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Bioaccumulation of anthropogenic contaminants by detritivorous fish in the Río de la Plata estuary: 1-Aliphatic hydrocarbons

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Abstract

The temporal variability and bioaccumulation dynamics of $C_{12–25}$ *n*-alkanes, isoprenoids and unresolved aliphatic hydrocarbons (UCM) were studied in a detritivorous fish (Sábalo: *Prochilodus lineatus*) collected from 1999 to 2005 in the sewage impacted Buenos Aires coastal area. Fish muscles contain huge amounts of *n*-$C_{12–25}$ (165 ± 93, 70 ± 48 or 280 ± 134 μg g^{-1}, dry, fresh and lipid weight, respectively) and UCM (931 ± 560, 399 ± 288 and 1567 ± 802 μg g^{-1}) reflecting the chronic bioaccumulation of fossil fuels from sewage particulates. On a temporal basis, lipid normalized aliphatic concentrations peaked by the end of 2001–2002 during the rainiest period over the last four decades (1750 vs. 1083 ± 4.6 mm in 1999, 2004 and 2005), reflecting an enhanced exposition due to massive anthropogenic fluxes from Metropolitan Buenos Aires in wet years. The hydrocarbon composition in fish muscles is enriched in *n*-$C_{15–17}$ and isoprenoids relative to a fresh crude oil and settling particulates, with fresher signatures during the 2001–2002 maxima. Fish/settling material bioaccumulation factors (BAFs: 0.4–6.4 dry weight or 0.07–0.94 lipid-organic carbon) plotted against K_{ow} showed a parabolic pattern maximizing at *n*-$C_{14–18}$ and isoprenoids. The optimal bioaccumulation window corresponds to highly hydrophobic ($\log K_{ow}$: 7.2–9.9), intermediate-size $C_{14–18}$ *n*-alkanes and $C_{15–20}$ isoprenoids (MW: 198–282; length: 17.9 to 25.4 Å) with melting points ranging from −19.8 to 28 °C. The uptake efficiency is inversely correlated to melting points and increased from 75% for *n*-C_{25} to above 90% for *n*-$C_{14–15}$ and isoprenoids.

Keywords: Sewage detritus; Hydrocarbons; Fish; Río de la Plata

1. Introduction

Fish detritivory is not a widespread feeding strategy but could represent an important route of energy flux and material cycling in aquatic ecosystems, especially in turbid, subtropical ecosystems such as the Río de la Plata (Bowen, 1983). This estuary is characterized by a huge suspended particulate matter load (90 million tons per year) transported by the Paraná and Uruguay Rivers from a 3 million km^2 basin in tropical and temperate areas of Brazil, Argentina, Paraguay, Bolivia and Uruguay (Esteves et al., 2000). The massive transport of allochthonous material feed a vast delta in front of Metropolitan Buenos Aires which concentrates one third of the total Argentinean population 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) and hydrocarbons (Colombo et al., 2005a,b, 2006a). 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., 2006b) which constitute the feeding ground of a specialized detritivorous fish, the Sábalo (*Prochilodus lineatus*).

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Sewage-derived organic matter has been recognized as an important energy subsidy for aquatic food webs which can lead to a fish production increase and a trophic structure alteration (deBruyn et al., 2003). These effects could be further amplified when highly specialized detritivorous fish feed directly on anthropogenic organic matter (Speranza and Colombo, 2006). In the Río de la Plata this niche is occupied by the Sábalo which dominates the fish community constituting over 60% of the ichthyomass. 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 specialization on detritivory and the presence of large discharges of untreated effluents in the Río de la Plata (e.g. main Buenos Aires sewer at Brazategui: ~2 million $m^3\ d^{-1}$), transformed the Sábalo in a critical pathway of persistent pollutants to humans (Colombo et al., 2000). Residues are also subjected to 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 transport of pollutants to remote areas along the Paraná Basin.

In this paper we report results on the temporal variation of aliphatic hydrocarbons in Sábalos captured in the main Buenos Aires sewer area from 1999 to 2005. The concentration, composition and bioaccumulation of individual hydrocarbons from settling material are discussed and correlated with contaminant physico-chemical properties.

2. Methods

Fish samples were obtained from local fishermen in the coastal area of Berazategui affected by crude industrial and sewage discharges (Fig. 1). Sampling was performed each 3–4 months covering the period from 1999 to 2005. 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. Settling particles were collected 1.5 m below the surface upstream and downstream the main Buenos Aires sewer at Berazategui (Fig. 1) during 13 trap deployments covering spring, summer, autumn and winter 2002–2006 (Colombo et al., 2006b).

In the laboratory, fish muscle samples were pooled (2–5 individuals) according to the size and weight of the fish based on the condition index: CI = total body weight (g)/standard length $(cm)^3$. The pooling criteria was adjusted to discriminate small (<1 kg), medium (>1 and <2.5 kg), large (>2.5 and <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 79 samples corresponding to 150 fish were analyzed (46 pools and 33 individual fish). The muscles were processed with 250 W blenders in glass jars using different equipments for small, medium and large fish. All material used was washed with hot water and detergent, rinsed with tap and distilled water, with a final rinse with pesticide grade petroleum ether.

The homogenized muscle samples were splitted for the determination of water content (100 °C, 24 h) and for chemical analyses (Colombo et al., 2000, 2005b). 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 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 lipid redissolved in petroleum ether was treated with sulphuric acid to partially remove the lipid material. The extracts were then fractionated by silica–gel chromatography. Individual aliphatic hydrocarbons 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

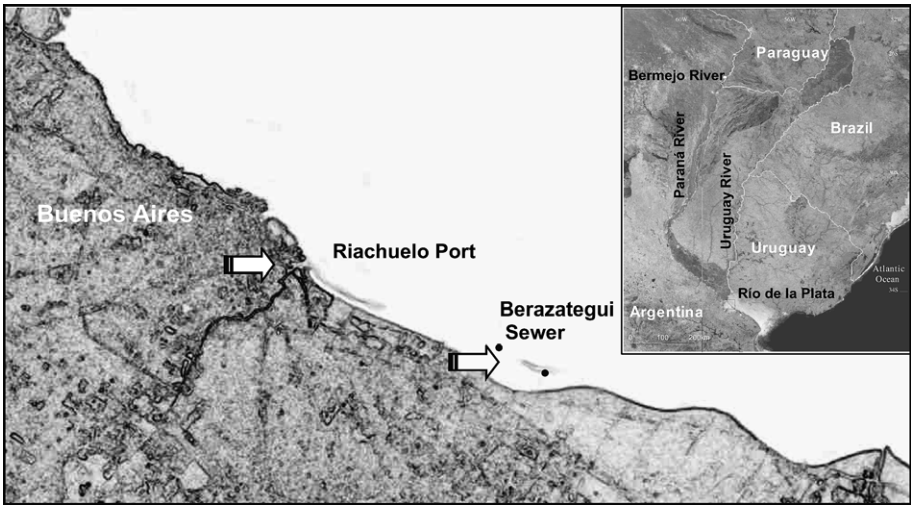

Fig. 1. Study area and sampling sites in the Berazategui sewer, Metropolitan Buenos Aires coast (based on a Landsat satellite image).

per segment, 50–550 amu). Quantification was performed by an external standard of 31 individual aliphatic hydrocarbons (*n*-C_{10} to *n*-C_{38} plus pristane and phytane; AccuStandard Inc.). Deuterated *n*-alkanes (*n*-C_{16}-d_{34} and *n*-C_{24}-d_{50}; Absolute Standards, Inc.) were used to control recovery yields. All samples were quantified by both detectors using the HRGC-MSD to confirm FID identities (*m*/*z*: 71, 85, 99) and to correct the possible co-elution of isoprenoids with linear alkyl benzenes (LABs, *m*/*z*: 91 and 105). According to MSD data, a contribution of <15 to ~40% C_{11-12} LABs to pristane and phytane as determined by FID was estimated in fish samples (Fig. 2). Method precision evaluated through repeated analysis of an internal reference fish material prepared with homogenized Río de la Plata *P. lineatus* muscle averaged 16% ($n = 5$). Duplicate and triplicate analysis of 18 fish samples yielded an average reproducibility of 14% for total aliphatic hydrocarbons. UCM was quantified by planimetry based on the response factor of resolved *n*-alkanes.

3. Results and discussion

3.1. Total hydrocarbon concentrations

Table 1 presents sample information together with average hydrocarbon levels in fish from 1999 to 2005 and in settling particulates collected in the sewer outfall area. Fig. 3 shows the full range variability of hydrocarbons in fish muscles. Sábalos contain huge amounts of C_{12-25} *n*-alkane hydrocarbons ranging from 13 to 465 μg g^{-1} dry weight (mean: 165 ± 93 μg g^{-1} dw), 2.8–242 μg g^{-1} fresh weight (70 ± 48 μg g^{-1} fw) or 108–713 μg g^{-1} lipids (280 ± 134 μg g^{-1} lip). In addition to these resolved components, Sábalos also contain large quantities of unresolved hydrocarbons (UCM), a typically petrogenic feature visible as a hump between *n*-C_{15-25} in the gas chromatograms (Fig. 2). The secondary hump observed at about 35 min corresponds to incompletely removed lipid residues. UCM concentrations in fish muscles range from 46–2271,

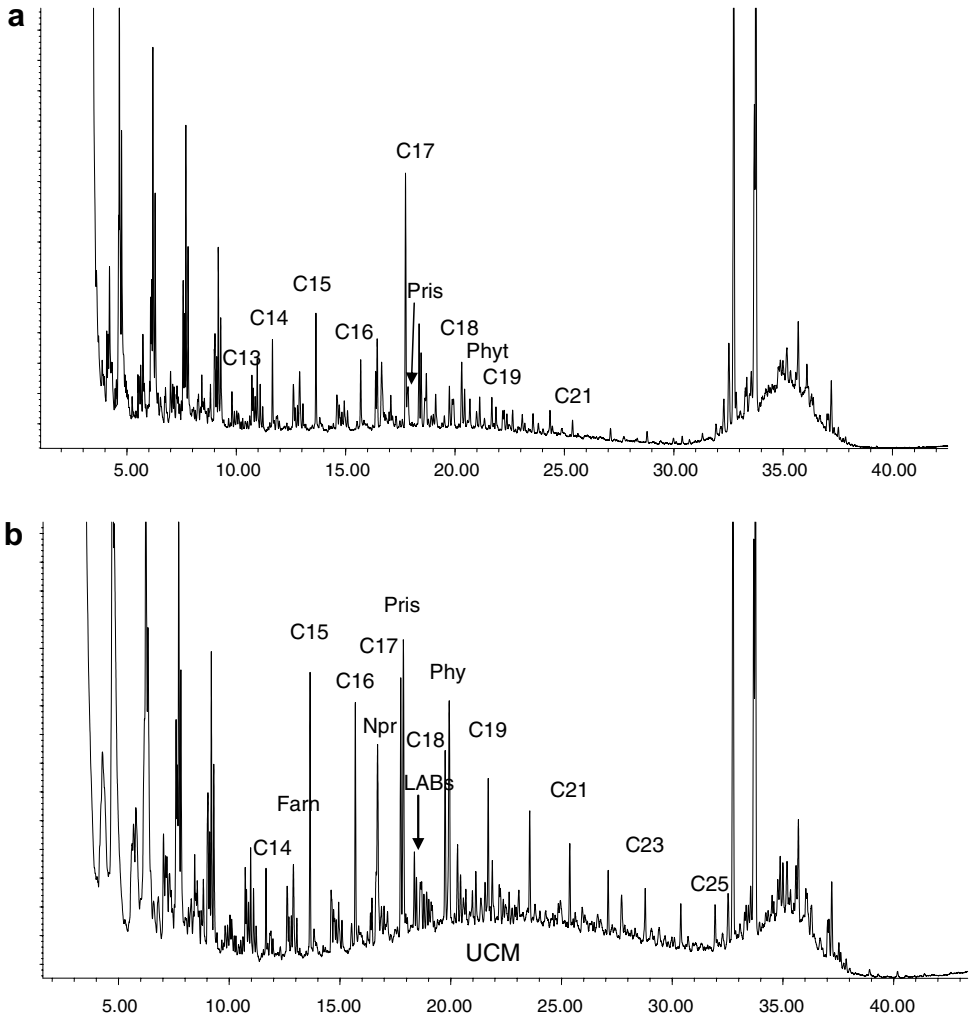

Fig. 2. Aliphatic hydrocarbon traces in muscle of small ((a) 1.4 kg, 22% lipids, 26 μg g^{-1} dw *n*-C_{12-25}) and large Sábalos ((b): 3.6 kg, 68% lipids, 245 μg g^{-1} *n*-C_{12-25}). Note the predominance of plankton-derived *n*-C_{17} and reduced UCM in the upper less polluted fish.

Table 1
Annually-averaged aliphatic hydrocarbon concentrations in Sábalo muscles and trap material

	Fish muscle							Traps
	1999	2000	2001	2002	2003	2004	2005	
Samples								
Pools	5	9	13	13	17	13	9	23
Fish (*n*)	5	9	25	24	37	30	20	
Std length (cm)	–	44.8	46.7	45.9	46.6	45.2	44.7	–
SD		7.6	6.8	6.0	4.3	5.3	3.8	–
Weight (kg)	–	2.7	3.2	3.1	3.2	2.9	2.6	–
SD		1.3	1.2	1.3	1.0	1.1	0.8	–
% Lipid–TOC	82.9	68.9	62.3	56.9	65.8	47.1	41.7	8.7[a]
SD	29.1	25.0	22.7	18.8	16.9	16.7	17.5	6.2[a]
Condition index		2.8	3.0	3.0	3.0	3.0	2.8	–
SD		0.2	0.4	0.4	0.4	0.3	0.4	–
Hydrocarbons ($\mu g\ g^{-1}$ dw)								
n-C_{12}	3.2	2.1	4.6	4.0	1.5	1.5	2.2	4.0
n-C_{13}	7.7	4.9	8.4	5.2	2.1	2.7	3.4	3.9
n-C_{14}	23.9	12.7	21.5	16.5	8.0	8.8	8.0	5.3
Farnesane	16.0	10.0	10.2	11.9	7.2	5.5	5.8	1.9
n-C_{15}	36.7	18.9	31.1	27.8	15.5	14.0	9.4	5.2
n-C_{16}	22.4	12.0	19.5	19.2	11.8	10.0	7.1	4.2
Norpristane	19.0	12.6	12.9	12.2	10.3	8.5	6.1	1.7
n-C_{17}	18.3	10.4	17.8	21.6	14.3	12.4	7.7	4.5
Pristane	24.2	17.5	18.0	20.5	16.0	12.4	7.5	2.7
n-C_{18}	14.2	8.9	14.5	17.0	10.1	8.8	5.0	4.0
Phytane	20.1	15.9	18.2	15.7	14.5	10.8	6.1	2.6
n-C_{19}	10.5	6.1	8.8	10.5	8.7	7.5	4.3	3.7
n-C_{20}	11.2	7.4	9.5	8.1	6.4	5.1	2.8	3.2
n-C_{21}	7.3	4.5	5.6	6.0	4.3	3.5	2.1	3.0
n-C_{22}	6.1	3.8	4.2	4.6	3.7	2.8	1.6	2.5
n-C_{23}	5.5	3.1	3.7	3.9	4.1	2.9	1.6	2.6
n-C_{24}	3.9	2.7	3.5	3.8	3.1	2.3	1.2	3.5
n-C_{25}	4.0	3.4	2.6	3.9	2.5	2.3	1.2	6.1
Total $C_{12–25}$ dw	254.3	157.0	214.5	212.3	144.1	121.7	83.2	64.5[b]
SD	63.6	69.0	115.1	103.8	57.9	77.5	47.1	63.5[b]
UCM dw	1229.0	980.2	1353.4	1053.5	916.3	742.9	274.2	371.3[b]
SD	424.6	479.6	584.5	600.7	457.9	487.7	139.1	281.2[b]
Total ALI dw	1483.3	1137.2	1567.9	1265.8	1060.4	864.6	357.4	435.8[b]
Total $C_{12–25}$ fw	112.3	68.4	97.2	91.2	62.2	44.3	33.3	
SD	35.8	34.6	61.3	56.7	30.6	33.9	23.6	
UCM fw	549.8	433.3	614.5	450.5	396.2	272.5	108.9	
SD	242.0	230.9	370.7	308.6	223.8	216.5	74.6	
Total ALI fw	662.1	501.7	711.7	541.7	458.4	316.8	142.2	
Total $C_{12–25}$ lip	322.1	232.1	365.2	388.4	219.5	249.8	186.7	731.3[c]
SD	47.1	60.1	185.7	147.2	83.4	107.9	51.8	519.6[c]
UCM lip	1537.8	1345.7	2389.5	1951.4	1361.3	1450.8	709.2	5927.6[c]
SD	367.7	390.8	871.2	888.9	613.2	637.9	359.5	5170.4[c]
Total ALI lip	1859.9	1577.8	2754.7	2339.8	1580.8	1700.6	895.9	6658.9[c]

dw: Dry weight; fw: fresh weight; lip: lipid based.
[a] Organic carbon.
[b] $C_{12–35}$ range: resolved *n*-alkanes = 111 ± 106, UCM = 928 ± 703 $\mu g\ g^{-1}$.
[c] Organic carbon basis $C_{12–35}$ range: resolved *n*-alkanes = 1337 ± 891, UCM = 14819 ± 12926 $\mu g\ g^{-1}$.

9–1269 and 240–4131 $\mu g\ g^{-1}$, dry, fresh and lipid weight, respectively. The total aliphatic hydrocarbon grand mean average in Sábalo muscles is around 1 $mg\ g^{-1}$ (165 ± 93 + 931 ± 560 $\mu g\ g^{-1}$ dw $C_{12–25}$ *n*-alkanes and UCM, respectively). These concentrations are among the highest ever reported for fish. Total *n*-alkane concentrations in Mediterranean fish are effectively 1–3 orders of magnitude lower, i.e. 0.5–11.1 $\mu g\ g^{-1}$ dw in *Merluccius*, *Mullus*, *Engraulis* and *Trachurus* sp., 1.4–13 $ng\ g^{-1}$ with 1.7–5.8 ng g^{-1} fw UCM in *Thunnus* sp. from Spain (Albaigés et al., 1987; Porte and Albaigés, 1993), 0.1–0.47 $\mu g\ g^{-1}$ fw in deep-fish from the Gulf of Lion (Solé et al., 2001), 0.8–33 $\mu g\ g^{-1}$ fw in Gulf of Naples fish (Amodio-Cocchieri and Cirillo, 2003), and 82 $\mu g\ g^{-1}$ fw in Portuguese Sardina (Ferreira et al., 2003). Similarly lower hydrocarbon concentrations have been reported for Colombian Cartagena Bay fish (13–37 $\mu g\ g^{-1}$ dw; Parga-Lozano et al., 2002), and Arabian Gulf fish (0.12–4.25 $\mu g\ g^{-1}$; Al-Hassan et al., 2003)

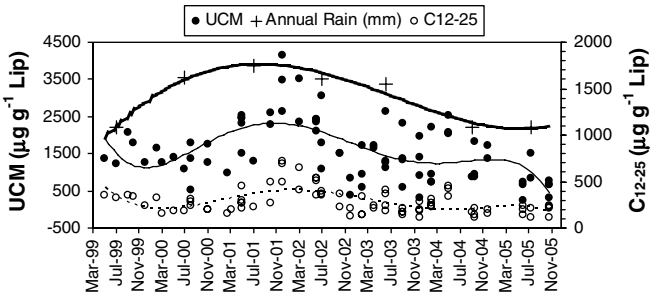

Fig. 3. Full range variability of lipid normalized total C_{12-25} *n*-alkanes and UCM concentrations in fish muscle compared to annual rain at Buenos Aires.

whereas mackerels and scad from the Gulf of Oman presented higher levels of petrogenic C_{10-28} *n*-alkanes (1.9–109 µg g^{-1}; Ahmed et al., 1998). Hydrocarbon concentrations in fresh water fish are also 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).

The exceptionally high hydrocarbon levels of Sábalos reflect a chronic fossil fuel exposition by crude effluent discharges to the Río de la Plata and point out the remarkable ability of this fish to bioaccumulate hydrophobic substances from sewage and industrial particulates. As a specialized detritivore, the energy benefit of this feeding strategy is based on the significant organic enrichment of the material collected by the traps (Speranza and Colombo, 2006). Effectively, relative to bottom sediments, the biochemical composition of the trap material is enriched in organic carbon (0.6 ± 0.5 vs. 8.7 ± 6.2% dw), lipids (0.5 ± 0.4 vs. 1.9 ± 2.0%), proteins (1.4 ± 0.9 vs. 3.2 ± 2.8%) and carbohydrates (1.7 ± 2.2 vs. 3.6 ± 3.1%), 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, 2006). Río de la Plata Sábalos are effectively exceptionally fatty (59 ± 22% dw), which further favors the accumulation of lipophilic substances such as aliphatic hydrocarbons and PCBs.

3.2. Temporal variability

Annually-averaged lipid normalized C_{12-25} *n*-alkane concentrations range from 187 to 388 µg g^{-1}, similar to previous reports from fish collected in 1996 (225–356 µg g^{-1} lipids; Colombo et al., 2000). This reflects the chronic hydrocarbon load to the estuary through industrial-sewer discharges which are used as feeding resource by the Sábalo. The annual variability for *n*-C_{12-25} and UCM averages 30–65%, 38–78% and 19–44% for dry, fresh and lipid normalized concentrations, respectively. The 1999–2005 grand mean relative standard deviations of C_{12-25}–UCM hydrocarbons are 57–60%, 68–72% and 48–51%, respectively. A significant amount of variability is related to differences in fish size and lipid contents. Aliphatic hydrocarbons effectively suggest a positive correlation with fish weight ($R^2 = 0.39$–0.47, UCM–C_{12-25}) and its covarying lipid contents (weight-lipid: $R^2 = 0.62$). The variability is emphasized by seven smallest fish (1.0 ± 0.2 kg) included in the data set which show lower lipid contents (16 ± 8.5%) and prevailing natural hydrocarbons (Fig. 2a). Lipid normalized concentrations reduce the size-related variability.

On a temporal basis, lipid normalized aliphatic concentrations in fish muscles present maximum values by the end of 2001 and beginning of 2002 (Fig. 3). Interestingly, 2001 was the rainiest year over the last four decades in Buenos Aires, with a total precipitation of 1750 mm, 60% higher than the dryer 1999, 2004 and 2005 period (1083 ± 4.6 mm). The seasonal study of sediment traps in the sewer area revealed that higher precipitation during warm months (October–March) resulted in increased contaminant fluxes with less degraded signatures due to a more efficient wash out of residues from Metropolitan Buenos Aires (Colombo et al., 2006b). Thus, the occurrence of highest hydrocarbon levels in fish during the rainiest year could be reasonably interpreted as resulting from an enhanced exposition resulting from massive discharges of anthropogenic residues in wet relative to less impacted dry years. The composition of hydrocarbons in the fish effectively indicates fresher signatures during 2001–2002, compatible with a pulse of less degraded contaminants in rainy years (see composition). The rapid transfer of this signal to the fish is favored by the feeding strategy of Sábalos who search the flocculent matter recently settled from industrial and sewer outfalls. However, a several-months lag is apparent in the data considering that the main rain pulse in 2001 occurred in January–March (780 mm) and that the highest aliphatic concentrations in the fish are registered from December 2001 to July 2002.

3.3. Hydrocarbon composition

Fig. 4 presents the annually-averaged composition of aliphatic hydrocarbons in Sábalo muscles discriminating

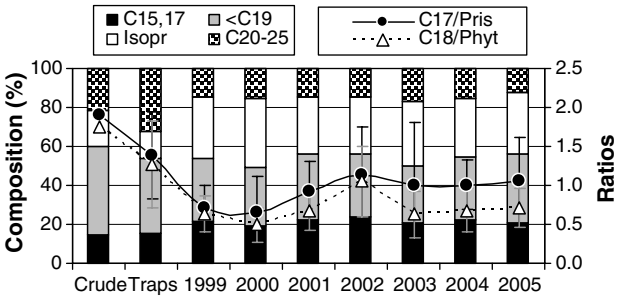

Fig. 4. Annually-averaged *n*-alkane composition and *n*-C_{17}/pristane *n*-C_{18}/phytane ratios in Sábalos compared to fresh crude oil and trap material.

potential biogenic sources such as algae (n-$C_{15,17}$), petrogenic labile ($<C_{19}$: n-C_{12-19}) and more recalcitrant components (isoprenoids: farnesane, norpristane, pristane and phytane), and higher molecular weight n-alkanes ($>C_{20}$: n-C_{20-25}). The general composition of resolved C_{12-25} aliphatic hydrocarbons in Sábalos is relatively conservative with a dominant contribution of lower molecular weight n-alkanes ($<C_{19} = 32 \pm 5.3\%$; $C_{15-17} = 22 \pm 3.7\%$), followed by isoprenoids ($31 \pm 6.5\%$) and $>C_{20}$ n-alkanes ($15 \pm 2.6\%$). This pattern results enriched in n-C_{15-17} and isoprenoids relative to a fresh crude oil (46%, 15%, 18% and 22%) and settling particulates (39%, 15%, 14% and 32% for $<C_{19}$, C_{15-17}, isoprenoids and $>C_{20}$ n-alkanes, respectively; Fig. 4). Trap figures include only the C_{12-25} n-alkane series determined in fish and excludes n-C_{25-35} with slight odd carbon predominance which represented $\sim$ 40% of the total (Colombo et al., 2006b; see Table 1). The higher proportions of n-$C_{15,17}$ in Sábalos relative to the crude and traps reflects the contribution of plankton derived organic matter enriched in $C_{15,17}$ in the diet of the fish (Fig. 2). In contrast, due to a preferential accumulation of medium chain length compounds (see bioaccumulation factors), higher molecular weight n-alkanes are underrepresented in the fish compared to the traps.

Sábalo muscles and traps present lower proportions of $<C_{19}$ n-alkanes relative to the crude oil reflecting an early alteration of the hydrocarbon signature. This is also indicated by the lower n-C_{17}/pristane and n-C_{18}/phytane ratios in fish (1.0 ± 0.5 and 0.8 ± 0.3) and trap material (1.4 ± 0.5 and 1.3 ± 0.5) compared to the crude oil (1.9–1.7, respectively), reflecting a progressive decay with selective preservation of more persistent isoprenoids. Due to the interference of algal derived n-C_{17} in fish, the n-C_{18}/phytane ratio seems more appropriate to evaluate the alteration of petrogenic traces. The increase of the more recalcitrant UCM relative to resolved components in fish and traps (UCM/n-$C_{12-25} = 5.7 \pm 2.5$ and 11.5 ± 8.2 vs. 1.1 in crude oil) also indicates an enhanced alteration of the hydrocarbon composition. In spite of the partial alteration indicated by these data, and considering the relative high susceptibility to degradation of aliphatics, the hydrocarbon signature of Sábalos looks still surprisingly fresh (Fig. 2). This implies a rapid and efficient transfer of the trap signal to the fish supporting the interpretation that Sábalos feed on recently-decanted flocculent matter. Sedimentary hydrocarbons in contrast, are extensively degraded as indicate the lower n-C_{17}/pristane (0.5 ± 0.2) and n-C_{18}/phytane ratios (0.4 ± 0.3) and higher UCM proportion (UCM/n-alkanes $= 49 \pm 31$; Colombo et al., 2005a).

On a temporal basis, in spite of the relative uniformity of the aliphatic composition, an enrichment of lower molecular weight n-alkanes with lower isoprenoid abundance is insinuated during the 2001–2002 hydrocarbon maxima (Fig. 4). Effectively, during both years the proportion of $C_{15,17}$ and $<C_{19}$ n-alkanes tends to be higher (56–57 vs. 49–56% in the other years), whereas isoprenoids are more reduced ($\sim$29 vs. 31–35%). This pattern is emphasized in fish with the highest hydrocarbon concentrations from December 2001 to July 2002 (average 60% lower molecular weight n-alkanes and 27% isoprenoids). The lower alteration of aliphatic traces in this fish compared to the other years is also supported by the higher n-C_{17}/pristane (1.2 ± 0.5 vs. 0.8–1.1) and specially n-C_{18}/phytane ratios (1.2 ± 0.4 vs. 0.6–0.8). These results support an enhanced exposition to less degraded hydrocarbons related to massive anthropogenic fluxes during rainy years.

3.4. Bioaccumulation factors

The presence of a specialized detritivorous fish feeding on well characterized sewage particulates provides a good opportunity to evaluate the bioaccumulation dynamics of individual hydrocarbons. Bioaccumulation factors (BAFs) were thus calculated with the average concentration of each compound in fish muscle and the trap material on a dry weight and lipid-organic carbon normalized basis. Fig. 5 presents a log–log plot of BAFs vs. octanol–water partition coefficients of aliphatic hydrocarbons.

The average n-alkane dry weight-based BAF is 2.8 ± 1.9 ($\log = 0.34 \pm 0.33$), similar to that of the UCM (2.5). Lipid-organic carbon BAFs are reduced to 0.41 ± 0.28 ($\log = -0.49 \pm 0.33$) and 0.26 for the UCM respectively, reflecting the proportionally higher lipid contents of fish (59%) relative to organic carbon in settling particulates (8.7% dw). The BAF–K_{ow} relationship show a very consistent parabolic model ($R^2 = 0.92$) maximizing at n-C_{14-18} (dw BAFs = 2.5–4.0; LipOC BAFs = 0.37–0.59) and decreasing values for lower and higher molecular weight n-alkanes. Isoprenoids seem to have the same pattern but shifted upwards (dw BAFs = 4.7–6.4; LipOC BAFs = 0.69–0.94), indicating a more efficient accumulation. In fact the first four n-alkanes of the series (C_{12-15}) display a significant linear relationship with K_{ow} ($R^2 = 0.99$; Fig. 5) implying an enhanced uptake with increasing hydrophobicity up to $\log K_{ow} \sim 7.7$. The subsequent BAFs decrease suggests reduced membrane permeability, i.e. steric hindrance or lower lipid solubility for higher molecular weight n-alkanes.

Since contaminant uptake in this detritivorous fish comprises the absorption from ingested particles, the decreasing

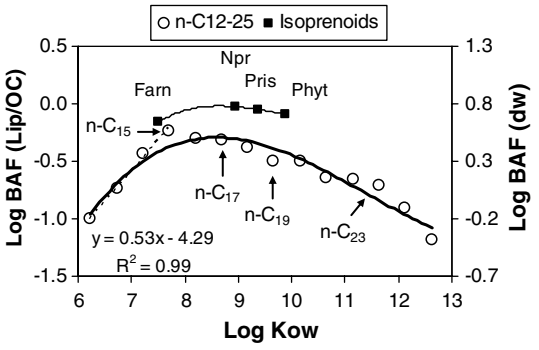

Fig. 5. Fish/trap bioaccumulation factors (BAFs) on a lipid-organic carbon and dry weight base vs. K_{ow} of individual aliphatic hydrocarbons.

BAFs for larger *n*-alkanes reflect basically a reduction of intestinal assimilation. Decreasing absorption efficiencies with increasing carbon and chlorine numbers have been previously reported for chlorinated benzenes, PCBs, and dioxin bioconcentration in fish (Sabljic and Protic, 1982) and for C_{14-32} *n*-alkanes fed intragastrically to rats (Kuksis, 1986). The ability for molecular discrimination of cellular membranes acting as structured soft polymers where diffusion occurs via holes created by random thermal motion has been also summarized (Hawker, 1990). In this context, molecular length rather than volume of hydrocarbons has been identified as the key parameter controlling their solubility in planar lipid bilayers with 21 linear-carbon chains being totally immiscible (Simon et al., 1977). Patton et al. (1984) reported a rapid fat solubility decrease of long chain compounds with increasing melting points (MP). In the same line, the study of fatty acid digestibility in Atlantic salmon indicated an inverse correlation between the absorption efficiency and MP (Sigurgisladottir et al., 1992). In view of the structural similarity of *n*-alkanes and fatty acids (linear-carbon chains), the uptake efficiencies of aliphatic hydrocarbons were estimated from MP based on the equation of digestibility vs. MP of fatty acids ($Abs\% = -0.000024\,MP^3 - 0.0026\,MP^2 - 0.11\,MP + 92.37$; $R^2 = 0.84$; Sigurgisladottir et al., 1992). These absorption efficiencies show a significant direct correlation with BAFs in Sábalos and increase in a continuous series from 75% for *n*-C_{24-25} to 94% for farnesane (Fig. 6). Lower chain *n*-C_{12-14} alkanes fall under the general relationship possibly reflecting their lower hydrophobicity. Evaporative losses could also contribute to this pattern, but this would apply for *n*-C_{12-14} in both fish and trap material. These results are conclusive evidence that the bioaccumulation dynamics of aliphatic hydrocarbons in this detritivorous fish is controlled by an efficient molecular discrimination during intestinal absorption. Similar *n*-alkane discrimination but favoring higher molecular weight C_{26-28} components has been reported for codling feed crude oil for 6 months (Hardy et al., 1974). In contrast, rainbow trout feed a 1% C_{13-22} *n*-paraffin diet for 7 months assimilated preferentially *n*-C_{14-15} (Cravedi and Tulliez, 1983), but with a hundred times lower overall BAF (0.029) relative to Sábalos possibly reflecting the distinct gastrointestinal absorption efficiencies of this predator relative to a specialized detritivorous fish. In Río de la Plata Sábalos, the optimal bioaccumulation window correspond to highly hydrophobic ($\log K_{ow}$: 7.2–9.9) intermediate-size C_{14-18} *n*-alkanes and C_{15-20} isoprenoids (MW: 198–282; length: 17.9–25.4 Å) with melting points ranging from −19.8 to 28 °C. Considering that at temperatures below the compounds MP, as K_{ow} increase fat solubility in fact decreases due to higher crystal lattice force strengths, i.e. "crystal loving" larger compounds (Patton et al., 1984), the aliphatic MP range for optimal bioaccumulation in Sábalos appear to reflect the thermodynamically most favorable absorption of liquid, miscible relative to solid hydrocarbons across the intestinal epithelium.

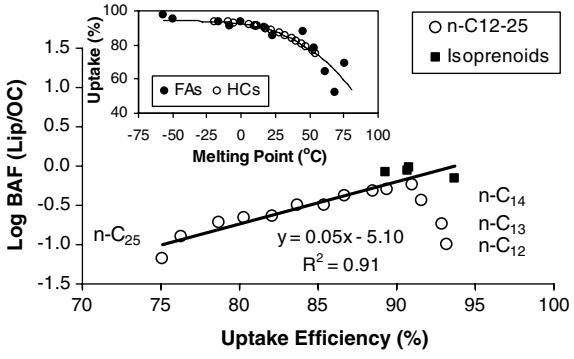

Fig. 6. Lipid-carbon BAFs of aliphatic hydrocarbons (HCs) in Sábalos vs. assimilation efficiencies estimated from melting points through the fatty acid (FAs) uptake-melting point relationship shown in the left upper corner. The linear regression shown include isoprenoids and *n*-alkanes excluding *n*-C_{12-14}.

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