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Accumulation of Polychlorinated Biphenyls (PCBs) in Navigation Channels, Harbors and Industrial Areas of the Bahía Blanca Estuary, Argentina

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ABSTRACT: The usage and production of polychlorinated biphenyls (PCBs) was banned in Argentina in 2002, approximately twenty to thirty years later than in other countries. A total of 29 sediment samples (up to 14 m deep) were analyzed for a mix of seven individual PCBs in a time series for over more than one year in twelve selected locations, including harbors, recreational docks and several industrialized coastal locations in Bahía Blanca Estuary, Argentina, South America. The GC/ECD results showed the dominance of three chlorinated compounds: CB180, CB52 and CB101, which showed a strong reduction with distance from the urban area. The principal components analysis differentiates light and heavy congeners variation, settling several hypotheses and the classification of sampling sites to determine the PCB burden. Considering literature reports, the present results were evaluated in the international PCB context, diminishing the scarcity of PCB data from the Southern Hemisphere and prompting the need of future monitoring approaches.

Key words: PCBs, Sediments, Coastal environments, Industries, Southern Hemisphere

INTRODUCTION

In Argentina, a developing country, although the release of persistent organic pollutants (POPs) into marine ecosystems has prompted diverse conservation measures, there is a lack of research studies and legal under-regulation on this topic. Polychlorinated biphenyls (PCBs) are a family of 209 hydrophobic chlorinated compounds characterized by high persistence, bioaccumulative potential and toxic properties, reflecting the lipophilicity and widespread distribution of these compounds in the environment (Sbriz *et al.*, 1998; Konat *et al.*, 2001; Frignani *et al.*, 2004; Samara *et al.*, 2006; Dercova *et al.*, 2009; etc.). PCBs bind strongly to soil and sediments and are not carried with rainwater or vertical infiltration water flux. As these compounds do not readily degrade, they might remain in these matrices for months or years. Generally, the rate of degradation depends on the number of chlorine atoms in PCBs, i.e., the more chlorine atoms contained in PCBs, the slower the degradation (ASTDR, 2000). PCBs were first synthesized in 1929, as various

(commercial) technical mixtures, including “Aroclor” (USA), “Clophen” (Germany), “Phenoclor” (France), “Fenclor” (Italy) and “Kanechlor” (Japan). PCBs were extensively used for different industrial applications (e.g., dielectric fluids, insulators for transformers and capacitors, hydraulic fluids, casting wax, carbonless carbon paper, compressors, heat transfer systems, plasticizers, pigments, adhesives, liquid cooled electric motors, etc.) until the late 1970’s when the production, processing and distribution of these substances were banned in most countries.

During the survey years of this research, an average of 62 tons/year of hazardous waste substances containing PCBs have been discarded in Argentina and 174 tons have been exported to European countries for authorized destruction (according to the National Environmental and Sustainable Development of Argentina, <http://www.ambiente.gov.ar>, this service is not available in Argentina). The Stockholm Convention estimates that 2.2 million tonnes of PCB oils and equipment will still

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need disposal by 2015, suggesting that the present occurrence and industrial usage of PCBs requires proper environmental monitoring. The usage and production of PCBs was banned in Argentina in 2002 (Law 25670), about twenty to thirty years after the ban in other countries (e.g., Japan banned the use of PCBs in 1972, while the USA imposed a ban in 1979 and the U.K. and Italy banned PCB use in 1981 and 1984, respectively). However, PCBs might still be in use in closed systems, such as capacitors, transformers, electronic equipment, etc. In fact, the disposal of household and industrial waste is a major source of PCB emissions into the environment (ASTDR, 2000). The Bahía Blanca Estuary (38° 500' S and 62° 300' W) has a total surface area of 2300 km², comprising 410 km² of islands and 1150 km² of intertidal sector. This estuary is a meso-tidal system with little fluvial input, covered by extensive tidal flats and salt marshes (Piccolo *et al.* 1990). Although, the Bahía Blanca Estuary presents intensive anthropogenic activity at the north shoreline: oil, chemicals, fertilizers and plastic factories, two commercial harbors and a large industrial city with more of 350,000 inhabitants, the inner regions of the estuary presents low urbanized/rural lands, a tourist area and a fishing/recreational port (Fig. 1). The rapid development, construction, urbanization and industrialization might affecting this area in the future, as many industries are presently colonizing the area and will modify the previous conditions of the estuary (e.g., higher emissions, deeper dredging, docks construction, increase of heavy marine traffic, etc.). Thus, there is a regional need to establish field PCBs background levels with enough periodicity to accurately detect differences between sites and/or times (Wu *et al.* 2008). Moreover, compared with the north hemisphere, information concerning the release and burden of PCBs in the South American environment is lacking. Highly fragmented data has been reported for PCBs in selected Argentinean marine environments (Colombo *et al.*, 1990; 2005) and there are no precedents for the occurrence of PCBs in any matrices at the area of study. Thus, the aim of this research was to establish a baseline of marine coastal burden of PCBs in a South Atlantic estuary to increase the scarcity of data at the southern hemisphere and test the null hypothesis that the PCB burdens in the southern hemisphere are negligible compared with those recorded in the northern hemisphere. These results will increase the awareness of this South American estuary as a part of the international PCB burden and set the basis for future tiered studies (including PCBs, dioxins and dioxin like-PCBs in biota) to estimate the actual human exposure risk through seafood consumption.

MATERIALS & METHODS

A total of 29 samples were obtained from twelve selected locations, including harbors, navigation

channels and several industrialized coastal locations (Fig.1). Five stations were fixed along the main navigation channel, namely Ing. White Hb. (5), Galván Hb. (4), Maldonado (3), Cuatros Hb. (2) and Villarino (1), sampled at three sampling legs between 2005 and 2006, and stored on board the “Buen día Señor” Research Vessel (15 samples). Based on a previous research on persistent organic compounds (Arias *et al.*, 2010), implicating the presence of a hydrophobic organic contaminants (HOC) hotspot in this area, a coastal industrial area was selectively sampled in two sampling legs, assuming higher levels of pollution. For sampling purposes, a total of 500 g of surface sediment was collected from each site using a grab sampler. The samples were immediately refrigerated, stored in solvent-cleaned glass containers to avoid exposure to light, and rapidly transported to the laboratory for deep-freezing prior to analysis. All chemicals used were of analytical and chromatographic grade with high purity. Seven congeners, called “indicator PCBs” (iPCBs), were measured, as these substances, rather than Aroclor or similar PCB technical mixtures, have been widely used to estimate “Total PCBs” (Babut *et al.*, 2009). These iPCBs bioaccumulate in the human diet and potentially represent all PCBs, as these substances are the predominant congeners in biotic and abiotic matrices (Bakker *et al.*, 2003; Baars *et al.*, 2004; ATSDR 2000). None of these iPCBs (i.e., congeners 52, 101, 118, 138, 153, and 180) exhibit dioxin-like activity, except for PCBs 28 and 118 (van den Berg *et al.*, 2006). For each sample, 5-10 g of wet superficial sediment was chemically dried (Na₂SO₄) and extracted. Prior to the analysis, as a standard protocol, the Soxhlet extraction apparatus was assembled and refluxed with Hexane-Acetone mixture (1:1) for two hours for each batch of samples. Subsequently, the dried samples were Soxhlet extracted for 12 h, using a Hexane-Acetone 1:1 solvent mixture (USEPA, 2000). The extracts were concentrated to 10 mL in a rotary evaporator using a low-temperature thermostatic bath and subsequently further concentrated to 2 mL under a gentle, high purity nitrogen flow. For the elimination of polar components, the extracts were passed through a 5% H₂O-deactivated alumina (5 g)/silica gel (10 g) column (1 cm i.d./15 cm), and the PCBs were eluted with 50 mL hexane/methylene chloride (8:1, v/v). Before the extract loading step, 1-2 g of Na₂SO₄ was added to the top of each column. The eluates were evaporated to 10 mL in a rotary evaporator and further concentration to 1 mL was achieved under Nitrogen flow at room temperature.

The instrumental method was optimized for the analysis of 7 PCBs (mix) using a GC (HP 6890 Series) with an ECD detector (⁶³Ni). The analysis was performed using a HP 5MS capillary column (Crosslinked 5% PH ME Siloxane, 30 m long and 2 mm ID). The oven

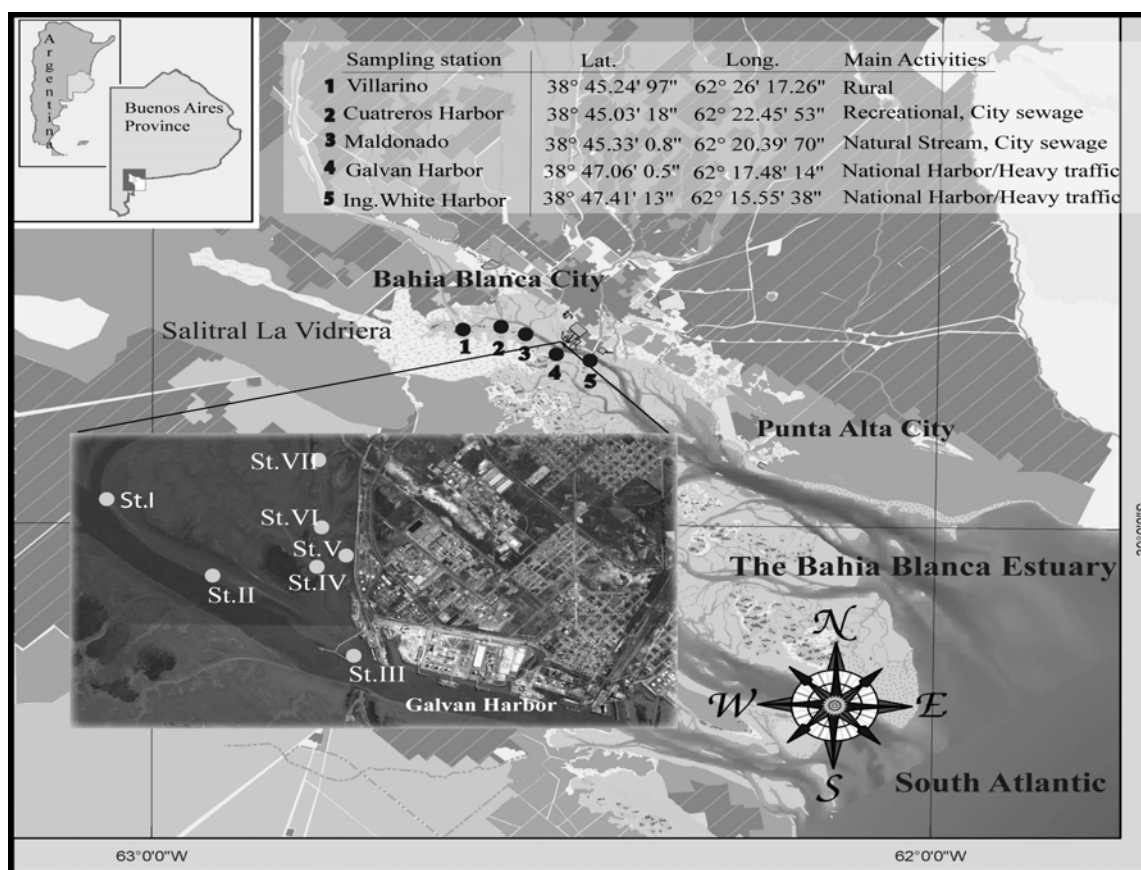


Fig. 1. Map of the study area indicating the sampling stations

Table 1. Name and IUPAC number of the indicator PCBs detected in this study

| IUPAC Number | IUPAC Name | Log (K _{ow}) |
|--------------|--------------------------------------|------------------------|
| CB28 | 2,4,4'-Trichlorobiphenyl | 5.67 |
| CB52 | 2,2',5,5'-Tetrachlorobiphenyl | 5.84 |
| CB101 | 2,2',4,5,5'-Pentachlorobiphenyl | 6.38 |
| CB118 | 2,3,4,4',5'-Pentachlorobiphenyl | 6.74 |
| CB138 | 2,2',3',4,4',5,5'-Hexachlorobiphenyl | 6.83 |
| CB153 | 2,2',4,4',5,5'-Hexachlorobiphenyl | 6.92 |
| CB180 | 2,2',3,4,4',5,5'-Heptachlorobiphenyl | 7.36 |

temperature was programmed from 90 °C (2 min) at 30 °C min⁻¹ to 180 °C (0 min) at 1 °C min⁻¹ to 200 °C (0 min) at 10 °C min⁻¹ to 300 °C (6 min). The injection port and detector temperature were maintained at 320 °C and the injection technique was split/splitless (2 µL). The helium (carrier gas) and nitrogen were maintained at flow rates of 6 and 60 mL.min⁻¹, respectively. Seven of the EPA-recommended iPCB congeners (US EPA, 1999) were analyzed (IUPAC numbers 28, 52, 101, 118, 138, 153, 180) and are listed in Table 1. The standards were purchased from Chem Service Inc. The standard solutions were generated from ultra pure solvent by injecting known volumes of polychlorinated biphenyls solutions in iso-octane, and the sample concentrations were calculated using the external standard method, based on seven experimental points distributed on the concentration axis. The minimum coefficient of

determination was 0.9898. The instrumental detection limit (IDL) of the individual PCBs was evaluated as the concentration of the extract sample producing a signal three times the peak-to-peak noise ratio, which was approximately 1 pg/L. Under the applied analytical conditions, using blank field samples and following the American Chemical Society criterion (Gibbons *et al.*, 2001), the Limit of Detection (LODs) for each compound was calculated as three times the blank standard deviation, ranging from 1 to 8 pg/L. The total PCB levels were calculated as the sum (Σ) of all seven determined congeners. The analytical quality control scheme included the periodic analysis of reactive blanks, electronic blanks and duplicate samples. The accuracy of the determination was routinely assessed by injection of the middle point of the calibration curve. For each set of 12 samples, blank procedural and matrix

samples were spiked with standards and used for monitoring interference, circumventing cross-contaminations and the % method recovery of congeners.

Finally, the total organic carbon, water content and particle size distribution were also analyzed. The total organic matter was estimated using a gravimetric method by ignition loss. First, a sub-sample of the wet sediment was weighed into a tared capsule and dried at 105 °C until a constant weight was achieved. Subsequently, the dried sediments were subjected to calcination in muffle oven at 450 °C for 4 h to obtain the ignition loss of the samples. At 450 °C, the ignition loss primarily involves the organic matter content in the samples (Commendatore et al. 2004). The total organic carbon (TOC) was calculated from this measure using a constant factor quotient (Margalef, 1979). The water content was determined by the sediment sub-sample weight loss at 100 ± 2 °C. For the grain size analysis, the sediment was dried in an oven and sifted using automated equipment with 2 mm and 63 µm mesh sieves. As a result, three fractions were obtained: gravel (particle sizes > 2 mm), sand (particle sizes between 0.063 and 2 mm), and silt-clay (particle sizes < 0.063 mm).

RESULTS & DISCUSSION

All sediment samples contained detectable amounts of iPCBs. Total iPCBs ranged from less than 1 ppb to more than 160 ppb. The overall mean total iPCBs (sum of seven congeners) recorded in this study was 24.16 ± 10.02 ppb, n=29 (all the results are expressed in dry weight). The highest total iPCB concentration was recorded at St. VI. This station had a shallow channel area located in the proximity of a petrochemical-industrial park and situated close to the mouth of the industrial wastewater discharge. Consistently, St. V and VII, located in the proximity of the latter, also exhibited high PCB concentrations. For this industrialized area (St. I to VII), the total iPCB levels ranged from 3.93 ng/g to more than 160 ng/g, with an average concentration of 31.53 ± 19.72 ng/g (n=14) (mean ± conf.int; samples = 14). For the remaining stations (stations: Ing. White Hb., Galván Hb., Maldonado, Cuatrerros Hb. and Villarino Viejo), the total iPCB levels ranged from 0.20 ng/g to 59.09 ng/g. This group of stations was located over the estuarine navigation channel (5 to 14 mts. depth, Fig 1 and 2a). However, sediments collected at Ing. White Hb. and Maldonado showed the highest mean concentrations for total iPCBs, with 18.69 ± 26.09 (n=3) and 22.79 ± 19.99 (n=3), respectively. These stations were located at the entrance of Ingeniero White National Harbor (one of the main national harbors) and the secondary main sewage network discharge. In addition, Maldonado station receives water input from Maldonado Stream, which runs through agriculture

lands and across the entire city. Industrial complexes were also settled within this area: oil, plastic polymers, and by-products from derivative refineries and a small commercial fishing fleet. However, Cuatrerros Hb. and Villarino Viejo stations, located in the vicinity of low urbanized/rural lands, showed reduced levels of Total iPCBs, with means of 3.25 ± 2.56 (n=2) and 9.31 ± 23.09 (n=3) ng/g, respectively (Fig. 2).

As shown in Fig. 3, the relative distribution of iPCBs was as follows: CB180 > CB52 > CB101 > CB28 > CB138 > CB153 > CB118. However, a different congener distribution was observed for the two sampled areas: for the stations located at the main navigation channel, the iPCB pattern was CB52 > C180 > CB101 > CB28 > CB153 > CB118 > CB138, while the distribution for the stations located close to the industries was: CB180 > CB52 > CB101 > CB138 > CB153 > CB28 > CB118.

The sediment iPCBs levels and composition results showed that apart from an outlier concentration recorded at Cuatrerros Hb. (which was discarded for media calculation), the total iPCBs levels increased proportionally to the distance from urban/industrial centers. This trend has been globally observed and reported in previous studies of persistent organic pollutants (Laflamme and Hites, 1978; Cantillo *et al.*, 1997; Miles and Delfino 1999). For example, Simcik *et al.* showed that the air emissions in the urban areas of Chicago increased the average coastal atmospheric concentrations above the continental background signal by factors of 12 and 4 for PAHs and PCBs, respectively (1998), while Hong *et al.* showed a negative gradient of HOC concentration when moving outwards from anthropogenic sources in Masan Bay, Korea (2003). Similarly, Motelai-Massei *et al.* showed that the PCB concentrations were reduced with increasing distance from the urban area, confirming the continuing role of urban/industrial areas as emission sources of PCBs (2005).

Consistent with the results discussed above, the lowest total iPCBs concentration in the area of study was detected at the Villarino station, located in the inner extreme point of the estuary, surrounded by agriculture lands. In contrast, the highest PCBs concentrations were detected in the industrial areas (St. I to St. VII). A previous analysis of wastewater samples from these discharge streams showed high HOC levels at this site (Arias *et al.*, 2010), indicating a “hot spot” occurrence. However, the comparison between the two sampled zones (the main navigation channel and the shallow channels close to the industrial park, with mean of 17.28 and 31.53 ppb, respectively) showed no statistically significant differences (test t, p=0.11) (Fig 1 and 2). Thus, the

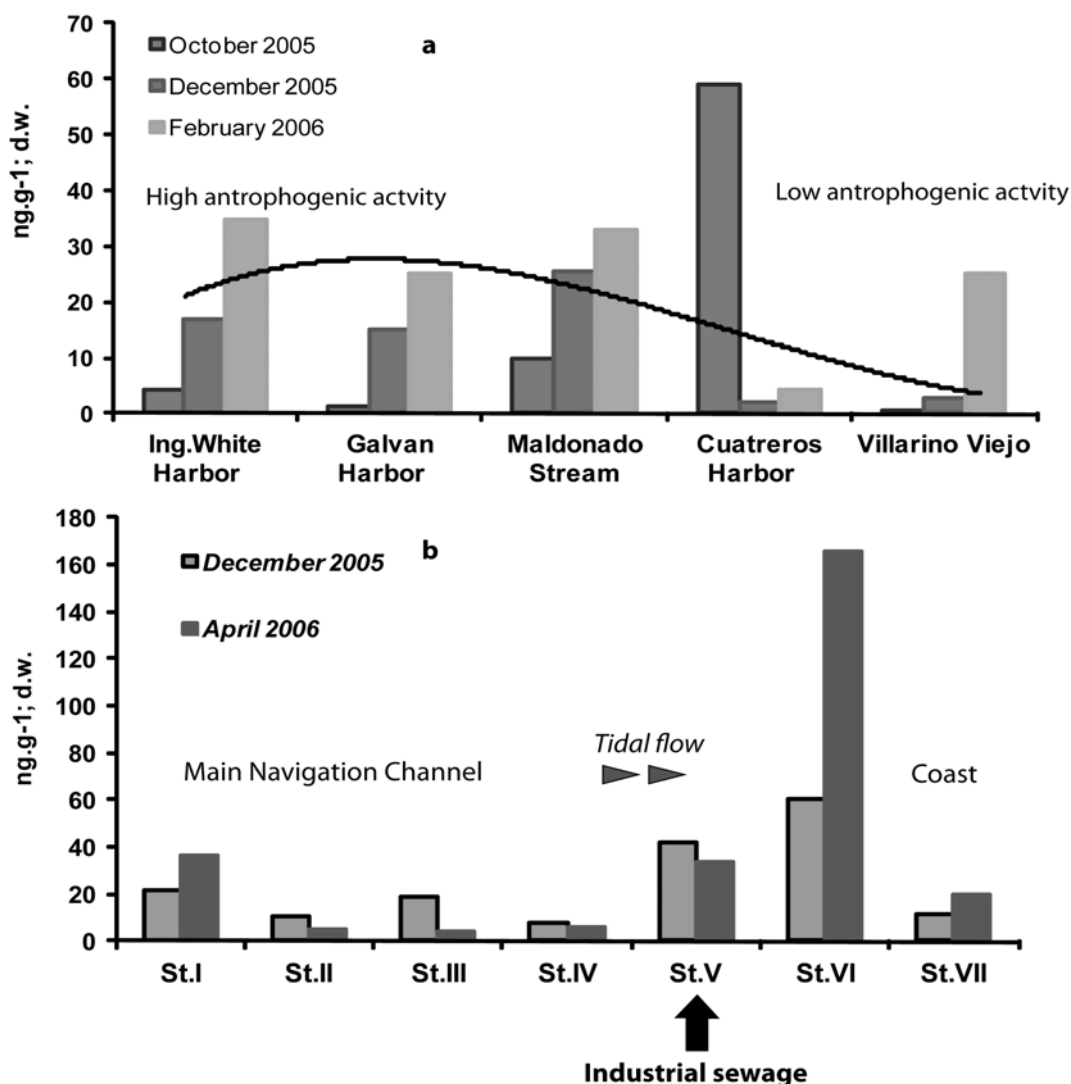


Fig. 2. a: The seven iPCBs from five sampling stations at the Principal Navigation Channel of the estuary from October 2005 to February 2006. b: Seven iPCBs from seven sampling stations located close to the industrial park

presumption of higher levels of PCBs at the industrial area could not be statistically demonstrated.

The environmental fate and behavior of hydrophobic organic compounds is ultimately determined by the physicochemical properties of each compound and sediment, namely, sediment organic matter content, size particle distribution, Octanol-Water partition coefficients (K_{ow}) and water salinity (Baker et al. 1991). To obtain a more comprehensive determination of the sediment toxicity, the relationship between the concentrations of iPCBs and the physicochemical parameters of the samples were examined. The sedimentary water content was generally high (41-55%). The total organic carbon (TOC) ranged from 0.06 to 4.10% along the sampled sites, with an average of 1.67%. This result was consistent with the general classification of Seiter et al. for the Argentinean Coast, considering that the

estuarine areas generally show higher TOC contents (2004). Apart from the Villarino station, which was classified as “Sandy”, the rest of the stations were classified as “Silty/Clay” sediments, as shown in Figs 4a and b. There is overwhelming evidence implicating organic carbon as the dominant sorption phase for nonionic organic chemicals in naturally occurring sediments (Di Toro *et al.*, 1985). A positive linear relationship between the sediment burden of persistent organic compounds and the TOC% is commonly observed in environmental samples (Nam *et al.*, 2008). This underlying hypothesis was specifically tested in the present study, and the results showed a positive correlation on two occasions: on the one side between the average total iPCBs concentration (ng/g, d.w.) vs. TOC % ($r = 0.29$) and on the other side between the average total iPCBs concentration (ng/g, d.w.) vs. the finest fraction of the sediment ($<63 \mu m$, $r=0.35$; Fig.

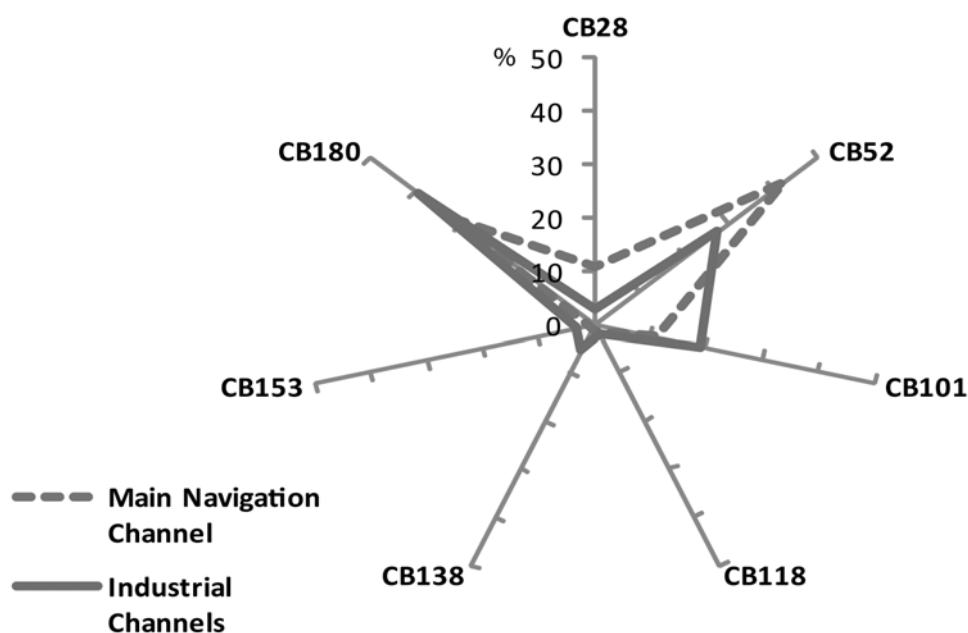


Fig. 3. Percent iPCB abundance over the two main sampling areas

4b). These results strongly suggest that these two physicochemical conditions of the sediments as main PCB bioavailability drivers for the areas of study. This finding should be considered in the future for building local sediment quality benchmarks, and consistent with the approach of Chouery *et al.*, the inclusion of site-specific characteristics when deriving South American quality benchmarks for sediments has generated more restrictive levels than those commonly used internationally (2009).

iPCBs have been reported in estuaries, harbors, near shore sediments and bays worldwide. There is a wide variety in the number of congeners reported and in the expression of the results, which generally makes comparisons difficult. However, to determine the burden of the studied iPCBs in an international context, selected literature iPCBs reports at several coastal locations were compiled in Table 2. The results showed various levels of PCB pollution, indicated by the variability in the occurrence of the iPCBs, from almost pristine sites (Dominican shore or the Hanoi freshwater canals in China) to extremely polluted sites (Strazsky canal at East Slovakia). On the one hand, the study area and other areas within South American environments have been characterized as moderately PCB-polluted sites. In fact, a similar trend was observed at a close coastal area, the Rio de La Plata Estuary (Colombo *et al.*, 2005). On the other hand, several European sites showed gross PCB contamination. A closer look to these sites generally reveals the existence of PCBs factories or heavy industries nearby.

Using internationally accepted criteria, a screening level analysis was performed to identify

potentially contaminated sites for further study. Most of the selected sediment quality guidelines interpret much of the sediment data. Effects range low (ERLs) and effect range median (ERMs; Long *et al.*, 1995) plus the Interim Sediment Quality Guidelines (ISQG) and probable effect levels (PELs; CCME, 1999) are based upon similar data compilations, but use different calculations (Buchman 1999). The ERL and ISQG values can be classified as threshold level effects below which adverse biological effects are not expected, whereas the ERM and PEL represent the levels above which adverse effects are frequently expected. The range of concentrations, with values between the “lower” and “upper levels”, represent the values at which toxicity might be occasionally observed in sensitive species. The data shown in Table 3 suggests that adverse effects are occasionally observed in sensitive species in approximately 40% of the sampled sediments. However, there were no samples exceeding the median or “upper” reference levels. Furthermore, the Sediment Quality Index (SeQI, CCME, 2001), which involves not only the reference value but also the TOC% of sediments, was calculated for two areas, the Principal Navigation Channel and the Industrial Area. The indices 68 and 65 (in a scale of 1-100 scale) can be interpreted as fair-quality sediments, representing the average for the harbor-industrial zone. Beyond the limits of the interpreting power of each guideline/index, the results clearly suggest concern for the sediments toxicity due to PCBs, settling the first baseline values for the area and prompting the need for future monitoring approaches.

Concerning potential PCB sources, it is known that PCB emissions to ambient likely reflect the

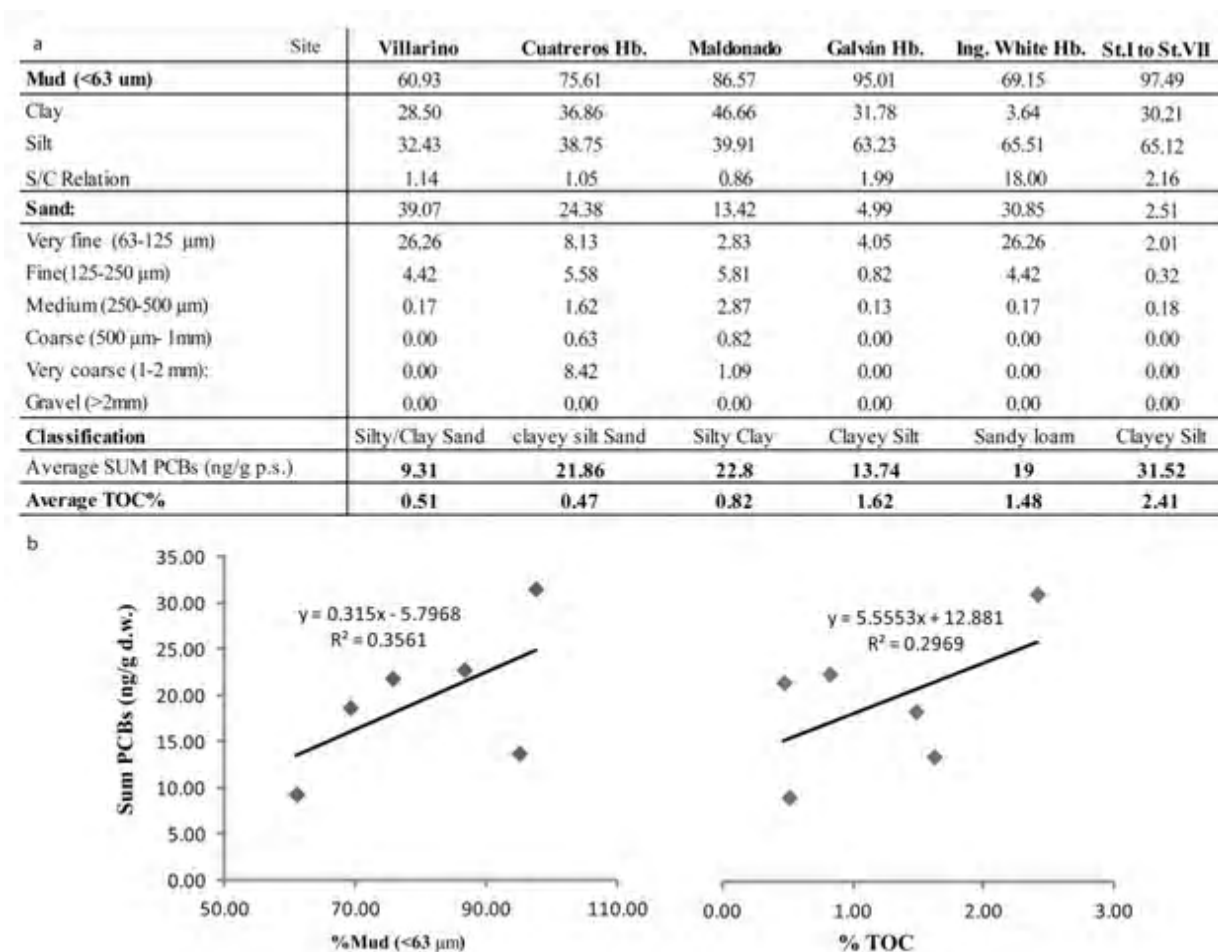


Fig. 4. a. Average granulometry of sediments at each sampling station. b. Correlation between SUM PCBs vs TOC% and % Mud (<63µm)

revolatilization of previously emitted compounds (Breivik *et al.*, 2002; Wania *et al.*, 1993; Harrad *et al.*, 1994) and the continued release from point sources, such as old industrial/urban areas, where these substances were previously heavily used and still exist (Motelay-Massei *et al.*, 2005). Because the incidence of runoff is great in urban and industrial areas close to the sampling points, it is possible that a significant contribution of PCBs (stations St. I to St.VII) was provided by the runoff of the 200 ha of industrially used lands. The aforementioned reduced break down of highly chlorinated PCBs might lead to the preferential transfer of heavy congeners to the sediment, in particular CB-180, which was dominant in those samples. It is not clear whether the estuary tributaries or the atmosphere transport and deposit PCBs in sediments. The results showed the simultaneous predominance of heavier congeners, such as CB180, and lighter congeners, such as CB52, CB101 and CB28. On the one hand, the presence of PCB congeners 138, 153 and 180 could reflect the input of technical mixtures (e.g., Aroclor 1260) into the environment from potential non-point sources, which follow water-transport pathways, such as terrestrial runoff, sewage and industrial

discharges (Froescheis *et al.*, 2000). On the other hand, one of the most abundant congeners was the CB52. This lightweight compound is widely contributed from atmospheric transport. Moreover, calculated air-soil exchange fluxes indicated that the contaminated soil is a secondary source to the atmosphere for lighter PCBs and as a sink for heavier PCBs (Bozlaker *et al.*, 2008), suggesting that the water-transport pathway could be a unique source. Assuming the preferential air-transport of the lighter PCBs congeners, the dominance of CB28 and CB52 over the estuary's principal channel samples suggests a substantial atmospheric contribution at these sites. In contrast, CB153, CB118, CB138 and CB 101 (higher weight PCBs) were diminished in compared with the pattern in the industrial area, where these congeners were higher in perceptual and absolute concentrations (Fig 3 a). The latter result strongly suggests an industrial main source in that area. This observation has been also reported in several similar environments. As an example, Hong *et al.* showed that the compositional pattern of PCB congeners exhibited a higher concentration of high-chlorinated congeners in the inner and most densely industrialized part of the study area (Masan Bay,

Table 2. The iPCB burden in selected coastal locations. Note: As indicated in the table, in some cases, the information for only selected congeners was considered. Note: The results are expressed in dry weight

| Location | Σ Mean (Sum of each congener average, ng/g) | Range (ng/g) | Number of congeners | N°sites/N°samples | Reference |
|---|---|--------------|---------------------|-------------------|----------------------------|
| Venice Lagoon and former industrial canals, Italy, Europe | 310.18 (*) | - | 12 | 7/13 | Frignani et al., 2004 |
| Southern Baltic Sea, Europe | 40 (**) | 1-149 | 7 | 30/60 | Konat et al., 2001 |
| Strazsky canal close to a former PCB's factory, East Slovakia, Europe | 347800 | 32640-92450 | 7 | 1/1 | Dercova et al., 2009 |
| Zemplinska srava water reservoir, East Slovakia, Europe | 330 | 2.5-187.8 | 7 | 1/1 | Dercova et al., 2009 |
| Hanoi Region, China | 7.67 | 0.01-4.81 | 6 | 12/12 | Nhan et al., 2001 |
| East River, China | 105.53 | 0.28-110 | 7 | 9/9 | Ren et al., 2009 |
| Salton Sea, California, USA, North America | 41.29 | 0-35.3 | 7 | 8/8 | Shapozhnikova et al., 2004 |
| Niagara River, USA, North America | 24.92 | 0-28 | 7 | 11/11 | Samara et al., 2006 |
| Dominican coastline; Central Atlantic, Central America | 2.61 | 0-1.62 | 7 | 11/11 | Sbriz et al., 1998 |
| Imperial River Salt Marsh, Chile, South America | 71.27 (†) | <0.01-13.46 | 8 | 1/5 | Barra et al., 2004 |
| Rio de la Plata Estuary, Argentina, South America | 34 (¥) | - | 8 | 14/14 | Colombo et al., 2005 |
| Bahia Blanca inner estuary, Argentina, South America | 24.16 | 1-160 | 7 | 12/29 | This study |

* To calculate this average, only superficial sediments were considered, up to 6 cm. Similarly, only 13 samples were considered for this calculation.

** To calculate this average, only superficial sediments were considered, up to 5 cm. Similarly, only 30 samples were considered for this calculation.

(†) To calculate this average, only superficial sediments were considered, up to 5 cm. The first sections of the corer sampling were considered for calculation.

(¥) Only sediments collected at 1 Km from the coast were considered, and the mean represents the average of three geographical areas.

Table 3. Reference PCBs guidelines and % of exceeding samples

| International reference values | Threshold Levels | | Median effect levels | |
|--------------------------------|------------------|-------------------------|----------------------|------------------|
| Name | ERL (1) | Canadian ISQG (TEL) (2) | ERM (1) | Canadian PEL (2) |
| PCBs Guideline (ng/g d.w.) | 22.7 | 21.5 | 180 | 189 |
| % of samples exceeding levels | 37% | 41% | 0% | 0% |

(1) Long et al., 1995

(2) Canadian Council of Ministers of the Environment, 1999

Korea) and a relatively low concentration of low chlorinated congeners in the outer (and less populated) area (2003).

The principal components analysis (PCA) is a multivariate analytical tool used to reduce the number of variables, e.g., the PCB content measured in bottom sediment samples, and extract underlying common factors (principal components, PCs) for analyzing the relationships among the observed variables. As a result of an effective extraction process, PC1 accounts for the major proportion of the total data variance, while the second and following PCs progressively explain smaller amounts of data variation. PCA has been applied to analyze variances in the persistent compound levels observed in some studies (Freeman and Catelli, 1990; Doong and Lin, 2004; Zhang *et al.*, 2004; Golobocanin *et al.*, 2004; Yim *et al.*, 2005). Then, in order to deepen the data analysis, a PCA was performed.

Prior to analysis, the values under the limit of detection (LOD) in the data set were replaced with random values under the LOD value. The concentrations of 7 iPCBs, as active variables, and 29 samples, as cases, were used. The number of factors extracted from the variables was determined according to Kaiser's rule, which retains only factors with eigenvalues that exceed one. Consistent with Golobocanin *et al.* (2004), a factor rotation was used to obtain the maximum number of positive loadings to achieve a more meaningful and interpretable solution. Two principal components vectors explained the majority of the variance (75%). PC1 explained 58.69% of the total variance and PC2 accounted for 16.22%. Figure 5a shows the loadings for the individual iPCBs in the principal components plot. PC1 had strong correlations (0.73-0.95) with CB101, CB118, CB138, CB153 and CB180. These compounds are the heavier congeners, formed from penta to hepta chlorine atoms (Table 1). These facts indicate PC1 as a heavy congeners correlation component, suggesting direct inputs through spills, and sewage or land runoff at the sampled sites. PC2 presented significant positive loadings for the lighter congeners CB28 and CB52. These tri and tetra chlorine compounds are typically associated with atmospheric transport; thus, PC2 explains the variation of the light congeners and

consequently, the likely atmospheric inputs at the sampled sites. Fig. 5b shows the score plot of the first two components, facilitating the characterization of the sampling stations according to the first and the second components. The plot reveals the relationships of the samples based on the measurements obtained. In this context, we identified two major groups of samples distributed along the PCs axis. Several samples from the industrial zone (IC: Industrial Channels; in e.g., St.VI, St.III and St. IV) were well differentiated according to the higher scores on the first component (X-axis). As previously observed, these samples are located in petro-chemical industrial park wastewater discharge zones, has areas that have previously been defined as hotspots for other pollutants (Arias *et al.*, 2010). A second group of samples, belonging to the main navigation channel, were coordinated along the second component (Y-axis). As mentioned before, the first possible explanation is that these areas received differential inputs from two major probable sources: either direct inputs or land runoff from the industries or atmospheric dry/wet deposition. The first source would certainly have led to the preferential input of heavyweight congeners, and was precisely the observed pattern at Industrial Channels (IC stations). The highest scores at PC1 were detected primarily at the Principal Navigation Channel (PC) of the estuary, suggesting the preferential atmospheric transport of PCBs at those sites (e.g., Maldonado Stream, Villarino Viejo and White Harbor). The remaining sampling stations likely received both contributions equally and could not be differentiated based on the distribution of these substances along the principal component axis. A probable second explanation to the observed differences between the sampled sites reflects the physicochemical/microbiological environment, which could have led to different degradation pathways for the PCBs congeners. The degradation of the PCBs can occur through two mechanisms: physical chemical weathering, including the evaporation and dissolution of the lighter and more soluble/volatile components, and microbial degradation (Saba *et al.*, 2011). Fava *et al.* showed that PCBs undergo reductive dechlorination mediated through endogenous sulfate-reducing and/or methanogenic bacteria (2003). In fact, as a general rule, several researchers have demonstrated the

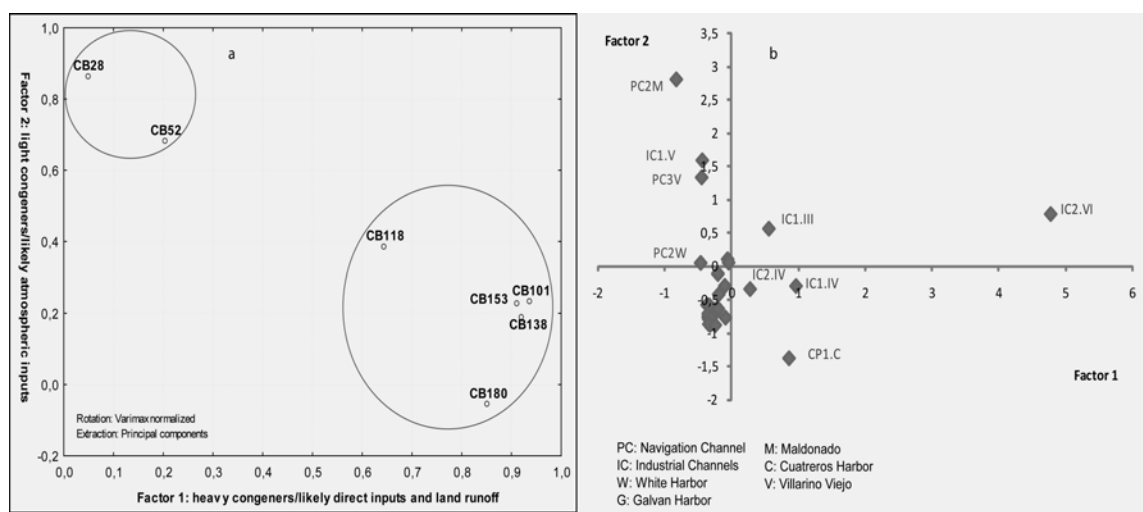


Fig. 5. a: PCA Factor Loadings, Factor 1 vs. Factor 2; b: Factor Scores

preferential weathering of PCBs in the form of losses of the lower chlorinated congeners, particularly the mono-, di-, and tri- homologue groups (Saba *et al.*, 2011, Rhee *et al.*, 1993; Wiegel and Wu, 2000; etc.). Thus, if the atmospheric input is constant, then the differential weathering could induce the dechlorination of the medium weight congeners up to CB 153 at the main estuary sites, as these congeners are diminished at those stations compared with the industrial sampling points. Consistent with the common degradation pattern, CB180 maintained low or no degradation at both areas. In fact, Fava *et al.* showed that this particular congener has a low dechlorination rate compared with less chlorinated molecules (2003).

CONCLUSION

The present survey of the PCBs concentration in coastal sediments showed different PCB concentrations in the study area, consistent with the anthropogenic activities of the surrounding area. A correlation between the PCB distribution, TOC% and the fine fraction was demonstrated for the area of study. The PCA analysis could differentiate between two principal signatures of iPCBs contributions, and this widespread abundance of light and heavy congeners suggests diverse input sources and/or the prevalence of preferential physical chemical weathering/losses, particularly in the mono-, di-, and tri- homolog groups in the principal channel stations. The levels of iPCBs identified in this study were detected between the moderately polluted environments. The results clearly show sediment toxicity due to PCBs, settling the first baseline values for the area and prompting the need of future monitoring approaches. This work highlights an emerging issue: the detection and quantification of atmospheric sources, which contribute to the PCB background at this coastal area. Using a tiered approach, the atmospheric deposition and water fluxes

of particulate matter are presently under study to assess the emerging hypotheses.

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