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# Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina

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## Abstract

Settling particles and underlying sediments collected at 1, 2.5 and 4 km along offshore transects in the urbanized sector of the Río de la Plata were analyzed to evaluate the sources and accumulation of PCBs. Total PCB concentrations range from <0.1 to 100 $\mathrm{ng\,g^{-1}}$ and include variability associated to North–South and offshore gradients reflecting the impact of coastal discharges. Highest concentrations were recorded in the industrialized Central area close to Buenos Aires ($61 \pm 37\ \mathrm{ng\,g^{-1}}$ at 1 km) relative to cleaner northern stations ($3.6 \pm 2.2\ \mathrm{ng\,g^{-1}}$) and southward sites ($37 \pm 2.8\ \mathrm{ng\,g^{-1}}$), affected by transport of particulate PCBs by coastal currents. Sediment traps deployed in the Central area revealed large depositional fluxes of total matter ($361 \pm 124\ \mathrm{g\,m^{-2}\,day^{-1}}$) and PCBs ($26 \pm 19\ \mathrm{\mu g\,m^{-2}\,day^{-1}}$) and high sedimentation rates ($5.0 \pm 1.7\ \mathrm{cm\,yr^{-1}}$). Uniform PCB concentrations (66–89 $\mathrm{ng\,g^{-1}}$) down to 20 cm in sediment cores suggest continued PCB discharges during the last 4 years. PCB composition was dominated by hexa ($43 \pm 6.4\%$), hepta ($23 \pm 5.1\%$) and pentachlorobiphenyls ($21 \pm 5.5\%$) with lower proportions tri–tetra ($7.4 \pm 5.4\%$) and higher chlorinated congeners ($5.1 \pm 3.3\%$). A consistent weathering pattern with loss of 3–5 chlorobiphenyls and enrichment in higher chlorinated PCBs corresponding to a shift from a 1:1 to a 1:3 1254:1260 Aroclor mixture, was observed offshore. A principal component analysis performed with the relative contribution of PCB congener classes confirmed the offshore weathering pattern indicating that transformer oils containing Aroclor 1254–1260 are the most probable sources. Sediment inventories, sediment trap fluxes and Fugacity II calculations indicate an accumulation ~500–800 kg PCB in superficial sediments of this coastal environment.

*Keywords:* Vertical fluxes; PCBs; Coastal sediments; Río de la Plata

## 1. Introduction

Among persistent organic pollutants targeted for monitoring, control and virtual elimination by international research projects and agreements (UNEP, 2001), polychlorinated biphenyls (PCBs) are ubiquitous contaminants in the aquatic environment. Owing to their

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high hydrophobicity, PCB dynamics is normally controlled by the particulate behavior of the system, including rapid adsorption to suspended particles and accumulation in underlying sediments which constitute long-term reservoirs and secondary sources. Large river-estuaries, lakes and coastal areas supporting heavy industrial and urban pressure are thus transformed in major sinks of these contaminants which can be buried, transported by coastal currents and sediment erosion, remobilized or bioaccumulated by organisms (Schwarzbauer et al., 2001; Tam and Yao, 2002; Hong et al., 2003; Hartmann et al., 2004).

The Río de la Plata (RLP) is a funnel-shaped, turbid, coastal-plain estuary with a total surface area of 35000 $km^2$ and a huge particulate load of 90 million tons of solids per year (see review in Urien, 1972; Framiñan et al., 1998; Esteves et al., 2000). This massive load of material feeds a vast delta in front of the Buenos Aires urban-industrial area which concentrates one third of the total Argentinean population and constitutes a major source of anthropogenic contaminants in the region (Barra et al., 2002). Earlier studies indicated that hydrophobic hydrocarbons, PCBs and other xenobitotics discharged daily to the estuary via small tributaries or untreated effluents associate to the abundant solid load of the system and enter the detritus food chain contaminating bivalves and fish (Colombo et al., 1990, 1995, 1997, 2000). However, the spatial extension and relative magnitude of the PCB load to sediments has not been assessed. In this paper, we evaluate the spatial distribution and horizontal transport of PCBs in coastal sediments and interpret PCB discharges through inventory calculations, depositional fluxes, and Fugacity II modeling in this urban estuary.

## 2. Methods

Sediment sampling was performed in April, August and September 2002–2003 using a 14 m boat equipped with GPS, sonar and electronic charting covering 50 km in the shallow (3–5 m depth) upper Río de la Plata Estuary (Fig. 1). Superficial sediments were collected with a "Van Veen" style Hydro-Bios stainless steel grab sampler along 13 transects perpendicular to the coast at 1, 2.5 and 4 km of the shore. In addition, sediments samples were also collected in the Sarandi stream and Riachuelo port which are main sources contributing to the coastal ecosystem. Sediment cores were collected at Riachuelo and Berazategui stations using a stainless steel Limnos Ltd. sediment sampler charged with 6–8 kg weight. Four sequential sediment slices were separated on board from the top 0–3 cm down to 15–25 cm depth. Sediment samples were stored in organic-free pre-cleaned glass jars maintained in portable coolers until arrival to the laboratory.

Settling particles were collected 1.5 m below the surface in the Central area (Fig. 1) during thirteen trap deployments covering spring, summer, autumn and winter in 2002–2004. Two sediment trap designs were used: a free-drifting 14.5 cm-diameter bi-cylindrical trap (total surface: 330 $cm^2$) which minimizes the possible overtrapping effect of currents, followed by the boat for 1.5–3 h, and two fixed 10 cm-diameter mono-cylindrical traps (total surface: 78.5 $cm^2$) which were deployed upstream and downstream the sewer area for 20–46 h. Although fixed equipments generally captured higher amounts of material (average: 14%), the results from both traps were considered in reasonable agreement given the strong spatial and temporal variability of set-

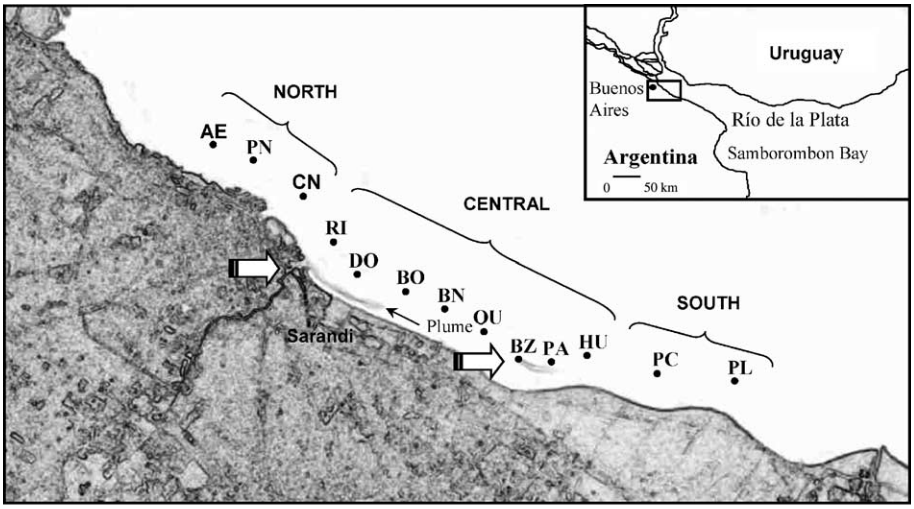

Fig. 1. Study area in the Río de la Plata estuary. Sampling station acronyms as in Table 1. From the three points sampled (1, 2.5 and 4 km from the shore), only the 2.5 km points are indicated. The arrows indicate major contaminant sources, i.e. Riachuelo and Berazategui sewer (note the dark water plumes).

tling fluxes and the difficulty to isolate the possible effect of the trap design.

Sediment samples were splitted for grain size analysis (sieve and pipette method), for the determination of water and organic matter content (100 °C for 24 h and 450 °C for 10 h), for total organic carbon and nitrogen analysis (catalytic combustion with a Thermo Finnigan, CE FlashEA 1112 elemental analyzer) and for the determination of trace organics (Colombo et al., 1990, 1995, 1997). Briefly, the analytical method included sediment drying at 30–35 °C in a clean, controlled oven, soxhlet extraction (40–50 cycles) with acetone:dichloromethane:petroleum ether (1:2:2), nitrogen concentration, activated copper treatment, silica gel fractionation with petroleum ether and petroleum ether:dichloromethane 1:3, and analysis by HRGC-ECD. Instrumental conditions (Agilent 6890N) comprised a split–splitless injector maintained at 250 °C, a μECD detector operated at 320 °C, a 0.25 mm × 30 m HP-5MS capillary column with He as carrier gas at constant flow and a temperature program from 65 °C (2 min) to 130 °C (1 min) at 10 °C/min and then to 305 °C (10 min) at 5 °C/min. Data were acquired and integrated with the Agilent Chemstation software. Quantification was performed by a external standard of 41 individual PCB congeners (IUPAC No.: 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199–201, 205, 206, 208, 209; Quebec Ministry, AccuStandard Inc.). Linear responses were obtained with 4-point calibration curves (10, 100, 500, 1000 pg μl$^{-1}$). Method accuracy evaluated through repeated analysis ($n = 7$) of certified sediment samples (NIST 1944) averaged 79 ± 24% for 24 individual PCB congeners. In addition, an internal reference sediment from La Plata harbor in the Río de la Plata was analyzed within each 10 sample batch to control method reproducibility. Total PCB concentration of this internal reference sediment averaged 22 ± 3.6 ng g$^{-1}$, i.e. 17% variability ($n = 12$). Duplicate and triplicate analysis of 15 samples yielded an average reproducibility of 22% for individual PCB congeners.

## 3. Results and discussion

### 3.1. Total PCBs in superficial sediments

Table 1 presents the concentration of selected congeners and total PCBs in surface sediments collected at 1, 2.5 and 4 km from the shore grouped in the North, Central and South areas. Fig. 2 shows total PCB levels compared to Canadian guidelines of sediment quality for protection of aquatic life and the effects range low value. Río de la Plata coastal sediments consist basically of sandy silts (57 ± 22% silt, 35 ± 25% sand) with low clay (7.5 ± 4.2%) and organic carbon contents (0.6 ± 0.5%). No significant spatial trends are observed in sediment texture as indicate the relatively homogeneous fine contents in the North (silt + clay: 63 ± 6.3%, 48 ± 30%, 85 ± 6.6% at 1, 2.5 and 4 km, respectively), Central (65 ± 22%, 73 ± 20%, 70 ± 27%) and South areas (70 ± 4.0%, 55 ± 22%, 72 ± 30%). In contrast, organic carbon contents show higher values in the Central area (1.1 ± 0.5%, 0.6 ± 0.3%, 0.4 ± 0.1% at 1, 2.5 and 4 km, respectively), relative to southern (0.8 ± 0.02%, 0.3 ± 0.1%, 0.4 ± 0.2%) and northern sites (0.3 ± 0.02%, 0.3 ± 0.3%, 0.5 ± 0.2%). These organic carbon contents are relatively low compared with environments with lower, i.e. Artic lakes (Muir et al., 1996), or higher PCB concentrations, i.e. Elbe river and tributaries (Schwarzbauer et al., 2001), reflecting the low productivity, shallow depth and prevailing oxic conditions in the water column of the Río de la Plata which lead to intense organic carbon degradation at the sediment interface (see below).

Total PCB concentrations are not homogeneous, they extend over 3 orders of magnitude from <0.1 to 100 ng g$^{-1}$, and include variability associated to North–South and offshore spatial gradients. PCB sedimentary levels in the Río de la Plata are higher than those reported for less affected or remote ecosystems such as Antarctica (1.1–5.9 ng g$^{-1}$; Montone et al., 2001), Hong Kong mangrove areas (0.5–5.8 ng g$^{-1}$; Tam and Yao, 2002), Canadian Artic lakes (2.4–39 ng g$^{-1}$; Muir et al., 1996), or similar to Masan Bay in Korea (10–148 ng g$^{-1}$; Khim et al., 1999; 1.2–41 ng g$^{-1}$; Hong et al., 2003) and Central Venice Lagoon (2.7–123 ng g$^{-1}$; Frignani et al., 2004), but they appear as relatively moderate compared to more polluted environments such as Lake Ontario (71–1200 ng g$^{-1}$; Oliver et al., 1989), the Elbe river and tributaries (109–3363 ng g$^{-1}$; Schwarzbauer et al., 2001), Narragansett Bay (21–1760 ng g$^{-1}$; Hartmann et al., 2004), or the industrial channels from Porto Marghera, Venice (73–41 639 ng g$^{-1}$; Frignani et al., 2004).

All the transects in the Río de la Plata show higher concentrations at 1 km reflecting the impact of coastal discharges, and decreasing offshore values. The Central area presents the highest concentrations (average: 61 ± 37 ng g$^{-1}$ at 1 km) due to the contribution from polluted streams (Sarandi), ports (Riachuelo) and crude sewers (Berazategui; Fig. 1). The analysis of sediment samples from these sources effectively confirmed very high PCB levels in Sarandi (98 ng g$^{-1}$), and specially in the port of Riachuelo (934 ng g$^{-1}$). In contrast to this impacted sector, northern stations show an order of magnitude lower values (3.6 ± 2.2 ng g$^{-1}$ at 1 km), indicating no major local sources. Although the Río de la Plata is a tidal estuary with current reversions induced by high tide and SE winds (CARP, 1989), these results indicate that the upward transport of pollutants is

Table 1
Concentration of total PCBs and selected congeners in Río de la Plata sediments collected at 1, 2.5 and 4 km from the coast

| Station | | PCBs (ng g$^{-1}$ dw) | | | | | | | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 km | | | | | | | | | 2.5 km | | | | | | | | | 4 km | | | | | | | | |
| | | 31–28 | 52 | 101 | 149 | 118 | 153 | 138 | 180 | Tot | 31–28 | 52 | 101 | 149 | 118 | 153 | 138 | 180 | Tot | 31–28 | 52 | 101 | 149 | 118 | 153 | 138 | 180 | Tot |
| *North area* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Aeroparque | AE | 0.02 | 0.02 | 0.05 | 0.11 | 0.03 | 0.10 | 0.12 | 0.06 | 1.0 | – | – | 0.003 | 0.01 | – | 0.01 | 0.01 | 0.004 | 0.1 | – | – | 0.02 | 0.06 | 0.03 | 0.04 | 0.06 | 0.03 | 0.5 |
| Puerto Norte | PN | 0.05 | 0.04 | 0.16 | 0.46 | 0.13 | 0.63 | 0.64 | 0.41 | 4.9 | – | – | – | 0.01 | – | 0.01 | 0.01 | 0.003 | 0.04 | – | – | 0.04 | 0.06 | 0.03 | 0.07 | 0.09 | 0.04 | 0.6 |
| Canal Norte | CN | 0.04 | 0.13 | 0.25 | 0.49 | 0.21 | 0.41 | 0.63 | 0.29 | 4.8 | – | – | 0.09 | 0.13 | 0.05 | 0.21 | 0.21 | 0.12 | 1.4 | – | – | 0.04 | 0.06 | 0.04 | 0.06 | 0.08 | 0.04 | 0.6 |
| Mean | | 0.04 | 0.06 | 0.15 | 0.35 | 0.12 | 0.38 | 0.46 | 0.26 | 3.6 | – | – | 0.05 | 0.05 | 0.05 | 0.08 | 0.08 | 0.04 | 0.5 | – | – | 0.03 | 0.06 | 0.03 | 0.06 | 0.07 | 0.04 | 0.5 |
| SD | | 0.02 | 0.06 | 0.10 | 0.21 | 0.09 | 0.27 | 0.30 | 0.18 | 2.2 | – | – | 0.06 | 0.07 | | 0.12 | 0.12 | 0.07 | 0.8 | – | – | 0.01 | 0.00 | 0.01 | 0.02 | 0.02 | 0.01 | 0.1 |
| *Central area* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Riachuelo | RI | 1.33 | 2.79 | 6.61 | 8.50 | 3.73 | 8.76 | 10.45 | 5.52 | 98.5 | 0.12 | 0.16 | 0.62 | 1.75 | 0.56 | 1.23 | 1.84 | 0.88 | 13.2 | 0.30 | 0.70 | 2.35 | 4.35 | 1.01 | 4.14 | 6.07 | 2.84 | 39.9 |
| Santo Domingo | DO | 0.27 | 0.51 | 1.38 | 1.63 | 0.88 | 1.81 | 1.99 | 0.85 | 18.6 | 0.13 | 0.61 | 0.43 | 0.63 | 0.22 | 0.54 | 0.84 | 0.35 | 7.5 | 0.08 | 0.05 | 0.12 | 0.23 | 0.06 | 0.16 | 0.25 | 0.13 | 2.4 |
| Don Bosco | BO | 0.10 | 0.27 | 0.66 | 0.79 | 0.40 | 0.86 | 1.08 | 0.49 | 9.3 | 0.02 | 0.04 | 0.18 | 0.48 | 0.12 | 0.41 | 0.58 | 0.31 | 4.2 | – | 0.01 | 0.08 | 0.23 | 0.05 | 0.17 | 0.29 | 0.14 | 1.9 |
| Bernal | BN | 2.35 | 2.60 | 6.63 | 8.16 | 4.25 | 9.10 | 10.91 | 5.11 | 95.6 | 0.19 | 0.27 | 2.08 | 3.43 | 2.43 | 4.18 | 5.56 | 2.70 | 40.2 | 0.10 | 0.09 | 0.10 | 0.26 | 0.08 | 0.20 | 0.33 | 0.15 | 2.6 |
| Quilmes | QU | 1.10 | 0.80 | 3.16 | 4.36 | 1.85 | 4.99 | 5.98 | 2.89 | 47.7 | 0.62 | 1.02 | 2.47 | 4.03 | 1.35 | 4.34 | 5.01 | 3.26 | 43.8 | 0.11 | 0.07 | 0.17 | 0.42 | 0.17 | 0.32 | 0.52 | 0.25 | 3.9 |
| Berazategui | BZ | | | | | | | | | | 5.32 | 1.53 | 3.88 | 5.34 | 2.10 | 5.54 | 8.59 | 4.68 | 85.1 | | | | | | | | | |
| Platanos | PA | 1.47 | 1.44 | 3.92 | 6.30 | 4.22 | 11.72 | 8.72 | 5.51 | 82.3 | 0.39 | 0.38 | 0.84 | 1.47 | 0.63 | 1.38 | 1.95 | 1.05 | 16.2 | 0.09 | 0.06 | 0.16 | 0.43 | 0.14 | 0.35 | 0.53 | 0.28 | 4.0 |
| Hudson | HU | 1.84 | 0.73 | 4.02 | 6.16 | 4.13 | 11.19 | 8.22 | 5.21 | 77.6 | 0.07 | 0.06 | 0.18 | 0.50 | 0.10 | 0.36 | 0.55 | 0.28 | 4.3 | – | | 0.32 | 0.59 | 0.38 | 0.33 | 0.57 | 0.11 | 4.8 |
| Mean | | 1.21 | 1.30 | 3.77 | 5.13 | 2.78 | 6.92 | 6.76 | 3.65 | 61.4 | 0.86 | 0.51 | 1.33 | 2.20 | 0.94 | 2.25 | 3.12 | 1.69 | 26.8 | 0.14 | 0.16 | 0.47 | 0.93 | 0.27 | 0.81 | 1.22 | 0.56 | 8.5 |
| SD | | 0.81 | 1.02 | 2.32 | 3.02 | 1.69 | 4.40 | 3.92 | 2.23 | 36.5 | 1.81 | 0.52 | 1.34 | 1.84 | 0.92 | 2.09 | 2.94 | 1.65 | 28.2 | 0.09 | 0.26 | 0.83 | 1.51 | 0.34 | 1.47 | 2.14 | 1.01 | 13.9 |
| *South area* | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| Punta Colorada | PC | 0.43 | 0.43 | 2.07 | 3.13 | 1.23 | 3.51 | 4.71 | 2.17 | 35.0 | 0.11 | 0.14 | 0.47 | 0.89 | 0.39 | 0.87 | 1.30 | 0.60 | 9.2 | 0.04 | 0.04 | 0.08 | 0.24 | 0.08 | 0.25 | 0.35 | 0.25 | 2.6 |
| Punta Lara | PL | 0.64 | 0.88 | 2.14 | 3.35 | 1.26 | 3.78 | 4.65 | 2.47 | 39.0 | 0.03 | 0.03 | 0.18 | 0.38 | 0.17 | 0.37 | 0.55 | 0.29 | 3.8 | 0.05 | 0.05 | 0.19 | 0.45 | 0.16 | 0.39 | 0.60 | 0.29 | 4.2 |
| Mean | | 0.53 | 0.66 | 2.10 | 3.24 | 1.25 | 3.65 | 4.68 | 2.32 | 37.0 | 0.07 | 0.08 | 0.33 | 0.64 | 0.28 | 0.62 | 0.93 | 0.45 | 6.5 | 0.05 | 0.04 | 0.14 | 0.35 | 0.12 | 0.32 | 0.48 | 0.27 | 3.4 |
| SD | | 0.15 | 0.32 | 0.05 | 0.16 | 0.02 | 0.19 | 0.04 | 0.22 | 2.8 | 0.06 | 0.08 | 0.21 | 0.36 | 0.16 | 0.35 | 0.53 | 0.22 | 3.8 | 0.01 | 0.00 | 0.08 | 0.15 | 0.06 | 0.10 | 0.18 | 0.03 | 1.1 |
| *km Avg* | | 0.80 | 0.89 | 2.59 | 3.62 | 1.86 | 4.74 | 4.84 | 2.58 | 42.9 | 0.70 | 0.42 | 0.95 | 1.46 | 0.74 | 1.50 | 2.08 | 1.12 | 17.6 | 0.11 | 0.13 | 0.31 | 0.61 | 0.19 | 0.54 | 0.81 | 0.38 | 5.7 |
| SD | | 0.80 | 0.94 | 2.34 | 3.06 | 1.73 | 4.36 | 4.00 | 2.22 | 37.0 | 1.63 | 0.50 | 1.21 | 1.72 | 0.84 | 1.89 | 2.65 | 1.48 | 24.8 | 0.09 | 0.23 | 0.65 | 1.19 | 0.28 | 1.14 | 1.67 | 0.78 | 10.9 |
| *Avg Sed. Trap* ($n = 13$) | | 1.87 | 1.07 | 5.17 | 6.40 | 2.64 | 9.95 | 10.75 | 4.77 | 74.8 | | | | | | | | | | | | | | | | | | |
| SD | | 4.06 | 1.65 | 4.14 | 4.08 | 2.50 | 7.49 | 7.19 | 2.73 | 44.5 | | | | | | | | | | | | | | | | | | |
| *Cores* (cm) | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| BZ 0–3 | | 4.23 | 1.37 | 5.40 | 4.53 | 2.08 | 4.63 | 5.62 | 4.60 | 71.7 | | | | | | | | | | | | | | | | | | |
| BZ 4–5 | | 3.41 | 2.50 | 3.83 | 5.06 | 2.39 | 5.69 | 6.80 | 4.08 | 70.5 | | | | | | | | | | | | | | | | | | |
| BZ 8–10 | | 4.60 | 2.52 | 4.15 | 5.62 | 2.49 | 6.03 | 7.31 | 4.83 | 75.4 | | | | | | | | | | | | | | | | | | |
| BZ 14–20 | | 1.53 | 3.62 | 5.90 | 6.21 | 3.91 | 4.98 | 5.43 | 2.35 | 69.8 | | | | | | | | | | | | | | | | | | |
| RI 0–3 | | 2.06 | 2.99 | 5.39 | 6.28 | 3.26 | 7.02 | 8.17 | 4.14 | 89.2 | | | | | | | | | | | | | | | | | | |
| RI 7–10 | | 2.10 | 2.56 | 5.42 | 6.74 | 3.33 | 7.70 | 8.80 | 4.27 | 87.4 | | | | | | | | | | | | | | | | | | |
| RI 14–16 | | 1.84 | 2.61 | 5.28 | 6.42 | 3.19 | 7.16 | 8.36 | 3.94 | 83.5 | | | | | | | | | | | | | | | | | | |
| RI 21–24 | | 1.11 | 2.00 | 4.05 | 4.74 | 2.40 | 5.12 | 6.01 | 2.76 | 66.2 | | | | | | | | | | | | | | | | | | |

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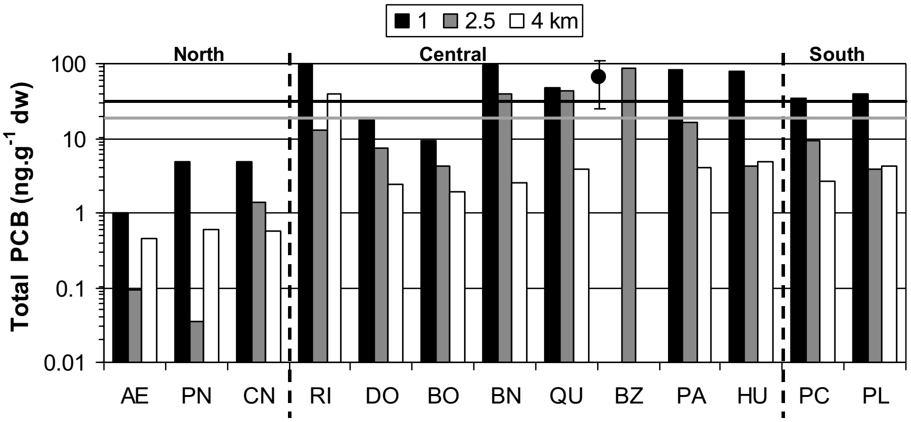


Fig. 2. Total PCB concentrations at 1, 2.5 and 4 km from the shore in the North, Central and South area of the Río de la Plata (note the logarithmic scale). The horizontal lines show guidelines of sediment quality for protection of aquatic life, in black the Canadian (34.1 $ng\,g^{-1}$) and in gray the effects range low value (22.7 $ng\,g^{-1}$). The average sediment trap concentration is shown as a filled circle in the central sector.

restricted, most probably due to sedimentation of particle-associated PCB close to major sources, i.e. Riachuelo and sewer. In contrast, the southward transport of residues is indicated by the relatively high and uniform concentrations at 1 km in Punta Colorada and Punta Lara (37 ± 2.8 $ng\,g^{-1}$), a vegetated zone without any significant human influence. This transport of particulate PCBs is favored by the strong freshwater discharge of the Paraná River (16000 $m^3 s^{-1}$), which reclined along the coast maintain relatively high PCB levels, 10 km downstream major sources. According to a descriptive model of sediment dispersion in the Río de la Plata, this is a depositional area with predominant onshore transport (Parker et al., 1987).

Following the general offshore decreasing pattern, at 2.5 km PCB concentrations are lower but maintain the spatial difference between cleaner northern sites (0.5 ± 0.8 $ng\,g^{-1}$), the most polluted Central area (27 ± 28 $ng\,g^{-1}$), and a rapid attenuation in southern stations (6.5 ± 3.8 $ng\,g^{-1}$). Excepted the most contaminated transect from Riachuelo, at 4 km from the coast PCB concentrations appear to reflect lower, more homogeneous background levels (0.6–5 $ng\,g^{-1}$). Nevertheless, northern stations still appear as less polluted (0.5 ± 0.1 $ng\,g^{-1}$) relative to central (3.3 ± 1.1 $ng\,g^{-1}$) and southern sites (3.4 ± 1.1 $ng\,g^{-1}$) indicating some offshore residue transport to 4 km in the most affected zone.

According to this distribution of PCB concentrations, 11 from 39 surface sediment samples exceeded recommended guidelines for protection of aquatic life, either the Canadian (34.1 $ng\,g^{-1}$; Canadian Council of Ministers of the Environment, 1999–2001) or the effects range low value (22.7 $ng\,g^{-1}$; Long et al., 1995) which is considered to rarely produce adverse biological effects. All the sites are located in the Central and South area, principally at 1 km (7 stations), but also at 2.5 km (3 sites) and 4 km of the shore (Riachuelo).

## 4. Total PCBs in settling particles

Sediment traps installed in the Central area collected a substantial amount of material ranging from 0.6 to 9 g for a total deployment of 1.5–45 h. The corresponding mass fluxes calculated, oscillate between 137 and 618 $g\,m^{-2}day^{-1}$, with a general mean of 361 ± 124 $g\,m^{-2}day^{-1}$. These large mass fluxes imply very high sedimentation rates which averaged 5.0 ± 1.7 $cm\,yr^{-1}$ in the Central area (sediment density of 2.65 $g\,cm^{-3}$). The contribution of resuspended bottom material to the traps can not be disregarded in this shallow estuary, specially during storm events which were specifically avoided in our sampling scheme. The large mass fluxes in the Río de la Plata reflect the turbid, deltaic characteristic of the estuary which receives a strong input of suspended mater transported basically by the Paraná River from tropical and sub-tropical areas of South America.

The concentration of PCBs in settling particles collected in the Central area ranged from 13 to 160 $ng\,g^{-1}$ with an average of 75 ± 44 $ng\,g^{-1}$ (Fig. 2), consistent with sediment concentrations at 1 km in this sector (61 ± 37 $ng\,g^{-1}$). This suggests that traps adequately represent depositional fluxes of PCBs in this area. In contrast, the carbon-normalized PCB average of settling particles (0.91 ± 0.54 $\mu g\,g^{-1}$) is lower than sediment values (5.0 ± 1.6 $\mu g\,g^{-1}$ at 1 km, see offshore gradients) reflecting the higher carbon contents of the trap material (8.2 ± 6.3 vs. 1.1 ± 0.5% in 1 km sediments). This rapid carbon attenuation between settling particles and sediments suggests intense biodegradation at the sediment–water interface.

The magnitude of depositional fluxes of PCB depend on concentrations in settling particles and on total mass fluxes, with both variables being normally inversely correlated due to dilution with organic-poor detrital material during high load episodes (e.g. Oliver et al., 1989; Schneider et al., 2002). The huge mass sedimentation in the Central area of the Río de la Plata combined with moderate PCB concentrations in the trap material results in large PCB fluxes ranging from 5 to 67 μg m$^{-2}$ day$^{-1}$ with a general mean of 26 ± 19 μg m$^{-2}$ day$^{-1}$. These PCB fluxes are much higher than those reported for deep lakes with lower sedimentation rates such as Lake Ontario (0.7–4.5 μg PCBs m$^{-2}$ day$^{-1}$ for a mass flux of 1.1–5.2 g m$^{-2}$ day$^{-1}$; Oliver et al., 1989), or Lake Michigan (0.01–0.3 μg PCBs m$^{-2}$ day$^{-1}$ for a mass flux of 0.01–24 g m$^{-2}$ day$^{-1}$; Schneider et al., 2002).

## 5. Vertical profiles of total PCBs

In order to evaluate the temporal variation of PCB inputs to the system, vertical profiles of PCBs were determined in polluted stations Riachuelo and Berazategui. Due to the proximity to major sources, these sediments contain higher and uniform organic carbon contents along the 20 cm cores: 1.5–1.8% at BZ and 1.9–2.3% at RI. Accordingly, sediment slices collected at 4–5 cm intervals down to 20 cm depth yielded very uniform total PCB concentrations at both sites ranging from 66 to 89 ng g$^{-1}$ (Table 1). These values are comparable to polluted superficial sediments and trap material from this Central area, suggesting relatively uniform PCB inputs in this sector.

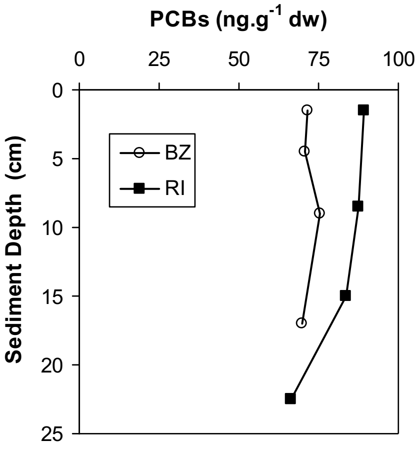


Fig. 3. Vertical sediment profiles of PCBs at most polluted Riachuelo and Berazategui stations.

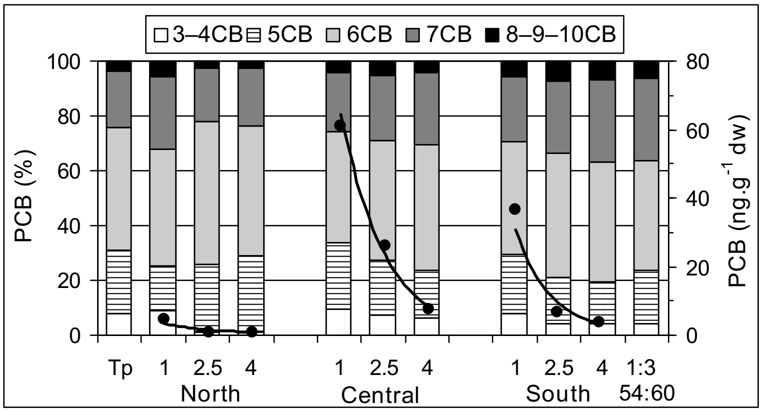
Vertical profiles show rather regular concentrations down to 15–20 cm depth, insinuating a decreasing trend below this depth (Fig. 3). Longer cores would be needed to confirm this apparent reduction in deeper sediment layers. According to the average sedimentation rate calculated from sediment trap data (5.0 cm yr$^{-1}$), these uniform levels down to 20 cm suggest that the actual depositional fluxes probably apply at least for the last 4 years prior to sampling (i.e. 1998).

## 6. Offshore gradients

Fig. 4 presents the exponential decrease of average PCB concentrations in the North, Central and South areas versus distance to the coast and the major compositional changes. The exponential regressions of PCBs with distance are very significant explaining 73–99% ($R^2$) of the total variability. The exponential coefficients suggest higher decay in the south area (0.80) relative to northern (0.63) and central sites (0.66). These average coefficients imply a 85–91% reduction of PCBs from 1 to 4 km. The coefficients of individual sites are more variable (0.27–1.20) but significant ($R^2$: 0.7–1.0) excepted less contaminated northern sites and most contaminated Riachuelo which present relatively high levels at 4 km (Table 1). These coefficients represent a 55–97% PCB reduction with distance to the shore. The lowest non-significant values correspond to less impacted northern stations with background concentrations (Fig. 7). The highest attenuations are observed in the Central sector located downstream principal sources.

Since the distribution of hydrophobic compounds is basically controlled by the organic content of sediments it is important to evaluate the effect of this association on offshore gradients. Fig. 5 shows the relationship of PCB concentrations with the organic carbon content of Río de la Plata sediments. The correlation is very significant at 1 km ($R^2 = 0.93$) reflecting the contribution of anthropic sources of organic matter and PCBs, it diminish at 2.5 km ($R^2 = 0.85$), and disappear at 4 km characterized by low organic contents and background PCBs levels. The PCB-organic carbon relationships at 1–2.5 km of the shore indicate that sediment quality guidelines are exceeded with organic carbon contents higher than 0.7–1%.

Organic carbon normalized PCB concentrations ranged from 0.05–9.4 μg g$^{-1}$ with more homogeneous higher values in the central area (5.0, 2.6, 2.3 μg g$^{-1}$ at 1, 2.5 and 4 km, respectively) relative to southern (4.5, 1.8, 0.9 μg g$^{-1}$) or northern sites (1.1, 0.1, 0.1 μg g$^{-1}$). The offshore decrease of PCB concentrations normalized to the organic carbon content is generally lower than dry weight based estimations but reflect the exponential reduction (Fig. 4). In contrast to dry weight results, exponential coefficients suggest a higher attenuation



| | | | | |
|---|---|---|---|---|
| DW | PCB= 4.81e$^{-0.63\ km}$<br>R$^2$=0.73 | PCB= 125 e$^{-0.66\ km}$<br>R$^2$=0.99 | PCB= 68.4 e$^{-0.80\ km}$<br>R$^2$=0.94 | ng/g |
| OC | PCB= 1.59e$^{-0.75\ km}$<br>R$^2$=0.76 | PCB= 5.94e$^{-0.26\ km}$<br>R$^2$=0.87 | PCB= 7.24 e$^{-0.52\ km}$<br>R$^2$=0.99 | **mg/g** |

Fig. 4. Average offshore gradients of PCBs in the North, Central and South area of the Río de la Plata. Exponential regression statistics on a dry weight and organic carbon normalized basis are shown below. Total concentrations are displayed on the right axis and relative abundance of tri–tetra (3–4 CB), penta (5 CB), hexa (6 CB), hepta (7 CB) and octa–nona–decachlorobiphenyls (8–9–10 CB) in the left percentage axis. The composition of sediment trap material (Tp) and a 1:3 Aroclor 1254:1260 mixture are included for comparison.

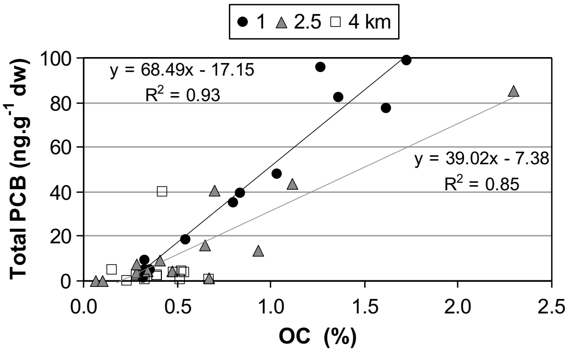


Fig. 5. Regression of total PCB concentrations versus organic carbon content of Río de la Plata sediments at 1, 2.5 and 4 km from the shore.

with distance to the coast in the North area (0.75), relative to the South (0.52) or Central sector (0.26). This apparent higher reduction in northern sites most probably reflects the reduction of organic carbon and associated background pollutants in inner organic-poor sands. The more uniform values in central sites confirm the persistence and offshore transport of organic carbon-associated PCBs.

## 7. PCB composition

PCB traces in Río de la Plata sediments were dominated by congeners ranging from 3–4 to 7 chlorines, including IUPAC 31–28, 52, 101, 110, 118, 149, 153, 138, 187, 174, 180, 170. The sum of these 13 congeners represented a fairly constant 67 ± 7.0% in all sediment samples, indicating a relatively uniform composition. The relative abundance of tri–tetra (3–4 CB), penta (5 CB), hexa (6 CB), hepta (7 CB) and octa–nona–deca chlorobiphenyls (8–9–10 CB) in sediments is shown in Fig. 4. For comparison, it also includes the proportions of the trap material and of a 1:3 Aroclor 1254:1260 mixture calculated based on the reported composition of technical formulations (Schultz et al., 1989). In general, sediments contain a dominant contribution of 6CB (43 ± 6.4%), followed by 7 CB (23 ± 5.1%) and 5CB (21 ± 5.5%), and lower proportions 3–4 CB (7.4 ± 5.4%) and higher chlorinated PCBs (5.1 ± 3.3%). According to the Aroclor composition, these results indicate that RLP sediments contain a prevailing contribution of Aroclor 1254:1260.

Over this general picture, some detailed compositional changes are observed along offshore transects. The basic trend is the decrease of the relative abundance of less chlorinated congeners (3–5 CB) with a parallel increase of higher chlorinated PCBs with distance to the coast. In the most contaminated central and southern sectors the contribution of 3–4 and 5 CB decrease from 8–9% to 4–6% and 21–25% to 17–19%, respectively, with a complementary increase of 6 CB (40–41% to 44–46%) and 7 CB (21–24% to 26–30%), from 1 to 4 km off the shore. The proportions of higher chlorinated congeners remains more stable around 4–7%. This compositional change of PCBs is probably related to the progressive disappearance of more soluble, volatile and labile congeners and relative enrichment of higher chlorinated PCBs with distance from major sources. Non-detection of lower chlorinated congener in less contaminated offshore stations could artificially amplify this trend. However, in the most polluted Riachuelo transect where all congeners were always detectable, the changes are even more marked, i.e. 3–4 and 5 CB decrease from 10% to 5% and 25% to 16% whereas 6 and 7 CB increase from 38% to 47% and 22% to 26%, respectively. The enrichment of higher chlorinated congeners in offshore sediments corresponds approximately to a shift from a 1:1 to a 1:3 1254:1260 mixture with distance to the coast. In less impacted northern stations the offshore changes of PCB composition are less consistent with an apparent higher preservation of 5 CB. This probably reflects the presence of residual background concentrations.

A detailed evaluation of the compositional changes and possible sources of PCBs in this coastal environment was carried out by principal component analysis performed with the relative abundance of all 5 PCB classes (3–4, 5, 6, 7 and 8–9–10 CBs) in Aroclor mixtures, 6 local transformer oil samples, average trap material and sediment samples (Fig. 6). The first two principal components (PC) explain 92% of the total variability of the data, 71% the first and 21% the second. PC1 is basically defined by the contribution of 3–4 CBs (+PC1) vs. 6 CBs (−PC1) i.e. Aroclor 1242 vs. 1260 and it mainly

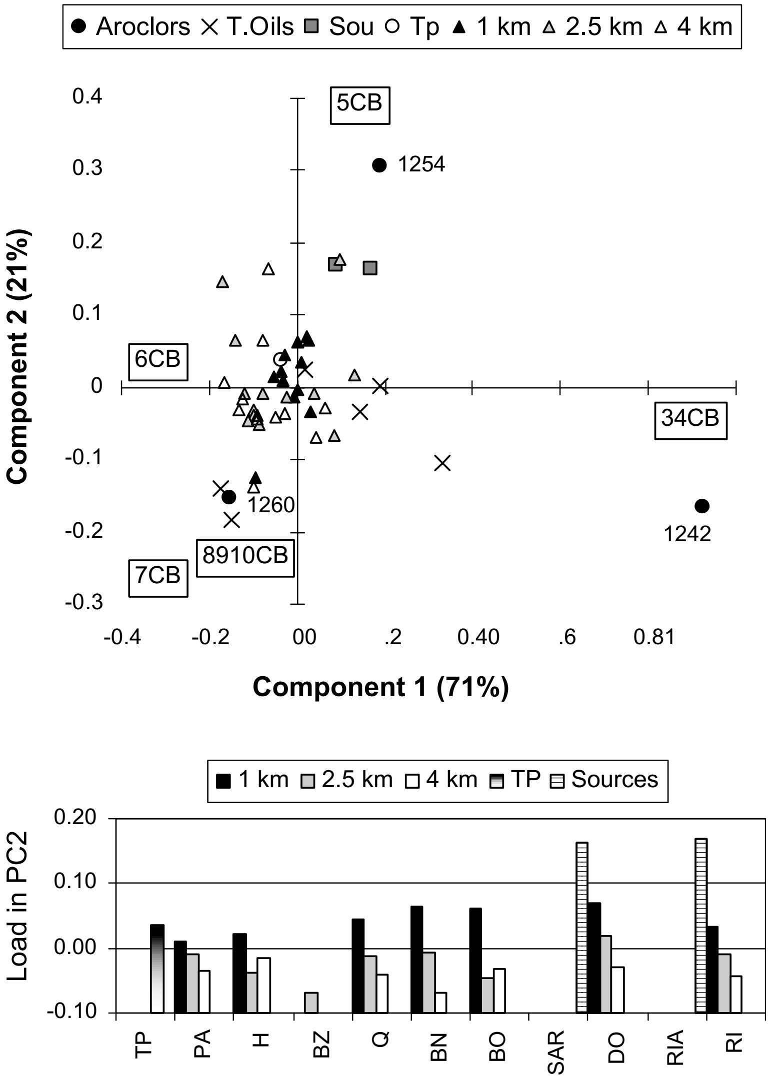


Fig. 6. Principal component analysis performed with the relative contribution of PCB containing 3–4 (3–4 CB), 5 (5 CB), 6 (6 CB), 7 (7 CB) and 8–9–10 chlorines (8–9–10 CB) in Aroclors mixtures, transformer oils, sediment and trap samples. The detailed load to principal component 2 is shown below for most contaminated stations from the central area.

reflects the composition of Aroclor 1242 and to a lesser degree a transformer oil sample enriched in this PCB mixture. PC2 has a prevailing contribution of 5 CBs (+PC2) vs. 7 and higher CBs (−PC2) i.e. Aroclor 1254 vs. 1260, and although it explains a lower amount of the total variability, it is the single most important factor which discriminates most samples.

Sediment samples spread mainly along a mixing line between the higher chlorinated mixtures 1254 and 1260. Samples collected at 1 km are generally closer to the 1254 formulation whereas 4 km sediments plot nearer 1260 reflecting the compositional shift related to the loss of low molecular weight PCB with distance to the coast. The average trap composition plots in the middle of the scatter, closer to 1 km samples. Sediments from sources contributing to the coastal zone, Sarandi stream and Riachuelo port, are discriminated by their higher predominance of 5 CB, i.e. closer to Aroclor 1254. This enrichment in lower chlorinated congeners in most contaminated Riachuelo port sediments and the progressive shift to 6, 7, 8–9–10 CB in 1 km samples supports the interpretation of the weathering process with distance to sources. This is shown in the detailed plot of the load to PC2 presented below the PCA (Fig. 6). There is a gradual shift from positive to negative values (i.e. from 1254 to 1260) from 1 km to 4 km in all stations from the most contaminated central area. In addition, Sarandi stream and specially Riachuelo port sediments present the highest loads on PC2 reflecting the abundance of 5 CBs, and complete the transitional pattern indicated by offshore sediments. Sediment traps show a relatively fresh signal similar to 1 km sediments whereas the sewer area sample (BZ) present a more weathered pattern closer to Aroclor 1260 as indicate the negative load on PC2. This suggests that this source discharges residues from a different origin or that they are more altered due to enhanced biodegradation.

The six transformer oil samples are dispersed in the virtual PCA space: one plot in the middle of the sediment scatter with a balanced contribution of 1254 and 1260, three have a higher proportion of 1242, and 2 contain basically Aroclor 1260. These results suggest that transformer oils could be the principal source of PCB residues found in sediments, principally oils containing Aroclor 1254 and 1260 mixtures. However, from more than 130 transformer oil samples analyzed in this laboratory for different industries and Government agencies, no one showed a contribution of Aroclor 1254 as high as that of most contaminated Riachuelo port sediments, suggesting the presence of other PCB source or oil type. On the other hand, in situ reductive dechlorination in anoxic Riachuelo sediments could alter PCB patterns producing an enrichment in lower chlorinated PCBs. Reduction of higher chlorinated congeners predominant in Aroclor 1260 an enrichment of 3–5 CBs, i.e. congeners 52, 49 and 44 has been demonstrated in polluted Housatonic River sediments (Bedard and May, 1996; Bedard et al., 1996). Further studies are needed to test this interpretation.

Overall, transformer oils containing Aroclor 1254–1260 appear to be the main source of PCBs in this coastal environment. In situ dechlorination in anoxic sediments from major sources followed by selective decay, fractionation and weathering with increasing distance to the shore could explain the observed shift of PCB patterns. As lower chlorinated congeners would be fractionated by selective dissolution, evaporation and degradation, the potential contribution of transformer oils enriched in 1242 could be underestimated in the weathered PCB signature of sediments.

## 8. Total PCB load to coastal sediments

In order to estimate the total amount of PCB introduced and accumulated in superficial sediments, three complementary approaches were employed: 1—calculation of sediment inventories of PCBs in the top 5 cm layer, 2—estimation of total PCB inputs from sediment trap fluxes, and 3—evaluation of a Fugacity II model. Table 2 present the parameters employed for the calculations and total PCB loads estimated.

The presence of strong offshore gradients complicate the calculation of accurate inventories in the most critical zone close to the shore where higher concentrations are expected. To integrate this variability, the exponential functions fitted to each transect were employed to model concentrations at each 0.5 km extending to 4 km offshore. In the sewer area (BZ), the concentration measured at 2.5 km was assumed to follow an exponential offshore decrease with coefficients averaged from those of nearby sites. At Riachuelo, the higher 4 km value was eliminated for the calculations. Fig. 7 present the exponential equations and the concentrations derived for the coastal zone. As expected, the peaks are concentrated close to the shore in the Central area with a rapid offshore attenuation. The southward transport of residues and the sewer impact are indicated by the elevation of the surface whereas northern sites show flat background levels. The highest values modeled for the 0–0.5 km sector (200–400 ng $g^{-1}$) should be considered with caution since the littoral fringe is bordered by fine sands and PCB levels could be overestimated by the exponential extrapolation (see below).

To calculate sediment inventories for the total surface, the exponentially derived concentrations at each 0.5 km were averaged for each square defined by the adjacent transects, i.e. in a $12 \times 8$ grid with a total surface of 182 $km^2$ (Table 2). The inventories in each square were calculated considering the top 5.0 cm layer which according to sediment trap data represents 1 year accumulation. The total sediment inventory of PCBs

Table 2
Environmental characteristics, PCB properties and estimations of PCB loads based on inventories, trap fluxes and Fugacity II calculations for Río de la Plata coastal sediments

| Environmental parameters | Surface ($km^2$) | | | |
|---|---|---|---|---|
| | North | Central | South | Total |
| Kilometers | | | | |
| 0.0–0.5 | 6 | 11 | 6 | 23 |
| 0.5–1.5 | 12 | 23 | 11 | 46 |
| 1.5–2.5 | 12 | 23 | 11 | 46 |
| 2.5–4.0 | 18 | 34 | 17 | 68 |
| Total | 48 | 90 | 44 | 182 |
| Sed OC (%) | 0.37 | 0.79 | 0.51 | 0.64 |
| Sed density ($g\,cm^{-3}$) | | | | 2.65 |
| Depth (m) | | | | 3 |
| SPM ($mg\,l^{-1}$) | | | | 45 |
| SPM OC (%) | | | | 8 |
| Fish density ($kg\,ha^{-1}$) | | | | 50 |
| Fish lipid (%) | | | | 65 |
| PCB properties (5–6 CBs) | | | | |
| MW | | | | 344 |
| Temp (°C) | | | | 25 |
| Log $K_{ow}$ | | | | 6.7 |
| $S$ ($g\,m^{-3}$) | | | | 0.063 |
| $V_p$ (Pa) | | | | 0.0028 |
| $H$ ($Pa\,m^3\,mol^{-1}$) | | | | 15.2 |
| MP (°C) | | | | 78 |
| Emission ($kg\,h^{-1}$) | | | | 0.06 |
| Reaction half-lives (h) | | | | |
| Air | | | | 600 |
| Water | | | | 70 000 |
| Sed/SPM/Biota | | | | 90 000 |

| Results | 1 yr Inventories (kg) | | | | | |
|---|---|---|---|---|---|---|
| | North | Central | South | Total | Trap flux ($kg\,yr^{-1}$) | Fugacity II (kg) |
| km | | | | | | |
| 0.0–0.5 | 1.7 | 266 | 51 | 319 | 107 | |
| 0.5–1.5 | 2.1 | 242 | 54 | 298 | 218 | |
| 1.5–2.5 | 1.0 | 89 | 23 | 113 | 218 | |
| 2.5–4.0 | 0.7 | 56 | 12 | 69 | | |
| Total | 5.5 | 654 | 140 | 800 | 543 | 724 |
| Total sediment mass: $2.4 \times 10^7$ tons | | | | | | |
| Sediment concentration ($ng\,g^{-1}$) | | | | | | |
| Measured grand mean: | | | 22 ± 30 | 33 | 23 | 28 |

calculated for the whole area amount to 800 kg. Excluding the 0–0.5 km coastal fringe were PCB levels could be overestimated, a more conservative estimation of 481 kg PCBs is obtained for a total area of 160 $km^2$. Most of the load is located in the first 1.5 km (62–77% for the conservative and total estimation, respectively). As expected from the North–South and offshore gradients discussed previously, the Central area contains the bulk of the PCB load (70–82% for the conservative and total estimation). The PCB inventories (481–800 kg) corresponding to one year accumulation for a total surface of 160–182 $km^2$, represent average depositional fluxes of 3–4 $mg\,m^{-2}\,yr^{-1}$, which is about 2–3 times lower than trap fluxes from the most contaminated Central area. The same calculation performed for the 0–2.5 km Central area inventory (330–595 kg in 45–56 $km^2$, for the conservative and total estimation) yields average PCB fluxes comparable to trap values (7–11 vs. 9.7 $mg\,m^{-2}\,yr^{-1}$). The total PCB inventory divided by the total mass of sediments ($2.4 \times 10^7$ tons) gives an average PCB concentration in the range of the values measured (Table 2).

The estimation of total PCB inputs from sediment traps is strongly dependent on the representativeness of the data for the total accumulating surface. Given the large North–South and offshore spatial variability

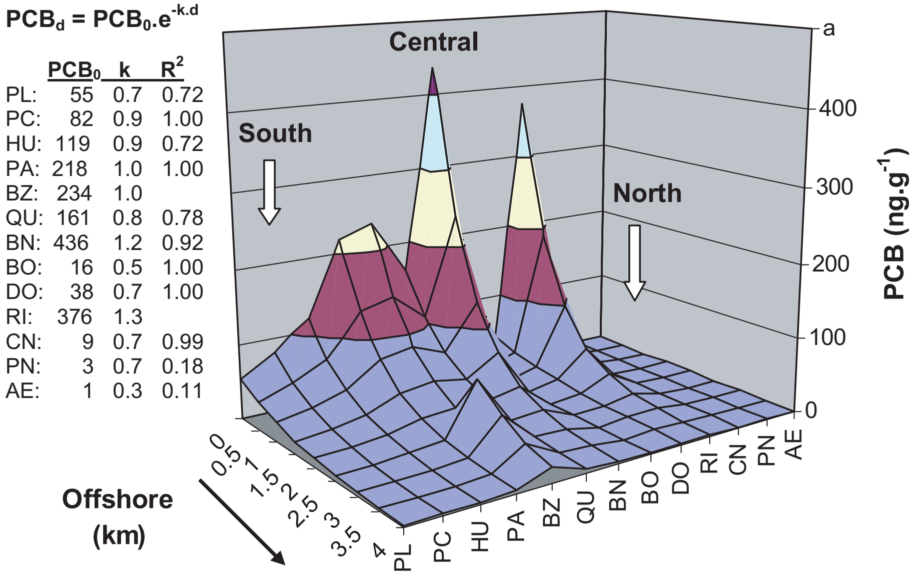


Fig. 7. Concentration surface of PCBs in Río de la Plata sediments modeled by the exponential equations fitted to each transect.

of this coastal zone, it is challenging to select an accurate surface to be considered. As our trap deployments covered basically the most polluted Central sector, results can not be extrapolated to distant, less impacted areas (i.e. North sites or stations situated >2.5 km offshore). For this reason, total PCB inputs for the Central area were calculated with the mean sediment trap flux (9.7 ± 6.8 mg m$^{-2}$ yr$^{-1}$), considering the surface of the 0–0.5, 0.5–1.5 and 1.5–2.5 km sectors (total surface: 56 km$^2$). The total PCB load estimated from trap data for the Central area (543 kg, Table 2) is comparable to the total sediment inventory (595 kg). However, the partial values for each sector indicates sub-estimation of PCB fluxes in the most affected costal fringe and overestimation in >1.5 km sediments, which appear consistent with the strong offshore gradients. In spite of these inconsistencies, and considering the large variability of vertical fluxes and sediment concentrations, trap data are in reasonable agreement with sediment inventories and confirm the ~500 kg magnitude of PCB inputs in this coastal ecosystem.

Fugacity models allow an estimation of the equilibrium partitioning of semi-volatile organic compounds according to physico-chemical properties, i.e. vapor pressure (VP), water solubility (S), octanol–water partition coefficient ($K_{ow}$), reaction half-lives, and environmental characteristics such as volume of each environmental compartment (air, soil, sediments, water, biota), the organic carbon content of sediments and lipid contents of biota (e.g. Mackay and Paterson, 1981; Mackay et al., 1992). A Fugacity level II model (Environmental Modelling Centre, 1999) including air, water, suspended particles, sediments and biota was evaluated for the Río de la Plata coastal area. The model parameters are presented in Table 2. The environmental characteristics have been adjusted for this coastal area and average PCB properties from the prevailing 5 and 6 chlorobiphenyls were considered for the calculations (Table 2; Priemer and Diamond, 2002; Sweetman et al., 2002). The standard atmospheric height of 1000 m and default advective flow residence time were used for the calculations. The emission rate input of PCBs to the system was estimated from sediment trap fluxes in the central area (543 kg yr$^{-1}$ or 0.06 kg h$^{-1}$).

The Fugacity II model results adjusted for Río de la Plata coastal environment indicate that with an emission of 60 g h$^{-1}$ to the system, sediments contain almost 98% of the total mass equivalent to 724 kg PCBs, comparable to the other figures estimated from inventories and trap fluxes (Table 2). The equilibrium concentration of PCB in sediments predicted by the model agree well with the grand mean calculated for the whole area (Table 2), suggesting a steady state condition. In addition, the predicted PCB concentration in fish (7.0 μg g$^{-1}$) is consistent with measured levels in a dominant, fatty detritivorous species collected in 1996 (5.9–6.6 μg g$^{-1}$; Colombo et al., 2000) or in more recent surveys (11 ± 5.9 μg g$^{-1}$; Colombo et al., unpublished). According to the model estimations, loss rates from sediments totalize 20 g h$^{-1}$ (34% of input emissions), through advection (14 g h$^{-1}$) and reaction (6 g h$^{-1}$).

Summing up, these calculations indicate that the total PCB load corresponding to one year accumulation in this coastal environment is about 500–800 kg. Residues are chiefly accumulated in the most contaminated Central area with a residual southward distribution, principally in 0–2.5 km offshore sediments. Based on the average trap sedimentation rate (5 cm yr$^{-1}$) and the relatively uniform 20 cm-depth sediment profiles, an additional amount of ~2000 kg would be buried in deeper sediment layers. This reservoir of ~3 tons PCBs could sustain for a long time high PCB levels in the water column and aquatic organisms through remobilization and erosive transport. Increasing PCB levels have been measured in a fatty, highly specialized detritivorous fish which transport the signal several hundred km North through the Paraná river during extensive reproductive migrations (Colombo et al., 2004). On the other side, the seaward transport of residues associated to resuspension of bottom material, bed load and suspended particulate transport is favored by the strong freshwater flow. The main sink of the particulate PCB discharge is the large and shallow Samborombon Bay, a 2800 km$^2$ mixo-haline environment situated down-stream the turbidity maximum zone of the estuary (Fig. 1). In this area, the flocculation of fines and double-layer estuarine circulation maintain a very high suspended solid charge which settle out in the muddy and flat Samborombon wetland.

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