs; $r=0.04$, $p\text{-value}>0.05$ for PCBs).

The points located in the inner estuary (points G01 to G10) presented the most part of OCs detected, with median concentration of 1.54 ng g^{-1} for PCB and 0.31 ng g^{-1} for OCP. PCBs were not detected in the mid-estuarine points (G11 to G17), while OCPs were detected only in points G16 and G17 at low concentrations (0.32 and 0.21 ng g^{-1} , respectively). In the outer estuary (G18 to G22), OCs were not detected.

The sampling points located in the inner estuary are related to the mouth of Cubatão and São João rivers, which originate in the Serra do Mar and crosses agricultural and industrial areas. Therefore, the source of OCs may be located outside the bay, related to fluvial input. The industrial activities in the margins of Cubatão and São João rivers, at the north of the estuary, had also been suggested as the main source of mercury to the region SANDERS *et al.* (2006). On the other hand, the detection of oxychlordanes may indicate a possible atmospheric source of OCPs to the area because this groups was not widely used in South America (BARRA *et al.*, 2006).

The DDT and their metabolites can be used to evaluate the occurrence of recent OCP inputs (HONG *et al.*, 2003; PENG *et al.*, 2005). Since DDD (*o,p'*-DDD and *p, p'*-DD) and DDE (*o,p'*-DDE and *p,p'*-DDE) are metabolites of DDT (*o,p'*-DDT and *p,p'*-DDT) under anaerobic and aerobic conditions, respectively, the lower values to DDD+DDE/DDT ratio suggests recent DDT input (GARRISON *et al.*, 2000; YU *et al.*, 2011). The DDD was the only metabolite detected in Guaratuba Bay, suggesting old DDT input and degradation under anaerobic conditions.

4.5. Vertical distribution and background levels of OCs in Guaratuba Bay

The dated sediment core was used to assess the background levels of OCs in Guaratuba Bay by determining concentrations preserved in a historical record (GÓMEZ-GUTIÉRREZ *et al.*, 2007). Neither PCB nor OCP was detected between 1926 and 1966 (Figure 4).

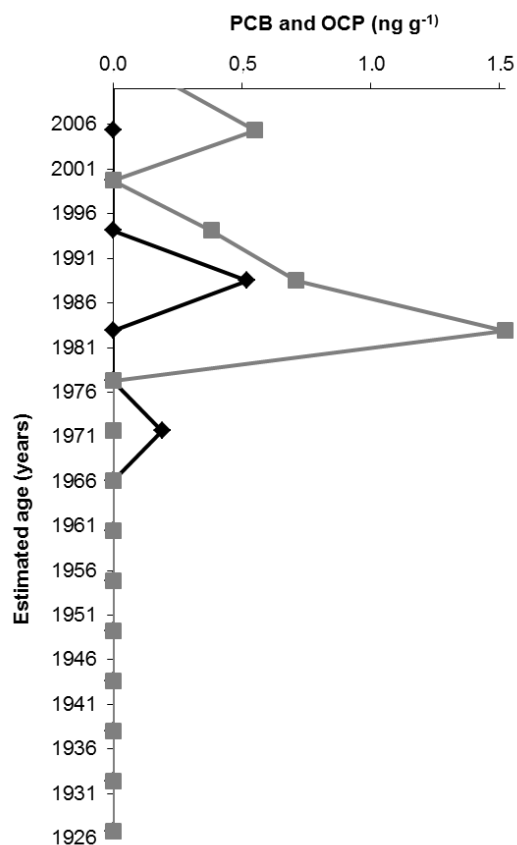


Fig. 4. PCB and OCP concentrations (ng g^{-1}) in T3 sediment core, according to the estimated age (years).

PCB was detected only at two sediment layers, corresponding to the years 1972 and 1989, and was not detected at the top of the sediment core (after the 1990's). This could be a consequence of the prohibition of PCB usage in Brazil in 1981, avoiding new inputs into the environment.

The first OCP input was detected only at 1983 and the concentrations remained mainly constant upwards, with a median value of 0.47 ng g^{-1} . The usage of OCPs was restricted in Brazil in 1985. The concentrations detected after that can be explained by the record of OCPs importation in Brazil of about 1,500 t from 1989 to 1990 and of about 87 t from 2000 to 2012 (MDIC, 2012).

Only three pesticides were detected in the sediment core: heptachlor heptoxide, *p,p'*-DDD, and oxychlordan. These OCPs are metabolites of heptachlor, DDT and chlordane, respectively, indicating degradation of pesticides in Guaratuba Bay.

5. Conclusions

The horizontal distribution of OCs suggests the riverine input as the major carrier of these compounds. The source of PCBs could be related to urbanized and industrialized areas located northward from Guaratuba Bay, while OCPs sources could be associated to the agricultural areas around Cubatão and São João rivers.

Although OCs concentrations have been continuously detected in studies on the Brazilian coast and despite their usage worldwide, in this study we detected very low concentrations of these compounds, which were comparable to those detected in remote and pristine areas. This data suggests little usage of this compound in the area. The data obtained can be considered as the background level of OCs in this region.

The detection and persistence of these compounds in remote and relatively uncontaminated areas highlights the need for monitoring programs to evaluate the effectiveness of regulatory efforts. Moreover, the long-range transport of POPs is a matter of global concern, and their study is necessary for understanding the behavior and providing data for a global inventory of these compounds.

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