Detritivorous fish contamination in the Río de la Plata estuary: a critical accumulation pathway in the cycle of anthropogenic compounds

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Abstract: Aliphatic hydrocarbons, chlorinated pesticides, polychlorinated biphenyls (PCBs), dioxins, furans, and trace metals have been quantified in fishes collected at four stations in Río de la Plata to determine contaminant sources, elucidate interstation and interspecies differences, and assess the health risks associated with fish consumption. Río de la Plata fish present low trace metal concentrations and moderate to high levels of organic pollutants, particularly aliphatic hydrocarbons and PCBs. The highest concentrations were recorded in *Prochilodus lineatus*, a dominant and remarkably specialized fatty detritivore that feeds on contaminated organic-rich flocculent matter. Lower levels were registered in *Cyprinus carpio* and especially in *Mugil cephalus*, reflecting different feeding preferences. A geographical pattern of higher contaminant concentrations close to the Buenos Aires urban center and lower levels in distant stations was also observed. The multivariate analysis of contaminant signatures indicated that most contaminated *Prochilodus* had fresh petrogenic and PCB traces, similar to fossil fuels and Aroclor 1254–1260, whereas *Mugil* and fish from distant sites presented a higher proportion of biogenic hydrocarbons and of more chlorinated PCBs. Toxicity equivalents ranged from 11 to 39 pg·g fresh weight⁻¹ in *Prochilodus*, exceeding the guideline of 25 pg·g⁻¹ for human consumption, with allowable consumption rates as low as 1 g fish-day⁻¹.

Résumé : Nous avons quantifié les hydrocarbures aliphatiques, les pesticides chlorés, les polychlorobiphényles (PCB), les dioxines, les furanes et les métaux-traces chez des poissons prélevés à quatre stations dans le Río de la Plata en vue de déterminer les sources de contaminants, d'éclaircir les différences entre stations et entre espèces et d'évaluer les risques pour la santé associé à la consommation de poissons. Les poissons du Río de la Plata présentent de faibles concentrations de métaux-traces et des teneurs modérées à élevées en polluants organiques, particulièrement les hydrocarbures aliphatiques et les PCB. Les concentrations les plus élevées ont été observées chez Prochilodus lineatus, poisson gras détritivore dominant et remarquablement spécialisé, qui se nourrit de matière floculée contaminée riche en substances organiques. Des concentrations plus faibles ont été enregistrées chez Cyprinus carpio et particulièrement chez Mugil cephalus, ce qui correspond à des différences sur le plan de l'alimentation. Nous avons aussi observé un patron géographique, les concentrations de contaminants étant plus élevées à proximité du centre urbain de Buenos Aires et plus faibles aux stations éloignées. L'analyse multivariée des signatures des contaminants a indiqué que la plupart des Prochilodus contaminés présentaient des traces fraîches de matériel pétrogénétique et de PCB, semblables à celles des combustibles fossiles et de l'Aroclor 1254-1260, tandis que les Mugil et les poissons des stations éloignées présentaient une plus forte proportion d'hydrocarbures biogéniques et des PCB les plus chlorés. Les valeurs des équivalents toxiques allaient de 11 à 39 pg·g poids frais⁻¹ chez *Prochilodus*, dépassant donc la limite de 25 pg·g⁻¹ fixée pour la consommation humaine, de sorte que la quantité autorisée à la consommation pouvait descendre à 1 g poisson jour⁻¹.

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Fig. 1. Río de la Plata estuary and sampling locations (arrows). TIG, Tigre; QUI, Quilmes; PL, Punta Lara; MG, Magdalena. The main urban centers are indicated.

Introduction

Organic pollutants and trace metals are ubiquitous contaminants in the global environment and they are usually concentrated in the waters, sediments, and biota of heavily populated estuaries of the world. The Río de la Plata estuary is, after the Amazon, the second largest river system in South America and conforms well to this generalization. The strong demographic and industrial pressure (about 13 million people and 50% of the country's industrial capacity) around Buenos Aires and La Plata cities (Fig. 1) produces a severe environmental impact. The widespread presence of hydrocarbons and chlorinated compounds in sediments and biota along the coast has been reported (Colombo et al. 1989, 1990). Petrogenic inputs predominate in polluted tributaries and nearby coastal areas whereas pirogenic hydrocarbons dominate in offshore areas. Chlorinated pesticides and polychlorinated biphenyls (PCBs) are abundant in aquatic organisms, with a composition denoting the integration of water column and sediment traces. Chlorinated organics and trace metals show geographical gradients of decreasing concentrations in suspended particles, sediments, and bivalves with increasing distance from the Buenos Aires area (Colombo et al. 1995; Bilos et al. 1998). The study of the long-term accumulation of xenobiotics, including dioxins and furans, in Asiatic clams indicated a doubling of the toxic equivalents over 4 years of clam growth (Colombo et al. 1997). These studies provided a general picture of the contamination status in the urbanized, freshwater area of the estuary. However, a detailed evaluation of the impact of anthropogenic contaminants on the rich local fisheries has not yet been performed.

The contamination of fish stocks by persistent organo-

chlorines such as PCBs and DDTs and degradation products produces economic as well as ecological and health-related effects. High PCB levels have triggered the periodic closures of commercial fisheries affected by the discharge of industrialized rivers and estuaries; the Atlantic coast striped bass (Morone saxatilis) and Great Lakes fisheries are perhaps the most illustrative examples (White et al. 1985; Bush et al. 1989; Fabrizio et al. 1991). The importance of fish as a critical pathway in the transfer of organochlorines to higher trophic level wildlife, e.g., birds and mammals, and humans is well established (e.g., Fox et al. 1991; Law and Gudaitis 1994; Tillitt et al. 1996). In this context, the epidemiological studies carried out in the Great Lakes during the last 25 years suggest a relationship between health effects and contaminated fish consumption in sport fishers, even in secondgeneration infants due to in utero exposure and breast milk residue transfer (Gilbertson 1985; Manno et al. 1995). In order to manage this health risk, fish consumption advisories have been issued, e.g., five consumption categories are recommended based on PCB levels (milligrams per kilogram fresh weight): (i) PCBs < 0.05, no restriction; (ii) PCBs = 0.05-0.2, 52 meals per year; (*iii*) PCBs = 0.2-1.0, 12 meals per year; (iv) PCBs = 1.0-1.9, six meals per year; (v) PCBs > 1.9, no consumption is recommended (Stow and Qian 1998).

In this paper, we study the accumulation of persistent organochlorines, hydrocarbons, and trace metals in four dominant fish species of the Río de la Plata estuary, including a highly specialized detritivore, collected at four stations with differing land uses. The objectives of the study are to (*i*) assess the contamination status of the biological resource, (*ii*) examine interspecies differences, (*iii*) investigate possible geographical patterns, (*iv*) examine the relationship be-

Table 1. Total concentrations and major components of organic contaminants and trace metals in Río de la Plata fish.

	Relative	e abundan	ce (%)									
	Sabalo				Carp					Mullet		
									Boga,			
	TIG	QUI	PL	MG	TIG	QUI	PL	MG	TIG	QUI	PL	MG
Aliphatic hydrocarbons												
<i>n</i> -C14	6.2	10.2	7.0	—	4.1	34.3	10.2	—	5.8	12.0	46.3	
Farnesane	5.3	5.7	5.4	—	4.7	4.9	3.6	—	8.9	6.9		
n-C15	11.6	13.6	9.6	—	6.5	15.4	9.5	—	7.0	7.2		
<i>n</i> -C16	7.4	9.2	12.7	—	9.2	17.5	10.9	—	5.3	4.1	_	
Norpristane	6.6	7.1	9.2	—	3.9	6.1	5.1	—	8.3	8.5	_	
<i>n</i> -C17	22.6	7.5	12.9		21.3	18.4	12.0		41.5	42.7	26.2	
Pristane	8.7	9.7	15.9		4.1	3.3	4.2		5.8	9.0	27.7	
<i>n</i> -C18	4.3	5.1	6.6		12.8	—	7.4		6.1	4.7		
Phytane	5.8	6.3	10.2		4.5	—	5.9		3.2	5.0		
Total (µg·g dry weight ⁻¹)	37.6	77.3	85.6		5.9	3.1	75.6		7.3	3.2	0.7	
Total (µg·g fresh weight ⁻¹)	9.5	34.6	27.9		1.2	0.7	21.0		2.1	0.9	0.2	_
Total (µg·g lipids ⁻¹)	135.6	224.9	356.2		244.8	284.4	287.6		16.9	70.9	20.9	
Mean \pm SD (µg·g lipids ⁻¹)		238.9	110.95			272.2	23.9			45.9	35.4	
PCBs												
52	2.9	3.2	2.8		1.4	2.2	3.1	2.2		3.0	2.6	3.3
49	2.0	2.7	2.0	_	0.7	_	2.0	1.2	_	1.9	_	2.2
95-66	4.2	4.3	3.8	8.1	3.7	3.6	4.6	4.7		4.4	2.8	5.0
101-90	7.7	7.8	7.6	5.6	8.4	8.7	7.5	9.0	4.8	9.0	7.9	10.1
110-77	3.0	3.0	3.0	3.1	4.4	4.7	4.0	4.3	3.7	4.1	3.2	4.2
149-123	5.4	5.1	5.3	6.2	7.2	7.1	5.3	7.2	2.5	6.6	3.8	4.8
118	4.1	4.2	4.2	3.1	4.3	4.9	4.1	4.2	4.5	4.1	3.4	4.5
153	8.9	8.7	8.7	11.5	14.3	14.8	8.4	12.6	18.4	13.3	9.7	11.5
138-160	5.6	5.2	5.3	8.0	8.4	9.4	5.5	8.3	8.4	7.4	6.6	7.3
180	4.0	3.5	3.4	7.8	4.2	5.1	3.2	4.0	5.6	4.9	3.3	3.6
170-190	3.1	2.9	2.9	10.1	2.9	3.8	2.8	2.7		3.3	2.1	4.0
Total (ug·g drv weight ⁻¹)	3.5	5.9	6.6	0.3	0.9	0.4	7.0	0.8	0.2	0.5	0.2	0.9
Total ($ug \cdot g$ fresh weight ⁻¹)	0.9	2.6	2.1	0.1	0.2	0.1	2.0	0.2	0.1	0.1	0.1	0.3
Total (ug·g lipids ^{-1})	12.7	17.1	27.6	2.2	38.4	39.1	26.8	68.3	0.4	10.2	5.7	14.1
Mean + SD ($\mu g \cdot g \cdot g \cdot h p \cdot ds^{-1}$)		14.9	10.5		2011	43.1	17.7	0010	0	10.0	4.2	1.111
Chlorinated pesticides												
v-BHC (lindane)	2.4	4.4	2.9	11.6	7.0	5.9	2.8	4.0	8.2	7.2	21.4	3.9
Heptachlor epoxide	3 5	5 5	3.4	5.2	2.5	69	1.6	0.0	7.8	9.8	3.8	49
<i>trans</i> -Chlordane	25.0	12.3	29.2	19.3	22.7	25.1	29.7	17.9	49	17.5	22.0	16.1
<i>cis</i> -Chlordane	12.2	8.8	11.8	10.5	9.6	9.0	12.2	7.6	3.6	11.3	13.4	11.5
trans-Nonachlor	9.5	77	9.5		9.8	6.0	93	27	27	7.8	67	7 5
DDF	13.1	25.1	19.0	26.8	21.8	19.6	28.4	40.8	52.9	16.6	11.2	28.0
TDF	19.1	14.9	12.3	117	21.0	19.6	11.1	11.8	72	14.6	10.8	13.2
DDT	12.0	10.0	7.0	29	1.5	23	0.3	11.0	7.2	93	2.0	9.0
Total (using dry weight ⁻¹)	0.50	0.34	1.15	0.05	0.08	2.5	0.5	0.07	0.06	0.05	0.05	0.14
Total (ug.g fresh weight ⁻¹)	0.57	0.15	0.37	0.05	0.08	0.04	0.74	0.07	0.00	0.05	0.05	0.14
Total (ug.g lipids ⁻¹)	2.12	0.15	1.91	0.01	3.17	4.07	2.83	6.14	0.02	1 15	1.44	2.17
Mean + SD (ug.g lipids ⁻¹)	2.12	0.98	2.0	0.54	5.17	4.07	2.65	0.14	0.15	1.15	0.5	2.17
Motels		2.1	2.0			4.1	1.5			1.0	0.5	
	70.2	70.0	61.6	72.0	00 /	02.2	<u>00 0</u>	80.0	72.5	926	70.2	020
	70.2 5.6	11.9	04.0	72.0	00.4	92.5	09.0	89.0 2.1	12.5	03.0	/0.5	02.0
	J.0	11.8	17.0	J.2	4.5	3.4	3.1	2.1	13.3	0.2	9.9 4 1	1.5
	15.2	ð.U 2 0	0.3	10.0	4.2	2.0	2.1	4.9	5.0	3.4 1.6	4.1	2.1
	4.2	5.2	/.4	0.1	1.9	0.4	3.5 1 E	1.9	4.5	1.0	10.6	3.1
INI	4.8	0.1	4./	0.1	1.2	1.2	1.5	2.2	2.8	3.2	5.0	3.9
Total ($\mu g \cdot g$ dry weight ')	24.6	13.1	10.1	20.0	55.9	57.4	/5.8	05.0	20.0	18.6	1/.5	∠1.9 5 7
iotal (µg·g fresh weight ⁻¹)	6.3	5.8	5.3	4.2	11.9	12.6	20.5	12.6	5.8	5.3	4.5	5.7

Note: TIG, Tigre; QUI, Quilmes; PL, Punta Lara; MG, Magdalena; ---, not detectable.

Table 2. PCDDs and PCDFs in sabalo from the Río de la Plata.

	Relative abundance (%)					
	TIG	QUI	MG			
PCDDs						
TCDDs			_			
PCDDs	30.0	14.3	_			
Hexa-CDDs		67.7	_			
Hepta-CDDs	34.9	9.7				
OCDD	35.0	8.3	100.0			
Total PCDDs (pg·g ⁻¹)	16.6	91.3	76.0			
PCDFs						
TCDFs	100.0	51.6				
PCDFs	_	48.4				
Hexa-CDFs	_	_				
Hepta-CDFs	_	_				
OCDF						
Total PCDFs (pg·g ⁻¹)	21.1	106.5				

Note: TIG, Tigre; QUI, Quilmes; MG, Magdalena; ---, not detectable.

tween feeding habits and bioaccumulation of xenobiotics, and (v) evaluate the possible health risks associated with fish consumption in the area.

Materials and methods

Three fish species that collectively make up >80% of the fish biomass in the Río de la Plata estuary, sabalo (*Prochilodus lineatus*), carp (*Cyprinus carpio*), and mullet (*Mugil cephalus*), were collected between October 26 and December 6 1996 at four stations with differing land uses (Fig. 1): Tigre, on the Paraná delta, upstream from the major urban/industrial center of Buenos Aires, Quilmes, in a heavily populated area downstream from Buenos Aires, Punta Lara, a popular beach located downstream from Quilmes and close to the La Plata City petrochemical port, and Magdalena, a less urbanized coastal area 100 km downstream from Buenos Aires. Due to the scarcity of mullet at Tigre, it was substituted by boga (*Leporinus obtusidens*).

At each station, between two and 10 adult individuals of each species were collected using gill nets, measured, weighed, and dissected to extract dorsolateral muscle samples. A total of 92 fishes of homogeneous standard lengths and weights with a higher proportion of females were collected (sabalo: 43 ± 1.9 cm (average \pm SD), 2.4 ± 0.6 kg, female to male ratio = 1.2, n = 29; carp: 53 ± 9.0 cm, 4.1 ± 2.1 kg, female to male ratio = 1.3, n = 30; mullet: 41 ± 2.0 cm, 1.2 ± 0.2 kg, female to male ratio = 2.1, n = 25; boga: 45 ± 2.4 cm, 1.9 ± 0.3 kg, female to male ratio = 1, n = 8). Pooled muscle tissue samples from each species at each site were transported to the laboratory in refrigerated glass flasks and frozen at -20° C. Initial sample processing included homogenization of muscle samples with a stainless steel blender and determination of the water content (24 h at 105° C).

For organic analyses, aliquots of 7–10 g of muscle homogenates were mixed with preextracted sodium sulfate (1:2) and Soxhlet extracted with a 1:1 dichloromethane – petroleum ether mixture. The extracts were concentrated at 25–30°C under a nitrogen flow to determine total lipids (gravimetry) and subsequently digested with 1 mL of concentrated sulfuric acid in 10 mL of petroleum ether. The supernatant was then purified on silica gel microcolumns (1 g, 5% hydrated) eluted with petroleum ether (F1: PCBs, aliphatic hydrocarbons) and 1:4 dichloromethane – petroleum ether (F2: chlorinated pesticides). Quantification was performed using a KONIK 3000 gas chromatograph equipped with a split-splitless injector operated at 250°C, a flame ionization and an electron capture detector, both operated at 320°C, and a 30-m DB5 capillary column programmed from 50°C (2-min hold) to 135°C (2-min hold) at 15° C min⁻¹ and then to 295° C (10-min hold) at 5° C min⁻¹. Aliphatic hydrocarbons were quantified using individual standards (Supelco) and local diesel fuel and crude oil samples. PCB response factors were calculated for each resolved peak using a 1:1:1 Aroclor 1242-1254-1260 mixture, the published complete composition of the formulations, and CLB1 individual congener standards from the Marine Analytical Chemistry Standards Program, CNRC (Colombo et al. 1995). Chlorinated pesticides were quantified using a standard solution containing α -, β -, and γ -benzene hexachloride (BHC), hexachlorobenzene (HCB), heptachlor, heptachlor epoxide, trans-chlordane, cis-chlordane, DDT and dechlorintation products (DDE and TDE), dieldrin, endrin, and methoxichlor; trans-nonachlor was identified using a technical chlordane solution. PCB method accuracy, checked through the analysis of mussel tissue reference material (NIST SRM 2974), averaged 92.5 \pm 27.5% for 17 certified congeners. PCB analytic precision calculated from duplicate fish analysis averaged 11% for 41 congeners. Detection limits ranged from 0.5 ng·g dry weight⁻¹ for chlorinated pesticides and PCBs to 100 $ng \cdot g^{-1}$ for hydrocarbons.

Selected lipid aliquots were analyzed at the "Ministère de l'Environnement et de la Faune du Québec" to determine coplanar PCBs, dioxins, and furans following previously reported procedures (Colombo et al. 1997). Briefly, extracts spiked with ¹³C12labelled PCBs and polychlorinated dibenzodioxin (PCDD) and dibenzofuran (PCDF) isomers were purified on multilayer silica columns followed by a fractionation of PCBs, planar PCBs, PCDD, and PCDF on alumina columns and additional cleanup on carbon columns for the PCDD/PCDF fractions. Planar PCBs and PCDD/PCDF were spiked with ¹³C12-labelled PCDDs and PCDFs and analyzed by HRGC/HRMS (Hewlett-Packard 5890-VG AutospecO, 34 eV, source at 260°C, static resolution of 10 000) using a 0.25 mm \times 60 m DB5 capillary column programmed from 100°C (1-min hold) to 200°C at 40°C·min⁻¹, from 200 to 235°C (10-min hold) at 3°C·min⁻¹, and to 310°C (15-min hold) at 8°C·min⁻¹. Relative response factors over a four-point calibration curve were calculated for each congener of PCDD/PCDF and planar PCBs. Procedural blanks and standard reference material (Carp-1, National Research Council of Canada) were processed along with the samples.

For trace metal analyses, muscle homogenates (1-2 g dry weight) were incinerated (16 h at 450°C) and then sequentially treated with nitric acid, hydrochloric acid, and hydrogen peroxide (5:1:2) at 90°C. After centrifugation, the extracts were diluted to 25 mL with deionized water and analyzed by flame atomic absorption spectrophotometry using a Perkin Elmer 3110 spectrophotometer equipped with deuterium background corrector, an airacetylene flame, and Perkin Elmer or ISTC hollow cathode lamps. High-purity Johnson Matthey PLC original standards were used to prepare calibration mixtures. The accuracy of the analytical procedure ranged from ± 3 to 11% of the values reported for a certified reference sediment (BCSS-1, National Research Council of Canada). The precision of the data ranged from 2 to 11% (RSD). Detection limits ranged from 0.4 to 0.5 μ g·g dry weight⁻¹ for Zn, Cd, Cu, and Mn, from 0.7 to 0.9 μ g g⁻¹ for Cr and Fe, and from 1.5 to 2.0 $\mu g \cdot g^{-1}$ for Ni and Pb.

Results and discussion

Contamination status of Río de la Plata fish

Tables 1 and 2 present total contaminant concentrations on a dry weight, fresh weight, and lipid basis as well as the major components of hydrocarbons, organochlorines, and trace metals in Río de la Plata fish. Figure 2 shows the total dry weight concentrations and the relative abundance of

Fig. 2. Concentrations of (*a*) aliphatic hydrocarbons, (*b*) chlorinated pesticides, (*c*) PCBs, and (*d*) trace metals in Río de la Plata fish. TIG, Tigre; QUI, Quilmes; PL, Punta Lara; MG, Magdalena. The boga sample collected at TIG is grouped with mullet (see text for explanation).



major components. Among the organic pollutants analyzed, aliphatic hydrocarbons exhibit the highest concentrations in fish muscle (0.7–86 μ g·g dry weight⁻¹), with a dominant contribution of lower molecular weight n-alkanes (n-C12-17) and isoprenoids (farnesane, norpristane, pristane, and phytane). In decreasing order, they are followed by PCBs $(0.2-7.0 \ \mu g g dry \ weight^{-1})$, with a clear predominance of penta- and hexa-chlorobiphenyls, and chlorinated pesticides $(0.04-1.1 \ \mu g g dry \ weight^{-1})$, chiefly as chlordanes (*trans*chlordane, cis-chlordane, and trans-nonachlor) and DDTs (DDE, TDE, and DDT). As expected, dioxins and furans are in the lower ppt range (17–91 and 21–106 pg·g dry weight⁻¹, respectively). Total trace metal concentrations oscillate between 13 and 74 µg·g dry weight⁻¹ with a clear predominance of Zn, especially in carp (88-92 versus 65-84% total metals in the other species).

Table 3 compares the average contaminant concentrations

in Río de la Plata fish with those in species from other environments. Overall, trace metals and organic micropollutants display a different situation; trace metal levels in Río de la Plata fish are in the low range of the reported values, except perhaps Cr, whereas organic contaminants are in the middle to high range, indicating a more critical situation. Among these compounds, hydrocarbon concentrations are quite high, with little data to compare from other environments. Nevertheless, a mean of $18 \,\mu g \cdot g^{-1}$ in sabalo with values as high as 35 μ g aliphatic hydrocarbons \cdot g⁻¹ with a clear petrogenic signature (see Sources and composition of fish microcontaminant residues section) denote the strong impact of oil discharges into the estuary. This corroborates previous findings (Colombo et al. 1989), indicating that discharges of petrochemical effluents, tanker ballast washings, and furtive spillages are still a major problem in this coastal area. PCBs also display a delicate situation; the concentrations are in the

		Concentration (ug·g fresh weig	(ht^{-1})				Concentr (pg·g fre	ation sh weight ⁻¹	^I)	
Environment	Species	Hydrocarbons	Pesticides	PCB	Zn	Cu	Cr	PCDD	PCDF	TEQ	Reference
Río de la Plata	Prochilodus lineatus Cyprinus carpio Mugil cephalus	18.0 5.7 0.4	0.17 0.06 0.02	1.44 0.60 0.14	3.6 12.5 4.1	0.47 0.44 0.44	0.27 0.28 0.25	16.1	11.2	39.3	This study This study This study
Buffalo River	Cyprinus carpio (middle aged)		0.15	4.3				25.0	42	75.0	Loganathan et al. 1995
Mean U.S. rivers	Cyprinus chrysops Ictalurus punctatus Castostomus commersoni		0.57 0.75 0.13	2.94 1.30 1.70				7.8 11.6 8.1	10.2 2.22 22.9	13.1 14.8 12.8	Kuehl et al. 1994 Kuehl et al. 1994 Kuehl et al. 1994
Polluted U.S. rivers	Cyprinus chrysops			30.74							Kuehl et al. 1994
Long Island – Hudson	Morone saxatilis			5.50							Bush et al. 1989
Lake Ontario	Oncorhynchus mykiss (pre- viously Salmo gairdneri)		0.66	2.13							Niimi and Oliver 1989
	Oncorhynchus kisutch Salvelinus namaycush		0.72 1.14	2.30 3.88							Niimi and Oliver 1989 Niimi and Oliver 1989
Michigan rivers	Cyprinus chrysops Oncorhynchus tshawytscha Catostomus commersoni		0.45 0.39 0.08	3.08 1.70 0.27						36.8 38.0 8.6	Giesy et al. 1994 Giesy et al. 1994 Giesy et al. 1994
Lake Michigan	Oncorhynchus tshawytscha		0.98	3.8							Miller 1994
Lahn River	Perca fluviatilis and Rutilus rutilus		0.03	0.78							Schüler et al. 1985
Western Mediterranean	Thunnus thynnus	1.74		0.02							Porte and Albaigés 1993
Western Mediterranean	Mullus barbatus Merluccius merluccius Engraulis encrasicholus	0.72 0.20 2.08	0.05 0.01 0.02	0.20 0.08 0.07							Albaigés et al. 1987 Albaigés et al. 1987 Albaigés et al. 1987
Israel coast	Mullus barbatus Merluccius merluccius		0.04 0.04	0.07 0.02							Ravid et al. 1985 Ravid et al. 1985
South and east coastal Asia	Multispecific average		0.03	0.01							Kannan et al. 1995
Tigris River	Cyprinus macrostomus Garra rufa				59.0 88.5	141 138					Gümgüm et al. 1994 Gümgüm et al. 1994
Jacarepaguá lagoons	<i>Mugil</i> sp. <i>Tilapia</i> sp.				2.20 2.20	0.40 0.20	0.09 0.08				Fernandes et al. 1994 Fernandes et al. 1994
Lake Balaton	Carassius auratus Esox lucius				14.8 10.5	1.24 1.38					Salánki et al. 1992 Salánki et al. 1992

Table 3. Contaminant concentrations in Río de la Plata fish compared with those in species from other environments.

Tanganyika Lake	Stolothrissa tanganyikae Oreochromis niloticus	29.5 4.4	1.10 0.18	Benemariya et al. 1991 Benemariya et al. 1991
African lakes	<i>Tilapia</i> sp.	9.12	2.87	Benemariya et al. 1991
Switzerland lakes	Perca fluviatilis	5.65	0.19	Benemariya et al. 1991
U.S. freshwater	Multispecific average	24.7	0.77	Benemariya et al. 1991
Six Ontario lakes	Catostomus commersoni	5.79	0.95	Miller et al. 1992

middle to high range, with sabalo values comparable with those of moderately polluted Great Lakes and U.S. river fishes. Chlorinated pesticides in Río de la Plata fish are in the middle to low range, lower than Great Lakes and U.S. river mean concentrations, whereas dioxins and furans are in the range of values commonly found.

In summary, the comparison of contaminant levels in Río de la Plata fish with values reported for other environments suggests a low impact of trace metals, corroborating previous results obtained for suspended particles, sediments, and Asiatic clams (Bilos et al. 1998). Organic compounds, on the other hand, evidence a more critical situation with hydrocarbons and PCBs as the most abundant contaminants, reflecting the continued discharge of these highly bioaccumulative compounds.

Interspecies and geographical differences

On a dry or fresh weight basis, all the organic contaminants examined showed a consistent interspecies pattern: the concentrations are higher in sabalo and lowest in mullet and boga. Only carp collected at Punta Lara show high levels, comparable with levels in sabalo from Tigre, Quilmes, and Punta Lara (Fig. 2). Hydrocarbon, PCB, and pesticide concentrations in fish from these four most contaminated sites are 11-22 times higher than the background levels registered in the other fish (e.g., high sabalo and carp versus background: 23 \pm 11 versus 1.0 \pm 0.7, 1.9 \pm 0.7 versus 0.13 \pm 0.07, and 0.22 \pm 0.11 versus 0.02 \pm 0.01 $\mu g \cdot g$ fresh weight^{-1} for hydrocarbons, PCBs, and pesticides, respectively). The background levels of PCBs and pesticides in fishes are comparable with the values registered in Asiatic clams along the Río de la Plata coast: 0.11 ± 0.05 and $0.05 \pm 0.02 \ \mu g \cdot g$ fresh weight⁻¹, respectively (Colombo et al. 1995). The contrasted loads of hydrophobic contaminants in fish are principally related to differences in lipid contents (average 25% in sabalo, 7.7% in carp, except at Punta Lara (26%), and 4.7% in mullet) and in feeding habits of the organisms. Lipid-normalized concentrations are comparable for sabalo and carp, but still clearly discriminate mullet and boga as the least contaminated species (Table 1). The low lipid-normalized values of boga result from the high lipid contents of this species (43%). Conversely, the high lipid-normalized values of carp relative to sabalo reflect the lower and also more variable lipid levels of carp (1.1-26 versus 14-34% in sabalo), suggesting interspecies differences in lipid metabolism. Further studies are needed to evaluate the significance of these sources of variability.

In addition to the differences in lipid content, feeding habits are a crucial factor to interpret the interspecies variations observed. The sabalo is a highly specialized ilyophagous species, which exclusively feeds on fine, organic-rich flocculent detritus. While detritus is certainly important for the other species, these organisms tend to be more selective, avoiding severely polluted muds and feeding primarily on benthic invertebrates, vegetal detritus, zooplankton, and algae (Sibbing 1988; Cardona et al. 1996). Sabalo has several mechanical and physiological adaptations to maximize the assimilation of detrital organic matter, e.g., sucking mouth, secreting pharyngeal diverticles, complex and mucous gillrakers to separate flocculent detritus from water, cardiac stomach, and a labyrinthine intestine with increased relief of

Fig. 3. PCA of the relative contribution of individual contaminants in Río de la Plata fish. Fish samples are identified by species (solid circles, *Prochilodus* (P); triangles, *Cyprinus* (C); open circles, *Mugil* (M) and *Leporinus* (L)) followed by the initial of the sampling station (T, Tigre; Q, Quilmes; P, Punta Lara; M, Magdalena). (*a*) Aliphatic hydrocarbons; sources: crude oil and oiled sediment (CR and OS, respectively, solid squares) and plankton (PK1 and PK2, open squares). (*b*) PCBs; sources: Aroclor 1242, 1254, and 1260 (A42, A54, and A60, respectively, crosses). (*c*) Chlorinated pesticides. (*d*) Trace metals; source: local macrophyte (SC, square).



the mucous membrane that produces a fourfold increase in the absorptive surface (Bowen 1983). Assimilation efficiencies of 30–60% of the organic matter ingested have been reported (Bowen et al. 1984). Due to this high specialization, in severely polluted habitats, sabalo acts as an efficient bioaccumulator of persistent, hydrophobic compounds that are concentrated in the organic muds. These characteristics, together with its large distribution area (the entire Río de la Plata basin, $>3 \times 10^6$ km²), vast abundance (>70% of the total fish biomass), and migrating habits (several hundred kilometres; Sverlij et al. 1993), make the sabalo an efficient carrier of persistent anthropogenic contaminants throughout the region. In addition, the comercial exploitation of the sabalo (87% of total Río de la Plata fishery), which is locally consumed, exported to Asiatic and African countries, e.g., >10 000 tons in 1982 (Sverlij et al. 1993), and used to produce oil and fish flour, converts this organism into a critical contamination pathway for humans.

The pattern of interspecies differences changes in the case of trace metals. Effectively, trace metal concentrations are more homogeneous, reflecting the well-know regulation capabilities of organisms for essential trace metals such as Zn. The most conspicuous trend observed for metals is the consistently higher concentrations in the carp. This pattern almost exclusively reflects the behavior of Zn, which comprised 65–92% of the total metals analyzed.

Superimposed on the interspecies differences, there are clear geographical variations in fish contaminant levels. Fish

from Quilmes and Punta Lara, located downstream from the Buenos Aires major urban/industrial center, present the highest concentrations of organics, whereas those from the more distant Tigre (upstream) and especially Magdalena sites (downstream) show lower levels. Surprisingly, these results suggest some degree of habitat fidelity for these species, some of them well-known migratory species such as sabalo and mullet. The multivariate analyses of the contaminant signatures effectively support these interspecies and spatial trends, suggesting that they could be useful for tracking fish from different locations. As indicated previously, trace metal results are more homogeneous and do not show marked differences between the four sampling stations. However, their relative abundance suggests some subtle trends (see the next section).

Sources and composition of fish microcontaminant residues

The evaluation of total contaminant concentrations in fish revealed the main interspecies and geographical trends. However, this approach does not adequately reflect the grouping of the samples according to their composition. To evaluate this aspect and elucidate the major contaminant sources, principal components analyses (PCA) were performed using the relative contribution of the individual constituents in fish samples and in known sources when available for each contaminant group.

In the case of hydrocarbons, the analyses were performed using the relative abundance of individual aliphatics in fish, a local crude, an oiled sediment from La Plata port, and two phytoplanktonic samples. The first two components explain 83% of the total variability, 55% PC1 and 28% PC2 (Fig. 3a). PC1 is defined by the contribution of odd low molecular weight *n*-alkanes (*n*-C15-17) on the positive side (+PC1), a typical signature of microalgae (Blumer et al. 1971), and of the other components on the negative side (-PC1). PC2 is chiefly determined by n-C14 and the acyclic isoprenoid pristane (+PC2), abundant in zooplankton (Colombo et al. 1996), and by the rest of the components which are clustered in the negative quadrant. Thus, this virtual space defines basically petrogenic (-PC1, -PC2) versus planktonic (+PC1, +PC2) influences. The crude oil and the oiled sediment sample are clustered together in the negative quadrant, close to sabalo from Quilmes and Punta Lara and carp from Punta Lara, indicating an almost exclusive petrogenic hydrocarbon source for these fish. The hydrocarbon profile of these organisms effectively shows a clear n-C12-25 continuous petrogenic pattern. The signal is only partially degraded, as indicated by the small change in the *n*-alkane/isoprenoid ratios relative to fossil fuels, e.g., C17/pristane (0.8-2.8 versus 1.7), and C18/phytane ratios (0.7-1.2 versus 2.5, fish versus crude). This minor degradation is surprising considering the relatively high susceptibility of aliphatics to decay, especially of low molecular weight components. These results suggest that the organisms are feeding on very fresh organic residues arising from petrochemical, industrial, and sewage discharges, e.g., La Plata and Buenos Aires ports, channels, and small polluted tributaries, or the main Buenos Aires sewage that discharges about 2×10^6 m³ of crude effluent per day upstream from Ouilmes.

The contrasting "natural" group in the PCA of hydrocar-

Table 4. TEQs of PCBs, PCDDs, and PCDFs in sabalo from the Río de la Plata.

	TEQ (pg∙g	TEQ (pg·g fresh weight ⁻¹)				
	TIG	QUI	MG			
PCBs						
77	0.0008	0.003	0.00003			
126	0.01	0.05				
118	3.14	9.69	0.06			
105	1.33	4.15	0.05			
156	2.48	8.46	0.09			
180	0.49	1.28	_			
170	2.51	7.23	0.11			
Total PCBs	9.96	30.86	0.31			
PCDDs						
1,2,3,7,8-PCDD	0.63	2.92				
1,2,3,6,7,8-hexa-CDD		1.00				
1,2,3,4,6,7,8-hepta-CDD	0.01	0.04				
OCDD	0.001	0.003				
Total PCDDs	0.641	3.963	_			
PCDFs						
2,3,7,8-TCDF	0.53	1.85				
2,3,4,7,8-PCDF		2.62				
Total PCDFs	0.53	4.47				
Grand total	11.13	39.30	0.31			

Note: TIG, Tigre; QUI, Quilmes; MG, Magdalena; —, not detectable.

bons is represented by mullet and boga samples, which are clustered in the planktonic area, reflecting dominant biogenic hydrocarbon sources. Interestingly, carp and sabalo from Tigre show an intermediate position, closer to petrogenic sources but with some biogenic influence. These results on the hydrocarbon composition agree well with the concentration patterns indicating prevalence of fresh petrogenic residues in the most contaminated sabalo and carp, specially at the Quilmes and Punta Lara sites, and dominance of biogenic hydrocarbons in the less polluted mullet and boga.

The PCA of PCBs was performed using the relative abundance of the different congeners in fish and in Aroclor 1242, 1254, and 1260 formulations. The first two components explain 56% of the total variability, 36% PC1 and 20% PC2 (Fig. 3b). This PCA is largely determined by the opposition between lower chlorinated PCBs (tri- and tetra-CBs) on the negative quadrant (-PC1, -PC2) and higher chlorinated congeners (hexa- and hepta-CBs) on the positive side, which includes highly recalcitrant and bioacumulative PCBs, e.g., 138, 153, and 180 (+PC1). This PCA again separates sabalo from Punta Lara, Tigre, and Quilmes with carp from Punta Lara, with the strongest contribution of lower chlorinated congeners, midway between the Aroclor 1254 and 1260 composition. The other samples show a progressive shift toward a higher contribution of more recalcitrant congeners, grouping the other carp samples with mullet from Quilmes. Varying Aroclor residue inputs along the coast are unlikely to explain this shift, since fish from the same locations are segregated into different groups, e.g., sabalo from Tigre and Quilmes and carp from the same sites. This trend most probably results from the selective elimination of lower chlorinated PCBs in less contaminated fish, which thus show

degraded PCB patterns dominated by the most recalcitrant hexa- (153, 138) and hepta-CBs (187, 183, 174, 180). Lower residue levels in fish with nondetection of less chlorinated congeners would produce an equivalent pattern. This is certainly the case for boga and also probably for sabalo from Magdalena, which are at the extremes of the trend (Fig. 3b), but not for the other samples, which show almost complete PCB detections. Furthermore, a similar decay of the Aroclor composition has been previously observed along the Río de la Plata coast and with increasing age of Asiatic clams (Colombo et al. 1995). These results indicate that most contaminated sabalo, together with carp from Punta Lara, show fresher PCB signatures with a higher proportion of less chlorinated congeners. This is consistent with hydrocarbon results, indicating that these organisms with the highest concentrations and adipose contents feed on fresh residues close to input sources and act as efficient accumulators with minimal degradation of the contaminant signature.

The PCA of chlorinated pesticides groups the samples according to the prevailing residues. The first two components account for 77% of the total variability, 62% PC1 and 15% PC2 (Fig. 3c). PC1 is basically determined by the contribution of chlordanes and TDE (-PC1) and DDE and heptachlor (+PC1). PC2 has a dominant contribution of BHCs, heptachlor epoxide, and HCB (+PC2). The most consistent cluster in this PCA is that formed by sabalo from Tigre and Punta Lara and carp from Quilmes, Tigre, and, to a lesser degree, Punta Lara, which are characterized by a higher relative abundance of chlordanes and TDE. Mullet and boga are again discriminated by their different composition but are distributed among BHC- (Punta Lara, Quilmes) and HCB/ DDE-dominated (Magdalena, Tigre) patterns. Sabalo from Magdalena and Quilmes are very close, showing a stronger contribution of heptachlor epoxide. The PCA of pesticides groups the samples in a manner different from that of hydrocarbons, reflecting the decoupling of industrial and rural signals (e.g., main hydrocarbon inputs are not primary sources of pesticides) and the variability of agricultural loads along the coast following the distribution of small plantations. This would explain the relatively high pesticide concentrations in mullet from the rural area of Magdalena (Table 1). Nevertheless, the PCA of pesticides supports the pattern of mullet and boga segregation from the other species and also the discrimination of Magdalena from the other sampling sites.

For the final PCA of trace metals, the relative abundances of the elements in fish and a common local aquatic macrophyte (Scirpus schenoplectum) were used for the calculations. The first two components explain 95% of the total variance, 78% PC1 and 17% PC2 (Fig. 3d). The opposition between Zn (+PC1) and Cr, Ni, and Cu (-PC1) largely determines the first component, whereas that of Mn (+PC2) and the rest (-PC2) defines PC2. In this space, carp samples are clearly discriminated by their high Zn contents, suggesting a specific physiological requirement. The other major trend in the data is the separation of sabalo from Tigre and Magdalena with a higher Mn contribution, closer to the local macrophyte. As Mn is a major natural element, very abundant in suspended particles and sediments (Bilos et al. 1998), this trend interestingly agrees with the hydrocarbon results, suggesting a more "natural" diet in these organisms. The other fish in the negative quadrant have a stronger contribution of predominantly anthropogenic metals such as Cr, Ni, and Cu. Mullet samples from Quilmes and Magdalena occupy an intermediate position between this group and carp.

Health risks associated with fish consumption

The possible health risks associated with consumption of Río de la Plata fish were evaluated considering the tolerances and action levels fixed for human consumption (U.S. Food and Drug Administration 1990), the allowable consumption rates of fish calculated from dose factors (U.S. Environmental Protection Agency 1997), and the total toxicity equivalents (TEQ) for PCBs, dioxins, and furans.

In the case of trace metals, Río de la Plata fish levels are one to two orders of magnitude below the limits acceptable for human consumption, e.g., 1000 and 30 µg·g fresh weight⁻¹ for Zn and Cu, respectively (Benemariya et al. 1991). The allowable fish consumption rates are estimates of exposure levels (milligrams per kilogram of body weight per day) that are not expected to cause adverse effects over a lifetime period. The allowable consumption of Río de la Plata fish for a 70-kg person based on the dose factors of Zn and Cu (200 and 15 $\mu g \cdot k g^{-1} \cdot da y^{-1},$ respectively), and considering only the fish pathway uptake, would be (Zn-Cu) 3700-2000, 1100–2300, and 3400–2400 g·day⁻¹ for average sabalo, carp and mullet, respectively. Considering a Cd dose factor $(1 \ \mu g \cdot k g^{-1} \cdot da y^{-1})$ and half of the detection limit in fish $(0.1 \ \mu g \cdot g^{-1})$, the allowable consumption would be 700 g $\cdot day^{-1}$. These results indicate that for trace metals, there is no risk associated with fish consumption in the Río de la Plata.

The concentrations of chlorinated pesticides in Río de la Plata fish are generally low, below the action levels, e.g., for DDTs, 0.003–0.14 versus a level of 5 μ g·g fresh weight⁻¹. Chlordane concentrations in fish are more critical, 0.006-0.51 versus an action level of 0.3 μ g·g fresh weight⁻¹. The allowable fish consumption rates for a 70-kg person based on the reference dose factors of DDTs and chlordane (0.5 and 0.06 µg·kg⁻¹·day⁻¹, respectively) would be (DDTs-chlordane) 480–20, 1400–43, and 3500–210 g fish day^{-1} for average sabalo, carp, and mullet, respectively. Heptachlor epoxide (dose factor 0.013 $\mu g \cdot k g^{-1} \cdot da y^{-1}$) is the next most critical pesticide, whereas lindane (dose factor 0.3 μ g·kg⁻¹. day⁻¹) is the least conflicting one, e.g., Punta Lara sabalo daily allowable consumption rate would be 8.3, 72, 240, and 2000 g fish·day⁻¹ based on chlordane, heptachlor epoxide, DDTs, and lindane, respectively.

The risk related to consumption of Río de la Plata fish is even more critical when PCBs, dioxins, and furans are considered. Effectively, total PCB levels range from a low value of 0.05 μ g·g⁻¹ in mullet to 2.2–2.6 μ g·g⁻¹ in sabalo, which exceeds the action level for human consumption (2 μ g·g⁻¹). The allowable fish consumption rate for a 70-kg person based on the reference dose factor of PCBs (0.02 μ g·kg⁻¹. day⁻¹) would be 1.0, 2.3, and 12 g·day⁻¹ for average sabalo, carp, and mullet, respectively. The value decreases to 0.5– 0.6 g·day⁻¹ for sabalo from Quilmes or Punta Lara.

A more precise estimation of the risk associated with fish consumption is obtained through the calculation of TEQs. These factors take into account the abundance and the individual toxicity of PCBs, dioxins, and furans relative to 2,3,7,8-TCDD (Ahlborg et al. 1994). Table 4 presents the TEQs of sabalo collected at Tigre, Quilmes, and Magdalena.

Total values range from 0.31–11.1 to 39 pg·g fresh weight⁻¹ at Quilmes, which exceeds the U.S. Food and Drug Administration advisory of 25 pg·g⁻¹. From these TEQs, PCBs account for about 80%, corroborating that these are the most critical contaminants in the Río de la Plata. This agrees with previous results from Asiatic clams whose TEQs ranged from 7 to 13 $pg \cdot g^{-1}$, with PCBs accounting for 83–88% (Colombo et al. 1997). The allowable consumption rates of Río de la Plata sabalo for a 70-kg person based on TEQ and U.S. Environmental Protection Agency reference doses, potency factors, and risk levels for carcinogenesis (0.6410 pg TEQs·kg⁻¹·day⁻¹ = risk level, 10^{-4} per potency factor, $1.56 \times$ 10^5) would be 145, 4.0, and 1.1 g·day⁻¹ for Magdalena, Tigre, and Quilmes, respectively. The Quilmes result is comparable with those reported for Buffalo River carp, 0.4-1.0 $g \cdot day^{-1}$ (Loganathan et al. 1995).

Persistent organic contaminants and trace metals have been quantified in four fish species from the Río de la Plata estuary collected at four station with differing land uses. Río de la Plata fish present low levels of trace metal pollution but a more critical situation regarding organic pollutants. The highest concentrations were recorded in the sabalo, a dominant and remarkably specialized fatty detritivore. Other known detritivores such as carp and especially mullet presented a lower degree of contamination, indicating different feeding preferences. Superimposed on these interspecies differences, a geographical pattern of highest concentrations in fish from the major Buenos Aires urban center and lowest levels in fish from distant stations was also observed.

The analysis of contaminant signatures by multivariate techniques revealed subtle compositional differences between species and stations. Most contaminated sabalo showed the presence of fresh petrogenic and PCB signatures in the flesh, with levels exceeding tolerance limits (2.2-2.6 μ g PCBs·g⁻¹). Mullet and, in general, fish from distant sites presented higher proportions of biogenic hydrocarbons and of more recalcitrant PCB congeners. Toxicity equivalents calculated for PCBs, dioxins, and furans ranged from 0.3 to >39 pg·g⁻¹, exceeding the recommended guideline. The calculation of allowable consumption rates based on reference dose factors indicated values as low as 0.6 g fish·day⁻¹ for contaminated sabalo from the industrial area with a clear residue hazard ranking: PCBs > (3.7 times) PCDD/PCDF > (3.5 times) chlordane > (8.3 times) heptachlor epoxide > (3.3 times) DDTs > (8.3 times) lindane \approx trace metals. Overall, these results indicate that, as a specialized detritivore, in contaminated areas, the sabalo acts as an effective accumulator of hydrophobic contaminants, feeding on polluted, organic-rich muds close to sewage and major industrial effluents. This feeding strategy probably represents a competitive advantage over other species, which avoid eating these materials. According to the contaminant load, carp appears to exploit a similar resource, most probably indirectly, i.e., not through direct mud ingestion but feeding on invertebrates inhabiting polluted sediments. The limited degradation of the contaminant signatures indicates that sabalo efficiently stores the residues in its rich adipose muscle compartment. Consequently, this fish constitutes a critical contamination pathway with potential health risks for humans. This would comprise foreign countries where the fish is exported and local fishers who include a significant proportion of Río de la Plata fish in their diets. These critical targets would be exposed to a much higher risk than the general Argentinean population, whose freshwater fish consumption is low. Nevertheless, the sabalo is frequently found in large supermarkets and food stores in the region, emphasizing the necessity for further studies to issue responsible management practices for this resource.

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