

Bioaccumulation of dioxin-like PCBs and PBDEs by detritus-feeding fish in the Rio de la Plata estuary, Argentina

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Abstract A comparative analysis of bioaccumulation behavior of dioxin-like polychlorinated biphenyls (dlPCBs) and polybrominated biphenyl ethers (PBDEs) was conducted involving simultaneous measurements in settling particles and a detritivorous fish (Sabalo, *Prochilodus lineatus*) collected in the sewage impacted Buenos Aires coastal area. Focalization of dlPCBs and PBDEs along the detritus food chain is reflected by a 30–40-fold increase of dry weight PBDE and dlPCB concentrations from settling particles to fish (1.8 ± 1.0 to 58 ± 31 and 6.8 ± 3.9 to 281 ± 155 ng g⁻¹ dry weight (dw), respectively). In this transference, dlPCB congeners presented more conservative patterns than those of PBDEs, basically due to debromination of BDE 99 and 153 to BDE 47 in fish. Lipid/organic carbon-based biota-sediment accumulation factors (BSAFs) ranged between 5 and 20 (7.3 ± 3.0 and 16 ± 8.0 for PBDEs and dlPCBs). Congener-specific BSAF of dlPCBs suggested a lower bioavailability of more planar *non-ortho*-PCB versus *mono-ortho*-PCB suggesting higher affinity to

organic matter. BSAFs of PBDEs differed markedly among bromine homolog groups, supporting the biotransformation-formation from higher brominated to lighter congeners. The log BSAFs-log K_{OW} relationship of dlPCBs and PBDEs presented a parabolic pattern maximizing at log K_{OW} 6–7, but PBDE curve differs reflecting biotransformation processes.

Keywords Dioxin-like PCB · PBDE · Biota-sediment accumulation factors (BSAFs) · Detritivorous · Rio de la Plata

Introduction

Hydrophobic organic pollutants like polychlorinated biphenyls (PCBs) and polybrominated biphenyl ethers (PBDEs) have a well-known affinity for organic phases and a prevailing particulated oriented behavior during their transport, distribution, and final deposition (Grant et al. 2011). Due to their deleterious effects in biota, PCBs and PBDEs are of national, regional, and global concern (UNEP 2009). Risk evaluation has been focused on a subset of 12 PCB congeners (*non-ortho*-PCB and *mono-ortho*-PCB) with similar toxic mechanisms to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (“dioxin-like PCBs” (dlPCBs); Van den Berg et al. 2006). PBDEs and PCBs present some similarities in terms of molecular and physicochemical properties. However, the ether linkage of PBDEs and the differential strength of bromine and chlorine bonds condition PBDE stability and thus determine a different environmental fate (Puzyn et al. 2008; Rodenburg et al. 2014).

Because of their persistence and bioaccumulation potential, focalization of these pollutants along the detritus food chain becomes a critical pathway for the contamination of aquatic biota and trophic transfer to humans (Zhou and Wong 2000). Bioaccumulation has a direct relationship with food digestibility (Arnot and Gobas 2004) and detritus-feeding fish optimize the ingestion of organic-rich particles, thus increasing

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the efficiency of pollutant bioaccumulation (Lee et al. 1990). This process is exacerbated when highly specialized detritus-feeding fish constitutes the basis of the trophic chain and a dominant component of fish community and freshwater captures, such as the Sabalo (*Prochilodus lineatus*) in the Rio de la Plata estuary (Colombo et al. 2000). Effectively, the large discharges of untreated effluents in the Rio de la Plata estuary (e.g., main Buenos Aires sewer at Berazategui: two million cubic meters per day; Cirelli and Ojeda 2008) and the dominance of the strict detritivorous Sabalo, which feed directly on anthropogenic organic matter (Speranza et al. 2013), generate a critical focusing pathway of persistent organic pollutants such as PCBs and PBDEs (Colombo et al. 2011).

In this study, we evaluate the concentrations and congener profiles of dlPCBs and PBDEs in *P. lineatus* muscle and detritus (settling particles), in order to assess the congener-specific bioaccumulation from diet, investigate the potential for biotransformation, and explore the relationship between bioaccumulation and physicochemical properties of compounds.

Methods

Field sampling was conducted each 3–4 months from March 2005 through September 2006 in the coastal area of Rio de la Plata (Fig. 1). A total of 37 fish were obtained from local fisherman. Immediately after the capture, fish were measured, weighed, and dissected to obtain a 10–30-g sample of dorso-lateral muscle. Samples were wrapped in clean aluminum foil

and freezed until analysis. Simultaneously to fish sampling, nine 10-cm-diameter sediment traps were deployed at 1.5-m depth during 20–48h in the sewer area to collect the settling material.

In the laboratory, fish muscle samples were pooled (two to five individuals) according to the size and weight of the fish based on the condition index:

$$CI = \text{total body weight (g)} / \text{standard length (cm)}^3$$

The pooling criteria was adjusted to discriminate small (<1 kg), medium (>1–2.5 kg), large (>2.5–3.5 kg), and very large fish (>3.5–4.5 kg) with similar CI. Fish with dissimilar morphometric characteristics were processed individually. A total of 15 samples were analyzed. Fish muscles sample were processed with 250-W blenders in glass jars using different equipment for small, medium, and large fish. All materials used were washed with hot water and detergent and rinsed with tap and distilled water, with a final rinse with pesticide grade petroleum ether (EP).

The homogenized muscle samples were splitted for the determination of water content (100 °C, 24 h) and for chemical analyses (Colombo et al. 2005). Prior to extraction, each sample was spiked with PCBs 103 and 198 (Absolute Standard, Inc.). Approximately 12 g of blended tissues were mixed with pre-extracted anhydrous sodium sulfate (1:3) and Soxhlet-extracted with acetone, dichloromethane, and EP (1:2:2). The extract was reduced to 3 ml, transferred to centrifuge tubes, and concentrated to constant weight under nitrogen to determine total lipids. An aliquot of 200-mg lipids was



Fig. 1 Sampling station of *Prochilodus lineatus* and settling particles in the Rio de la Plata estuary

redissolved in EP and treated with sulfuric acid to partially remove the lipid material. The supernatant phase was concentrated under nitrogen and fractionated on successive chromatography on silica gel and silica gel-charcoal columns.

The trap material was immediately centrifuged and splitted for total organic carbon and nitrogen analysis (TOC-TN: catalytic combustion; ThermoFinnigan, CEFlashEA 1112 elemental analyzer) and for the determination of trace organics. Air-dried samples were spiked with internal standards (PCBs 103 and 198) and ultrasonically extracted with acetone/dichloromethane/EP (1:2:2). The extracts were concentrated under nitrogen, treated with activated copper and fractionated on successive chromatography on silica gel and silica gel-charcoal columns.

dIPCBs were quantified by high-resolution gas chromatography (GC Agilent 6890 and 6850) using 30-m-length DB 5 MS columns and equipped with a ^{63}Ni electron capture detector (*mono-ortho*-PCBs) and mass spectrometer (5973N) used to confirm *mono-ortho*-PCBs and mandatory to quantify *non-ortho*-PCBs. The mass detector was operated in SIM mode at m/z 290 and 292, 324 and 326, 354 and 358, and 392 and 394 to identify tetra-, penta-, hexa-, and hepta-CBs, respectively. Quantification was performed using an external standard of 28 congeners (Accustandard C-WNN; five-point calibration curve). PBDEs were analyzed by high-resolution gas chromatography/mass spectrometry using negative chemical ionization mode (Perkin Elmer Clarus 500) in simultaneous scan (m/z 70–700) and SIM modes (m/z 79 and 81) and a 30-m DB 5 MS column. Quantification was done with an external standard of 39 PBDEs (Accustandard BDE-AAP-A; four-point calibration curve).

The detection limits (3:1 signal versus noise value) ranged between 4–19 pg g^{-1} for dIPCBs and 2–6 pg g^{-1} for PBDEs in dry trap material, and 20–90 pg g^{-1} for dIPCBs and 11–29 pg g^{-1} for PBDEs in dry fish muscle. Procedural and instrumental blanks (one for every batch of twelve samples) were below the detection limits, and surrogate recovery ranged between 60 and 110 %.

Concentration of dIPCBs and PBDEs are expressed in dry weight (dw), wet weight (ww), lipid weight (lw), or TOC-normalized as indicated. The evaluation of dIPCB and PBDE profiles was carried out by principal component analysis using XLSTAT 2011 (Addinsoft).

Results and discussion

Total concentration of dIPCBs and PBDEs

Concentrations of dIPCBs and PBDEs (dry weigh, wet weight, and lipid/TOC basis) in fish muscle and settling particles, as well as relative abundance of individual congeners, are summarized in Table 1. On a dry weight basis, total

Table 1 Average dIPCB and PBDE concentrations in fish muscle and settling particles

	Relative abundance %			
	Settling particle		Fish muscle	
	Mean	DS	Mean	DS
dIPCBs congeners (%)				
77	3.7	1.8	3.3	2.1
126	0.5	0.2	0.3	0.1
169	0.8	1.2	0.1	0.1
105	19	5.0	17.1	2.5
118	47	6.0	54.3	3.8
123	6.7	2.6	4.4	4.6
156	13	3.3	13.0	1.2
167	5.4	1.8	6.0	0.8
189	4.2	5.3	1.4	0.4
Total dIPCBs (ng g^{-1} ww)			109	76
Total dIPCBs (ng g^{-1} dw)	6.8	3.9	281	155
Total dIPCBs (ng g^{-1} lipid/TOC)	67	26	770	219
TEQ (pg g^{-1} ww fish or dw particle)	4.5	2.8	43	29
PBDEs congeners (%)				
15	1.5	1.6	0.3	0.1
17	1.5	0.7	0.3	0.1
28/33	0.9	0.7	2.0	0.4
49	2.8	1.9	5.0	0.6
47	36	7.9	69	4.0
66	0.8	0.4	2.4	0.7
100	5.3	1.5	6.3	0.6
99	40	8.2	12	3.2
154	2.8	1.7	1.7	0.3
153	5.0	3.5	0.9	0.3
183	3.8	3.3	0.1	0.1
Total PBDEs (ng g^{-1} ww)			22	14
Total PBDEs (ng g^{-1} dw)	1.8	1.0	58	31
Total PBDEs (ng g^{-1} lipid/TOC)	25	22	166	67

dIPCB concentrations ranged from 1.2 to 14 ng g^{-1} ($6.8 \pm 3.9 \text{ ng g}^{-1}$) in settling particles and from 88 to 590 ng g^{-1} ($281 \pm 155 \text{ ng g}^{-1}$) in fish muscle. PBDE concentrations varied from 0.6 to 4.2 ng g^{-1} dw ($1.8 \pm 1.0 \text{ ng g}^{-1}$) in the trap material and 18 to 127 ng g^{-1} dw ($58 \pm 31 \text{ ng g}^{-1}$) in fish. These results imply a 30–40-fold average increase of dry weight PBDE and dIPCB concentrations from settling particles to fish (Fig. 2).

In the trap material, concentrations of dIPCBs and PBDEs were within the ranges reported for low to moderately impacted areas (Table 2). The mean dIPCB concentration ($6.8 \pm 3.9 \text{ ng g}^{-1}$ dw) is similar to values reported for settling matter from the Detroit (Marvin et al. 2002) and Niagara River (Marvin et al. 2007) and is one order of magnitude lower than values reported for the impacted Trenton Channel (Marvin

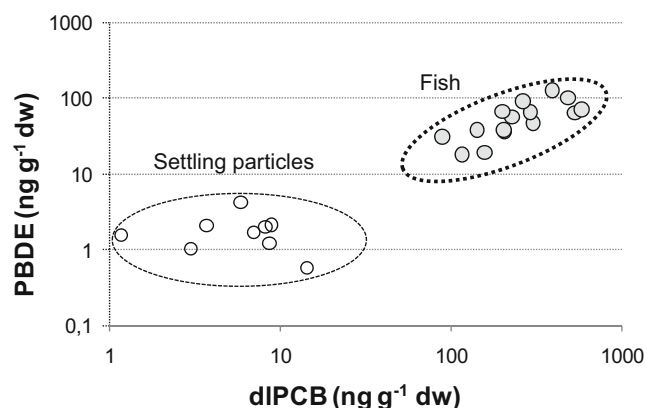


Fig. 2 dlPCB and PBDE concentrations (dry basis) in fish muscle and settling particles

et al. 2002). The total equivalent toxicity of dlPCBs calculated for the trap material was principally due to *non-ortho*-tetra-CB 126 ($60 \pm 24\%$) and *mono-ortho*-penta-CBs 156 and 118 (25 ± 20 and $18 \pm 14\%$, respectively). Mean PBDE concentration in settling particles was comparable to reports for suspended sediment from a non-impacted area of Lake Erie and lower than values published for the Niagara River (Marvin et al. 2007).

Compared with other fish reports, concentrations of dlPCBs and PBDEs in *P. lineatus* were comparable to results from moderate to highly polluted areas (Table 2). Average wet weight dlPCB concentrations are ~ 1 – 2 orders of magnitude higher than values reported for European eel from the Mondengo Estuary, Portugal (Nunes et al. 2011), and similar to Lake Ontario trout (Hickey et al. 2006). This trend is sustained even with lipid-normalized concentrations (770 ± 219 in *P. lineatus* vs $21 \text{ ng g}^{-1} \text{ lw}$ in eel and 356 – $2546 \text{ ng g}^{-1} \text{ lw}$ in trout). Mean TEQ concentration are similar

to reports for Great Lakes trout (Hickey et al. 2006) and various fish species from a superfund site in Kalamazoo River (Kay et al. 2005).

Average PBDE concentration in *P. lineatus* muscle was more than one order of magnitude higher than values reported for fish collected near populated areas in Swiss lakes (Zennegg et al. 2003) and comparable to reports for Lake Ontario smelt (Dodder et al. 2002). In contrast to dlPCBs, these differences are not maintained by lipid-normalized concentrations ($166 \pm 67 \text{ ng g}^{-1} \text{ lw}$ in *P. lineatus* vs 36 – $165 \text{ ng g}^{-1} \text{ lw}$ in Swiss Lakes and $240 \pm 30 \text{ ng g}^{-1} \text{ lw}$ in Lake Ontario).

dlPCB and PBDE congener profiles

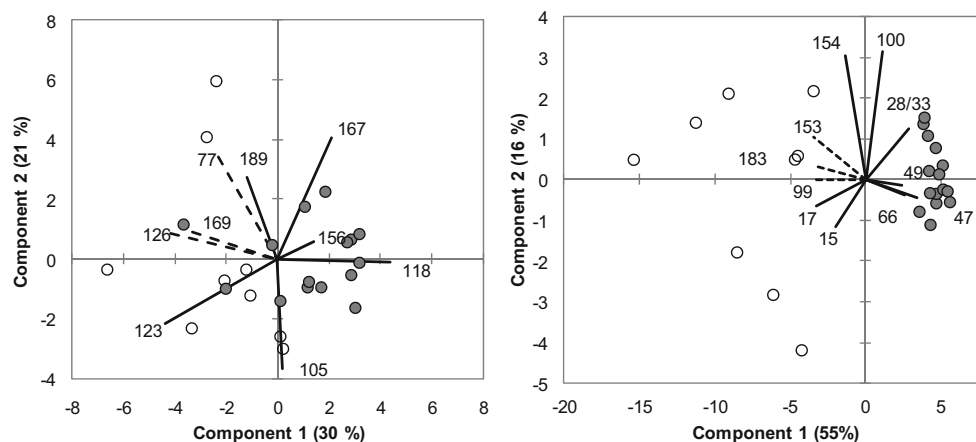
The composition of dlPCBs in the trap material and fish is relatively homogeneous, with a marked contribution of congeners 118, 105, and 156 (Table 1). In contrast, PBDEs show more contrasted compositional differences between both matrices (i.e., opposite patterns of 47 and 99). The detailed evaluation of dlPCB and PBDE profiles was carried out by principal component analysis (PCA) based on the relative contribution of individual congeners (9 dlPCBs and 12 PBDEs; Fig. 3).

In the case of dlPCBs, components 1 (PC1) and 2 (PC2) account for 51 % variability (30 and 21 %, respectively); PC1 has a prevailing contribution of CB 118 (positive) and CBs 77, 126, and 169 (negative), whereas PC2 is basically determined by CB 167 (positive) and CB 105 (negative). In spite of the general compositional homogeneity of dlPCBs, PCA results show trap samples mostly spread on the negative PC1 with stronger contribution of *non-ortho*-PCBs (CBs 77, 126, and 169), whereas fish samples are shifted to the positive side with higher proportions of hexa-CBs 156 and 167 and specially

Table 2 dlPCB and PBDE concentrations in particles and fish from the Rio de la Plata compared with other environments

Location		% Lipid	dlPCB	PBDE	TEQ	References
Trap/suspended sediment			ng g ⁻¹ dw	pg g ⁻¹ dw		
Rio de la Plata			6.8±3.9	1.8±1.0	4.5±2.8	This study
Detroit River			1.3–18		1.1–6.8	Marvin et al. (2002)
Trenton Channel			68–137		22–35	Marvin et al. (2002)
Lake Erie				<5		Marvin et al. (2007)
Niagara River (2002)			5	5–20		Marvin et al. (2007)
Fish species			ng g ⁻¹ ww	pg g ⁻¹ ww		
Rio de la Plata	Sabalo	14±7.6	109±76	22±14	43±29	This study
Lake Ontario	Smelt	7.8±1.0		18±1		Dodder et al. (2002))
Swiss lakes	Whitefish	4.5±1.7		1.6–7.4		Zennegg et al. (2003)
Kalamazoo River	Several species	3.7			51±27	Kay et al. (2005)
Lake Ontario	Trout	18±1.6	64–441		2–192	Hickey et al. (2006)
Mondengo Estuary	European eel	21	2.8			Nunes et al. (2011)

Fig. 3 Principal component analysis performed with relative abundance of individual dI PCBs and PBDEs in settling particles (open circles) and fish samples (gray circles)



mono-ortho-penta-CB 118 (46–60 % in fish vs 36–55 % in the trap material). The predominance of PCB 118 has been observed in different environmental matrices and along food webs (Nunes et al. 2011). This general dI PCB profile evidences a subtle shift of congener patterns from particles to fish probably reflecting the most favorable chemical properties (e.g., hydrophobicity, molecular size) of five to six CBs for bioaccumulation (Colombo et al. 2007; see next section on bioaccumulation factors).

In the PCA of PBDEs, the first two components explain 71 % of the total variability (55 % PC1 and 16 % PC2); PC1, defined by the opposing contribution of BDEs 28/33, 47, 49, and 66 (positive) and BDEs 17, 99, 153, and 183 (negative) is the most discriminative reflecting basically well-known debromination schemes reported for fish (i.e., 99→47; Stapleton et al. 2004; Echols et al. 2013; Mizakawa et al. 2013). PC2 has a dominant contribution of BDEs 100 and 154 which are more resistant to debromination (Roberts et al. 2011; Zeng et al. 2012). Due to the higher reactivity of PBDEs, their PCA produces a better discrimination of settling particles (negative PC1) with higher proportions of precursor congeners (i.e., BDE 99: 40 vs 12 % in fish; BDE 153: 4.9 vs 0.9 % in fish, Table 1), from fish samples (positive PC1) which

show higher proportions of debromination products (i.e., 47: 69 vs 35 % in the trap material, Table 1).

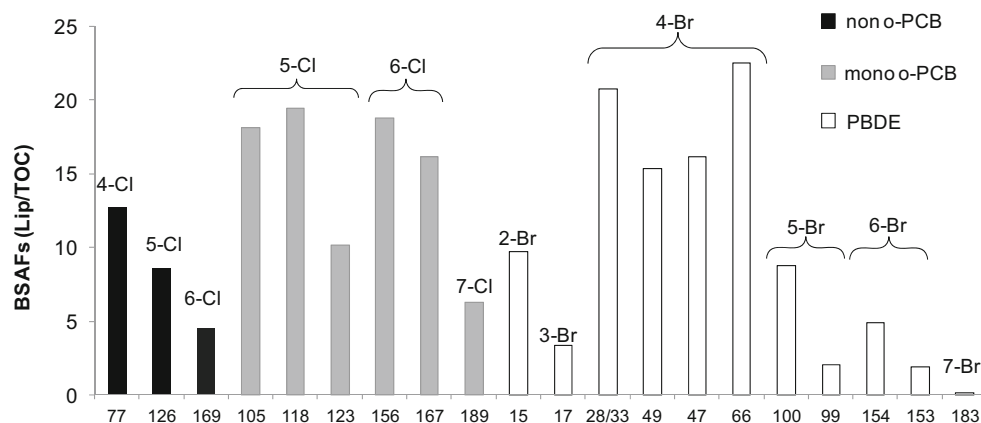
Summarizing, dI PCB patterns are more conservative than those of PBDEs but still display some subtle changes from settling particles to fish, whereas PBDE profiles display major differences following debromination patterns (enrichment of BDE 47 and reduction of BDEs 99 and 153).

dI PCB and PBDE bioaccumulation factors

The equilibrium partitioning between fat concentrations of aquatic organisms and organic carbon equivalent concentrations in sediments is reported as the biota-sediment accumulation factor (BSAF; Lee 1998). In the case of a strict detritus-feeding fish such as the Sabalo, this partition coefficient calculated with settling particle concentrations allows the evaluation of the absorption behavior along the most significant route of pollutant uptake (bioaccumulation or magnification through detritus). Fish muscle (lipid-normalized) and settling particles (TOC-normalized) BSAFs were thus calculated to evaluate the overall and congener-specific bioaccumulation dynamics of dI PCBs and PBDEs.

Most BSAFs range between 5 and 20, with some of the lowest values for PBDEs (Fig. 4). Consequently, average total

Fig. 4 Average biota-sediment accumulation factors (BSAFs) of individual *non-ortho*-PCBs (black), *mono-ortho*-PCBs (gray) and PBDEs (open bar)



BSAF of dIPCBs doubled that of PBDEs (16 ± 8.0 vs 7.3 ± 3.0). Congener-specific BSAFs of dIPCBs ranged from 4.6 to 19, comparable to values reported for crucian carp from Japan (1.6–26; Kajiwara et al. 2007) and for Lake Michigan's trout (0.3–14; Burkhard et al. 2004). BSAFs were relatively uniform for four to six chlorine dIPCBs (tetra, 13 ± 5.3 ; penta, 18 ± 10 ; hexa, 17 ± 8.0) but dropped markedly for hepta-CB (6.3 ± 3.5). Chlorine position showed a marked influence on BSAFs with higher values for *mono-ortho* relative to *non-ortho*-PCBs (15 ± 5 vs 8 ± 5), consistent with results reported for bass (Naito et al. 2003) and crucian carp from Japan (Kajiwara et al. 2007). These results emphasize the role of substitution pattern in the bioaccumulation of dIPCBs and suggest a lower bioavailability of more planar compounds due to their high affinity to organic matter (Jonker and Koelmans 2002).

BSAFs for PBDE congeners ranged from 0.1 to 23, comparable to Pearl River estuary fish reports (0.04–17; Xiang et al. 2007) but lower than Hadley Lake fish results (16–38; Dodder et al. 2002). In contrast to dIPCBs, BSAFs differed markedly among bromine homolog groups (Fig. 4). Lighter PBDEs presented higher BSAFs (tetra, 16 ± 10 ; tri, 8.2 ± 4.6 ; di, 6.0 ± 8.8) compared to heavier PBDEs (hexa, 2.9 ± 1.0 ; penta, 2.8 ± 0.9 ; hepta-BDE, 0.2 ± 0.2) reflecting their bioformation from higher brominated congeners. Metabolic degradation pathways such as *meta*- and *para*-debromination (Stapleton et al. 2004) would explain the lower BSAFs found for penta-BDE 99 and hexa-BDE 153 in this study (1.9–2.0). On the other side, bioformation of BDEs 47 and 49 explain the elevated BSAFs found for these congeners (15–16). The formation of tri-BDEs through further *meta*-, *ortho*-, and/or *para*-cleavage of bromine from BDEs 47, 49, and 66 has been also suggested (Isosaari et al. 2006; Munschy et al. 2011) and would explain the highest BSAFs observed in this study for tri-BDEs 28–33 (7–60).

In order to evaluate the role of physical-chemical properties in bioaccumulation, Fig. 5 presents the log BSAFs for individual dIPCBs and PBDEs plotted against their log octanol-

water partition coefficients (log K_{OW} ; Braekvelt et al. 2003; Paasivirta and Sinkkonen 2009). To compare dIPCBs and PBDE with *ortho*-PCBs, the previously reported *P. lineatus* particle BSAFs versus K_{OW} curve has been included as a solid, thicker line (log BSAFs = $0.38 \log K_{OW}^2 + 5.16 \log K_{OW} - 15.8$; $R^2 = 0.46$; Colombo et al. 2007). BSAFs for dIPCBs show a consistent decrease with increasing K_{OW} in the range (log $K_{OW} \geq 7$) where bioaccumulation factors are expected to decrease due to hydrophobic and steric hindrance effects (Oppenhuizen and Stokkel 1988; Burkhard et al. 2004). *Non-ortho*-PCBs display a lower curve than *mono-ortho*-PCBs, and both BSAF- K_{OW} curves plot below *ortho*-PCBs. The reduced BSAFs of dIPCBs cannot result from biotransformation since this is very limited in fish (Campbell et al. 2003; Buckman et al. 2006; Paterson et al. 2010) but basically from a reduced bioavailability and lower intestinal assimilation due to enhanced and/or irreversible adsorption of planar molecules onto ingested particles, as has been reported for PAH and PCBs (Jonker and Smedes 2000; Bucheli and Gustafsson 2003). In this context, a differential bioaccumulation according to planarity of PCBs is expected (*non-ortho* < *mono-ortho* < *ortho*-PCBs; Bucheli and Gustafsson 2003), which is consistent with the pattern of BSAFs curves (Fig. 5).

The log BSAFs-log K_{OW} relationship of PBDEs also presents a parabolic pattern maximizing at log K_{OW} 6–7 with a lower value for BDE 99 (2.0 ± 0.6), coincident with the debromination pathways described above. Within a similar log K_{OW} range (5–7), the BSAFs of tri-tetra-BDE are comparable to those of *ortho*-PCB, suggesting comparable bioaccumulation, but BSAFs of lighter congeners are overestimated due to bioformation processes. Conversely, the BSAFs of penta- to hepta-BDEs gradually decrease from the PCB curve reflecting their more limited bioaccumulation due to bioconversion. This differential bioaccumulation of dIPCBs and PBDEs in a detritus-feeding fish is consistent with patterns described for Lake Michigan trout (Streets et al. 2006) and for South China fish (Wu et al. 2008), basically attributed to different rates of metabolism of individual congeners.

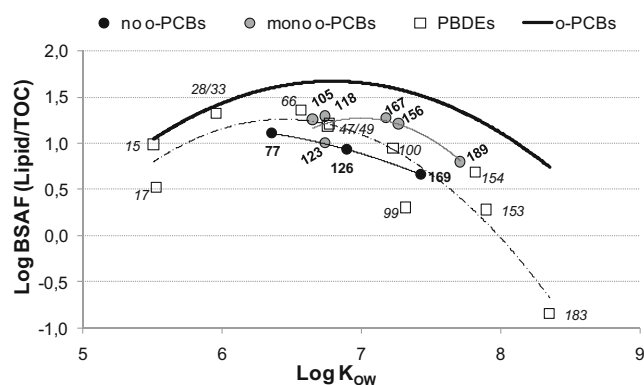


Fig. 5 Log BSAFs versus log K_{OW} of individual *non-ortho*-PCBs, *mono-ortho*-PCBs, PBDEs, and predicted curve for *ortho*-PCBs (log BSAFs = $0.38 \log K_{OW}^2 + 5.16 \log K_{OW} - 15.8$; Colombo et al. 2007)

Conclusions

Focalization of dIPCBs and PBDEs along the detritus food chain was reflected in the 30–40-fold increase of dry weight PBDE and dIPCB concentrations from settling particles to fish. In this transference, dIPCB congeners presented more conservative patterns than those of PBDEs. A detailed evaluation of the individual congener kinetics revealed an enhanced bioaccumulation of *mono-ortho* relative to *non-ortho*-PCBs, suggesting a lower bioavailability of more planar compounds due to their higher affinity to organic matter (adsorption). Metabolic degradative processes controlled the differential

bioaccumulation of individual PBDEs, resulting in the prevailing accumulation of lighter brominated congeners relative to heavier homologs which are selectively debrominated.

References

- Amot J, Gobas F (2004) A food web bioaccumulation model for organic chemicals in aquatic ecosystems. *Environ Toxicol Chem* 23:2343–2355
- Braekevelt E, Tittlemier S, Tomy G (2003) Direct measurement of octanol-water partition coefficients of some environmentally relevant brominated diphenyl ether congeners. *Chemosphere* 51:563–567
- Bucheli TD, Gustafsson O (2003) Soot sorption of non-ortho and ortho substituted PCBs. *Chemosphere* 53:515–522
- Buckman AH, Wong CS, Chow E, Brown SB, Solomon KR, Fisk AT (2006) Biotransformation of polychlorinated biphenyls (PCBs) and bioformation of hydroxylated PCBs in fish. *Aquat Toxicol* 78:176–185
- Burkhard L, Cook PM, Lukasewycz MT (2004) Biota-sediment accumulation factors for polychlorinated dibenzofurans in Southern Lake Michigan Lake trout (*Salvelinus namaycush*). *Environ Sci Technol* 38:5297–5305
- Campbell LM, Muir DCG, Whittle DM, Backus S, Norstrom RJ, Fisk AT (2003) Hydroxylated PCBs and other chlorinated phenolic compounds in lake trout (*Salvelinus namaycush*) blood plasma from the Great Lakes region. *Environ Sci Technol* 37:1720–1725
- Cirelli A, Ojeda C (2008) Wastewater management in Greater Buenos Aires, Argentina. *Desalination* 218:52–61
- Colombo JC, Bilos C, Remes Lenicov M, Colautti D, Landoni P, Brochu C (2000) Detritivorous fish contamination in the Río de la Plata estuary: a critical accumulation pathway in the cycle of anthropogenic compounds. *Can J Fish Aquat Sci* 57:1139–1150
- Colombo JC, Cappelletti N, Barreda A, Migoya MC, Skorupka CN (2005) Vertical fluxes and accumulation of PCBs in coastal sediments of the Río de la Plata estuary, Argentina. *Chemosphere* 61:1345–1357
- Colombo JC, Cappelletti N, Migoya MC, Speranza E (2007) Bioaccumulation of anthropogenic contaminants by detritivorous fish in the Río de la Plata Estuary: 2-Polychlorinated biphenyls. *Chemosphere* 69:1253–1260
- Colombo JC, Cappelletti N, Williamson M, Migoya MC, Speranza E, Sericano J, Muir DCG (2011) Risk ranking of multiple-POPs in detritivorous fish from the Río de la Plata. *Chemosphere* 83:882–889
- Dodder NG, Strandberg B, Hites R (2002) Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the northeastern United States. *Environ Sci Technol* 36:146–151
- Echols KR, Peterman PH, Hinck JE, Orazio CE (2013) Polybrominated diphenyl ether metabolism in field collected fish from the Gila River, Arizona, USA—levels, possible sources, and patterns. *Chemosphere* 90:20–27
- Grant P, Johannessen S, Macdonald R, Yunker M, Sanborn M, Dangerfield N, Wright C, Ross P (2011) Environmental fractionation of PCBs and PBDEs during particle transport as recorded by sediments in coastal waters. *Environ Toxicol Chem* 30:1552–1532
- Hickey JP, Batterman S, Chernyak SM (2006) Trends of chlorinated organic contaminants in great lakes trout and walleye from 1970 to 1998. *Arch. Environ Contam Toxicol* 50:97–110
- Isosaari P, Hallikainen A, Kiviranta H, Vuorinen PJ (2006) Polychlorinated dibenzo-p-dioxins, dibenzofurans, biphenyls, naphthalenes and polybrominated diphenyl ethers in the edible fish caught from the Baltic Sea and lakes in Finland. *Environ Pollut* 141:213–225
- Jonker M, Koelmans A (2002) Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot and soot-like materials in the aqueous environment: mechanistic consideration. *Environ Sci Technol* 36:3725–3735
- Jonker MTO, Smedes F (2000) Preferential sorption of planar contaminants in sediments from Lake Ketelmeer, The Netherlands. *Environ Sci Technol* 34:1620–1626
- Kajiwara Y, Kashiwagi N, Kadokami K (2007) Nationwide study of dioxins in the freshwater fish *Carassius auratus (gibelio) langsdorfii* (crucian carp) in Japan: concentrations and estimation of source contribution ratios. *Chemosphere* 69:1177–1187
- Kay D, Blankenship A, Coady K, Neigh A, Zwiernik M, Millsap S, Strause K, Park C, Bradley P, Newsted J, Jones P, Giesy J (2005) Differential accumulation of polychlorinated biphenyl congeners in the aquatic food web at the Kalamazoo River Superfund site, Michigan. *Environ Sci Technol* 39:5964–5974
- Lee II H (1998) Methods for Assessing Sediment Bioaccumulation in Marine / Estuarine Benthic Organisms. National Sediment Bioaccumulation Conference. EPA
- Lee H, Boese B, Randall R, Pelletier J (1990) A method for determining gut uptake efficiencies of hydrophobic pollutants in a deposit-feeding clam. *Environ Toxicol Chem* 9:215–219
- Marvin C, Alaee M, Painter S, Charlton M, Kauss P, Kolic T, Macpherson K, Takeuchi D, Reiner E (2002) Persistent organic pollutants in Detroit River suspended sediments: polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like polychlorinated biphenyls and polychlorinated naphthalenes. *Chemosphere* 49:111–120
- Marvin C, Williams D, Kuntz K, Klawunn P, Backus S, Kolic T, Lucaciu C, Macpherson K, Reiner E, Erie F (2007) Temporal trends in polychlorinated dibenzo-p-dioxins and dibenzofurans, dioxin-like PCBs, and polybrominated diphenyl ethers in Niagara river suspended sediments. *Chemosphere* 67:1808–1815
- Mizukawa K, Yamada T, Matsuo H, Takeuchi I, Tsuchiya K, Takada H (2013) Biomagnification and debromination of polybrominated diphenyl ethers in a coastal ecosystem in Tokyo Bay. *Sci Total Environ* 449:401–409
- Munschy C, Héas-Moisán K, Tixier C, Boulesteix L, Morin J (2011) Classic and novel brominated flame retardants (BFRs) in common sole (*Solea solea* L.) from main nursery zones along the French coasts. *Sci Total Environ* 409:4618–4627
- Naito W, Jin J, Kang Y-S, Yamamuro M, Masunaga S, Nakanishi J (2003) Dynamics of PCDDs/DFs and coplanar-PCBs in an aquatic food chain of Tokyo Bay. *Chemosphere* 53:347–362
- Nunes M, Marchand P, Vernisseau A, Le Bizec B, Ramos F, Pardal M (2011) PCDD/Fs and dioxin-like PCBs in sediment and biota from the Mondego estuary (Portugal). *Chemosphere* 83:1345–1352
- Opperhuizen A, Stokkel R (1988) Influence of contaminated particles on the bioaccumulation of hydrophobic organic micropollutants in fish. *Environ Pollut* 51:165–177
- Paasivirta J, Sinkkonen SI (2009) Environmentally relevant properties of all 209 polychlorinated biphenyl congeners for modeling their fate in different natural and climatic conditions. *J Chem Eng Data* 54:1189–1213
- Paterson G, Liu J, Haffner GD, Drouillard KG (2010) Contribution of fecal egestion to the whole body elimination of polychlorinated biphenyls by Japanese koi (*Cyprinus carpio*). *Environ Sci Technol* 44:5769–5774
- Puzyn T, Suzuki N, Haranczyk M (2008) How do the partitioning properties of polyhalogenated POPs change when chlorine is replaced with bromine? *Environ Sci Technol* 42:5189–5195

- Roberts SC, Noyes PD, Gallagher EP, Stapleton HM (2011) Species-specific differences and structure-activity relationships in the debromination of PBDE congeners in three fish species. *Environ Sci Technol* 45:1999–2005
- Rodenburg L, Meng Q, Yee D, Greenfield B (2014) Evidence for photochemical and microbial debromination of polybrominated diphenyl ether flame retardants in San Francisco Bay sediment. *Chemosphere* 106:36–43
- Speranza ED, Tatone LM, Cappelletti N, Colombo JC (2013) Cost-benefit of feeding on anthropogenic organic matter: lipid changes in a detritivorous fish (*Prochilodus lineatus*). *Ichthyol Res* 60:334–342
- Stapleton HM, Letcher RJ, Baker JE (2004) Debromination of polybrominated diphenyl ether congeners BDE 99 and BDE 183 in the intestinal tract of the common carp (*Cyprinus carpio*). *Environ Sci Technol* 38:1054–1061
- Streets SS, Henderson S, Stoner AD, Carlson DL, Simcik MF, Swackhamer DL (2006) Partitioning and bioaccumulation of PBDEs and PCBs in Lake Michigan. *Environ Sci Technol* 40:7263–7269
- UNEP (2009) Conference of the Parties of the Stockholm Convention on Persistent Organic Pollutants. Fourth Meeting. Recommendations of the Persistent Organic Pollutants Review Committee of the Stockholm Convention to amend Annexes A, B or C of the Convention Geneva, 4–8 May, 2009
- Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L, Rose M, Safe S, Schrenk D, Tohyama C, Tritscher A, Tuomisto J, Tysklind M, Walker N, Peterson RE (2006) The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds. *Toxicol Sci* 93:223–241
- Wu J-P, Luo X-J, Zhang Y, Luo Y, Chen S-J, Mai B-X, Yang Z-Y (2008) Bioaccumulation of polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs) in wild aquatic species from an electronic waste (e-waste) recycling site in South China. *Environ Int* 34:1109–1113
- Xiang C-H, Luo X-J, Chen S-J, Yu M, Mai B-X, Zeng E (2007) Polybrominated diphenyl ethers in biota and sediments of the Pearl River Estuary, South China. *Environ Toxicol* 26:616–623
- Zeng Y-H, Luo X-J, Chen H-S, Yu L-H, Chen S-J, Mai B-X (2012) Gastrointestinal absorption, metabolic debromination, and hydroxylation of three commercial polybrominated diphenyl ether mixtures by common carp. *Environ Toxicol Chem* 31:731–738
- Zennegg M, Kohler M, Gerecke A, Schmid P (2003) Polybrominated diphenyl ethers in whitefish from Swiss lakes and farmed rainbow trout. *Chemosphere* 51:545–553
- Zhou H, Wong M (2000) Accumulation of sediment-sorbed PCBs in tilapia. *Water Res* 34:2905–2914