HISTORIC PCB RECORDS IN A SEDIMENT CORE FROM AN ESTUARINE WETLAND IN THE RIO DE LA PLATA, ARGENTINA

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Introduction

Estuarine wetlands are highly dynamic, transitional environments increasingly recognized for their ecological value which are exposed to strong natural and anthropogenic-related fluctuations, i.e. tides, storm surges, floods, droughts, effluent discharges [1,2]. The Samborombon Bay in the outer Río de la Plata estuary (Fig. 1) is an extensive (2240 km^2), little urbanized, very shallow, mixohaline depositional environment declared RAMSAR site in 1997 with a high particulate load from the turbidity maximum zone of the estuary [3] and a continuously prograding coast [4]. In addition to the terrestrial discharge of the Río de la Plata, which includes polluted inputs from Buenos Aires metropolitan area [5,6], the meandering Salado River drains a vast agricultural and livestock farming region (90000 km^2) in the east-central Buenos Aires Province plain. The natural drainage of the Bay has been modified by several hydraulic projects to control major floods, i.e. Channel 15 enlarged in 1997 drains more than 70% of the Salado River discharge [7]. In order to interpret historical PCBs inputs to the basin, in this paper we report a detailed study of a sediment core collected in high sedimentation area at the Salado River embouchure in the Samborombon Bay.

Materials and Methods

A 115 cm-long sediment core collected in 2015 using a 10.3 cm diameter PVC tube [2] in a salt marsh area from the Salado River (057°22.38' W 35°44.73' S; Figure 1) was divided in twenty three 4-6 cm height slices. Analysis included the determination of the grain size composition (sieve and pipet method), total organic carbon contents (TOC; Thermo Finnigan Flash EA 1112), and of 41 individual PCBs congeners (HRGC-ECD, Agilent 6890N, [5]). Deposition rates were derived from ^{210}Pb dating [2]. Table 1 presents grain size, TOC and total PCBs in the core.

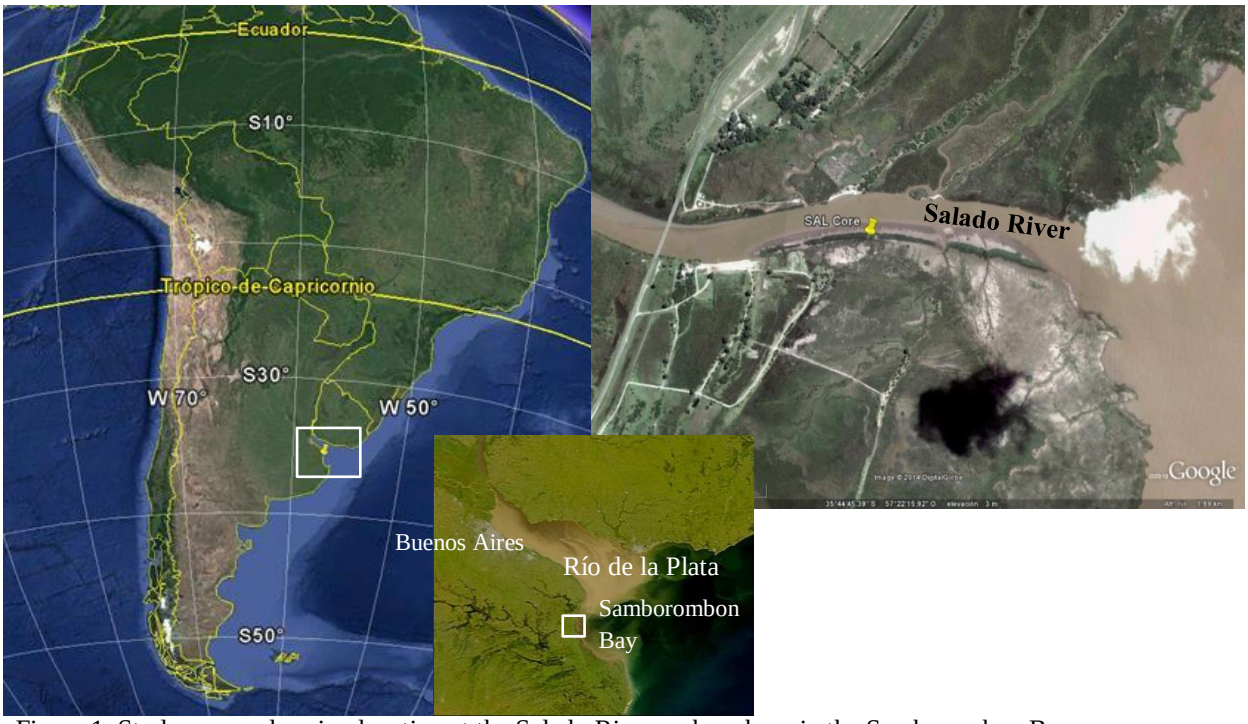

Figure 1. Study area and coring location at the Salado River embouchure in the Samborombon Bay.

Results and Discussion

The core is relatively homogeneous in terms of grain size composition, i.e. silty-clays with low sands (clay: 71±9.3; silt: 27±9.3; sand: 1.9±1.3%), and TOC contents (2.2±0.6 %) with no clear trends, indicating uniform source contributions from the turbidity maximum and Salado River along the 40 years represented by the core which show an uniformly high deposition rate of 2.62 cm/y [2]. In contrast, the C/N ratios (11-22) show a progressive downcore increase (Fig. 2) suggesting higher terrestrial inputs in the past and/or preferential N decay. The C/N maxima buried at 70-80 cm denoting extreme terrestrial inputs coincides with the once-in-the-century flood occurred in 1982-83 during a strong El Niño event, ENSO [8], indicated by high ONI values [9] (Fig. 2). Some secondary C/N peaks also matches later El Niño episodes (i.e. 1987, 2002) but the synchronism is not perfect, i.e. 1997 high ONI missing in C/N record. PCB concentrations are low (0.6-3.8 ng/g) reflecting relatively unpolluted conditions of this site distant from major urban industrial sources (> 200 km downstream Buenos Aires). Yet, PCBs show higher variability (40% vs. 13% for clay or 29% for TOC) basically due to a clear downcore increasing pattern reflecting the historical shift of anthropogenic inputs not related to ENSO events (Fig. 2). The peak buried at 80-90 cm, i.e. 1980's coincides with Argentina's estimated maximum PCB usage of 170-210 tons/year in 1974-80 [10]. The upward PCB reduction corresponds to an exponential decay of 4.2% per year, similar to the reduction rates reported for historic PCB trends in sediments from the Baltic, Lake Greifensee and Erie which peaked (15-65, 132 & 136 ng/g) earlier in 1960-70 [11,12,13].

Table 1. Grain size composition, TOC, C/N ratio and total PCB contents of the Salado core.

Depth	Sand	Silt	Clay	TOC	C/N	PCBs
cm	%					ng/g
0-4	1.7	23.8	74.5	3.0	14.0	0.75
4-8	4.1	24.1	71.8	1.9	11.0	0.60
8-12	3.5	18.0	78.5	2.0	11.8	0.84
12-16	1.4	55.4	43.2	1.6	11.3	0.96
16-20	6.1	22.5	71.4	1.7	12.4	1.06
20-26	1.3	23.5	75.2	1.7	12.2	0.92
26-32	1.7	31.0	67.2	2.2	14.7	1.02
32-38	2.0	22.8	75.2	1.7	12.7	1.45
38-44	0.4	20.3	79.3	1.5	12.6	1.77
44-50	1.9	36.7	61.5	1.4	12.7	1.26
50-55	3.2	39.2	57.6	3.1	16.0	1.57
55-60	2.6	32.7	64.7	1.9	13.6	1.72
60-65	1.3	26.2	72.5	1.8	13.5	1.43
65-70	1.3	21.3	77.4	2.6	15.7	1.92
70-75	3.1	18.3	78.6	2.5	12.8	1.97
75-80	1.3	12.8	85.9	3.8	21.7	2.26
80-85	1.5	21.0	77.4	2.9	17.6	2.67
85-90	1.4	20.0	78.6	2.7	17.2	3.77
90-95	1.0	33.0	66.1	2.1	17.5	1.56
95-100	0.6	25.7	73.7	2.1	16.2	2.00
100-105	0.7	25.8	73.4	1.7	15.1	1.30
105-110	1.8	34.1	64.1	1.6	17.3	1.08
110-115	0.9	38.4	60.7	2.7	20.7	1.35
Mean	**1.9**	**27.2**	**70.8**	**2.2**	**14.8**	**1.92**
SD	1.3	9.3	9.3	0.6	2.9	0.73

The lowest (< 1 ng/g) PCB concentrations in the top 30 cm agree well with PCB banning in 2001/02. PCB composition (Fig. 2) show a general predominance of chlorobiphenyls (CB) with 6, 7 and 5 chlorines with reduced variability (6CB: 49±7.8; 7CB: 21±4.4; 5CB: 17±7.7; 8-10CB: 9.4±4.5; 3-4CB: 3.5±5.4 %). The most variable 3-4CB show higher contributions in deeper layers, suggesting burial of fresher mixtures enriched in lighter congeners. The labile/recalcitrant tetra 101/hexaCB 153 ratio increases downcore and correlates with C/N (R^2= 0.44) supporting the burial of fresher PCB mixtures, but the PCB peak at 80-90 cm denotes a heavier composition with a lower ratio (Fig. 2). The congener composition buried in deeper sediment layers resembles an Aroclor 1254:1260 (1:2) mixture with increased ageing of the signal in more recent layers, similar to a weathered Aroclor 1260 profile.

Conclusions

A sediment core collected in a turbid and rapidly growing salt marsh precisely traced historic PCB burdens peaking at 80-90 cm depth (i.e. 1980) with a downcore increase of lighter congeners. ENSO variability correlated with C/N peaks but not with PCBs which showed an exponential 4.2% per year decrease from the buried maxima to the present with a weathered Aroclor 1260 profile.

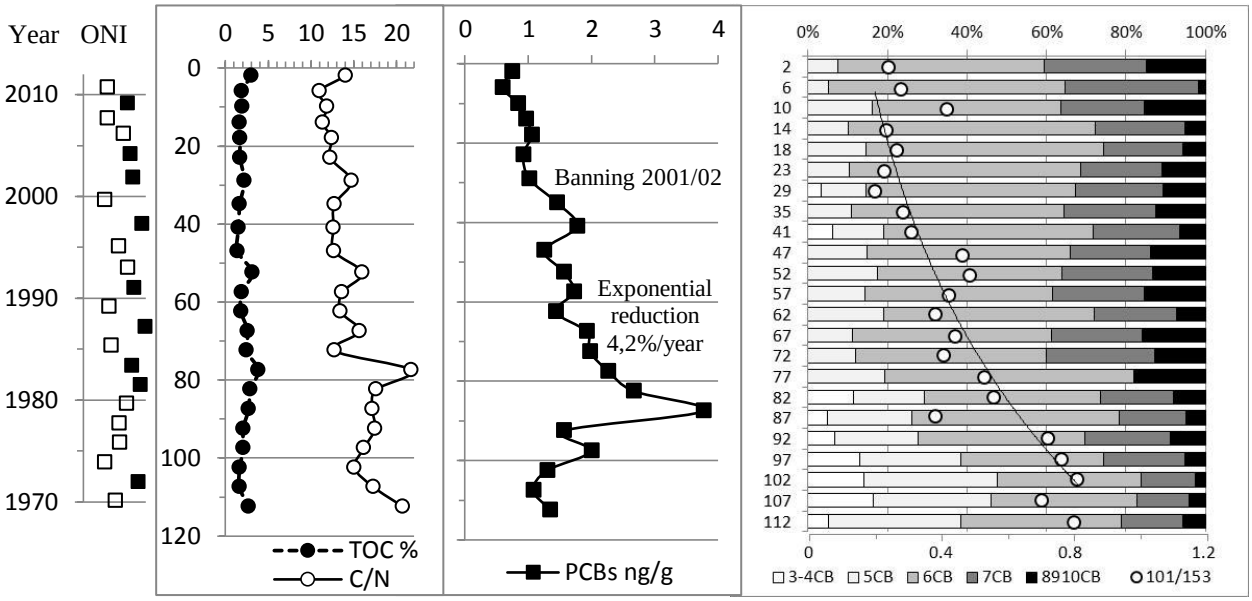

Figure 2. TOC, C/N and PCB profiles and composition in the Salado core. Age and the Oceanic El Niño Index (ONI) on the left (black squares denote warm-rainy El Niño events).

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