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Long-Term (1970−2017) Temporal Trends of Polychlorinated Biphenyls in Fish, Settling Material, and Sediments from Populated and Remote Sites in Río de la Plata Estuary, Argentina

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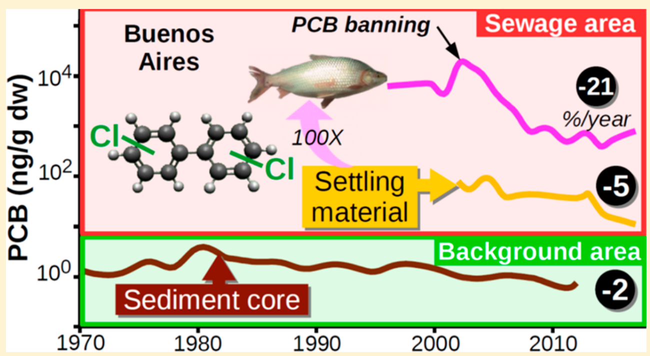
Supporting Information

ABSTRACT: Temporal trends of polychlorinated biphenyls (PCBs) were studied for detritivorous fish (1996−2017) and settling material (2002−2017) from polluted Buenos Aires coast and for a dated sediment core (1970−2013) from the outer Río de la Plata estuary. In spite of contrasting concentrations [5.3 ± 6.3 $\mu g \cdot g^{-1}$ dry weight (dw) for fish, 48 ± 26 $ng \cdot g^{-1}$ dw for settling material, and 1.5 ± 0.7 $ng \cdot g^{-1}$ dw for core], all three revealed exponentially decreasing trends over time (97%, 83%, and 83%, respectively). Time trends showed peak maxima coincident with Argentina's period of maximum PCB usage in 1973−1980 (80 cm depth in the core) and pulse discharges related to PCB banning in 2001−2002 (fish) with a lighter signature enriched in less persistent tri- and tetrachlorobiphenyls. The log−linear PCB time trends compare well with the predicted decrease for a high emission scenario from global emission data; the best fit was observed for the less impacted sediment core (−2%·$year^{-1}$ versus −3%·$year^{-1}$ for emission scenario). Steeper slopes are observed for the more polluted settling material (−5%·$year^{-1}$) and especially for fish, in which the background decline trend tripled after the 2001 PCB pulse (from −7%·$year^{-1}$ to −21%·$year^{-1}$). These PCB time trends in related environmental compartments from contrasted sites provide rare evidence for evaluating the effectiveness of control measures in southern South America.



INTRODUCTION

Global concern about persistent organic pollutants (POPs), highlighted by the Stockholm Convention treaty (2001), led to the development of multiple monitoring programs worldwide for the effectiveness evaluation of POP reduction based on recommended matrices of air and breast milk.[1] Yet a considerable amount of baseline information and temporal patterns of dichlorodiphenyltrichloroethanes (DDTs) and polychlorinated biphenyls (PCBs) in biota and sediments had been gathered 30−50 years prior to enactment of the treaty. This long-term information allows a practical assessment of the contamination status and efficacy of management practices. However, these long-term data are primarily restricted to the Northern hemisphere, where numerous monitoring programs have been developed by national agencies, for example, in the California coast,[2] the Great Lakes region,[3−5] the Arctic,[6,7] the Baltic and Swedish lakes,[8,9] the Rhine and Meuse rivers,[10] the Mediterranean Sea,[11] and the Asian Pacific.[12] In South America, economic constraints and political instability restricted the sustainability of monitoring efforts, resulting in scattered and temporally discontinuous data.[13]

In Argentina, the first DDT and PCB data for Río de la Plata fish and sediments were published in the early 1990s.[14,15] Later studies continued to monitor detritivorous fish,[16−20] settling material as a useful proxy to characterize the flocculent detritus arriving to the bottom and associated downward PCB flux,[21,22] and more recently, breast milk[23] and air.[24] In this paper, we summarize previously published data and add new information

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from ongoing projects in order to evaluate long-term temporal trends of PCBs in the Río de la Plata basin. Environmental compartments with different accumulation/decaying patterns and a trophic relationship; for example, detritivorous fish (21 years monitoring) and settling detrital material captured by sediment traps in polluted Buenos Aires coast (15 years) are compared with a dated sediment core from a mixohaline environment from the estuary mouth to the sea, distant from populated areas (42 years).

MATERIALS AND METHODS

In this work, new information from ongoing sampling campaigns in the Rio de la Plata estuary has been added to previously published data covering 1996–2006,[17,18,21,22] to have updated temporal coverage of fish and settling material. The Rio de la Plata estuary is the second largest basin of South America (>3 million km^2, 500–800 km^3 of freshwater and 90 $\times 10^6$ tons of solid load per year) with an abundant ichthyomass dominated by the detritivorous fish *Prochilodus lineatus*.[19] This strict detritivore has been chosen for PCB monitoring due to its special adaptations to ingest organic matter: suckerlike mouth, gill raker filtering structure, and numerous pyloric ceca that allow the fish to directly feed on flocculent sewage-industrial organic matter, leading to a rapid accumulation of fat and associated organic pollutants.[19] Although *P. lineatus* migrates 1000–1200 km north for reproduction, chemometric analysis of its biochemical and pollutant profile indicated a high degree of habitat fidelity to Buenos Aires, where the fish find an abundant and highly energetic food supply.[20] Sampling methods and general analytical procedures have been described in previous papers.[17,18,21] Briefly, fish were obtained from local fishermen from 1996 to 2017 along Metropolitan Buenos Aires coast, a freshwater area affected by untreated industrial and sewage discharges (Figure 1). Dorsolateral muscle samples were pooled according to fish size and weight (average size, 45 ± 4.9 cm; weight, 2.7 ± 0.9 kg; n = 442 fish in 109 pools and 57 individual samples). Settling material was collected 1.5 m below the surface in a 5–6 m water column near Buenos Aires main sewer at Berazategui (Figure 1) during 34 trap deployments covering 2002–2017. To minimize the capture of resuspended bottom material in this shallow coastal area, storm events were specifically avoided in the sampling scheme. Due to the large anthropogenic discharges (Buenos Aires main sewer: ~2 million $m^{-3} \cdot day^{-1}$) and high turbidity of the estuary, the fixed 10 cm diameter bi- and tricylindrical traps (total surface 157–235 cm^2) deployed for 20–48 h collected a large amount of material (total flux 140–700 $g \cdot m^{-2} \cdot day^{-1}$). In order to compare temporal patterns of PCBs in a more pristine, high-sedimentation, mixohaline, transitional environment in the Samborombon Bay (200 km SE from Buenos Aires to the sea), a 115 cm long sediment core was collected in the Salado River mouth (Figure 1) in 2013 using a 10.3 cm inner diameter poly(vinyl chloride) (PVC) tube (25), which was divided into 23 4–6 cm thick slices.

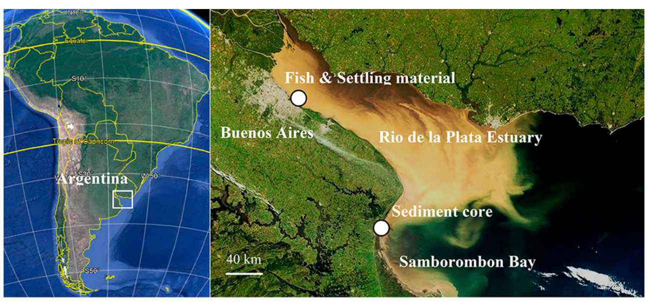

Figure 1. Study area and sampling locations of fish and settling material (Buenos Aires Metropolitan coast) and sediment core (Samborombon Bay).

Analyses included the determination of grain size composition (sieve and pipet method), total organic carbon (TOC) contents by high-temperature catalytic combustion (Thermo Finnigan Flash EA 1112), and 41 individual PCBs by high-resolution gas chromatography and electron capture detection (Agilent 6890N, Agilent 7890N).[17,18,21,22] PCB quantification was performed with the linear response (2, 10, 50, and 250 $pg \cdot \mu L^{-1}$) of 41 PCBs (IUPAC numbers 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; C-QME-01, AccuStandard Inc.). PCBs 103 and 198 (Ultra) were added to control recovery yields. Blanks included in every eighth sample batch gave negligible results. PCB method detection limit for the trap material ranged from 0.05 to 0.15 $ng \cdot g^{-1}$ dw; half of these values were used in case of nondetected congeners. Repeated analysis of an internal reference sediment from La Plata harbor in the Río de la Plata (21 ± 3.6 ng of $PCB \cdot g^{-1}$) indicated an average variability of 17–22%. Method accuracy, evaluated through the analysis of certified reference materials (sediment, NIST 1944; cod liver oil, COD1588a), averaged 79% ± 12% for 24 individual PCB congeners in sediments and 87% ± 16% for 22 certified congeners in fish. For age determination of the sediment core,[25] radionuclide analyses (excess ^{210}Pb and ^{137}Cs as an independent control on ^{210}Pb-derived ages) were conducted on 10–15 g of dried sediments by γ-spectrometry (high-purity germanium detectors, Canberra BE3830P). The year of deposition of sediment layers was derived from the constant rate of supply (CRS) dating model based on unsupported ^{210}Pb activity.[25] PCB usage and high emission data for the country were obtained from global historical emission inventories for 22 PCB congeners from the Norwegian Institute for Air Research.[26] Descriptive statistics and regression and correlation analyses were performed with Excel 2010 and Python (SciPy, NumPy, and SciKit-learn).

RESULTS AND DISCUSSION

Yearly averaged total PCB contents in fish, settling material, and sediment core are presented in Table 1, and temporal trends for all data are displayed in Figure 2. Lipid content of muscle from detritus-feeding fish from Metropolitan Buenos Aires is high (grand mean 44% ± 23% dw, n = 166), reflecting feeding on organic-rich, polluted anthropogenic detritus. This produces a higher body mass gain [condition index (CI) = (body mass)$\cdot$(standard length)$^{-3}$ = 3.0 ± 0.5], enhanced hepatomegaly [hepatosomatic index (HSI) = (liver)$\cdot$(body mass)$^{-1}$ × 100 = 1.4 ± 0.4], and lipogenesis, possibly reinforced by the obesogen role of PCBs.[19] In contrast, fish from northern Paraná and Paraguay Rivers (>1000 km north from Buenos Aires), with a diet based on vegetal detritus, are lean with smaller livers (13% ± 8.4% lipids dw; CI = 2.4 ± 0.4; HIS = 0.7 ± 0.2).[20] Accordingly, fatty Buenos Aires fish show a high bioaccumulation of PCBs with dry weight concentrations 2 orders of magnitude higher compared to the organic-rich

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Table 1. Annual PCB Averages and Compositional Ratios for Fish, Settling Material, and Sediment Core[a]

	fish ($\mu g \cdot g^{-1}$)					settling material ($ng \cdot g^{-1}$)				sediment core ($ng \cdot g^{-1}$)		
year	dry wt	fresh wt	lipid wt	3−4/6 CB	*n*	dry wt	TOC wt	3−4/6 CB	*n*	dry wt	TOC wt	3−4/6 CB
1970										1.35	49.5	0.13
1972										1.08	66.2	0.44
1974										1.30	78.0	0.39
1976										2.00	96.0	0.37
1978										1.56	75.8	0.16
1980										3.77	139.1	0.09
1982										2.67	91.7	0.26
1983										2.26	59.0	0.00
1985										1.97	79.6	0.00
1987										1.92	73.6	0.00
1989										1.43	78.5	0.00
1991										1.72	91.6	0.00
1993										1.57	50.0	0.00
1995										1.26	88.4	0.00
1996	5.9−6.6	2.2−2.6	17.1−27.6	0.49	2							
1997										1.77	116.6	0.12
1998												
1999	7.1 ± 2.6	3.2 ± 1.5	8.8 ± 1.9	0.46	5							
2000	6.1 ± 2.7	2.7 ± 1.5	8.7 ± 2.3	0.40	9					1.45	86.5	0.00
2001	4.7 ± 1.9	2.2 ± 1.3	7.8 ± 3.3	0.56	10							
12/2001	21 ± 12	8.5 ± 5.8	47 ± 22	1.04	3							
2002	17 ± 4.9	7.0 ± 1.9	39 ± 28	0.64	13	79.6	491	0.19	1	1.02	46.3	0.06
2003	16 ± 6.0	7.3 ± 3.7	24 ± 7.0	0.40	16	57−68	334−1627	0.47	2			
2004	11 ± 4.6	3.8 ± 2.2	20 ± 5.0	0.35	12	87 ± 34	1976 ± 1591	0.19	6	0.92	53.9	0.00
2005	5.2 ± 2.9	2.1 ± 1.5	12 ± 2.9	0.30	9	76 ± 33	1286 ± 903	0.38	4			
2006	2.9 ± 2.0	1.1 ± 0.9	11 ± 4.5	0.29	12	39 ± 22	580 ± 238	0.78	4	1.06	61.8	0.00
2007	1.7 ± 0.8	0.5 ± 0.3	8.3 ± 6.5	0.31	10							
2008	0.8 ± 0.5	0.2 ± 0.1	3.1 ± 1.5	0.42	3	44	466	0.76	1	0.96	58.7	0.00
2009	0.9 ± 0.3	0.3 ± 0.1	2.8 ± 1.4	0.28	8					0.84	42.2	0.00
2010	0.8 ± 0.6	0.2 ± 0.2	2.7 ± 1.7	0.34	9							
2011	0.5 ± 0.3	0.2 ± 0.1	2.3 ± 1.9	0.45	17					0.60	31.3	0.00
2012	0.6 ± 0.3	0.2 ± 0.1	2.0 ± 0.7	0.39	12	37 ± 5.1	349 ± 125	1.23	4	0.75	24.6	0.00
2013	0.7 ± 0.4	0.2 ± 0.1	2.1 ± 0.7	0.42	9	45 ± 32	384 ± 200	1.08	4			
2014	0.4−0.5	0.13−0.14	1.2−2.1	0.46	2	21−31	720−1060	0.34	2			
2015	0.52−0.54	0.1−0.2	1.5−1.8	0.47	2	15 ± 7.7	692 ± 164	0.25	3			
2016												
2017	0.8 ± 0.4	0.3 ± 0.2	1.9 ± 0.6	0.42	3	11 ± 5.8	827 ± 425	0.54	3			
total					166				34			

[a]Some values are given as arithmetic mean ± standard deviation. 3−4/6 CB is the tri+tetra/hexachlorobiphenyl ratio. 12/2001 indicates December 2001 peak concentration in fish after massive dumping.

(8.3% ± 4.5% TOC) settling material collected by the traps (0.11−35, 5.8 ± 7.0 $\mu g \cdot g^{-1}$ dw versus 7.0−154, 50 ± 34 $ng \cdot g^{-1}$ dw, respectively).

The less polluted sediment core from Samborombon Bay shows homogeneous grain size composition and lower TOC contents (sand, 1.9% ± 1.3%; silt, 27% ± 9.3%; clay, 71% ± 9.3%; TOC, 2.2% ± 0.6%), revealing very low baseline PCB concentrations for the basin at 30-fold below Buenos Aires' trap material values (0.6−3.8, 1.5 ± 0.7 $ng \cdot g^{-1}$ dw). As expected, the differences between lipid- and organic carbon-based PCB concentrations are lower but still show the same pattern, with fish averaging 20 times higher than the trap material value which, in turn, is 7 times higher than the sediment core average (11 ± 13 $\mu g \cdot g^{-1}$ lipid for fish, 478 ± 384 and 71 ± 27 $ng \cdot g^{-1}$ TOC for settling material and sediment core, respectively).

In spite of the large differences in PCB concentrations, the variability of the data [relative standard deviation (RSD) 120% for fish and ~50% for settling material and sediment core] includes significant exponentially decreasing trends over time in all three environmental compartments ($r^2 = 0.57−0.89$, $p < 0.001$; Figure 2). When the decrease from peak maxima to more stable final periods of the time series is considered (December 2001 to 2008−2017 for fish, 2002−2005 to 2015−1017 for settling material, and 1980 to 2011−2012 for sediment core), the exponential decrease in total PCBs averages 97% for fish (from 21 to 0.7 $\mu g \cdot g^{-1}$ dw), 83% for settling particles (from 76 to 13 $ng \cdot g^{-1}$ dw), and 82% for sediment core (from 3.8 to 0.7 $ng \cdot g^{-1}$ dw). The initial lower concentrations and peak maxima observed in fish and sediment core data introduce significant variability in the time series.

The time trend of fish data shows a large variability associated with a peak maximum by the end of 2001 when PCB phase-out associated with a severe economic crisis, illegal dumping, and heavy rains resulted in a strong pulse of PCBs into the estuary.[17,18] Effectively, PCBs from transformer oil

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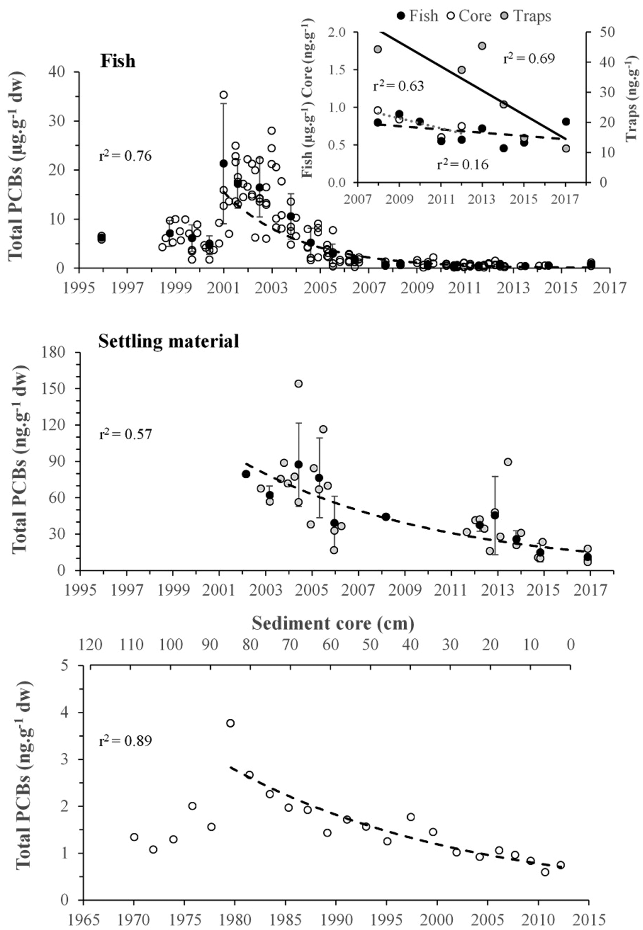

Figure 2. Temporal trends of PCBs in fish, settling material (traps), and sediment core from the Río de la Plata estuary. (○) Individual measures; (●) arithmetic year averages ± standard deviations. Exponential decrease trends (dashed lines) are displayed after 2001 for fish and after 1980 for sediment core. Recent linear trends are shown for the 2008–2017 period (top, inset).

residues discharged in heavily polluted channels and ports were efficiently washed out to the estuary, producing concomitant extreme PCB concentrations in fish from December 2001 (13–35 $\mu g \cdot g^{-1}$ dw; Figure 2). A similar situation has been suspected to explain PCB increases in Meuse River eels in 2000 after the Belgium dioxin crisis.[10] The large variability of Buenos Aires' fish averages for December 2001 and the years 2002 and 2003 (Figure 2) reflects mixing of fish with different exposures. In fact, from December 2001 to 2003, 29 out from 32 fish samples ranged from 13 to 35 μg of PCB$\cdot g^{-1}$ dw (mean 18 ± 5.4 $\mu g \cdot g^{-1}$ dw), tripling the already high previous PCB concentrations of fish from this polluted area (from 1996 to October 2001, 5.8 ± 2.4 $\mu g \cdot g^{-1}$ dw; n = 26), whereas only three animals maintained similar concentrations in 2001–2003 (6.4 ± 0.5 $\mu g \cdot g^{-1}$ dw). The dampening of this PCB pulse in fish appears to be largely completed approximately in 2006–2007. While depuration/elimination kinetics might play a role in this decrease, the exceptionally high muscle lipid depot of the fish, which is maintained even during migration efforts when visceral fat is consumed, act basically as a long-term reservoir for persistent pollutants, minimizing their remobilization.[20] Thus, the most likely explanation of PCB attenuation in fish is the general population turnover, where heavily polluted fish are progressively replaced by less contaminated specimens from subsequent cohorts. According to the most recent local fishery study,[27] the age-class distribution of this fish is maximal between 2 and 6 and 9–10 years, supporting the interpretation of a relatively rapid 6–7 year replacement of fish after the 2001–2002 PCB pulse. From 2008 to 2017, PCB concentrations stabilized as shown by the nonsignificant fit of the linear trend (0.68 ± 0.16 $ng \cdot g^{-1}$ dw; r^2 = 0.16, p > 0.28; Figure 2, inset), suggesting that 7 years after the official phase-out of PCBs, fish approached a new steady state, at levels 9 times lower than the prepulse PCB concentrations. These results indicate that despite the typically large variability of fish data, this dominant and highly specialized detritivorous fish, with a very short trophic chain based on anthropogenic organic matter, provides useful and reliable information to evaluate the effectiveness of management practices related to the Stockholm Convention.

Although the time series of settling material has a limited time coverage that begins just after the major PCB pulse observed in fish (August 2002), the highest concentrations in the trap material match the time frame of fish maximum (2002–2005) with a significant decrease afterward. Effectively, the average PCB concentration in the trap material during 2002–2005 (80 ± 29 $ng \cdot g^{-1}$ dw) decreased 2–3-fold after 2008 and displayed a larger relative variability (31 ± 20 $ng \cdot g^{-1}$ dw). Shorter time series (1984–1991) of settling material in Lake Superior presented an even faster decrease over time.[28] During the 2008–20017 period, annual PCB averages of settling material continue decreasing (from 37–45 to 11–15 $ng \cdot g^{-1}$ dw; r^2 = 0.69, p < 0.05 for the linear regression), contrasting with the more stable fish pattern (Figure 2, inset). This may be attributed to the direct impact of input discharges on the trap material, in contrast to fish, where the pattern is also influenced by bioaccumulation/depuration kinetics, longevity, migration, and population dynamics. Organic carbon-normalized PCB concentrations in settling material also show a maximum in 2004–2005 and lower values afterward (from 1300–2000 to 350–890 $ng \cdot g^{-1}$ TOC; Table 1) but during 2014–2017, concentrations increases significantly due to the average 5-fold reduction of TOC (9.9% ± 3.5% to 2.1% ± 0.8%) related to the construction of a wastewater treatment plant, resulting in a nonsignificant exponential fit of TOC-based concentrations and years (r^2 = 0.11, p = 0.32) . These results indicate that the main Buenos Aires sewer is a significant source of TOC but not of PCBs and confirms the flaws of TOC-normalized data for time trend analysis.[8]

The sediment core collected in the distant, more pristine, and mixohaline Samborombon Bay covers an extended 42-year time frame with 1–2 orders of magnitude lower PCB concentrations than Buenos Aires' settling particles and a different temporal pattern than fish and trap material. The sediment core presents a PCB maximum at 80 cm depth (3.8 $ng \cdot g^{-1}$ dw) dated to 1980, which is in good agreement with Argentina's period of maximum PCB usage of 200–350 tons$\cdot$year^{-1} from 1973 to 1980[26] but does not reflect the 2001–2002 pulse maximum of Buenos Aires' fish. This suggests that this remote area reflects background inputs related to the general magnitude of PCB usage in the country rather than local pulses from the most industrialized and populated area, where the very high sedimentation rates (5.0 ± 1.7 cm$\cdot$year^{-1})[21] and associated PCB fluxes (26 ± 19 $\mu g \cdot m^{-2} \cdot day^{-1}$)[21] favor the rapid burial of hydrophobic pollutants near main sources. Similar to trap material, the more recent surficial PCB

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concentrations in the core suggest a decreasing trend, but it is statistically nonsignificant due to few data points (~1 to 0.6 ng·g^{-1} dw; $r^2 = 0.63$, $p < 0.20$; Figure 2, inset). As observed for settling material, the TOC-normalized sediment core concentrations also decrease from 1980 to 2012 (from 139 to 25 ng·g^{-1} TOC, Table 1) but show a poorer yet significant exponential fit ($r^2 = 0.52$, $p < 0.001$ for TOC and $r^2 = 0.89$, $p < 0.001$ for dw data), thus supporting the use of dry weight concentrations in time trend analysis.

Log–linear PCB time trends in fish, settling material, and sediment core from the Río de la Plata are compared with usage/emission patterns and Argentina's management milestones in Figure 3. In general, all three environmental compartments compare well with the predicted decline emission scenario with a best fit for the remote environment, away from major pollution sources. The log–linear slope of this more pristine sediment core (−2%·year^{-1}, $p < 0.001$) is lower than the decline slope derived for the high-emission scenario (−3%·year^{-1}). More polluted settling material from Buenos Aires present higher slopes (−5%·year^{-1}, $p < 0.001$) and especially fish data, whose slope shows a 3-fold increase after the 2001 pulse (−7%·year^{-1}, $p < 0.001$, excluding the 2001 peak to −21%·year^{-1}, $p < 0.001$). Overall, Río de la Plata's declining PCB trends are comparable to those reported for other environments (2−5%·year^{-1} for sediments and 2−11%·year^{-1} for fish) with a proportionally higher decrease for settling particles compared to the core and especially for fish after the 2001 PCB pulse. Table S1 provides Río de la Plata dry weight-, fresh weight-, and lipid-based declining PCB trends compared to other environments. The 1980−2012 decrease of PCBs in Río de la Plata sediment core is comparable to that reported for a core covering 1968−1990 in the Stockholm Archipelago[8] and 3 times lower than a 1940−1990 Baltic core's declining trend.[8] PCB burial and sediment core slopes are significantly influenced by sedimentation rates and resuspension.[8] The high sedimentation rate estimated for the Salado core from ^{210}Pb data (2.62 cm·year^{-1})[25] indicates a relatively rapid burial of the PCB signal, and the uniformly fine texture of the core (clay, 71% ± 9.3%; silt, 27% ± 9.3%) suggests that resuspension and mixing with coarser material is probably not relevant. As observed in Río de la Plata data, the Baltic temporal PCB trends also show consistently lower slopes for sediment cores compared to biota.[8]

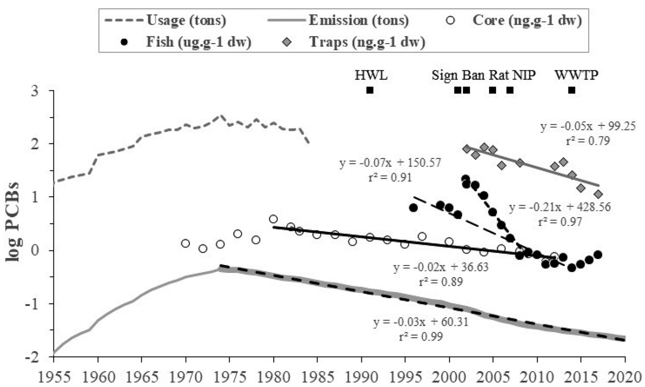

Figure 3. Temporal trends of total PCBs (log basis) in fish, settling particles (traps), and sediment core compared with usage and high-emission scenarios and management milestones (HWL, hazardous residue law, 1991; Sign, Stockholm Convention signature, 2001; Ban, PCB banning, 2002; Rat, Stockholm Convention ratification, 2005; NIP, National Implementation Plan, 2007; WWTP, wastewater treatment plant, 2014). Annual percentage decreases are indicated by the slopes of the log−linear trends.

Settling material from Buenos Aires showed a higher PCB decrease trend from 2002 to 2017 compared to the Río de la Plata core but lower than the 1984−1991 temporal decline reported for Lake Superior,[28] where trap material PCB concentrations were more than an order of magnitude higher with total mass fluxes 3 orders of magnitude lower than Buenos Aires coastal area.[22] Excluding the 2001−2002 pulse, PCB decline in Buenos Aires' fish is on the high end of the 2−11%·year^{-1} range observed for most locations.[4,8,29,30] After the 2001−2002 pulse, the 3-fold increase in PCB decline is comparable only to the extreme 1975−2010 PCB reduction reported for Lake Michigan salmon.[31] Contrasted scenarios are observed in the time trends relative to management practices. Fish data show paradoxical results, with a 3-fold PCB increase after their banning in 2001−2002 with a subsequent rapid decline. On the other hand, construction of the wastewater treatment plant effectively contributed to an average 5-fold reduction of trap TOC with lower dry weight PCB contents.

Figure 4 presents the average composition of PCBs in fish, settling material, and sediment core and its annually averaged variability. Overall, hexachlorobiphenyls predominate in all three compartments but especially in the remote sediment core, which shows a heavier PCB signature (6CB, 36% ± 3.4% in fish, 35% ± 9.9% in trap material, and 49% ± 7.8% in core). Fish and settling material from Buenos Aires' coast display a similar and lighter PCB pattern, evidence of the impact of fresher discharges enriched in less persistent tri-, tetra-, and pentachlorobiphenyls, with a more homogeneous signature in fish. Pentachlorobiphenyls are the next most abundant congeners in fish and settling material, followed by heptachlorobiphenyls (5CB, 23% ± 5.0% and 24% ± 3.1%; 7CB, 21% ± 4.7% and 18% ± 6.2%, respectively), but this trend is reversed in the sediment core (5CB, 17% ± 7.7%; 7CB, 21% ± 4.4%). Tri- and tetrachlorobiphenyls are variable in all three environmental compartments (3−4CB, 15% ± 4.6% in fish, 17% ± 6.8% in traps, and 3.5% ± 5.3% in core) with higher proportions during peak PCB concentrations. This is especially evident in fish, where they account for 27% of total PCBs with the highest 3−4/6 chlorobiphenyl ratio (~1) during the December 2001 PCB peak, denoting the input of fresh residues. Afterward, tri- and tetrachlorobiphenyls decrease progressively in fish until 2005−2006 (to 10−11%), with a steeper decline of the 3−4/6 CB ratio (to ~0.3). This pattern is also evident in the sediment core, which shows increased proportions of 3−4 CBs from 1972 to 1982 (10−15% of total PCBs) with higher 3−4/6 chlorobiphenyl ratios (~0.4) during the period of maximum PCB usage in Argentina, whereas lower chlorinated congeners almost disappear in upper sediment layers, which show very low 3−4/6 CB ratios (<0.1). The relationship of lighter PCB signatures during peak contamination episodes and progressive attenuation of the signal due to increased volatility and degradation of lighter chlorinated PCBs has also been reported for Swedish lakes.[9] Settling material shows variable PCB composition with an apparent increase in lower chlorinated congeners and highest 3−4/6 chlorobiphenyl ratios between 2006 and 2013, with intermediate concentrations.

Summing up, PCB time trends in detritivorous fish and settling material from the polluted Buenos Aires coastal area and a more pristine, dated sediment core from the mixohaline

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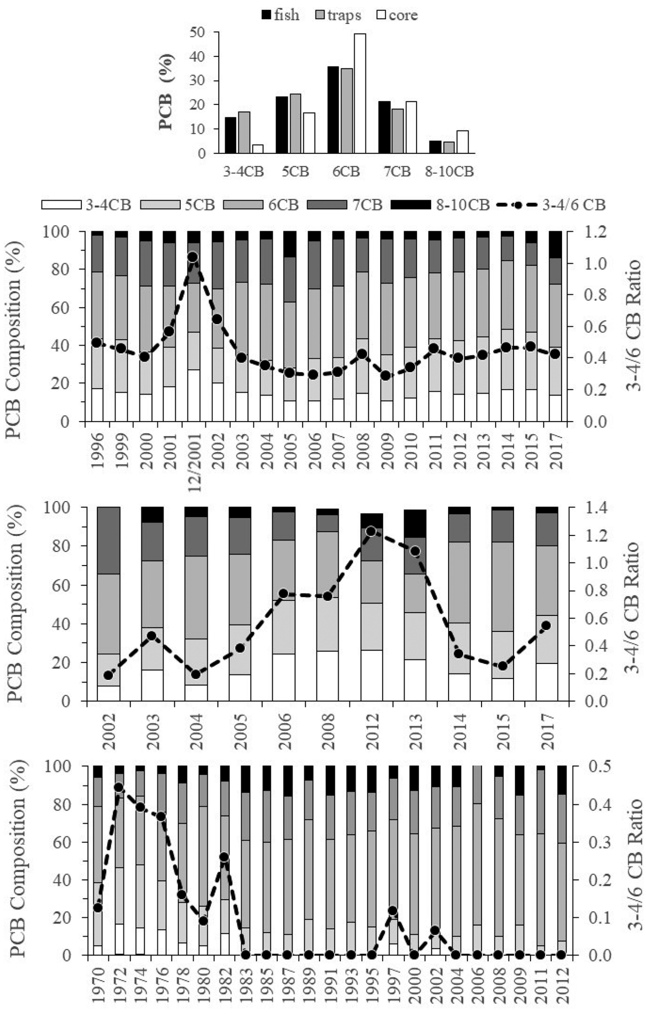

Figure 4. (Top panel) Average PCB composition in fish, settling material, and sediment core and annually averaged variability for (second panel) fish, (third panel) settling material, and (bottom panel) sediment core from the Río de la Plata estuary. PCBs are grouped by Cl contents in tri-tetra- (3–4CB), penta- (5CB), hexa- (6CB), hepta- (7CB). and octa–decachlorobiphenyls (8–10 CB). The lower/higher chlorinated 3–4/6 CB ratio is also shown.

outer Río de la Plata estuary provide rare and valuable evidence of consistent, exponentially decreasing trends over time in southern South America. Temporal patterns showed peak maxima associated with Argentina's period of maximum PCB usage in 1973–1980 in the longer time series represented by the sediment core and pulse discharges related to PCB banning in 2001–2002 in the fish, with a lighter signature enriched in less persistent tri- and tetrachlorobiphenyls. The log–linear PCB time trends in all three compartments compare well with those reported for the Northern hemisphere with an annual decrease of 2–5% for sediments and 2–11% for fish. A higher PCB decline is observed for settling material compared to the core and especially for fish after the 2001 pulse, which showed a rapid 21%·year^{-1} reduction until 2006–2007.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b04403.

One table comparing PCB time trends in sediments and fish from different environments (PDF)

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Notes

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