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Risk ranking of multiple-POPs in detritivorous fish from the Río de la Plata

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ABSTRACT

To evaluate the bioaccumulation and the risk associated to consumption of lipid-rich detritivorous fish, a comprehensive set of organic pollutants ($n = 213$) including polychlorinated biphenyls (PCBs), dioxin like PCBs (dlPCBs), chlorinated pesticides (CHLPs), chlorobenzenes (CBzs), polybrominated diphenyl ethers (PBDEs), polychlorinated dibenzo dioxins and furans (PCDD/F), resolved (ALI) and unresolved aliphatic hydrocarbons (UCM) and linear alkyl benzenes (LABs) were analyzed in Sábalo fish (*Prochilodus lineatus*) collected in the polluted Metropolitan Buenos Aires coast and in migrating specimens. Fatty fish muscles (lipids: 74 ± 9.3% dry weight) contained homogeneous (24–51% variability) and very high-concentrations of organic pollutants ranging from 60 to 1300 μg g^{-1} fresh weight (fw) ALI + UCM; 10–40 μg g^{-1} fw LABs and PCBs; 0.1–1 μg g^{-1} fw dlPCBs, DDTs, chlordanes, CBzs and PBDEs; 0.01–0.1 μg g^{-1} fw mirex, endosulfans, aldrin, dieldrin, endrin and 0.07–0.2 ng g^{-1} PCDD/F. Total toxicity equivalents (TEQs) ranged from 60 to 395 pg g^{-1} fw (34 ± 17 and 213 ± 124 pg g^{-1} TEQs for PCDD/F and dlPCBs respectively). These are among the highest concentrations reported for fish and point out the remarkable ability of Sábalo to feed on anthropogenic organic-enriched particles and tolerate a high pollutant load. Contaminant signatures show partial alteration with still abundant lower molecular weight components indicating that fish feeds directly in the outfalls. Consumption limits based on reference doses ranged from 0.1 (PCBs) to >12 000 g d^{-1} (endosulfan) allowing a comprehensive risk-based ranking of contaminants in this long-range migrating, detritivorous fish.

1. Introduction

Fish detritivory is only limited to a few species but represent a prevailing route of energy flux in turbid, subtropical aquatic ecosystems such as the Río de la Plata Basin (Bowen, 1983). With a total fresh water flow of 16–28 × 10^3 m^3 s^{-1}, the Río de la Plata is the second largest hydrographic system in South America covering more than 3 million km^2 in tropical and temperate areas of Brazil, Argentina, Paraguay, Bolivia and Uruguay (Esteves et al., 2000). Approximately 90 million tons of suspended particulate matter are transported annually to the estuary, mostly derived from rainy Andean food plains through the muddy Bermejo River discharge (suspended solids ~6000 mg L^{-1}) to the Paraná River, 1300 km north to Buenos Aires (Fig. 1). The massive transport of allochthonous material feed a vast delta in front of Buenos Aires City which concentrates one third of the total Argentinean population (~40 millions) and most of its industrial capacity. This results in a heavy impact in the coastal zone which receive crude effluent discharges containing persistent organic pollutants (POPs), hydrocarbons and trace metals (Colombo et al., 2005a, 2005b, 2006; Tatone et al., 2009). Massive vertical fluxes of organic carbon (1.2 ± 1.2 g cm^{-2} y^{-1}), hydrocarbons (15 ± 14 mg cm^{-2} y^{-1}) and PCBs (1.1 ± 0.8 μg cm^{-2} y^{-1}) have been measured in this area (Colombo et al., 2007a) which constitutes the feeding ground of a specialized detritivorous fish, the Sábalo (*Prochilodus lineatus*).

Sewage-derived organic matter has been recognized as an important energy subsidy for aquatic food webs which can lead to trophic structure alterations and an increase of fish production (deBruyn et al., 2003). These impacts are probably amplified in the Río de la Plata basin where the ichthyomass is dominated by the Sábalo which actively search flocculent anthropogenic organic matter as an enriched feeding resource (Speranza and Colombo, 2009). The Sábalo is a strict detritivorous with a sucker-like mouth, filtering oral ridges, a highly muscularized grinding stomach and an increased intestinal absorptive surface. This strong

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Fig. 1. Study area showing the Río de la Plata basin (shaded area in South America) and the sampling sites at Buenos Aires, Goya and Empedrado (based on a NASA World Win image).

specialization on detritivory and the presence of large discharges of untreated effluents in the Río de la Plata (e.g. main Buenos Aires sewer: ~2 million $m^3\ d^{-1}$), transformed the Sábalo in a critical pathway of POP cycling in the basin with direct outcomes for the human population. Residues are also subjected to trophic biomagnification since the Sábalo is a principal food item for major predators such as the shovelnose catfish (*Pseudoplatystoma* sp.) and the dorado (*Salminus maxillosus*). The Sábalo also moves in large schools upstream for hundreds kilometers in a reproductive, flood-controlled migration (Agostinho et al., 2004) facilitating the active biotransport of pollutants to remote areas along the Paraná and Uruguay Rivers.

In this paper we perform a comprehensive multi-POP screening in detritus-feeding Sábalo fish collected in Metropolitan Buenos Aires coast and in migrating specimens captured 800 km north along the Paraná River to evaluate the bioaccumulation and produce a comparative risk ranking associated to consumption of this dominant fish.

2. Methods

Fish samples were obtained from local fishermen in the coastal area of Metropolitan Buenos Aires affected by crude industrial and sewage discharges in December 2003, February, May and September 2004, and from Goya and Empedrado, 700–850 km north along the Paraná River (Fig. 1). Immediately after the capture, fish were measured, weighed and dissected to obtain a 10–30 g sample of dorso-lateral muscle which was wrapped in clean aluminum foil and freezed until analysis. In the laboratory, fish muscle samples were pooled (2–3 individuals) according to the size and weight of the fish discriminating medium ($1 < x < 2.5$ kg), large ($2.5 < x < 3.5$ kg) and very large fish ($3.5 < x < 4.5$ kg). Fish with dissimilar morphometric characteristics were processed individually. The muscles were processed with 250 W blenders in glass jars using different equipments for medium and large fish.

The homogenized muscle samples were split for the determination of water content (100 °C, 24 h) and for chemical analyses (Colombo et al., 2000, 2007b). Briefly, blended tissues were mixed with pre-extracted sodium sulphate (1:3) and then Soxhlet extracted with acetone, dichloromethane and petroleum ether (1:2:2). The extracts were evaporated, transferred to centrifuge tubes and concentrated to constant weight under nitrogen to determine total lipids. The concentrated lipid extracts were split for a multi-residue analysis scheme which included dlPCBs, ALI and LABs (Laboratorio de Química Ambiental y Biogeoquímica, Argentina), PCBs, CHLPs, CBzs, PBDEs (Environment Canada, Water Science and Technology Directorate, Aquatic Ecosystem Protection Research Division, Canada) and PCDD/Fs (Geochemical and Environmental Research Group, USA). The analytical protocol for dlPCBs, ALI and LABs included the dissolution of 200 mg lipid with petroleum ether, treatment with sulphuric acid and fractionation by silica-gel chromatography (F1: petroleum ether; F2: petroleum ether: dichloromethane 3:1). After instrumental analysis the F1 was further fractionated in 20% charcoal:silica gel columns separating multi (F1), mono (F2) and no-ortho PCB congeners (F3; Cappelletti et al., 2005). Aliphatic hydrocarbons and LABs were quantified by high resolution gas chromatography (Agilent 6890N and Agilent 6850) with FID and MSD detection (Agilent 5973N: EI 70 eV, 2.94 scans per segment, 50–550 amu). Quantification was performed by an external standard of 31 individual aliphatic hydrocarbons (n-C10–n-C38 plus pristane and phytane; AccuStandard Inc.) and 25 LABs provided by a local Petrochemical Company. Deuterated n-alkanes (n-C_{16}-d34 and n-C_{24}-d50; Absolute Standards, Inc.) were used to control recovery yields. All samples were quantified by both detectors using the MSD to confirm ALI identities (m/z: 71, 85, 99) and to correct the possible co-elution with linear alkyl benzenes (m/z: 91 and 105). The UCM was quantified based on total surface area and the response factor of resolved n-alkanes. Dioxin-like PCBs were analyzed by HRGC with ECD detection with confirmation by GC–MS in ion selective mode (m/z 290, 292, 326, 328, 360, 362) using authentic standards (IUPAC No. 77, 105, 118, 123, 126, 157, 167, 169, 189; AccuStandard Inc.). Method precision evaluated through repeated analysis of an internal reference fish material prepared with Rio de la Plata *P. lineatus* muscle averaged 16% ($n = 5$) for aliphatic hydrocarbons.

The analysis of PCBs, POCLs, CBzs, toxaphene and PBDEs was performed as described by Muir et al. (2004). In brief, lipid extracts diluted with hexane:dichloromethane (DCM) 1:1 were spiked with internal recovery surrogates of 1,3-dibromobenzene (1,3-DBB), endrin ketone, PCB-30 and PCB 204. The extract was reduced to approximately 1 mL volume on a rotary evaporator and lipid was removed by automated gel permeation chromatography (GPC; Bio-Beads SX3 column). The extract was then evaporated and exchanged into hexane and reduced to 1 mL. Extractable lipids were determined gravimetrically in the discarded fraction from the GPC column. Sample extracts were fractionated on a 100% activated silica gel column to separate PCBs from other POCLs including HCH isomers and chlorinated bornane components (toxaphene). The column was eluted into two fractions. Fraction 1 (hexane) contained PCBs, p,p′-DDE and toxaphene congener B8-1413 (Parlar 26) and PBDE congener 47 (BDE47). Fraction 2 (DCM:hexane 50:50) contained chlordane and DDT-related compounds, toxaphene congeners and other PBDEs. PCB congeners and organochlorine pesticides were determined by high resolution capillary gas chromatograph (GC) with electron capture detection using a Hewlett Packard 6890 GC equipped with a

30 m × 0.25 mm, 0.25 μm film thickness DB-5 column programmed at 15 °C min^{-1} to 150 °C and 3 °C min^{-1} to 265 °C. Carrier gas was H2 (about 1 mL min^{-1}) and make-up gas was N2 (40 mL min^{-1}). PCB congeners and OC pesticides were quantified by GC-ECD using a series of external standards based on a five-point calibration curve. Cod liver oil SRM 1588a (National Institute of Standards and Technology, Gaithersburg MD) was analyzed with the seven samples. Results averaged within 25% of certified values for 32 certified analytes.

Toxaphene and PBDEs were determined by GC–mass spectrometry in electron capture negative chemical ionization (ECNI) mode (Muir et al., 2004, 2006) using an Agilent 6890 GC-5973 MSD with an HP5-MS capillary column (30 m × 0.25 mm × 0.25 μm). All PBDEs were monitored at *m/z* 79/81 and were quantified using an external standard consisting of 36 congeners (BDEs 7, 8, 10, 11, 12–13, 15, 30, 32, 28–33, 35, 37, 49, 47, 66, 71, 75, 77, 85, 99, 100, 105, 119, 116, 155–126, 138, 140, 153, 154, 166, 181, 183, 190). In the case of toxaphene, hexa- (*m/z* 309–311), hepta- (*m/z* 343–345), octa-(*m/z* 377–379), and nonachlorobornanes (*m/z* 411–413) were monitored by selected ion monitoring in ECNI mode. Individual congeners were quantified with a series of authentic external standards of each compound obtained from Ehrenstorfer GmbH (Germany) (Muir et al., 2004). Total toxaphene was quantified by a single response factor based on a technical toxaphene standard. Results for BDE 47, 99 and 100, as well as for total toxaphene and congeners B8-1413 (P26) and B9-1679 (P50) were within 25% of reference values (NIST, 2007).

The analysis of PCDD/Fs PCBs followed the method described by Gardinali et al. (1996) after spiking with isotopically ($^{13}C_{12}$) labeled 2,3,7,8-subsitituted PCDD/Fs (Cambridge Isotope Laboratories, Andover, Massachusetts, USA). Briefly, the sample extract was initially run through a mixed-bed silica column with a mixture of concentrated sulfuric acid/silica gel (Silica Gel 60, EM Science, Gibbstown, New Jersey, USA) to remove lipids and further purified by basic alumina column (Alumina, Activated, 80–200 mesh, EM Science, Gibbstown, New Jersey, USA) followed by charcoal column fractionation (20:1 mixture of Silica Gel 60, EM Science, Gibbstown, New Jersey, USA and AX-21 Super Activated Carbon, Anderson Inc., Adrian, Michigan, USA). The analysis of PCDD/Fs was performed on a VG Autospec Ultima (VG Analytical, Manchester, UK) double focusing instrument working at >10 000 resolution power (10% valley) in electron impact mode at 36 eV coupled to a HP-5890 Series11 gas chromatograph (Hewlett–Packard, Wilmington, Delaware, USA). PCDD's and PCDF's are analyzed according to previously reported methods (USEPA, 1990) against authentic standards (Cambridge Isotope Laboratories, Andover, Massachusetts, USA).

3. Results and discussion

3.1. Total contaminant concentrations

Table 1 presents the size, weight and lipid content of fish and the total fresh weight contaminant concentrations. Sábalo muscles are remarkably fatty (74 ± 9.3% lipids) reflecting the facilitated absorption of organic matter from sewage-industrial particles which are enriched in organic carbon (8.7 ± 6.2% vs. 0.7 ± 0.4%) and labile components (i.e. fatty acids, proteins) relative to natural detritus (Speranza and Colombo, 2009). The concomitant uptake of organic pollutants is evidenced by the very high and relatively uniform levels registered in fish muscles (Table 1). The UCM, typical petrogenic hump between n-C_{15-25}, and ALI range from 60 to 1300 μg g^{-1} fresh weight with a relative standard deviation (SD) of 37–51%. LABs and PCBs follow in the 10–40 μg g^{-1} range with ~25% variability; 1–2 orders of magnitude below follow dlPCBs, DDTs, CHLDs, CBzs, and PBDEs in the 0.1–1 μg g^{-1} range with 25–55% SD; mirex, endosulfans and drins (aldrin, dieldrin, endrin) range from 0.01 to 0.1 μg g^{-1}, 9–69% SD; and PCDD/Fs in the low ppt range (145 ± 55 pg g^{-1} fresh weight; SD: 38%). Sábalos collected in northern sites (Goya, Empedrado) present similar lipid contents and pollutant loads than Río de la Plata fish indicating a

Table 1
Morphometric parameters and total concentrations of organic pollutants in fish.

	EMP	GOY	BA Dec. 2003	BA Dec. 2003	BA Feb. 2004	BA May 2004	BA Sep. 2004	Mean	SD
Length (cm)	50.5	48.3	43	50.5	49	50.5	48	48.2	2.8
Weight (kg)	4.1	4.07	2.64	4.24	3.56	3.92	3.89	3.8	0.5
Lipids (% dw)	87.1	80.4	79.6	77.2	67.2	64.0	63.1	74.1	9.3
μg g^{-1} fw									
ALI	222.0	184.9	66.9	118.1	74.9	121.2	58.8	121.0	62.2
UCM	1287.1	1028.3	750.7	581.8	533.6	719.5	507.0	772.6	287.9
LABs	23.8	25.0	35.4	35.6	39.4	21.4	26.2	29.5	7.1
PCBs	12.6	11.0	16.0	17.2	10.2	9.5	10.1	12.4	3.1
dlPCBs	1.10	0.81	0.53	0.59	0.29	0.49	0.28	0.58	0.29
HCHs	0.011	0.009	0.002	0.018	0.001	0.010	0.013	0.009	0.006
CHLDs	0.60	0.34	0.16	0.45	0.09	0.26	0.28	0.31	0.17
DDTs	0.50	0.34	0.38	0.38	0.22	0.27	0.27	0.34	0.09
tCHLPs	1.25	0.82	0.62	1.01	0.38	0.66	0.68	0.77	0.29
CBzs	0.23	0.27	0.22	0.44	0.21	0.37	0.50	0.32	0.12
PBDEs	0.24	0.19	0.22	0.17	0.16	0.13	0.12	0.18	0.04
pg g^{-1} fw									
PCDD/Fs	193.9	75.3	257.2	171.2	202.8	131.5	68.7	157.2	69.3
TEQs (pg g^{-1} fw)									
dlPCBs	311.7	310.0	250.0	358.9	122.7	87.7	48.8	212.8	124.3
PCDD/F	62.2	21.2	25.4	35.6	46.9	34.8	11.6	34.0	16.9
Total	373.9	331.2	275.4	394.5	169.6	122.5	60.4	246.8	130.4

EMP: Empedrado; GOY: Goya, northern sites; BA: Metropolitan Buenos Aires; dw: dry weight; fw: fresh weight; SD: standard deviation; ALI: C12–25 resolved aliphatic hydrocarbons plus four isoprenoids (*n* = 18); UCM: unresolved aliphatic complex mixture; LABs: C10–14 linear alkyl benzenes (*n* = 21); PCBs: mono-deca polychlorinated biphenyls (*n* = 103); dlPCBs: dioxin-llike PCBs (mono and no-ortho substituted; *n* = 9); HCHs: hexachloro cyclo hexanes; CHLDs: heptachlor and epoxide, oxychlordane, trans and cis chlordanes and nonachlors; DDTs: p,p and o,p DDE, DDD and DDT; tCHLPs: total chlorinated pesticides (*n* = 22); CBzs: di-hexa chlorobenzenes (*n* = 9); PBDEs: tri-hexa polybrominated diphenyl ethers (*n* = 13); PCDD/Fs: tetra-octa polychlorinated dibenzo dioxins and furans (*n* = 17); TEQs: WHO toxicity equivalents.

common provenance (see composition) and the preservation of fatty reserves and associated pollutants along the 700–850 km upriver migration. In contrast to salmons which exhaust their fatty reserves leading to a POPs magnification during migration (Debruyn et al., 2004), the abundant visceral fat of the Sábalo (~7% body weight) is sufficient to sustain the energetic demand of migration (Speranza and Colombo, 2009).

The analysis of toxaphene residues in both northern fish samples indicated moderate levels (0.05 μg g^{-1} fw) with a clear predominance of hepta homologs (79–85%) and B7-1450 as the major congener followed by B8-2229, an order of magnitude below. These concentrations are lower than those registered in Lake Trout from Lake Superior (0.89 ± 0.90 μg g^{-1} fw) and Lake Michigan (0.44 ± 0.16 μg g^{-1} fw) but similar than those from Lake Siskiwit (0.06 ± 0.03 μg g^{-1} fw; Stapleton et al., 2001; Muir et al., 2004).

The scarcity of comprehensive multi-contaminant surveys in fish and differences in concentration units in which are expressed the results (dry, fresh or lipid weight), makes difficult the comparison of the data. However, as a general trend, the concentrations in Sábalos are among the highest reported for fish, only comparable to those from polluted Great Lakes Salmonids and Hudson River Stripped Bass. Hydrocarbons are particularly difficult to compare since they have not been measured on a routine basis in fresh water fish, but reported concentrations of resolved aliphatics are normally in the low μg g^{-1} range, i.e. 0.17–1.96 and 1.7–26 μg g^{-1} fresh weight in Texoma Lake and Arkansas River (Martin, 1992; Baker et al., 1995). Within the large PCB data base, only polluted Great Lakes salmonids and carps, and Hudson River Stripped Bass present concentrations in the 1–10 μg g^{-1} fresh weight range as observed in Sábalos (Rasmussen et al., 1990; Oliver and Niimi, 1988; Ashley et al., 2000; Kannan et al., 2000; Jackson et al., 2001). The concentrations of LABs in Sábalos are 1–2 orders of magnitude higher than those reported for Southern California White Croaker impacted by sewage discharges, i.e. 0.17–0.75 μg g^{-1} fresh weight (Phillips et al., 2001). Sábalo PBDE levels are also in the high range of reported values; e.g. 0.008–0.17 μg g^{-1} fresh weight in Washington Rainbow Trout, Carps and Channel Catfish (Jackson et al., 2001), 0.08 μg g^{-1} in Lake Ontario salmonids, (Manchester-Neesvig et al., 2001), 0.05–0.13 μg g^{-1} in mountain White Fish, (Rieck, 2004) and 0.0004–0.57 μg g^{-1} fresh weight in Bleak fish from Cinca River, Spain, (Eljarrat et al., 2005), but are lower than the highest value reported for Virginia Carps, 1.1 μg g^{-1} fresh weight (Hale et al., 2001). The concentrations of PCDD/Fs in Sábalos are also high compared to other reports, 4–68 pg g^{-1} fresh weight in Buffalo River carp (Loganathan et al., 1995) and 176–214 pg g^{-1} in Great Lakes trout and carp (Niimi, 1996; Tillit et al., 1996). Chlorinated pesticides appear in a lower level again comparable to data published for Great Lakes fish, i.e. DDTs: 0.04–0.6 μg g^{-1} fresh weight (Giesy et al., 1994); DDTs: 0.17 μg g^{-1} fresh weight in Lake Ontario Chinook salmon (O'Toole et al., 2006).

The exceptionally high contaminant levels of Sábalos reflect a chronic exposure to crude effluent discharges to the Rio de la Plata and point out the remarkable ability of this fish to benefit from feeding on sewage and industrial organic-enriched particles while tolerating a high pollutant load. This is probably linked to a physiological–biochemical or genetic adaptation to minimize toxic effects as has been observed in other fish living in contaminated sites (Nacci et al., 2009, 2010). As a specialized detritivore, the energy benefit of this feeding strategy is based on the significant organic enrichment of anthropogenic particles (Speranza and Colombo, 2009). Compared to bottom sediments, the biochemical composition of settling material from Metropolitan Buenos Aires coast is enriched in organic carbon (8.7 ± 6.2% vs. 0.6 ± 0.5% dw), lipids (1.9 ± 2.0% vs. 0.5 ± 0.4%), proteins (3.2 ± 2.8% vs. 1.4 ± 0.9%) and carbohydrates (3.6 ± 3.1% vs. 1.7 ± 2.2%), and is similar to the stomach contents of the fish (lipids: 2.4 ± 2.9%, proteins: 2.0 ± 1.6%, carbohydrates: 5.4 ± 2.9%). This industrial-sewage material is the principal feeding resource of Sábalos, allowing an enhanced growth and fat accumulation in the Río de la Plata compared to the Northern basin where the diet is composed of organic-poor vegetal detritus (Speranza and Colombo, 2009).

3.2. Fish consumption limits and contaminant risk ranking

In order to estimate recommended fish consumption limits according to Sábalo's contaminant levels and prioritize the risks for the human population, allowable consumption limits were calculated based on available reference doses (EPA IRIS). In the case of aliphatic hydrocarbons, the reference dose of most toxic C_{6-16} alkanes (0.03 mg kg^{-1} d^{-1}; EPA, 2006) and their average abundance in fish (39 ± 3.8% of total hydrocarbons) were considered. For LABs, the reference dose was estimated from the no observed adverse effect levels (NOAEL) for reproductive toxicity in rats (5 mg kg^{-1} d^{-1}; Robinson and Schroeder, 1992) applying a 10-fold uncertainty factor. In the case of PCDD/Fs and dlPCBs the FAO/WHO 70 pg TEQ kg^{-1} $month^{-1}$ reference dose was considered (JECFA, 2001). Fig. 2 presents fish consumption limits calculated for a 70 kg person in a decreasing order and contaminant reference doses in logarithmic scale.

As expected from the high PCB concentrations of Sábalos which are sixfold higher than the 2 ppm guideline for human consumption (USFDA, 2006), these are the most critical residues with the lowest daily consumption limit (0.1 g). In a decreasing risk order follows dlPCBs (0.8 g) and PCDD/Fs (4.8 g d^{-1}). Surprisingly, the next most hazardous compounds in Sábalos are aliphatic hydrocarbons which are not very toxic with reference doses 3–7 orders of magnitude higher than PCBs and PCDD/Fs but reach ~0.1% by weight in fish muscle. PBDEs present a consumption limit comparable to aliphatic hydrocarbons (~40 g d^{-1}), although the reference dose is five orders of magnitude lower and fish concentrations ~1000 times lower. DDTs and Chlordane follow allowing a consumption of about 100 g fish per day. The consumption limits increase to 100–1000 g per day for drins and mirex and are highest for LABs, CBzs, HCHs, and endosulfan which are the least hazardous residues in fish (1000–10 000 g d^{-1}). On a longer-term basis, the no-consumption limit of half a meal (227 g) of fish per month is exceeded by PCDD/Fs which are the third most critical residues.

3.3. Contaminant composition

Figs. 3 and 4 present the composition of organic contaminants in Sábalo muscles compared to fresh sources (i.e. a crude oil, LAB, Aroclor and PBDE mixtures) with individual components grouped by carbon, chlorine or bromine contents. For aliphatic hydrocarbons, potential biogenic inputs from algae (n-$C_{15,17}$), petrogenic labile (<C_{20}: n-C_{12-19}) and more recalcitrant components (isoprenoids: farnesane, norpristane, pristane and phytane), and

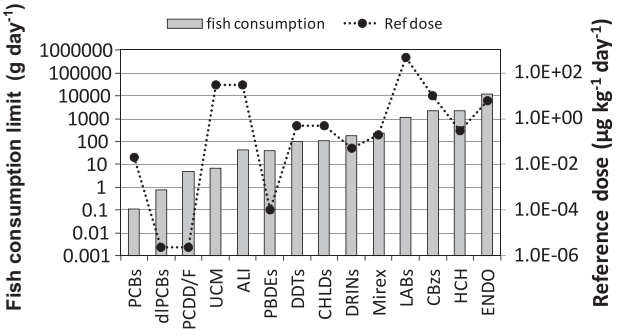

Fig. 2. Fish consumption limits calculated for a 70 kg person based on available reference doses (logarithmic scale) in a decreasing risk order.

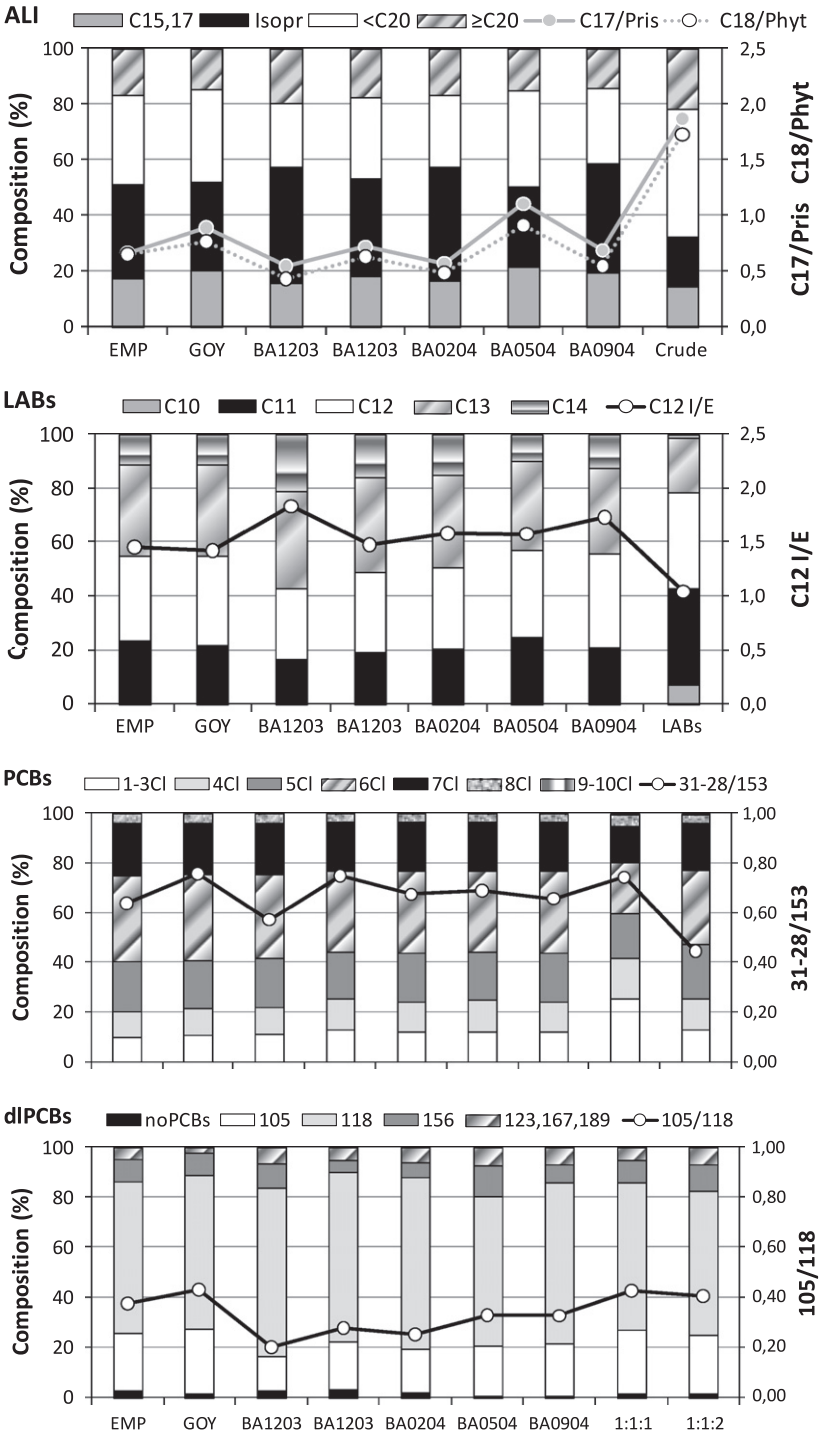

Fig. 3. Relative abundance of major compounds grouped by carbon or chlorine contents and compositional ratios of aliphatic hydrocarbons, linear alkylbenzenes, PCBs and dlPCBs in fish muscles (noPCBs: non-ortho PCBs).

higher molecular weight n-alkanes ($\geqslant C_{20}$: n-C_{20-25}) were discriminated. Selected compositional ratios are also shown to evaluate the relative change of the signatures.

The general composition of resolved C_{12-25} aliphatic hydrocarbons in Sábalos shows a dominant contribution of lower molecular weight n-alkanes (C_{15-17} = 19 ± 2.2%; $<C_{20}$ = 29 ± 4.5%), followed by isoprenoids (36 ± 5.0%) and $\geqslant C_{20}$ n-alkanes (16 ± 2.0%). This pattern is enriched in n-C_{15-17} and specially isoprenoids relative to the fresh crude oil (15% and 18%, respectively). The higher proportion of n-$C_{15,17}$ in Sábalos may reflect some contribution of plankton-derived $C_{15,17}$ (Colombo et al., 2007b). However, the aliphatic profile of fish has a clear petrogenic signature with an incipient alteration as indicated by the lower abundance of $<C_{20}$ relative to crude oil (29% vs. 46%), enrichment of more persistent isoprenoids (36% vs. 18%) and UCM compared to resolved components (UCM/ALI: 7.0 ± 2.2 vs. 1.1) and the lower C_{17}/Pris (0.7 ± 0.2 vs. 1.9) and C_{18}/Phyt ratios (0.6 ± 0.2 vs. 1.7 in the crude; Fig. 3). The variation of these parameters in the individual samples indicate that fish from Buenos Aires from December 2003 and February 2004 present the most degraded aliphatic signature (higher isoprenoids and lower ratios) whereas fish from May 2004 show the opposite fresher pattern (Fig. 3). Considering the relative high

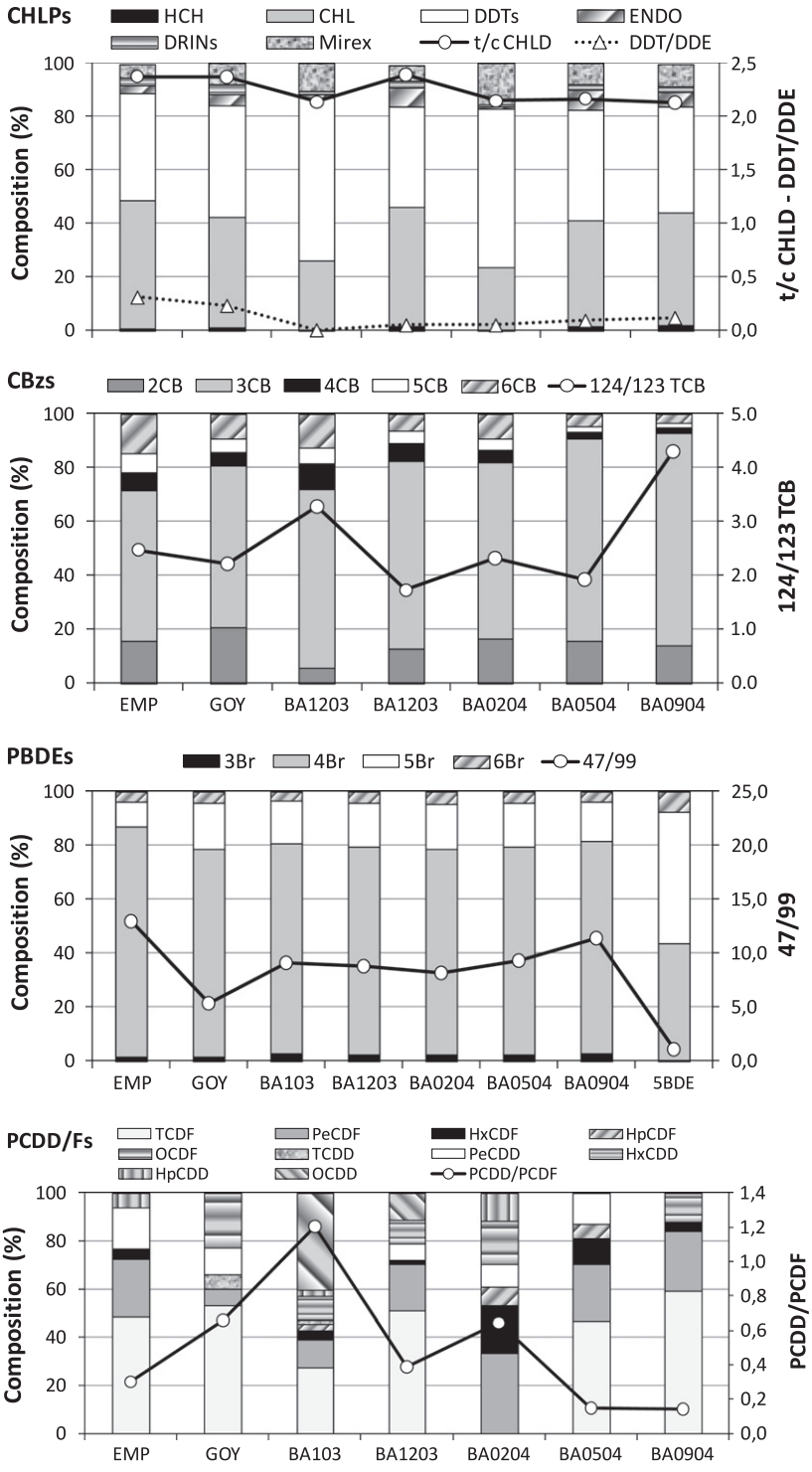

Fig. 4. Relative abundance of major compounds grouped by chlorine or bromine contents and compositional ratios of chlorinated pesticides (CHLPs), chlorobenzenes (CBzs), PBDEs (5BDE: penta-brominated commercial mixture) and PCDD/Fs in fish muscles.

susceptibility to degradation of aliphatics, the hydrocarbon signature of Sábalos looks surprisingly fresh with still abundant lower molecular weight components. This supports the interpretation that Sábalos feed on recently-decanted flocculent matter. Sedimentary hydrocarbons in contrast, are extensively degraded as indicate the lower n-C_{17}/Pris (0.5 ± 0.2) and n-C_{18}/Phyt ratios (0.4 ± 0.3) and higher UCM proportion (UCM/ALI = 49 ± 31; Colombo et al., 2005a).

The composition of LABs in fish muscles shows a fairly homogeneous contribution of isomers with 11–13 carbons which account for a grand mean average of 85% (C_{11} = 20 ± 2.8%, C_{12} = 31 ± 2.9%, C_{13} = 34 ± 1.5%), followed by C_{14} (14 ± 3.8%) and minor amounts of C_{10} LABs (0.6 ± 0.3%). Compared to the local fresh LABs mixture, this signature is depleted in low molecular weight LABs (i.e. C_{11}: 20% vs. 36%, and specially C_{10}: 0.6% vs. 7.1%), and enriched in C_{13} (34% vs. 20%) and C_{14} components (14% vs. 1.4% in the LAB formulation; Fig. 3), suggesting also an incipient decay. The ratio of internal to external C_{12} isomers (I/E = 6C_{12}–5C_{12}/4C_{12}, 3C_{12}, 2C_{12}; Fig. 3), indicative of LABs biodegradation due to more rapid attack of external isomers, is higher in the Sábalos (1.6 ± 0.2) relative to

the fresh LAB formulation ($I/E \sim 1.0$), supporting an initial alteration. In agreement with hydrocarbon data, fish from Buenos Aires December 2003 also present the most degraded LAB pattern (lower C_{12-13} and higher C_{14} and C_{12} I/E ratio), but the other samples look more conservative probably reflecting the higher recalcitrance of LABs compared to hydrocarbons (Colombo et al., 2007a).

As observed for ALI and LABs, the composition of PCBs in fish muscles is relatively homogeneous with a prevailing contribution of penta, hexa and heptachlorobiphenyls which collectively account for average 73% of total PCBs (5 Cl = 20 ± 0.4%, 6 Cl = 34 ± 0.9%, 7 Cl = 20 ± 0.6%), followed by tetra (4 Cl = 12 ± 0.9%), monotri (1–3 Cl = 12 ± 1.1%), octa (8 Cl = 3.5 ± 0.2%) and nona-deca chlorobiphenyls (9–10 Cl = 0.2 ± 0.03%). This average composition is similar to a 1:1:2 Aroclor 1242:1254:1260 mixture (Fig. 3). However, the ratio of tri to hexachlorobiphenyls 31 + 28/153 in the fish are closer to a 1:1:1 Aroclor mix, suggesting that other lower chlorinated PCBs than 31–28 abundant in Aroclor 1242 are depleted in the fish resulting in a general pattern resembling the higher chlorinated 1:1:2 Aroclor proportion. Interesting, the 31 + 28/153 ratio is lowest in Sábalos from Buenos Aires December 2003, which in view of the higher susceptibility to microbial attack of lower chlorinated congeners, supports the stronger alteration observed for ALI and LABs which are more susceptible to decay than PCBs.

The composition of dlPCBs is dominated by pentachlorobiphenyls, especially 118 (64 ± 3.7%) and 105 (20 ± 4.0%), followed by hexachlorobiphenyl 156 (8.4 ± 2.6%), and lower proportions of penta-heptachlorobiphenils 123, 167, 189 (5.5 ± 1.7%) whereas no-ortho PCBs (tetra 77, penta 126, and hexaCB 169) account for a minor fraction of the total (2.2 ± 1.1%). This dlPCB composition in fish is similar to that of Aroclor mixtures with slightly lower proportions of 105 (20% vs. 23%) and higher of 118 (64% vs. 57%; Fig. 3), which may imply a selective preservation of 118. The 105/118 ratios in fish (0.31 ± 0.08) are generally lower than in Aroclor formulations (0.41–0.43), especially in the Sábalo from Buenos Aires December 2003 (0.20). In view of the behavior of compositional ratios of ALI, LABs and PCBs indicating a higher alteration in this sample, this lower 105/118 ratio supports a higher stability of 118. The proportion of coplanar PCBs in fish tends to be higher than in the Aroclor mixtures but the variability is large (0.8–3.5% vs. 1.7–1.9%).

Chlorinated pesticides show a clear predominance of DDTs (46 ± 9.8%) and chlordanes (38 ± 9.4%) accounting for 84% of total residues, followed by mirex (8.7 ± 3.5%) and endosulfans (4.1 ± 2.5%) and minor proportions of aldrin, dieldrin and endrin (drins: 2.2 ± 1.1%) and HCH isomers (1.1 ± 0.7%). The signature of chlordanes but specially that of DDTs indicate an alteration compared to fresh sources (Fig. 4). The trans/cis Chlordane ratio is uniformly higher in fish relative to a local chlordane mixture (2.2 ± 0.1 vs. 1.2) suggesting a selective preservation of the trans isomer as has been previously observed in Río de la Plata bivalves and fish (Colombo et al., 1995; Colombo et al., 2000). The alteration of DDTs residues is more extensive as indicate the very low proportion of the parent vs. derived components (DDT/DDE = 0.12 ± 0.11) reflecting an older signal compatible with the past utilization of this pesticide.

The composition of chlorobenzenes show a strong predominance of trichlorobenzenes (67 ± 8.0%) followed by 2CB (15 ± 4.6%) with lower proportions of tetra, penta and hexaCB (5.3 ± 2.6%, 4.3 ± 2.0% and 8.7 ± 4.1%, respectively; Fig. 4). The large abundance of 3CB could reflect its widespread use in industrial applications (e.g. solvents, chemical intermediates, lubricants), pesticide and herbicide formulations and/or its presence as a major component of old transformer dielectric fluids (e.g. Askarels) which are the principal source of PCBs in this coastal area (Colombo et al., 2005a). The imbalance of TCB and PCBs in fish (0.3 and 12 $\mu g\ g^{-1}$ fw) relative to the usual 35–65% proportion in Askarels could be related to the higher mobility (more volatile and water soluble) and lower persistence of TCB which lead to comparatively lower bioconcentration factors compared to penta-hepta PCBs (log BCF: 3.1–3.4 vs. ~5–6 for PCBs; Lu et al., 2000).

PBDEs present a major and uniform contribution of tetra-brominated components (78 ± 3.1%) basically PBDE 47 (74 ± 5.2%), followed by 5 Br PBDEs (15 ± 2.7%) composed by comparable contributions of congener 100 (6.6 ± 2.6%) and 99 (8.4 ± 2.6%), and minor proportions of 6 and 3 Br PBDEs (4.1 ± 0.4% and 2.4 ± 0.5%, respectively). As has been previously reported for fish (Hale et al., 2001; Ikonomou et al., 2006; Labandeira et al., 2007), this composition is significantly enriched in congener 47 compared to a penta-brominated commercial mixture (Fig. 4). The 47/99 ratio captures this difference increasing from 1.1 in the penta-brominated mixture to 9.3 ± 2.4 in the fish, possibly reflecting the selective biotransformation of 99 in favor of 47, i.e. de-bromination from 5 to 4 Br PBDE (Stapleton et al., 2004).

Within PCDD/Fs, polychlorinated dibenzofurans generally predominate accounting for 73 ± 11% of the total with a prevailing contribution of tetra (43 ± 20%) and penta PCDF congeners (21 ± 8.1%), and minor contributions of hexa (6.5 ± 6.7%) and hepta PCDFs (2.6 ± 3.4%) and none of octa PCDF. The 27% represented by dioxins is composed basically by hexa (11 ± 8.7%) and penta PCDDs (8.2 ± 6.4%) with reduced abundances of hepta (3.1 ± 4.6%), octa (2.9 ± 5.0%) and tetra PCDDs (1.3 ± 2.3%; Fig. 4). The general predominance of PCDF over PCDD and of lower chlorinated congeners could be related to the input of mixed industrial–urban effluents along the coast. However this pattern is also possibly shifted by the discrimination of higher molecular weight components abundant in air-borne PCDD/F sources (Armitage et al., 2009; Sundqvist et al., 2009) during intestine absorption. Further studies and a more precise local PCDD/Fs fingerprint characterization are needed to assess the prevalent sources of these compounds in the area.

3.4. Pollutant transport during migrations

Both the total contaminant load and the detailed composition of the different compounds (chemical signature) show a remarkable uniformity in all samples suggesting that fish collected 700–850 km north are in fact migrating specimens that feed in Metropolitan Buenos Aires coast. The 7-year database of Sábalos collected trimonthly at Buenos Aires indicate a consistent high-concentration, fresh pattern of aliphatic hydrocarbons and PCBs (Colombo et al., 2007b, 2007c), with contaminant levels 2–3 orders of magnitude higher than in extreme north (>1000 km) fish which show more degraded signatures enriched in recalcitrant components. Both fish ensembles could be also distinguished by morphometric and biochemical parameters, with southern fish being heavier (length/weight relationship ~3.5), fatty (>50%) and contaminated compared with lean, non-polluted north fish (Speranza and Colombo, 2009). As indicated previously, Sábalos are a predominant component of the fish community of the basin totaling an estimated production ~70 000 tons $year^{-1}$ in the lower Río Paraná, Uruguay and Río de la Plata (23 500 km^2). Considering a total upward migration of Río de la Plata Sábalos ~3500 tons $year^{-1}$ distributed in different distant-ranges with most frequent recaptures (70%) in the 0–400 km range and the rest up to 500–1500 km (Sverlij et al., 1993), the annual transport of contaminants would amount to >3 tons hydrocarbons (ALI + UCM), 100 kg LABs, 40 kg PCBs, 2 kg dlPCBs, 1 kg each of CHLDs, DDTs and CBzs, and 0.6 kg PBDEs as major pollutants.

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