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Environ. Sci. Technol., **1995**, 29 (4), 914-927 • DOI: 10.1021/es00004a011 • Publication Date (Web): 01 May 2002

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Bioaccumulation of Polychlorinated Biphenyls and Chlorinated Pesticides by the Asiatic Clam *Corbicula fluminea*: Its Use as Sentinel Organism in the Río de La Plata Estuary, Argentina

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Individual PCBs and chlorinated pesticides (CHLPs) were determined in water, suspended particles (SPM), sediments, and Asiatic clams to study their bioaccumulation kinetics and evaluate the usefulness of the clams as sentinel organisms. Bioaccumulation depended on the routes of uptake and bioavailability determined by compound hydrophobicity. CHLPs were mainly present in the dissolved phase, showed a positive correlation between the bivalve-water BAFs and K_{ow} 's and reached steady-state levels before 70 days in a caging experience. These facts reflect an efficient water-gill partitioning process. In contrast, PCBs were only detected in the SPM, showed essentially K_{ow} independent bivalve-sediment and bivalve-SPM BAFs with the lowest values for superhydrophobic heptachlorobiphenyls 174, 180, and 170, and did not reach steady-state levels during a 140-day exposure period. This suggests that the uptake was hindered by their stronger affinity for SPM and the interference of steric factors during intestine absorption. *Corbicula fluminea* are reliable sentinel organisms and showed clear geographical trends along 150 km of the Río de La Plata coast: a progressive decrease of PCB levels and more degraded patterns dominated by recalcitrant congeners, i.e., 153, were observed with increasing distance from the major La Plata-Buenos Aires urban center. A size-related trend overlapped with this spatial gradient: older clams usually showed higher levels and a more degraded PCB signature. CHLPs showed less clear geographical trends due to the presence of multiple sources. CHLP patterns showed a strong dominance of

chlordan-related compounds, particularly *trans*-chlordan which was 2-5 times more abundant than the *cis* isomer. On a temporal scale, from 1986 to 1993, Asiatic clams presented sustained PCB levels but showed a significant decrease of chlordan and DDT, which suggests reduced inputs in recent years.

Introduction

Because of their sedentarism, wide distribution, extensive populations, filtering habits, and capacity to bioaccumulate organic xenobiotics, bivalves have been early recognized as useful sentinel organisms of contamination in aquatic ecosystems (1, 2). This led to the implementation of the mussel watch approach, chiefly based on the study of mussels and oysters, first in the U.S. east and west coasts and Australia and recently as a coordinate International Program including Central and South America (3-6). Although considerably less developed, the same approach has been employed in freshwater ecosystems using other bivalve species such as *Anodonta piscinalis*, *Dreissena polymorpha*, and Asiatic clams (7-10). Within the latter group, the successful invader *Corbicula fluminea* presents several characteristics that make them very interesting for biomonitoring purposes: long life span, worldwide distribution, high biotic potential, high filtration rates, resistance, and easy collection (11). Previous works in the Río de La Plata indicated that *C. fluminea*, which entered the estuary in the early 1970s, is widely distributed (12, 13) and that it is an efficient bioaccumulator of organochlorine compounds (OCL) (14).

Based on this previous experience, in 1992 a project was designed to validate the potential use of *C. fluminea* as a sentinel organism in the Río de La Plata. In this paper, we describe the results obtained for polychlorinated biphenyls (PCBs) and chlorinated pesticides (CHLPs) in bivalves collected at seven locations along 150 km of the Argentinean coast of the estuary and in transplanted organisms which have been used to study the bioaccumulation kinetics of these xenobiotics over a 140-day exposure experience.

Study Area and Sampling

The Río de La Plata is after the Amazon, the second largest River in South America. With a surface of 35 000 km², a huge drainage basin (more than 3 million km²), and freshwater runoff (16 000-28 000 m³/s), it receives about 80 million t/y of particulated matter from temperate and tropical regions of South America (15). The first 80 km of the estuary (from Buenos Aires City to La Plata City) is heavily populated, supporting one-third of the total Argentinean population (≈33 million). Previous studies in the area demonstrated that the heavily industrialized area near La Plata is an important source of petrogenic and pyrogenic hydrocarbons and chlorinated compounds and that Río de La Plata fishes and bivalves reflect this heavy load of xenobiotics presenting high levels of PCBs and CHLPs (14, 16).

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[§] Died March 1994.

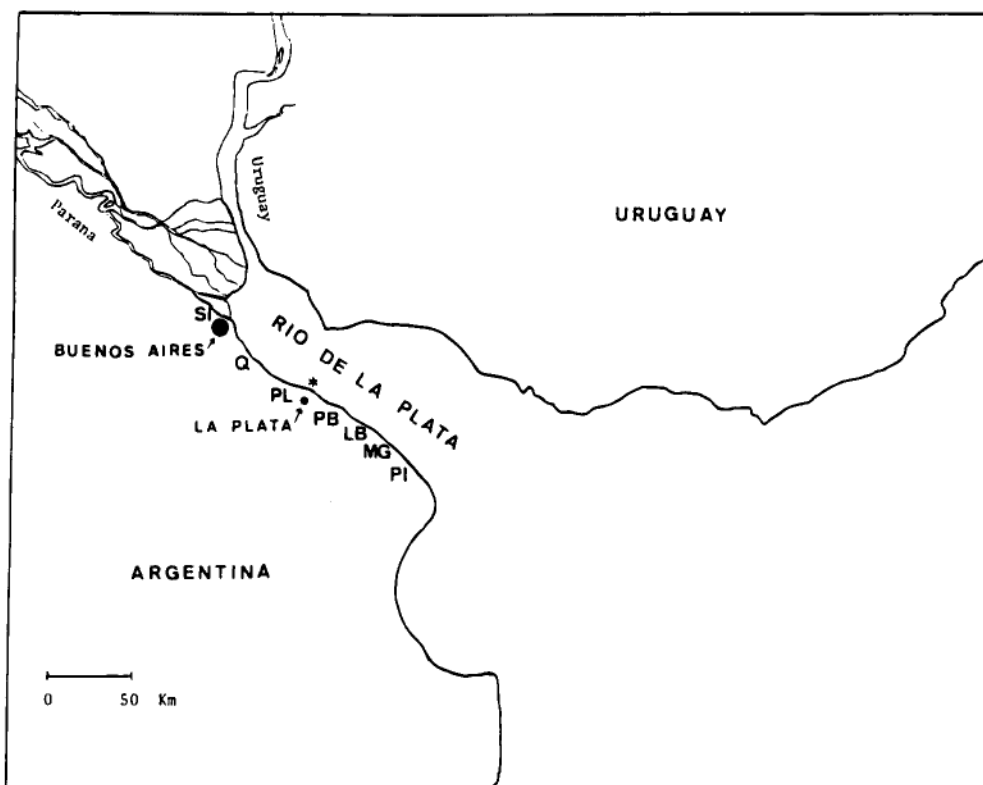


FIGURE 1. Sampling stations along the Argentinean coast of the Río de La Plata: SI, San Isidro; Q, Quilmes; PL, Punta Lara; PB, Palo Blanco; LB, La Balandra; MG, Magdalena; PI, Punta Indio. Asiatic clams collected in MG were transplanted to La Plata port embouchure (marked by an asterisk) for the bioaccumulation experiment.

TABLE 1

Concentration of Total Chlorinated Pesticides and Relative Contribution of Individual Compounds in Dissolved and Particulated Phases of the Río de La Plata^a

pesticide	% total pesticides						
	PI	MG	LB	PB	PL	Q	SI
dissolved							
α-BHC	8.6	15.8	6.9	9.1	10.5	8.5	8.4
β-bBHC	2.5	2.0	2.9	3.6	3.4	4.0	5.9
γ-BHC	43.3	57.9	72.7	69.0	60.1	54.2	55.3
total BHCs	54.5	75.7	82.4	81.7	74.1	66.6	69.6
heptachlor	45.5	24.0	7.5	9.9	11.9	20.0	9.1
heptachlor epoxide	—	—	5.2	3.5	5.5	3.9	6.4
trans-chlordane	—	—	5.0	2.5	5.9	5.0	10.3
cis-chlordane	—	—	—	2.5	2.6	4.4	4.6
trans-nonachlor	—	—	—	—	—	—	—
total chlordane	45.5	24.0	17.6	18.3	26.0	33.4	30.4
total concn (ng/L)	3.4	1.2	1.9	3.1	3.3	5.3	1.9
heptachlor/heptachlor epoxide	—	—	1.4	2.9	2.1	5.1	1.4
trans/cis-chlordane	—	—	—	1.0	2.3	1.1	2.3
particulated							
DDE	100.0	66.7	50.6	57.1	100.0	71.7	48.2
TDE	—	33.3	28.9	23.5	—	28.2	22.6
DDT	—	—	20.4	19.3	—	—	29.2
total DDTs	100.0	100.0	100.0	100.0	100.0	100.0	100.0
total concn (ng/g dw)	6.0	18.3	68.5	37.8	9.3	17.7	22.6
DDT/TDE	—	—	0.7	0.8	—	—	1.3

^a PI, Punta Indio; MG, Magdalena; LB, La Balandra; PB, Palo Blanco; PL, Punta Lara; Q, Quilmes; SI, San Isidro. (—) not detected.

Field sampling was carried out in July 1993 at seven locations along the Argentinean coast of the Río de La Plata: San Isidro (SI), Quilmes (Q), Punta Lara (PL), Palo Blanco (PB), La Balandra (LB), Magdalena (MG), and Punta Indio (PI) (Figure 1). At each site, water (in 12-L containers), integrated surficial sediments (top 0–2 cm, covering the area inhabited by the clams), and bivalves were hand-

collected along the beach during low tide. About 1000 clams were collected in this field campaign. For the bioaccumulation experiment, 124 bivalves were sampled again in October at MG. A total of 87 organisms was immediately transferred in a plastic cage at a station located at the embouchure of La Plata harbor channel in the Río de La Plata (Figure 1).

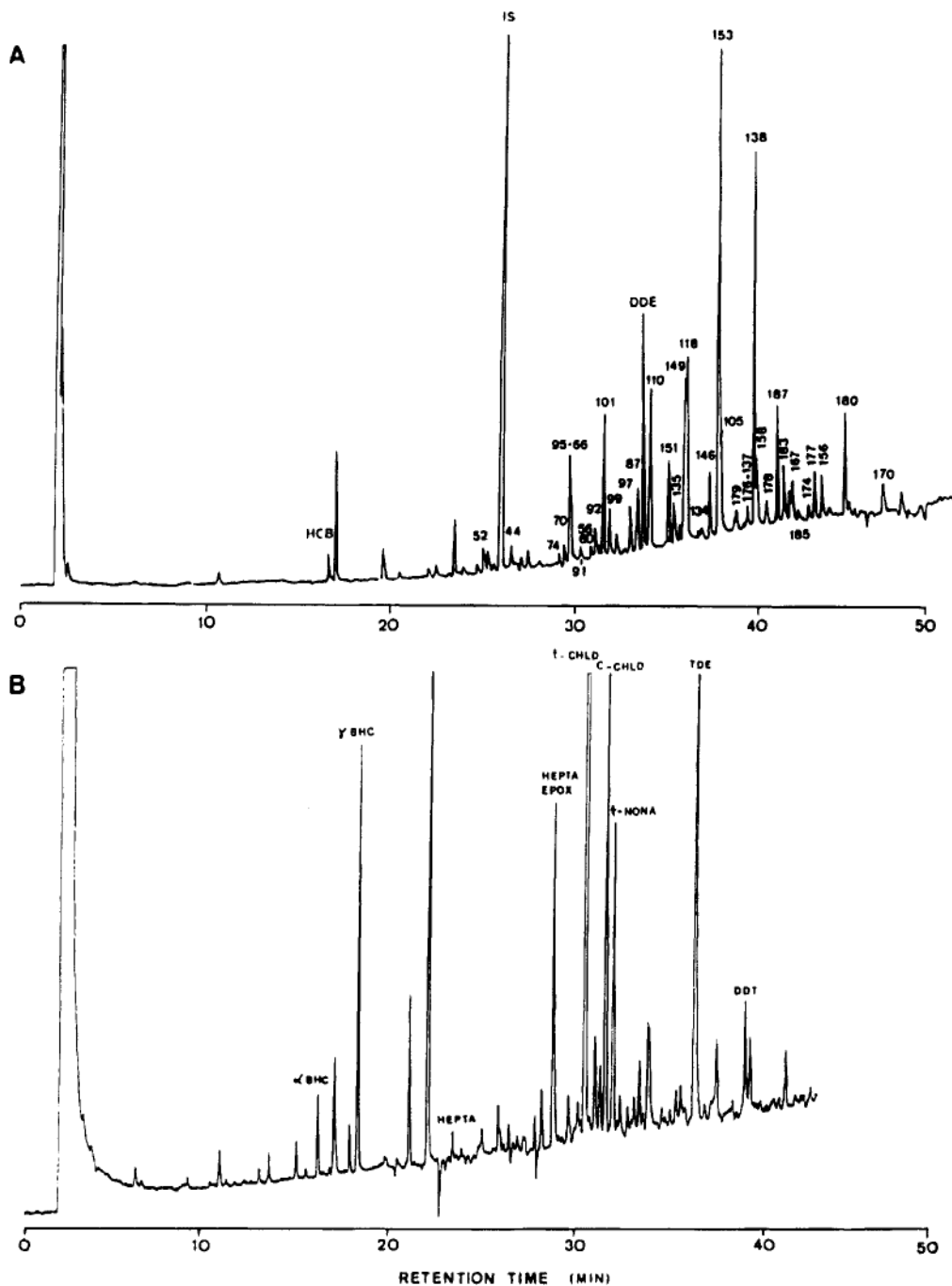


FIGURE 2. Gas chromatograms of silica gel fraction 1 (mainly PCBs) (A) and fraction 2 (mainly chlorinated pesticides) (B) in Asiatic clams collected at Punta Lara (PL).

Methods

Water samples were refrigerated, and suspended particulate matter (SPM) was separated by filtration of 3–6 L under N_2 pressure using solvent-rinsed Delrin filter holders and previously extracted Whatman GF-F glass fiber filters (12.5 cm diameter). Filtered water was simultaneously extracted in 6.5-L Erlenmeyer flasks with 250 mL of *n*-hexane under magnetic agitation. Homogenized sediments were subsampled for the determination of water content (24 h at 110 °C), ignition loss (20 h at 420 °C), grain size analysis (sieve and pipet methods), and extraction of organic compounds. Between 70 and 590 mg dw of SPM and 70 g dw of sediments were extracted (five times) using a 1:4 acetone–petroleum ether mixture and sonication. Bivalves were measured (anterioposterior length), classified into three arbitrary size classes (small: <20 mm; medium: 20–30

mm; and big: >30 mm), and frozen at –20 °C until analysis. Soft bivalve tissues were rinsed with deionized water to remove sand grains, pooled, and homogenized with a stainless steel blender. Aliquots of 5–10 g wet weight were mixed with sodium sulfate (1.5–2 times in wet mass) and, after the addition of aldrin as internal standard, were extracted with the 1:4 acetone–petroleum ether mixture under sonication. The extraction was repeated five times. A 1-mL aliquot of the combined extracts was separated for the gravimetric determination of total lipids, and the rest was evaporated under N_2 , redissolved in 10 mL of petroleum ether, and treated with concentrated sulfuric acid to remove lipids (17). Further purification and separation of PCBs (fraction 1, 3.5 mL of petroleum ether) and most CHLPs (fraction 2, 4 mL of 1:4 dichloromethane–petroleum ether) was achieved by microcolumn chromatography using

TABLE 2

Concentration of Total PCBs and Relative Contribution of Individual Congeners in Suspended Particulate Matter and Sediments of the Rio de La Plata^b

PCBs	% total PCBs													
	SPM							sediments						
	PI	MG	LB	PB	PL	Q	SI	PI	MG	LB	PB	PL	Q	SI
31-28	-	8.3	5.5	4.5	-	-	4.9	-	-	-	-	-	1.7	0.7
33-53-20	-	-	-	4.4	-	-	-	-	-	-	-	-	1.1	-
22-51	-	-	-	-	-	-	-	-	-	-	-	-	0.8	-
45	-	-	-	-	-	-	-	-	-	-	-	-	1.1	-
46	-	-	-	-	-	-	-	-	-	-	-	-	0.4	-
52	-	-	-	7.4	-	-	-	-	-	-	-	-	3.0	-
47-48-75	-	-	-	-	-	-	-	-	-	-	-	-	1.6	-
44	-	-	-	-	-	-	2.5	-	-	-	-	-	1.3	1.3
41-64	-	-	-	-	-	-	2.8	-	-	-	-	-	2.3	0.8
40	-	-	-	-	-	-	-	-	-	-	-	-	-	-
74	-	-	-	-	-	-	-	-	-	-	-	-	2.0	-
70	-	-	-	-	-	-	-	-	-	-	-	-	1.9	-
95-66	-	-	9.4	6.5	8.2	5.8	5.2	-	-	-	-	4.9	4.9	4.1
91	-	-	-	-	-	-	-	-	-	-	-	-	0.4	-
56-60	-	-	-	-	-	-	-	-	-	-	-	1.2	0.5	0.7
92	-	-	-	-	-	-	-	-	-	-	-	-	1.0	0.9
84	-	-	-	-	-	-	-	-	-	-	-	-	0.8	1.7
101-90	-	18.0	9.2	7.5	7.2	7.3	7.0	-	-	-	-	8.1	7.5	7.3
99	-	-	-	-	-	3.4	-	-	-	-	-	3.2	2.5	2.1
97	-	-	-	-	-	2.3	-	-	-	-	-	2.6	1.7	1.5
87-115	-	-	-	-	3.2	3.3	1.9	-	-	-	-	3.2	2.4	2.2
136	-	-	-	-	-	-	-	-	-	-	-	-	1.6	-
110-77	10.8	9.0	7.4	5.6	6.0	5.3	3.9	19.5	-	11.1	5.7	6.4	4.8	4.4
82	-	-	-	-	-	-	-	-	-	-	-	-	0.3	-
151	-	-	-	-	2.2	2.8	2.7	-	-	-	-	2.0	1.7	2.0
135	-	-	-	-	-	3.8	3.0	-	-	-	-	-	1.8	2.1
107	-	-	-	-	-	-	-	-	-	-	-	1.0	0.6	0.7
149-123	13.4	16.7	10.2	7.8	7.4	6.9	6.0	-	-	21.1	12.0	6.4	5.0	5.3
118	-	-	6.7	5.4	5.2	5.5	5.4	-	-	-	-	5.0	4.1	3.9
134	-	-	-	-	-	-	-	-	-	-	-	-	0.6	0.6
131	-	-	-	-	-	-	-	-	-	-	-	-	-	1.3
146	-	-	-	-	-	2.1	-	-	-	-	-	1.8	1.1	0.7
153-132	36.5	30.3	19.4	16.9	18.5	14.0	16.0	48.9	57.5	39.6	27.2	15.2	8.9	13.5
105	-	-	-	-	-	-	-	-	-	-	-	3.2	2.3	2.4
141	-	-	4.8	4.9	4.7	5.2	4.0	-	-	-	-	2.1	1.2	2.1
176-137	-	-	-	-	-	-	-	-	-	-	-	1.3	0.9	0.8
138-160	16.2	10.4	8.0	6.3	8.4	6.5	5.8	19.8	35.1	18.8	12.9	8.0	5.5	6.6
158	-	-	-	-	-	-	-	-	-	-	-	2.0	1.4	1.6
178-129	-	-	-	-	-	-	-	-	-	-	-	-	0.9	0.9
175	-	-	-	-	-	-	-	-	-	-	-	-	-	2.6
187	-	-	3.1	3.0	2.4	2.1	2.7	-	-	2.8	5.6	2.2	1.2	-
183	-	-	-	1.0	1.2	1.3	1.4	-	-	-	-	1.2	0.7	1.2
128	-	-	-	3.0	2.9	3.3	2.6	-	-	-	-	3.0	1.7	2.2
185	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.7
174	-	-	4.0	2.7	2.2	1.9	2.3	-	-	-	6.0	2.0	1.4	1.6
177	-	-	-	2.0	1.9	1.3	1.7	-	-	-	5.1	1.3	0.9	1.3
171-156-202	-	-	-	4.5	5.8	5.4	6.3	-	-	-	-	3.3	3.1	4.5
201-173-157	-	-	-	-	-	-	-	-	-	-	-	-	2.0	1.9
180	13.9	7.7	5.3	5.1	5.5	3.7	4.8	11.9	7.3	6.5	11.9	3.7	2.8	5.2
193	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-
191	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2
170-190	9.2	7.6	7.1	3.7	4.1	3.3	3.7	-	-	-	8.8	3.6	2.2	3.7
199	-	-	2.4	1.1	1.0	0.8	1.1	-	-	-	1.9	0.5	0.4	0.5
203-196	-	-	2.8	-	1.2	1.2	1.3	-	-	-	3.0	1.0	0.5	0.8
189	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1
195-208	-	-	-	-	-	0.8	-	-	-	-	-	-	0.3	0.4
194	-	-	-	1.3	0.7	0.7	1.1	-	-	-	-	0.6	0.4	0.7
205	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.1
total concn (ng/g dw)	5.3	11.1	29.2	29.0	37.2	54.2	23.7	0.07	0.05	0.05	0.07	0.48	2.23	2.42
153/138	2.3	2.9	2.5	2.7	2.2	2.2	2.8	2.5	1.6	2.1	2.1	1.9	1.6	2.0

* PI, Punta Indio; MG, Magdalena; LB, La Balandra; PB, Palo Blanco; PL, Punta Lara; Q, Quilmes; SI, San Isidro. (-) not detected.

Pasteur pipets filled with 1 g of 3% deactivated silica gel.

Quantification of chlorinated compounds was carried out by high-resolution gas chromatography using a Shimadzu GC-7AG gas chromatograph equipped with a 0.25 mm × 30 m SPB-5 silica column, a split-splitless injector

(split ratio = 8), and an electron capture detector operated at 320 °C. The column temperature was programmed from 135 (1-min hold) to 295 °C (8-min hold) at 3.5 °C/min. PCB congeners were quantified with individual response factors for each resolved peak calculated using a 1:1:1 mixture of

TABLE 3

Concentration of Total PCBs and Relative Contribution of Individual Congeners in Asiatic Clams from the Rio de La Plata^a

PCBs	% total PCBs															station and size					bioaccumulation experiment									
																PBS	PBM	PBB	PLS	PLM	PLB	QS	OM	SIS	SIM	day 0	day 4	day 22	day 68	day 140
	PIS	PIM	PIB	MGM	MGB	LBS	LBB	PBS	PBM	PBB	PLS	PLM	PLB	QS	OM	SIS	SIM	day 0	day 4	day 22	day 68	day 140								
18-17	-	-	-	-	-	-	-	-	-	0.1	-	-	0.8	-	-	0.8	0.8	-	-	-	-	-	-	-	-	-				
15	-	-	-	-	-	-	-	0.1	0.1	-	-	-	0.2	-	-	0.2	0.2	-	-	-	-	-	-	-	-	-	-			
24-27	-	-	-	-	-	-	-	0.1	-	0.1	-	-	0.1	-	-	0.1	0.2	-	-	-	-	-	-	-	-	-	-			
16-32	-	-	-	-	-	-	0.3	0.2	0.2	0.2	0.2	0.2	0.3	0.4	0.2	0.3	0.3	-	-	-	-	-	-	-	-	-	-			
31	-	-	-	-	-	-	0.6	0.6	0.4	0.4	0.4	0.4	0.6	0.6	0.6	0.7	0.7	-	-	-	-	-	-	-	-	-	-			
28	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.9	0.9	0.3	-	-	-	-			
33-53-20	-	-	-	-	0.2	-	-	0.4	0.1	0.1	0.2	0.2	0.2	0.5	0.3	-	0.3	-	-	-	-	-	-	-	-	-	-			
22-51	-	-	-	-	-	-	-	0.5	-	-	0.2	0.2	-	0.4	0.3	0.2	0.2	-	-	-	-	-	-	-	-	-	-			
45	-	-	-	-	-	-	-	0.7	0.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3			
46	-	-	-	-	-	-	-	-	-	-	-	-	0.3	-	-	-	0.0	-	-	-	-	-	-	-	-	-	-			
52	-	-	-	-	1.4	0.8	2.3	2.3	1.9	2.2	2.2	2.4	2.0	2.8	2.9	3.8	4.2	-	-	-	2.0	2.8	2.8	2.3	2.3	2.4	2.4			
49	-	-	-	-	0.7	-	-	1.1	1.1	2.3	-	-	7.6	7.5	-	-	-	-	-	-	-	-	-	-	-	-	4.7			
47-48-75	-	-	-	-	0.5	-	1.2	1.1	0.9	1.0	0.9	0.7	1.8	1.7	1.1	1.4	-	-	-	-	-	1.5	1.5	1.2	1.2	1.2	0.6			
44	-	-	-	-	0.3	0.5	0.7	0.9	0.6	0.7	0.8	1.0	1.4	1.4	2.3	2.7	-	-	-	-	0.9	1.1	1.1	1.2	1.2	0.6	0.3			
14-59-37	-	-	-	-	-	-	0.4	0.5	0.2	0.3	0.4	0.4	0.5	0.5	0.5	-	-	-	-	-	-	-	-	-	-	-	0.3			
41-64	-	-	-	-	0.6	0.2	1.1	1.1	0.8	0.8	1.0	0.8	0.6	1.1	1.1	1.7	1.9	-	-	-	1.2	1.5	1.5	1.5	1.5	1.5	0.7			
40	-	-	-	-	0.5	0.1	0.3	0.3	0.3	0.3	-	0.1	-	-	0.4	0.2	-	-	-	-	-	-	-	-	-	-	0.0			
74	-	-	-	-	0.6	0.1	0.9	0.8	0.7	0.8	1.0	1.0	1.0	1.0	0.8	1.7	1.6	-	-	-	-	-	-	-	-	-	0.3			
70	-	-	-	-	0.9	0.4	1.6	1.5	1.1	1.4	1.6	1.6	1.1	2.1	1.8	3.5	3.6	-	-	-	0.9	1.4	1.4	1.2	1.2	0.5	0.5			
95-66	2.6	0.5	-	2.0	3.0	3.7	5.4	5.0	6.2	4.6	5.4	6.7	6.3	6.8	7.4	7.5	-	-	-	-	4.3	6.3	6.3	6.4	6.4	4.9	4.9			
91	-	-	-	-	0.1	0.5	0.4	0.4	0.4	0.5	0.4	0.6	0.6	1.0	0.9	0.9	0.8	-	-	-	-	-	-	-	-	-	0.4			
56-60	-	-	-	-	0.6	0.2	0.2	0.6	0.4	0.4	0.5	0.4	0.4	1.2	1.0	1.6	1.8	-	-	-	-	-	-	-	-	-	0.7			
92	-	-	-	-	1.5	1.0	1.3	1.4	1.3	1.5	1.7	1.5	2.0	2.0	2.0	2.2	1.8	-	-	-	2.4	0.8	0.7	0.7	0.7	1.7	1.7			
84	-	-	-	-	0.6	0.2	0.5	0.6	0.4	0.4	0.6	0.7	1.4	1.3	2.2	2.2	1.8	-	-	-	-	-	-	-	-	-	0.9			
101-90	5.3	5.8	5.1	4.5	4.8	7.3	8.1	7.7	7.4	8.1	9.0	8.5	8.1	8.1	9.6	8.9	-	-	-	-	6.3	7.6	7.6	7.9	7.9	9.1	9.1			
99	-	-	-	2.4	2.3	2.9	3.2	3.0	2.6	2.8	3.3	3.0	3.2	3.2	3.4	4.4	-	-	-	-	4.3	6.3	6.3	6.4	6.4	4.9	4.9			
83	-	-	-	-	0.3	0.8	0.0	0.3	0.0	0.2	0.3	0.2	0.5	0.5	0.7	-	-	-	-	-	-	-	-	-	-	-	0.4			
97	-	-	-	1.5	1.7	2.6	1.7	2.0	1.9	1.8	1.8	2.1	2.2	2.1	2.4	2.4	-	-	-	-	-	-	-	-	-	-	0.2			
87-115	-	-	-	-	0.4	1.8	0.6	1.8	1.7	1.4	1.8	1.8	1.7	2.3	2.3	3.5	3.4	-	-	-	-	-	-	-	-	-	0.2			
136	-	-	-	-	-	-	0.7	0.6	1.3	0.8	1.0	1.2	1.3	1.9	1.9	-	-	-	-	-	-	-	-	-	-	-	1.5			
110-70	3.8	2.9	3.1	1.6	2.5	4.2	4.1	3.9	3.8	3.9	4.1	4.4	4.5	4.6	5.8	6.3	-	-	-	-	4.0	4.5	4.5	4.8	4.8	4.4	4.4			
82	-	-	-	-	1.3	0.1	-	0.4	-	-	0.2	0.2	0.3	0.3	-	0.6	0.7	-	-	-	-	-	-	-	-	-	0.6			
151	3.9	2.4	2.2	2.6	2.0	3.7	2.6	2.6	2.7	2.6	2.8	2.7	2.0	2.2	1.9	1.7	-	-	-	-	2.1	2.4	2.4	2.6	2.6	2.6	2.6			
135	4.6	-	-	1.7	1.5	3.3	1.9	2.0	2.1	2.0	2.1	1.9	1.5	1.9	1.7	1.7	-	-	-	-	1.6	1.8	1.8	1.9	1.9	2.2	2.2			
107	-	-	-	-	0.3	0.6	0.8	0.9	0.6	0.8	0.6	0.5	0.5	0.5	0.7	0.7	-	-	-	-	0.6	0.5	0.5	0.5	0.5	0.9	0.9			
149-123	8.4	7.8	9.1	6.8	7.0	7.1	6.1	5.6	6.2	5.6	5.6	5.7	4.8	4.7	3.8	3.5	-	-	-	-	5.8	5.2	5.2	5.3	5.3	5.3	5.3			
118	4.9	4.6	1.8	4.3	4.1	5.2	4.0	4.2	4.0	4.0	4.9	4.9	4.7	4.5	4.5	3.8	-	-	-	-	4.3	4.0	4.0	4.5	4.5	4.0	4.0			

134	-	-	-	-	-	0.2	0.7	0.7	0.5	0.8	0.4	0.4	0.2	0.4	0.6	0.3	0.3	0.4	-	-	-	-	-	-	0.5	0.5	1.2
146	2.4	4.0	3.3	2.9	3.0	2.4	1.9	2.3	2.0	2.3	2.0	1.9	1.9	1.3	1.3	1.2	1.2	1.2	2.2	2.6	2.2	2.2	2.2	2.2	1.7	1.7	2.2
153-132	30.5	38.3	44.7	36.2	18.7	33.7	16.0	15.4	20.3	16.6	16.1	19.5	10.8	12.2	12.5	10.0	10.0	34.6	29.1	34.6	29.1	34.6	29.1	17.1	17.1	16.4	18.5
105	0.9	-	-	-	-	-	0.4	0.6	0.3	0.6	0.4	0.4	0.2	0.2	0.3	0.1	0.2	0.2	0.4	0.2	0.4	0.2	0.4	0.8	0.7	1.1	-
141	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
179	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
130	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
176-137	-	0.8	-	1.0	1.3	0.7	1.0	1.8	1.4	1.2	0.9	1.1	0.9	0.7	0.6	1.9	2.2	1.1	1.0	0.4	0.4	0.4	0.4	0.9	0.8	0.8	1.7
138-160	11.5	11.3	11.3	9.9	10.4	7.6	7.3	6.2	5.5	6.1	6.6	6.1	5.7	4.5	4.3	4.6	4.3	9.9	8.7	9.9	8.7	9.9	8.7	6.5	5.9	6.3	
158	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
178-129	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
182-187-159	6.2	5.4	5.5	4.9	4.2	2.7	2.7	2.2	2.0	2.0	1.9	1.7	2.0	1.0	0.9	0.9	0.6	2.9	3.6	2.9	3.6	2.9	3.6	2.5	1.2	1.8	
183	1.7	1.7	1.6	1.0	1.2	1.0	0.8	1.0	0.8	0.9	0.8	0.8	0.8	0.5	0.5	0.4	1.1	0.8	3.6	2.4	1.1	0.8	2.1	1.7	2.1	1.8	
128	3.9	2.3	1.5	1.9	1.6	1.1	2.2	1.4	1.4	1.4	1.1	1.2	1.3	1.3	1.1	1.5	1.7	2.4	1.8	1.9	1.8	1.9	1.9	1.8	1.8	2.1	
167	1.1	2.0	2.5	1.1	1.4	0.3	1.5	0.4	0.4	0.6	0.4	0.4	0.6	0.3	0.5	0.5	0.3	1.4	0.8	0.6	0.5	0.8	0.6	0.6	0.5	0.8	
185	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
174	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
177	3.5	2.2	2.2	2.1	2.2	1.3	1.3	1.6	1.2	1.3	1.0	1.1	1.0	0.6	0.7	0.6	0.6	1.6	1.4	1.6	1.4	1.8	1.3	1.0	1.0	1.2	
171-156-202	-	1.6	3.9	2.0	1.5	1.2	1.8	2.6	2.0	2.4	2.3	2.2	2.3	1.6	1.6	1.7	1.4	1.8	0.9	1.8	0.9	1.4	1.4	2.3	2.3	2.2	
201+173+157	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
180	4.6	4.3	5.5	3.9	3.5	2.0	2.2	1.6	1.6	1.9	1.4	1.4	1.4	0.8	0.9	0.6	0.6	2.7	2.4	2.4	2.4	2.4	1.8	1.8	1.8	2.7	
193	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
191	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
170-190	-	1.4	1.3	1.2	0.6	0.6	0.7	0.7	0.6	0.5	0.4	0.4	0.7	0.3	0.4	0.1	0.1	0.2	0.9	0.7	0.7	0.7	0.4	0.7	0.7	0.5	
198	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
199	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
203-196	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
total concn (µg/g of L)	0.5	0.9	0.8	3.3	3.5	5.0	6.7	4.8	6.7	6.2	7.1	8.1	9.8	9.6	9.9	9.5	8.8	2.8	2.6	2.6	2.6	2.6	4.9	9.2	9.2	11.6	
SD	0.1	0.1	0.3	0.8	0.8	0.4	0.6	0.5	1.2	1.2	1.2	0.8	1.0	1.0	1.0	0.8	1.4	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.7	
153/138	2.6	3.4	4.0	3.9	3.5	2.5	4.6	2.6	2.8	3.3	2.5	2.7	3.4	2.4	2.9	2.7	2.3	3.5	3.3	3.5	3.3	3.5	2.6	2.8	2.8	2.9	
length (mm)	12.6	21.9	31.8	24.7	33.6	15.6	39.5	14.3	27.7	35.4	17.1	22.8	38.0	17.2	24.2	17.4	20.7	24.9	26.7	24.9	26.7	25.6	26.5	26.5	26.5	29.5	
SD	3.1	3.5	1.1	2.1	2.9	2.8	3.8	4.1	2.3	6.1	2.1	1.9	4.0	1.8	6.3	1.7	0.7	1.8	2.8	2.8	2.8	2.1	1.7	1.7	1.7	1.4	

^a PI, Punta Indio; MG, Magdalena; LB, La Balandra; PB, Palo Blanco; PL, Punta Lara; Q, Quilmes; SJ, San Isidro; S, small; M, medium; B, big; L, lipid. ^b (-) not detected.

TABLE 4
Concentration of Total Chlorinated Pesticides and Relative Contribution of Individual Compounds in Asiatic Clams from the Rio de La Plata^a
 % total pesticides

pesticide	station and size																bioaccumulation experiment					
	PIS	PIM	PIB	MGM	MGB	LBS	LBB	PBS	PBM	PBB	PLS	PLM	PLB	OS	QM	SIM	day 0	day 4	day 22	day 68	day 140	
HCB	0.6	0.6	-	0.4	0.2	0.6	0.3	0.6	1.0	0.9	0.9	1.1	0.6	1.6	2.6	0.3	0.5	1.1	1.1	1.1	1.3	0.7
α -BHC	11.5	11.1	9.0	6.2	4.6	1.9	3.5	2.6	1.6	0.9	1.2	1.3	1.6	2.8	4.5	1.0	2.3	2.1	3.1	2.8	1.5	1.5
β -BHC	3.7	2.0	1.3	2.1	1.8	0.7	1.1	1.0	0.9	0.6	0.9	0.8	0.9	1.5	1.3	0.6	1.7	1.6	1.8	1.8	1.2	1.2
γ -BHC	20.2	15.7	14.3	17.2	17.2	6.4	8.8	5.2	4.8	3.9	5.8	6.6	7.0	8.4	12.1	1.9	7.2	12.1	8.9	6.2	6.6	6.6
total BHCs	35.3	28.7	24.6	25.6	23.6	9.0	13.4	8.8	7.2	5.4	7.9	8.7	9.5	12.8	17.8	3.6	11.3	15.7	13.9	10.8	9.3	9.3
heptachlor	3.4	2.8	3.3	2.1	2.0	3.0	2.6	4.9	7.2	6.2	3.4	3.9	2.1	2.6	4.2	5.4	8.6	7.3	4.3	3.7	3.3	3.3
heptachlor epoxide	5.3	4.1	3.8	5.0	5.4	3.8	4.2	4.1	4.9	5.7	7.0	6.0	6.2	4.4	4.0	6.6	2.4	4.1	5.5	4.0	5.0	5.0
trans-chlordane	19.0	27.6	30.6	22.6	25.0	28.4	24.5	30.1	28.0	28.8	28.5	28.8	32.9	27.3	24.7	29.3	22.7	28.4	27.4	30.7	29.6	29.6
cis-chlordane	4.7	5.0	6.1	5.5	4.9	9.0	7.2	12.4	11.1	11.5	10.0	8.8	9.3	10.5	9.1	11.0	8.3	10.5	12.0	10.9	11.5	11.5
trans-nonachlor	5.3	4.4	4.2	4.2	3.9	5.3	5.1	7.4	6.1	6.8	6.2	5.2	5.2	4.8	4.0	5.8	6.6	5.9	8.0	7.3	8.7	8.7
total chlordane	37.7	43.9	48.0	39.5	41.2	49.5	43.5	59.0	57.3	59.1	55.1	52.6	55.7	49.6	46.0	58.1	48.6	56.3	57.2	56.6	58.1	58.1
DDE	6.3	8.5	10.0	10.1	5.9	14.6	12.9	8.2	11.1	10.1	14.7	15.5	10.3	8.1	12.6	9.2	14.6	6.7	8.3	10.7	10.1	10.1
TDE	16.4	12.7	13.3	18.3	22.8	19.1	22.0	17.1	17.0	18.5	16.9	18.0	20.1	22.0	17.3	16.8	19.2	16.7	15.8	17.4	19.2	19.2
DDT	3.7	5.5	4.0	6.1	6.2	7.2	7.9	6.4	6.4	5.9	4.6	4.0	3.9	5.9	3.7	12.1	5.9	3.5	3.7	3.2	2.6	2.6
total DDTs	26.4	26.8	27.4	34.5	34.9	40.9	42.9	31.7	34.5	34.6	36.1	37.6	34.3	36.0	33.5	38.1	39.7	26.9	27.9	31.3	32.0	32.0
total concn (μ g/g of L)	0.4	0.5	0.4	1.2	1.5	2.0	2.2	3.9	3.6	3.7	2.4	2.2	3.7	4.5	3.1	6.0	0.7	1.3	2.4	3.3	3.4	3.4
SD	0.1	0.7	0.9	0.4	0.4	0.8	0.6	1.2	1.5	1.1	0.5	0.6	0.3	0.6	1.0	0.8	0.0	1.8	0.8	0.9	0.6	0.6
heptachlor/ heptachlor epox	0.6	0.7	0.9	0.4	0.4	0.8	0.6	1.2	1.5	1.1	0.5	0.6	0.3	0.6	1.0	0.8	0.0	1.8	0.8	0.9	0.6	0.6
trans/cis-chlordane	4.0	5.5	5.0	4.1	5.1	3.1	3.4	2.4	2.5	2.5	2.8	3.3	3.6	2.6	2.7	2.7	2.7	2.7	2.3	2.8	2.6	2.6
DDT/DE	0.2	0.4	0.3	0.3	0.3	0.4	0.4	0.4	0.4	0.3	0.3	0.2	0.2	0.3	0.2	0.7	0.3	0.2	0.2	0.2	0.2	0.1

^a Abbreviations as in Table 3. (-) not detected.

Aroclors 1242, 1254, and 1260 and the published complete composition of the formulations (18). These response factors were compared with those calculated from solutions of 15 individual congeners (CLB1) purchased from the Marine Analytical Chemistry Standards Program of the Canadian National Research Council. The results were fairly comparable with somewhat higher responses (average 13%) for the CLB1 mixtures. This discrepancy is probably related to the effect of coeluting congeners in the Aroclor mixture (19). As these mixtures are the origin of the residues found in the environment which also present several coeluting peaks, it was considered that quantification using Aroclor-derived response factors was more accurate. Identification and quantification of CHLPs were carried out with a standard solution of 14 pesticides (α -, β -, and γ -BHC, HCB, heptachlor, heptachlor epoxide, *trans*-chlordane, *cis*-chlordane, DDE, DDT, TDE, dieldrin, endrin, and metoxichlor). A solution of technical chlordane was used to identify *trans*-nonachlor, which was quantified using the response factor of chlordanes. Standards were passed at least once during each working day and usually twice, at the beginning and end of the day. Bivalve samples were analyzed as duplicate or triplicate depending on the availability of material. The reproducibility of the analytical method averaged 12% for total PCBs and 17% for total CHLPs (RSD). Figure 2 show representative chromatograms of PCBs and CHLPs in clams.

Results and Discussion

1. Partitioning of OCLs in Water, SPM, and Sediments.

Tables 1 and 2 show the concentrations of PCBs and CHLPs in these three compartments. Most CHLPs were detected only in the dissolved phase where total concentrations ranged from 1.2 to 5.3 ng/L; DDTs were the sole pesticides found in the SPM (6.0–68 ng/g; Table 1). In contrast to most CHLPs, PCBs were always below the detection limit in the dissolved phase but were clearly present in the SPM at levels ranging from 5.3 to 54.2 ng/g (Table 2). This preferential partitioning of PCBs in the SPM is related to their high hydrophobicity and strong affinity for fine particles. In major European rivers, the distribution coefficients (K_d) SPM–water of individual PCBs ranged between 10^4 and 10^6 (20). Assuming a maximum dissolved PCB concentration equal to our detection limit for the Aroclor mixture (≈ 1 ng/L) and taking the average PCB level in SPM (27 ng/g), the K_d estimate would be $\geq 2.7 \times 10^4$. The detection of PCBs in the particulated phase was probably enhanced by the retention of very small particles enriched in organic matter (SPM ignition loss: 7–32%) and PCBs (20). The nominal cutoff of GF/F filters must have been considerably lower than $0.7 \mu\text{m}$ after filtration of a few milliliters of Río de La Plata turbid waters (44–260 mg SPM/L). The detailed composition of SPM has not been examined, but previous studies indicated that in common with other turbid rivers it is dominated by silt-sized minerals with a strong contribution of terrestrial detritus and a comparatively lower abundance of planktonic organisms. The dominance of CHLPs, especially of BHCs, in the dissolved phase is not unexpected considering the usually higher water solubility of these compounds and the abundance of dissolved organic matter in Río de La Plata waters, which after filtration still displayed a marked yellowish color.

Due to the well-known reduced affinity of chlorinated compounds with coarse sediments, PCB concentrations

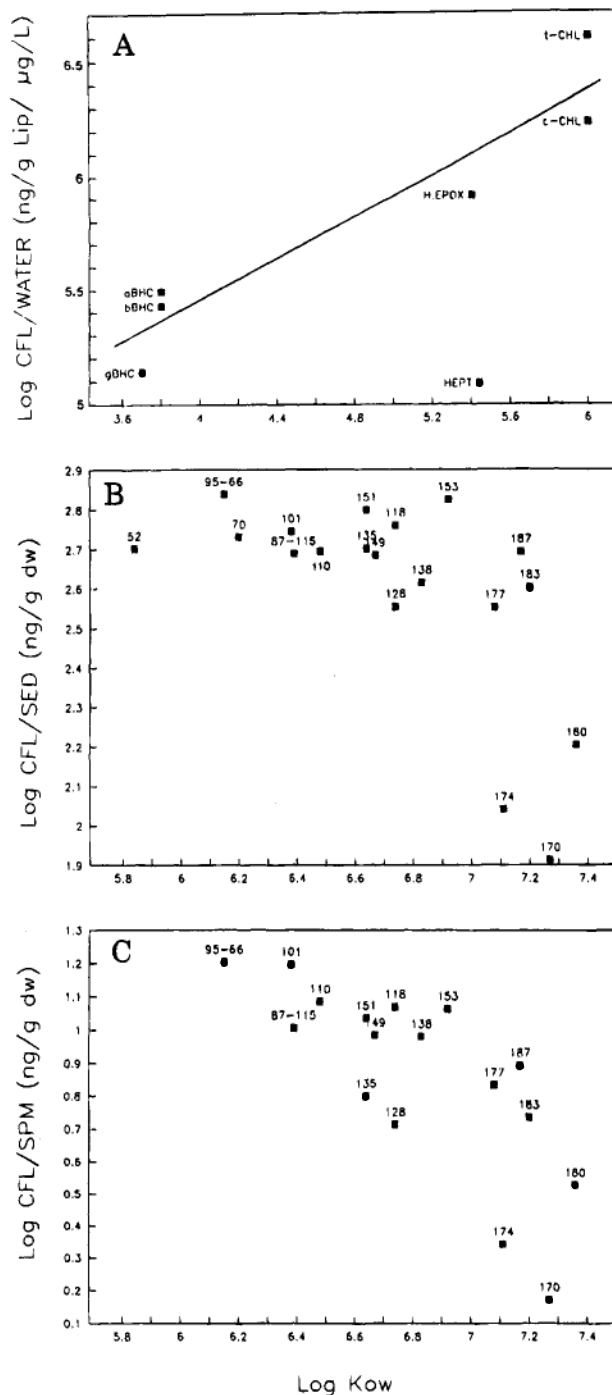


FIGURE 3. Bioaccumulation factors in *Corbicula fluminea* (CFL) collected at Quilmes versus octanol–water partition coefficients: (A) CFL/water BAFs of chlorinated pesticides; (B) CFL/sediment BAFs; and (C) CFL/SPM BAFs of individual PCB congeners.

are much lower (0.05–2.4 ng/g; Table 2) in Río de La Plata beach sediments composed of 93–99% sand with very low organic matter contents (0.5–1.1% ignition loss). Some CHLPs, i.e., DDE, were only discernible as minute peaks in a few sediment samples.

2. Concentrations of OCLs in Asiatic Clams: Temporal Trends. The concentrations of PCBs and total CHLPs in Asiatic clams from the Río de La Plata ranged from 0.5 to 12 and from 0.4 to $6 \mu\text{g/g}$ lipids, respectively (Tables 3 and 4). Compared to other freshwater bivalves, these PCB levels are higher than those reported for caged *Anodonta piscinalis* exposed in an unpolluted area, $0.09 \mu\text{g}$ of PCBs/g of lipids, which increased to $2.4 \mu\text{g/g}$ (in the range of our values) in

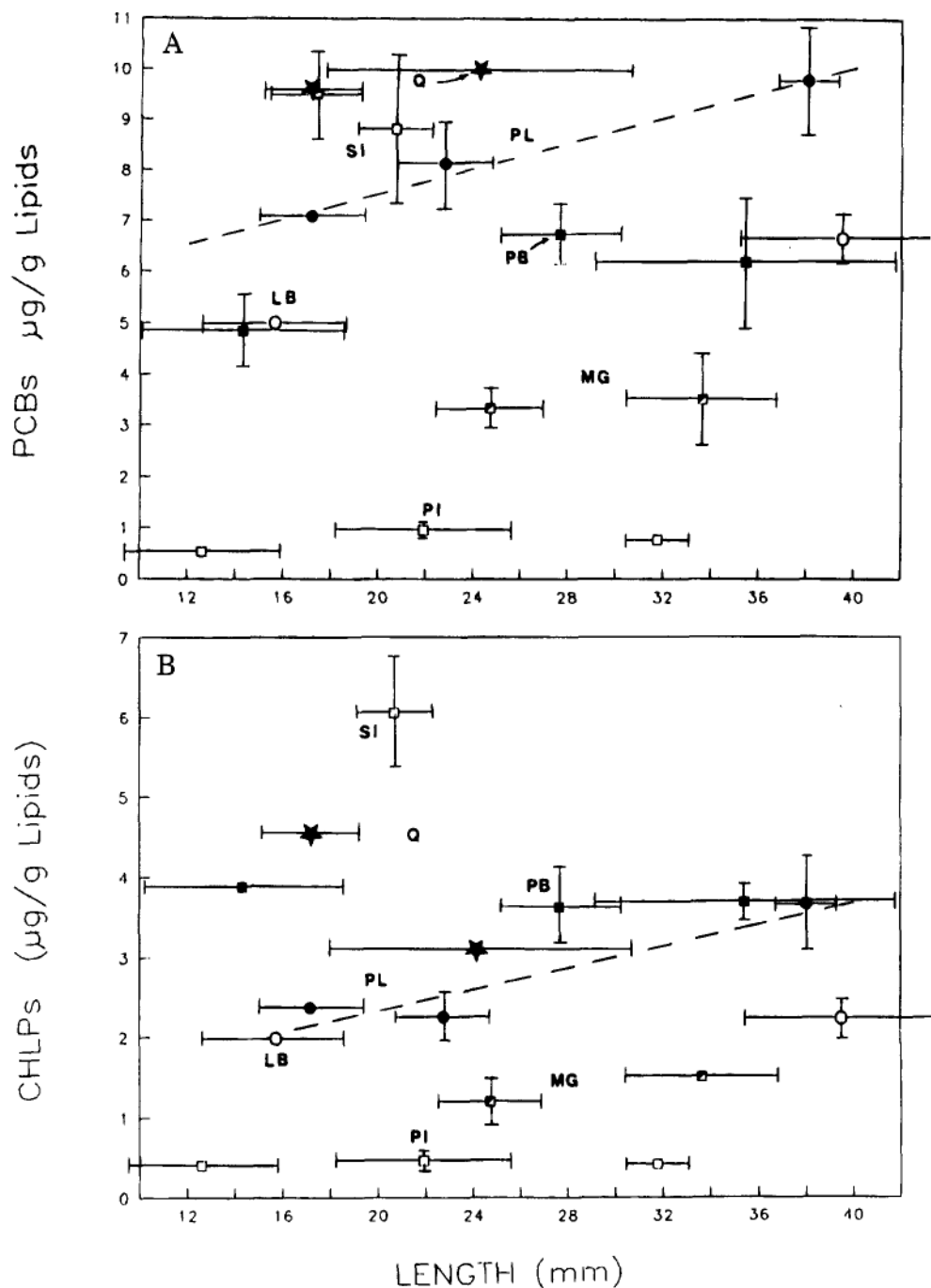


FIGURE 4. Total concentrations of PCBs (A) and chlorinated pesticides (B) in Asiatic clams versus clam length.

organisms exposed to polluted effluents (7). Zebra mussels (*Dreissena polymorpha*) collected along the Mosel River presented similar PCB levels (2.5–10 µg/g of lipids) (10) whereas in Lake Créteil, Paris, the same organisms presented much higher PCB (25–57 µg/g of lipids) and CHLP concentrations (6.2–26 µg/g of lipids) (8). Considering the results published for marine species, on a dry weight basis, total PCB and DDT concentrations in Río de La Plata Asiatic clams (43–1300 and 7–315 ng/g, respectively) are much higher than those reported for nonpolluted bivalves from Brazil (2.5–10.5 and 1.2–5.6 ng/g) and the Arabian Sea (0.1–69 and 0.1–8.4 ng/g), which may represent baseline levels due to atmospheric transport from distant sources (21). Our PCB and DDT values are comparable to those published for bivalves from industrialized areas such as the Baltic Sea (179–778 and 62–739 ng/g), Irish Sea (57–1070 and 92–590 ng/g), Spanish and French Mediterranean

(11–1825 and 60–288 ng/g), and U.S. Northeast Pacific Ocean (607–2052 and 5.4–1077 ng/g) (21).

Comparing our results for Río de La Plata Asiatic clams collected in 1993 with those previously reported for organisms sampled in 1986 (14), PCBs and CHLPs evidence different temporal trends. Over this 7-y period, PCBs show sustained levels while CHLPs evidence an average 3-fold decrease, suggesting a significant reduction in the use of these agrochemicals. Total PCB levels in 1986 Corbicula (7.2–7.6 µg/g lipids) lie in the range of those registered in 1993 at PB and PL stations (4.8–9.8 µg/g lipids), 5 and 8 km downstream and upstream, respectively, of the previous sampling site. The concentrations of total CHLPs on the contrary decreased from about 10 to 2.2–3.9 µg/g of lipids from 1986 to 1993. This total decrease hides markedly different individual pesticide behaviors; from 1986 to 1993, lindane shows sustained levels (0.2–0.3 to 0.1–0.3 µg/g of

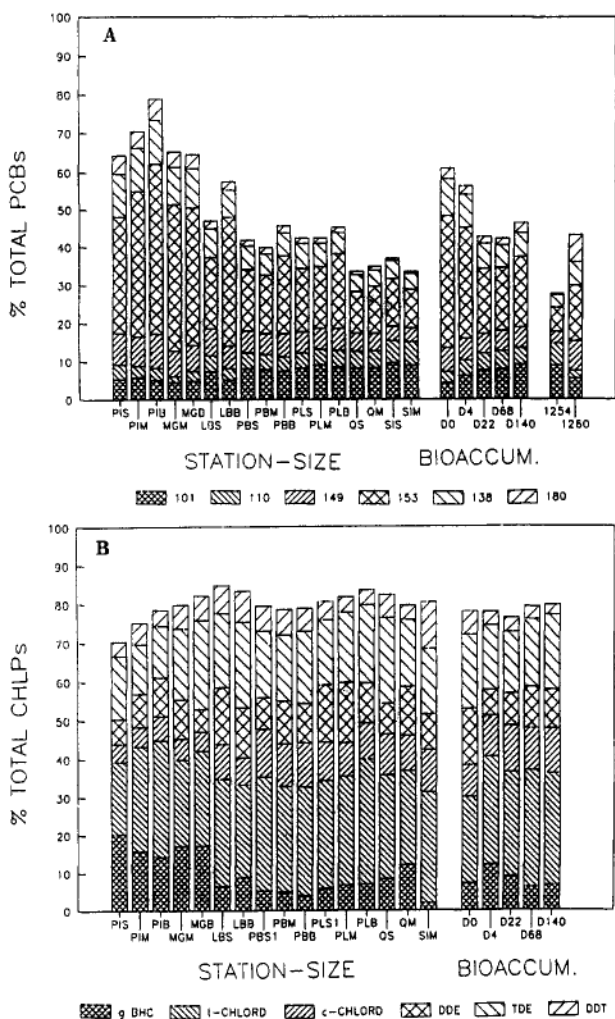


FIGURE 5. Relative composition of PCBs (A) and CHLPs (B) in Asiatic clams collected in the field (by station and size) and from the bioaccumulation experiment. Aroclors 1254 and 1260 are included in (A) for comparison.

lipids), *trans*-chlordane evidences an intermediate decrease (2.4–2.6 to 0.6–1.2 $\mu\text{g/g}$), while DDT shows the strongest decline (1.3–1.4 to 0.1–0.25 $\mu\text{g/g}$). This decreasing trend of chlordane and DDT inputs is also supported by the higher parent compound/degradation product ratios registered in the 1986 bivalves. The average heptachlor/heptachlor epoxide, DDT/DDE, and DDT/TDE ratios decrease from 4.6 to 0.9, from 1 to 0.5, and from 0.4 to 0.3, respectively, from 1986 to 1993, indicating more recent inputs in 1986. Significant decreases in the concentration of DDTs in bivalves and fish have been also reported for the U.S. coast, the Gulf of Mexico, the Baltic Sea, and the Finnish Sea (4, 21).

3. Bioaccumulation Factors. The bioaccumulation factors (BAF) of bivalves with respect to water (average: 130 600 for lindane and 7 373 000 for *trans*-chlordane), sediments (380–9700 for total PCBs), and suspended particulate matter (9.2–39 for total PCBs) confirm that Asiatic clams are efficient OCL concentrators. This is related to their relatively high lipid contents (5–16% dry weight) and the marked hydrophobicity of the compounds analyzed. As expected, the lipid-based bivalve–water BAFs are the highest, and they rise with increasing octanol–water partition coefficients (K_{ow}) of the compounds (22, 23) (log BAF = $0.46 K_{ow} + 3.59$, $R^2 = 0.90$, $n = 6$ at Quilmes; Figure 3A). Heptachlor was excluded from the calculations

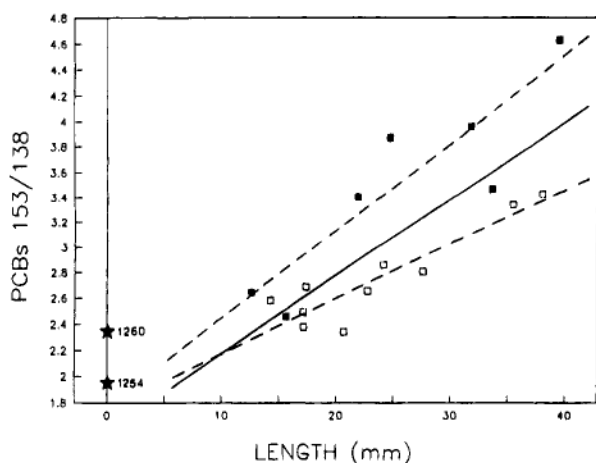


FIGURE 6. Evolution of the 153/138 PCB ratios in Asiatic clams versus clam length. Filled points are samples from PI, MG, and LB.

because the BAF is extremely low, possibly reflecting the biodegradation of the pesticide by the clams.

Owing to the higher affinity of PCBs for sediments and especially for SPM, the BAFs calculated with respect to these phases are much lower. At Quilmes, the log bivalve/sediment BAFs of 19 individual congeners range from 1.9 to 2.8 and show a parabolic form when plotted against K_{ow} 's (24) (Figure 3B). Basically, the same pattern is observed in the bivalve/SPM BAFs plot (Figure 3C). These BAFs are perhaps the most ecologically significant ratios: PCBs are mainly found in SPM, (see section 1), and Asiatic clams are very active filtrators (0.3–2.5 L/h) which efficiently remove fine particles ($\leq 1-10 \mu\text{m}$) constituting major seston traps in rivers (11). In both the bivalve/sediment and bivalve/SPM BAF plots, heptachlorobiphenyls 174, 180, and 170 show the lowest values, indicating an enhanced difficulty for bioaccumulation. Similar results with maxima at about $\log K_{ow} = 6$ and declining values for more hydrophobic compounds have been reported for oligochaete/sediment (25) and fish/water BAFs (26). This is interpreted as an indication that bioaccumulation is governed by compound hydrophobicity up to $\log K_{ow} \approx 6$ whereas for superhydrophobic molecules other factors such as a lower lipid solubility or steric effects interfere reducing the BAFs (26).

4. Geographical Trends in OCL Concentrations. The concentrations of OCL in waters, SPM, and sediments show a rather consistent increasing trend from PI to Q–SI (Tables 1 and 2). However, some high intermediate values are also apparent in the case of CHLPs. These trends are confirmed by the OCL concentrations in the Asiatic clams. Figure 4 shows the lipid-based PCB and CHLP concentrations plotted against the average size of the bivalves. PCB levels show a clear geographical trend increasing progressively with proximity to the major La Plata–Buenos Aires urban center (PL, Q, and SI stations). According to their PCB loads, the Asiatic Clam populations from the Río de La Plata coast are divided in four main geographical groups. From the least to the most contaminated they are as follows: PI ($0.7 \pm 0.2 \mu\text{g/g}$) < MG ($3.2 \pm 0.4 \mu\text{g/g}$) < LB = PB ($5.9 \pm 0.9 \mu\text{g/g}$) < PL = Q = SI ($9.0 \pm 1.0 \mu\text{g/g}$). Superimposed to this clear geographical pattern, a length (i.e., age)-related trend is also insinuated; bigger animals usually show higher PCBs levels. The regression analysis performed for PL animals (PCBs = $0.1 \text{ length} + 5.1$, $R^2 = 0.98$) displayed in Figure 4A suggests that organisms may duplicate their PCB levels during growth from a 0.25-mm newly released juvenile (11) to a 40-mm clam, which could

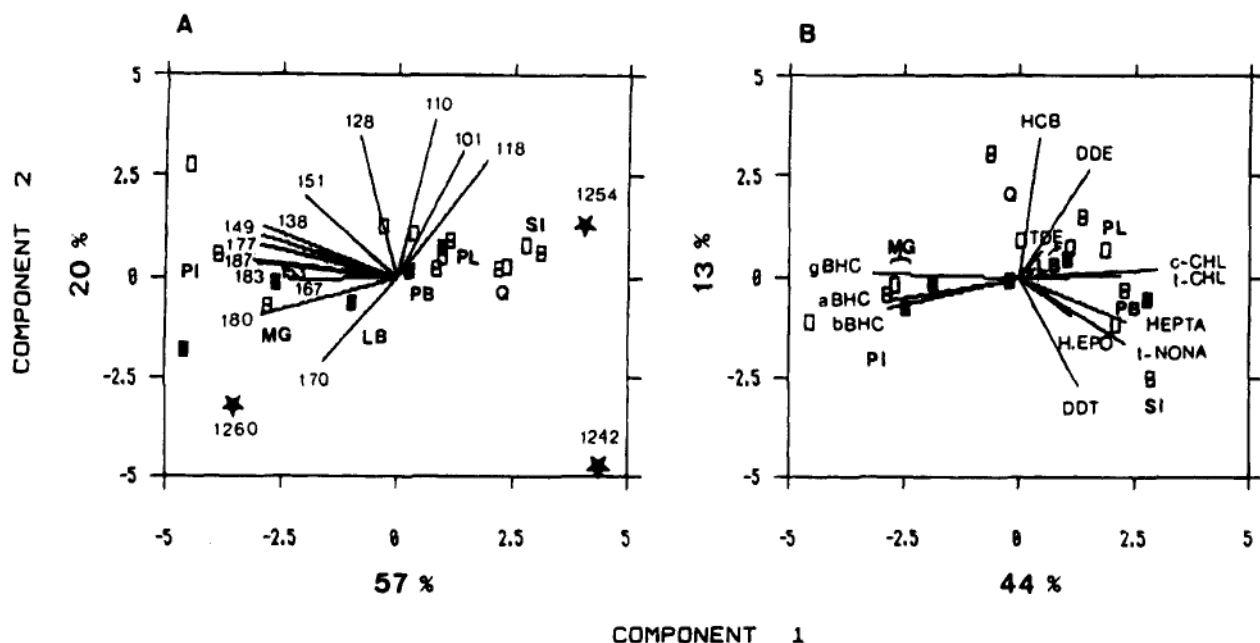


FIGURE 7. Representation of the first two components of a principal component analysis carried out with the relative contribution of 14 PCBs (A) and 11 CHLPs (B) in Asiatic clams. The rays represent the original variables while the squares represent the samples. Open squares stand for small organisms, hatched squares stand for medium clams, and solid squares stand for big animals.

take 3–4 years (average growth of 10–15 mm/yr) (11). However, due to the analytical error (10%), the concentration differences between PL medium and big animals are not significant. More data are needed, especially of tiny larvae, to confirm these results.

The geographical trend of CHLPs is less clear than that of PCBs; although the concentrations are the lowest at PI and the highest at SI, intermediate stations overlap. This confirms that, in contrast to PCBs whose major source is the big La Plata–Buenos Aires urban center, other sources of CHLPs are spread along the coast. Small coastal plantations are abundant in the area and are the most probable source of these residues. The high CHLP levels of the clams collected at PB (Figure 4B) are probably related to the contribution of a small rivulet which drains a nearby orchard area. The length-related trend discussed for PCBs is also insinuated in the case of CHLPs. For PL organisms, the regression (CHLPs = 0.07 length + 0.99, $R^2 = 0.89$; Figure 4B) suggests that CHLPs levels almost quadruplicate from a 0.25 to a 40-mm organism.

5. Geographical Trends in OCL Composition. The composition of PCBs in Río de La Plata SPM, sediments, and Asiatic clams shows a marked dominance of penta- and hexachlorobiphenyls (Tables 2 and 3). The patterns resemble most the Aroclor 1260 formulation in SPM and sediments and the Aroclor 1254 mixture in bivalves, which do not efficiently bioaccumulate higher chlorinated congeners (see section 3). Following the gradient observed for the concentrations, the composition of PCBs show clear geographical trends. In more distant and less polluted stations (PI, MG, and LB), the aging and decay of the PCB signal are evidenced by the depletion of several congeners and the strong dominance of 153 which account for 30–40% of the total (cf with 10–15% in more contaminated sites). PCB 153 is one of the most persistent congeners and is usually a major component in environmental samples (27–29). This geographic compositional change was reproduced in the bioaccumulation experiment; the proportion of 153 decreased from 35 to 16–18% along the 140-

day experience (Figure 5A), reflecting the rejuvenation of the PCB signal. The relative increase of major peaks such as PCB 153 in remote sites results in part from the nondetection of some minor congeners. However, the evolution of the ratios of two major recalcitrant hexachlorobiphenyls (153/138) vs clam length (Figure 6) indicates that the main factor which determines the selective persistence of 153 is its inherent recalcitrance. The progressive increase of the ratios (general equation $y = 0.060x + 1.77$, $R^2 = 0.61$, $n = 17$) reflects the selective persistence of 153 during decay with increasing clam age. The geographical trend is also present in the data; less polluted clams from PI, MG, and LB (filled points) present higher ratios (enhanced decay) whereas PB to SI clams show lower values (less alteration). Both regression lines converge close to the Aroclor 1254 ratio ($y = 0.069x + 1.72$, $R^2 = 0.79$, $n = 7$ for PI–MG–LB and $y = 0.042x + 1.59$, $R^2 = 0.61$, $n = 10$ for PB to SI clams), i.e., the geographical differences are attenuated in smaller organisms which have a fresher signature.

The composition of CHLPs in the dissolved phase presents a marked dominance of the more soluble BHCs and lower abundances of chlordanes whereas in the particulated phase DDE is the most abundant component. In Asiatic clams, chlordanes-related compounds predominate, accounting for 38–59% of total residues whereas DDTs and BHCs represent 26–43 and 5.4–35%, respectively (Table 4). Owing to the already discussed presence of multiple CHLPs sources, the compositional differences along the coast are less clear than for PCBs. Bivalve data suggest a gradual reduction of the relative abundance of γ -BHC from PI to SI (Figure 5B). Chlordane compounds show another interesting trend. Among this group, *trans*-chlordane stands out clearly (19–33% total CHLPs) and is 2.5–5.5 times more abundant than the *cis*-isomer. Considering that the *trans/cis*-chlordane ratio of a local technical chlordane formulation is about 1.2, similar to those reported in the literature (1–1.4) (30) and to those found in the dissolved phase (1.0–2.3; Table 1), these results suggest a

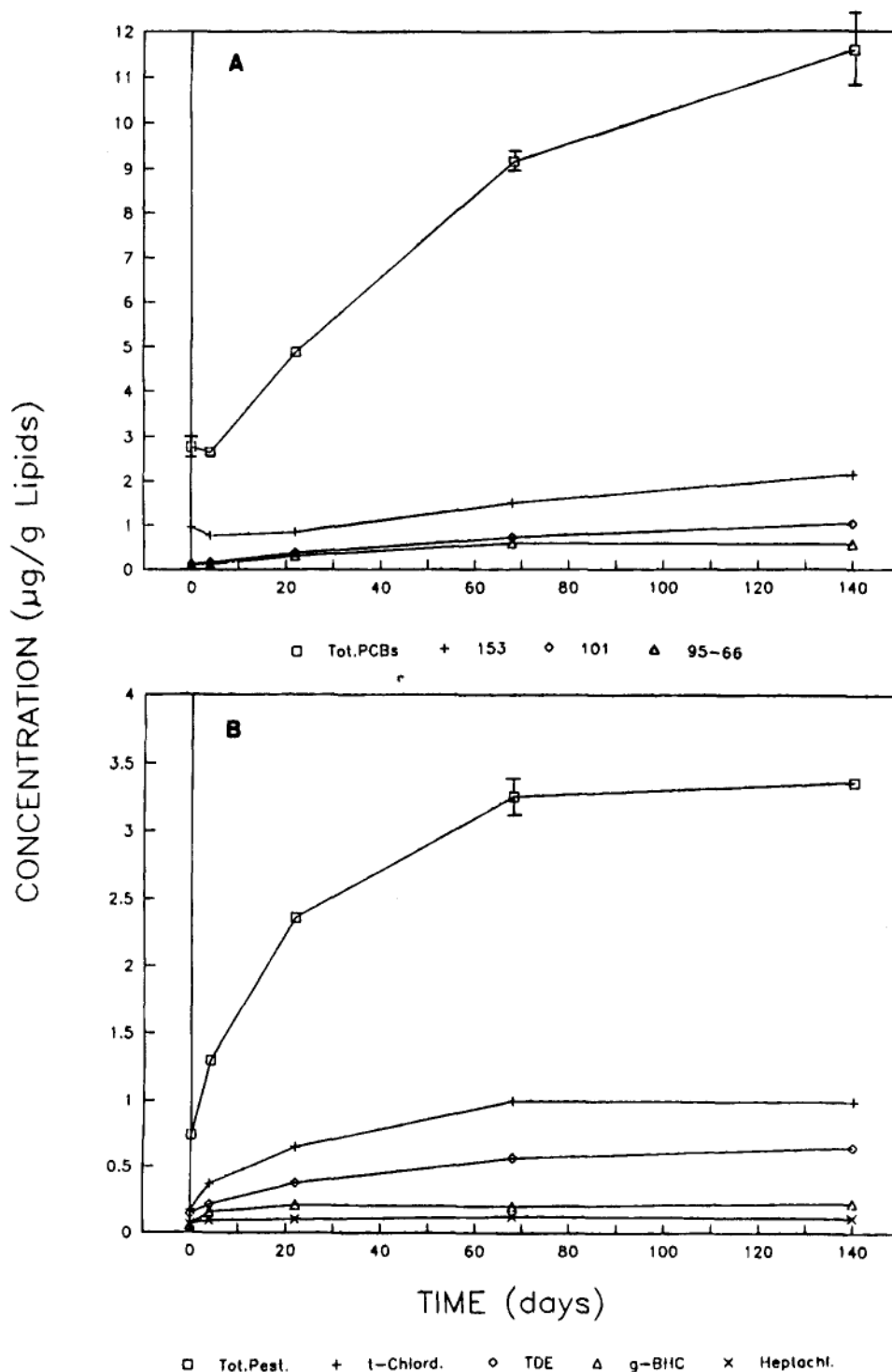


FIGURE 8. Bioaccumulation kinetics of PCBs (A) and CHLPs (B) in Asiatic clams transplanted from Magdalena (MG) to La Plata port embouchure.

selective preservation of the *trans*-isomer in the organisms. The gradual decrease of *trans/cis*-chlordane ratios (4.0–5.5 to 2.6–2.7) from less to more contaminated clams (Table 4) gives further support to this interpretation. These ratios and the heptachlor/heptachlor epoxide relationship are good indicators of the freshness of chlordane residues; recent applications are indicated for the clams sampled at PB and at MG in October for the caging experience (day 0 in Table 4), which show low *trans/cis*-chlordane and high heptachlor/heptachlor epoxide ratios.

The conclusion of a selective preservation of *trans*-chlordane in Río de La Plata Asiatic clams agree with its previously reported marked abundance in bivalves and

fishes of the area (14) but contradict literature reports which indicate an enhanced preservation of *cis*-chlordane in remote environments (30–32). Laboratory depuration experiments in fish indicated clearance rates 1.8 times faster for the *trans*-isomer (33) whereas in more recent studies in rats an opposite trend was observed (34). The reported enhanced persistence of *cis*-chlordane in remote environments (Arctic, Antarctic, northern North Pacific) may be related to the selective photochemical or chemical degradation of *trans*-chlordane during atmospheric dispersion (35, 36). This effect is particularly intense in summer when *trans/cis*-chlordane ratios as low as 0.37–0.66 have been reported for air samples from Norway and the Canadian

Arctic (35, 36). Another factor which might also be involved is the co-elution of nonachlor-III with *cis*-chlordane (37). Nonachlor-III, a minor component of the mixture ($\approx 1\%$), is very stable and is biomagnified in higher trophic levels (38).

6. Multivariate Analysis of OCL Composition in Clams.

To study the covariation of several parameters and the grouping of the samples, principal component analyses were performed with the standardized relative abundances of 14 PCBs and 11 CHLPs in the samples. Figure 7 shows the original variables (rays) and samples (squares) represented in the same plane to facilitate the visual interpretation of the results. Close rays are positively correlated variables; opposite rays denote negative correlation.

In the case of PCBs, principal components 1 (PC1) and 2 (PC2) account for 57 and 20%, respectively, of the total variability. PC1 is chiefly determined by the contribution of hexa- and heptachlorobiphenyls 151–170 (–PC1) and to a lesser degree of pentachlorobiphenyl 118 (+PC1). PC2 presents a strong contribution of congeners 118–128 (+PC2) and 170 (–PC2). Both components discriminate the samples according to the aging of the PCB signal: PC1 reflects the geographic variation (more contaminated and fresher signal: +PC1; less polluted and more altered: –PC1) whereas PC2 seems to describe the age-related differences (small: +PC2; big: –PC2). Most contaminated samples (single cluster formed by SI and Q) present more balanced PCB compositions similar to Aroclor 1254 (+PC1) whereas in less polluted clams (PI and to a lesser degree MG) the signal is degraded with higher proportions of recalcitrant hexa- and heptachlorobiphenyls, closer to the 1260 formulation (–PC1 and –PC2). The other samples occupy intermediate positions: LB big are midway between MG and the cluster formed by LB small, PB, and PL.

In the PCA of CHLPs (Figure 7B), PC1 (44%) and PC2 (13%) account for a much smaller percentage of the total inertia than in the case of PCBs. This is related to the much less clear environmental gradients observed for these compounds which have multiple sources along the coast (see section 5). PC1 is determined by the contribution of chlordane-related compounds (+PC1) which are negatively correlated with BHCs (–PC1). PC2 presents a strong contribution of HCB and DDE (+PC2) and DDT (–PC2). The samples are thus separated according to the different contribution of BHCs and chlordanes (PC1) and HCB, DDE, and DDT (PC2). PI and MG are clearly discriminated by their elevated proportion of BHCs (–PC1), whereas PB presents a dominant contribution of chlordanes (+PC1). PL, LB, and Q occupy an intermediate position, presenting a higher contribution of HCB, particularly QM (+PC2). SI is discriminated by its higher percentage of DDT (–PC2). Thus, Asiatic clams from this station present fresher residues of both PCBs and DDTs.

7. Bioaccumulation Experiment. Figure 8 shows the bioaccumulation curves of PCBs and CHLPs obtained during the 140-day exposure period of clams transplanted from MG to La Plata port embouchure. Both compound classes show an approximate 4-fold increase reflecting the pollution gradient, but their accumulation kinetics is markedly different: CHLPs are accumulated more rapidly and reach steady-state concentrations before 70 days whereas PCBs show a slower accumulation kinetics and do not appear to reach steady-state levels during the experience. This difference is probably related to the routes of uptake and bioavailability of the compounds, which are

determined by their hydrophobicity. The faster equilibration of CHLPs is consistent with a more efficient partitioning from the dissolved phase where, except DDTs, these pesticides are mainly found (see section 1). In contrast, the bioaccumulation of PCBs depends mainly on the ingestion of SPM, which presents a higher affinity for superhydrophobic molecules. This would make the partitioning process difficult, especially for higher chlorinated congeners. The unfavorable stereochemistry of these components would be an additional impeding factor. This interpretation is supported by the fact that only lower chlorinated PCBs such as 95–66 with moderate K_{ow} (≈ 6.2) appear to reach steady-state concentrations during the experience (Figure 8A). This penta-tetrachlorobiphenyl presents the highest clam/SPM BAF at Quilmes station (Figure 3C). The importance of the route of uptake on PCB absorption was demonstrated in laboratory experiments: in fish, when water was the vehicle of PCBs, the BAF increased with $\log K_{ow}$ (even for heptachlorobiphenyls) but when food was the PCB source, all heptachlorobiphenyls did not bioaccumulate more than congener 44 due to lower intestinal uptake efficiencies (39, 40). In the deposit feeder bivalve *Macoma nasuta*, the sediment uptake efficiencies declined from about 90% for trichlorobiphenyl 18 to 0% for decachlorobiphenyl 209 (41), reflecting the difficulty for the intestine absorption of higher chlorinated PCBs.

Acknowledgments

Financial support was provided by the Argentinean National Research Council (CONICET) and by the Research Commission of the Province of Buenos Aires (CIC).

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Received for review May 17, 1994. Revised manuscript received August 25, 1994. Accepted October 12, 1994.*

ES9403064

* Abstract published in *Advance ACS Abstracts*, November 15, 1994.