CADMIUM, ZINC AND TOTAL MERCURY LEVELS IN THE TISSUES OF SEVERAL FISH SPECIES FROM LA PLATA RIVER ESTUARY, ARGENTINA

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Abstract. A survey of the concentrations of heavy metals – cadmium, zinc and total mercury – in the tissues of fifteen fish species from Samborombón Bay, La Plata river estuary, in Argentina, has been carried out. Liver appeared to be the main organ accumulating cadmium and zinc, while both liver and muscle showed a similar ability for accumulating mercury. The bioaccumulation process was verified for the three metals analyzed, even though low concentrations have been determined. The biomagnification process of the metals studied was not verified in this environment. The highest metal concentrations were recorded in *Mugil liza*, and particulate matter and sediments – which are closely related to its trophic and ecological habits – seemed to be the main source of metals for this species. Both *Micropogonias furnieri* and *Mugil liza* were recognized as possible indicator species for future monitoring programmes for heavy metals in Samborombón Bay. Considering the present results, this area of La Plata river estuary is characterized as a non-polluted environment.

1. Introduction

Among studies relating to environmental quality, those concerning the heavy metal pollution of ecosystems are of the utmost importance. This is so because of the potential transference of hazardous substances to man through food, mainly in view of the tragic events of the '50s and '60s involving mercury and cadmium poisoning (Wittmann, 1983). Thus, a number of studies has been carried out to assess the level of metals in organisms, sediments and water from different environments. Each of these compartments provides a partial image of the occurrence of metals within the system. However, the advantage of studying organisms is that the results reflect the bioavailability of the pollutants, and consequently mark the real degree of pollution in the environment assessed (Pertilla *et al.*, 1982).

The concentration of heavy metals in fish species from the Southwestern Atlantic Ocean may have not been extensively studied yet, and only a few papers are available (Peréz *et al.*, 1986; Marcovecchio *et al.*, 1988(a)); moreover, information on fish from La Plata river estuary has still not been reported.

The main purpose of this paper is to supply basic data on the heavy metal levels – cadmium, zinc and total mercury – of several fish species from Samborombón Bay, in La Plata river estuary (Argentina). Simultaneously, some ecological processes – such as bioaccumulation or biomagnification – were considered. Furthermore,

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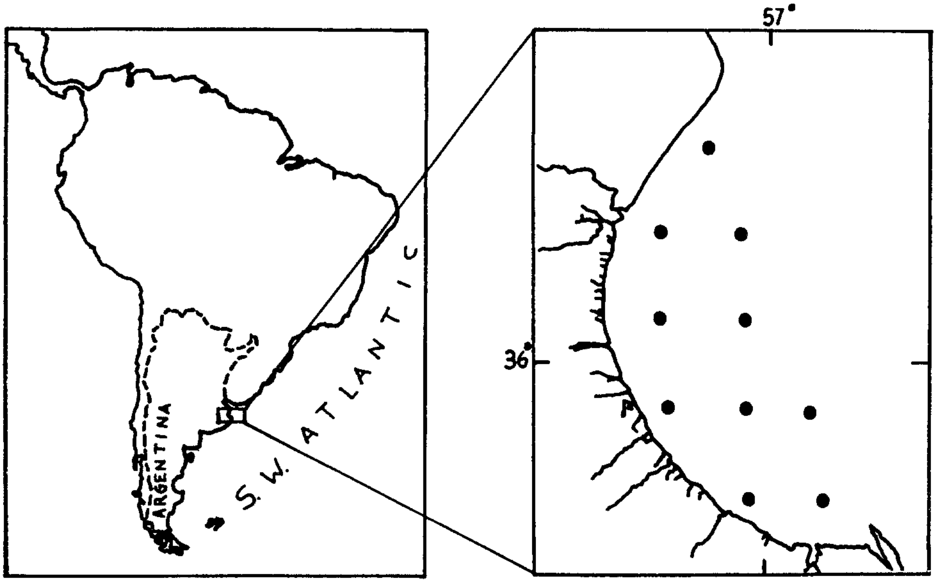

Fig. 1. Location of sampling station in Samborombón Bay, La Plate river estuary.

the data of all species were compared, to identify suitable bioindicators for the environment studied.

2. Materials and Methods

Samborombón Bay is a particular area of the very large La Plata river estuary, in Argentina. This bay is located between 32°57′ and 36°18′S, and 56°48′ and 57°08′W, at the Southeastern La Plata river outlet (Figure 1). On this side of the river, the most important industrial concentration of the country exists, including petrochemical plants, smelters, and all kind of industrial factories. Furthermore, there are large harbours upstream, with the attendant necessity for harbour operation, dredging and filling, etc. A fraction of the freshwater volume as discharged by La Plata river goes into Samborombón Bay, and in this way sediments and particulate matter transporting pollutants can enter this ecosystem.

During 1987 and 1988 samples of fifteen fish species were periodically (every 30–40 days) obtained from ten sampling stations in Samborombón Bay (Figure 1). The location of these stations was selected statistically, and sampling operations were carried out with commercial fishing vessels from this area. After appropriate morphometric measurements, dorsal muscle (anterior to dorsal fin) and liver were removed. They were kept in plastic bags, and maintained in a freezer at −20°C until treatment in the laboratory. Cadmium and zinc were determined in acid digests

TABLE I
Percentages of recovery in the analysis of reference material to assess analytical quality.

Metal analyzed	Percentage of recovery (range)
Cd	91.4 – 99.3 %
Zn	96.5 – 102.3 %
Hg	93.2 – 99.6 %

through atomic absorption spectrophotometry (AAS), with air-acetylene flame, and deuterium lamp background correction (Marcovecchio *et al.*, 1988(a)). For total mercury determination flameless atomic absorption spectrophotometry was utilized, after acid mineralization, according to the method described by Moreno *et al.* (1984). A Shimadzu AA-640-13 with potentiometric recorder was utilized to carry out the corresponding analysis. Analytical reagents were used for blanks and calibration curves, and a certified reference material ('mussel standard') – provided by the National Institute for Environmental Studies, NIES, Tsukuba, Japan – was utilized in order to assure the accuracy of the data. Recovery percentages obtained in the analysis of this reference material are shown in Table I. Detection limits of the utilized methods were 0.05 μg/g for mercury (Perěz and Moreno, 1984), and 0.04 μg/g for cadmium and zinc (Marcovecchio, 1988(b)).

Comparisons between metal concentrations in species were performed by one-way analysis of variance (ANOVA).

3. Results and Discussion

Cadmium, zinc and total mercury levels and their distribution in muscle and liver of fifteen fish species from Samborombón Bay, in Argentina, were determine (Table II). Cadmium and zinc exhibited a similar pattern of distribution, and their concentrations were significantly higher in liver than in muscle of all the analyzed species ($p < 0.01$). This cadmium and zinc distribution trend as found in fish species from Samborombón Bay agreed well with previous reports on 'arctic cod', *Boreogadus saida* from Strathcona Sound, in Canada (Bohn and McElroy, 1976); on *Pagothenia borchgreviki* from Antarctic (Honda *et al.*, 1983); and on 'eperlan', *Osmerus mordax*, from St. Lawrence estuary, in Canada (Arnac and Lessus, 1985) (Table II). On the other hand, mercury showed a different distribution pattern in the considered fish species, and similar levels were found in both muscle and liver, corresponding analysis of variance showing no significant differences ($p < 0.01$). This trend is consistent with those reported by Buggiani and Vanucchi (1980) on fish from La Spezia and Livorno, in Italy; and by Hilge *et al.* (1984) in the 'cod'

TABLE II
Metal concentrations (μg/g wet weight) in tissues of each fish species. Mean value $\pm$ Standard deviation. N.D.: non-detectable. N: number of samples.

Species	N	Length (mm)	muscle	liver	muscle	liver	muscle	liver
1. Brevortia aurea	65	175–390	0.21±0.05	0.20±0.05	0.07±0.05	3.88±0.91	14.94±4.89	172.82± 44.8
2. Mugil liza	56	290–435	0.40±0.06	0.53±0.11	0.34±0.05	9.15±1.27	48.83±4.05	52.23± 4.10
3. Cyprinus carpio	47	320–465	0.19±0.07	0.15±0.05	0.09±0.04	7.99±1.32	30.36±5.97	47.64± 7.64
4. Parona signata	29	235–435	0.21±0.09	0.24±0.15	0.02±0.03	7.59±1.09	4.98±1.09	49.66± 9.20
5. Stromateus brasiliensis	27	100–175	0.09±0.07	0.06±0.05	N.D.	1.32±0.49	7.22±1.88	59.52± 2.53
6. Rhamdia sapo	26	245–375	0.13±0.04	0.11±0.03	N.D.	2.67±0.57	21.15±4.29	32.31± 3.95
7. Netuma barbus	29	200–370	0.11±0.04	0.10±0.03	N.D.	2.26±0.53	17.38±4.43	30.00± 5.63
8. Basilichthys sp.	46	150–350	0.13±0.05	0.09±0.06	0.04±0.04	1.14±0.74	14.53±5.14	55.53±11.59
9. Micropogonias furnieri	98	180–470	0.11±0.04	0.13±0.04	N.D.	3.03±1.08	20.54±5.26	44.30± 6.21
10. Pogonias cromis	61	320–700	0.22±0.15	0.19±0.12	0.11±0.12	3.08±1.71	19.99±9.69	31.79± 9.93
11. Cynoscion striatus	90	185–460	0.14±0.08	0.16±0.07	N.D.	3.69±1.08	11.75±2.93	127.42±47.52
12. Macrodon ancylodon	83	175–410	0.12±0.05	0.11±0.05	N.D.	3.59±0.85	12.93±4.57	43.03± 9.67
13. Conger orbignyanus	46	390–685	0.29±0.07	0.34±0.11	0.22±0.07	2.16±0.66	24.89±7.11	40.48± 7.75
14. Myliobatis goodei	35	350–630	0.31±0.06	0.26±0.06	0.04±0.05	5.87±1.30	7.14±1.37	33.66± 4.78
15. Paralichthys sp.	74	180–370	0.30±0.09	0.40±0.11	0.09±0.07	5.53g±1.19	19.03±6.24	179.27±17.06

Gadus morhua from the Southern Baltic Sea (Table III).

Even though the abovementioned trends were observed in all the fish analyzed, species-to-species differences in heavy metal concentrations were highly variable. Thus, in the case of cadmium, the liver contents showed a general mean value – for the fifteen assessed species – of 4.14 ppm, with individual values ranging between 0.17 and 12.4 ppm (Table IV). Simultaneously, mean values of hepatic cadmium among species varied between 1.14 ppm in *Basilichthys sp.*, and 9.15 ppm in *Mugil liza* (Table IV). When the mean contents of muscular cadmium in each

TABLE III
Metal concentrations (μg/g wet weight) reported by different authors for fishes from different environments.

Analyzed Species	Metal concentration (μg/g)			Reference
	Hg	Cd	Zn	
Boreogadus saida	–	0.620	90.00	Bohn & McElroy, 1976
Pagothenia borchgrevinki	0.052	0.020	5.65	Honda *et al.*, 1983
Osmerus mordax	–	0.02–0.19	19–38	Arnac & Lassus, 1985
Gadus morhua	0.008	0.050	4.70	Brzezinska *et al.*, 1984
Mugil cephalus	1.100	1.000	17.00	Windom *et al.*, 1973
Pleuronectes platessa	–	0.180	29.70	Wright, 1976
Pleuronectes limanda	–	0.150	30.30	Wright, 1976
Micropogonias sp.	–	0.150	10.30	Pfeiffer *et al.*, 1985
Cynoscion sp.	–	0.030	5.34	Pfeiffer *et al.*, 1985
Cyprinus carpio	0.320	0.170	61.81	Fernandez Aceytuno *et al.*, 1984
Mugil sp.	0.270	0.120	31.90	Fernandez Aceytuno *et al.*, 1984
Cyprinus carpio	0.710	–	–	Cooper, 1983
Solea solea	0.170	–	–	Vos *et al.*, 1986
Pleuronectes platessa	0.240	–	–	Vos *et al.*, 1986
Perca pluviatilis	0.400	–	–	Luten *et al.*, 1987

species were considered, variation between non-detectable values (i.e. *Stromateus brasiliensis*, *Rhamdia sapo*, *Netuma barbus*, *Micropogonias furnieri*, *Cynoscion striatus* and *Macrodon ancylodon*), and 0.34 ppm (*Mugil liza*) were found (Table II). These values can be compared with those previously reported by Windom *et al.* (1973) for *Mugil cephalus* from the Northern Atlantic Ocean; by Wright (1976) for *Pleuronectes platessa* and *P. limanda* from north-eastern coast of England; and by Pfeiffer *et al.* (1985) for *Micropogonias sp.* and *Cynoscion sp.* from the Sepetiba Bay, in Brasil (Table III).

In the case of zinc, the mean hepatic content for the fifteen species analyzed was 68.7 ppm, with individual concentrations varying between 6.15 ppm and 254 ppm (Table IV). Considering the hepatic mean values of each analyzed species, variations ranged between 30.0 ppm – in *Netuma barbus* – and 179 ppm – in *Paralichthys sp.* – (Table II). Furthermore, the average muscular zinc content for all the species analyzed was 19.2 ppm, with individual variations from 0.26 to 59.8 ppm (Table IV). The mean zinc levels of each fish species showed to be ranged between 4.98 ppm (*Parona signata*) and 48.83 ppm (*Mugil liza*) (Table II). These zinc concentrations as found in fishes from Samborombón Bay can be compared with earlier reports on *Boreogadus saida* from Northern Canada (Bohn

TABLE IV
Metal concentrations (μg/g wet weight) in tissues of Samborombón Bay fishes (data of all species together). S.D.: standard deviation. CV%: coefficient of variation. min-max: minimum and maximum values.

		Liver	Muscle
Mercury	mean	0.20	0.20
	S.D.	0.14	0.14
	CV%	71%	71.6%
	min-max	0.00–0.79	0.00–2.00
Cadmium	mean	4.14	0.17
	S.D.	2.49	0.11
	CV%	60.1%	155.0%
	min-max	0.17–12.4	0.00–0.44
Zinc	mean	68.7	19.2
	S.D.	54.4	11.4
	CV%	79.1%	59.5%
	min-max	6.15–254.0	0.26–59.8

and McElroy, 1976); on *Cyprinus carpio* and *Mugil liza sp.* from Doñana, in Spain (Fernandez Aceytuno *et al.*, 1984); and on *Micropogonias sp.* and *Cynoscion sp.* from the Sepetiba Bay, in Brasil (Pfeiffer *et al.*, 1985) (Table III).

Concurrent analysis of mercury showed a mean concentration in the liver of the fifteen species analyzed of 0.20 ppm, with individual values oscillating between non-detectable levels and 0.79 ppm (Table IV). When the hepatic mean concentrations of each analyzed species were assessed, variations between 0.06 ppm – in *Stromateus brasiliensis* – and 0.53 ppm – in *Mugil liza* – were found (Table II). Furthermore, the mean content of muscular mercury for all the species analyzed was 0.20 ppm, with individual variations between non-detectable levels and 2.0 ppm (Table IV). Simultaneously, the mean mercury concentrations in muscle among the species considered varied between 0.09 ppm (*Stromateus brasiliensis*) and 0.40 ppm (*Migil liza*) (Table II). These mercury concentrations as obtained in the fish species from Samborombón Bay can be compared with previous reports on *Cyprinus carpio* from Nevada, U.S.A. (Cooper, 1983); on *Solea solea* and *Pleuronectes platessa* from the coast of Holland (Vos *et al.*, 1986); and on *Perca fluviatilis* (Luten *et al.*, 1987) (Table III).

The levels of all three metals analyzed – cadmium, zinc and total mercury – in the tissues of fish species from Samborombón Bay were not very high as compared with the international literature for similar environments. In fact, the values were similar to or even lower than those reported for the same species caught in the Argentine Sea (Peréz *et al.*, 1986), and showed to be significantly lower ($p < 0.01$)

than those of the same species caught in Bahia Blanca estuary (Marcovecchio *et al.*, 1988(c); 1988(d)), which has been recognized as a heavy metal hot-spot in Argentina.

Heavy metal concentrations were studied in relation to the total length of the organisms analyzed. A direct relationship between the size of the fish and the total mercury concentration was found in both muscle and liver, despite the low level of metals observed. This trend was true for most of the species studied (i.e. *Micropogonias furnieri*, Figure 2). On the other hand, cadmium and zinc did not show so clear a trend as mercury did. Thus, while zinc accumulated in both muscle and liver, cadmium did so only in liver, and its muscular concentrations were non-detectable or close to the detection limit of the method for most of the species analyzed. Furthermore, both metals seemed to accumulate up to certain levels; then, the concentration appeared to remain closely constant (i.e. Cd and Zn accumulation in *Parona signata*, Figure 3). This would suggest that several mechanisms may regulate the content of these metals in fish, and it probably happened because of the low metal levels as they are incorporated in Samborombón Bay. The trends observed for the three metals analyzed (Cd, Zn and total Hg) allow us to suggest that a bioaccumulation process occurs in the organisms of the environment studied, even though the metal concentrations of the fish species were found to be low. This result, which indicates that the heavy metals accumulation process can occur even at a very low pollutant level, fully coincides with the reports of Amiard *et al.* (1987) and Amiard-Triquet *et al.* (1987(a); 1987(b)).

None of the metals analyzed showed an increase in their levels through the corresponding trophic web (Figure 4), contrary to earlier papers – mainly on mercury – which report the occurrence of a biomagnification process (Ratkowsky *et al.*, 1975; Bryan, 1979; Surma-Aho *et al.*, 1986; Marcovecchio *et al.*, 1986). Metal concentrations higher than those observed in fish species from Samborombón Bay are probably required to develop the biomagnification process, but more research is necessary to clarify this topic.

The highest contents of the three metals analyzed were found in both muscle and liver of *Mugil liza*. This result was unexpected because of the low trophic level it occupies in Samborombón Bay food than, considering that the top predators are usually known to be most important heavy metal accumulators. It has been reported that *Mugil liza* is a detritivorous feeder (Oliver *et al.*, 1972). This is a very important fact because suspended particulate matter was recognized to be the main carrier of heavy metals from La Plata river to Samborombón Bay (Marcovecchio, unpublished data). In earlier papers Salomons and Forstner (1984) and Pfeiffer *et al.* (1986) have underlined the fact that particulate matter coming from polluted rivers is the main input of heavy metals to the estuarine environment. Consequently, in this way heavy metals could be accumulated in the tissues of *Mugil liza* in Samborombón Bay.

Several of the species studied were analyzed in order to identify any possible heavy metal bioindicator species. In this respect, the organisms must have certain

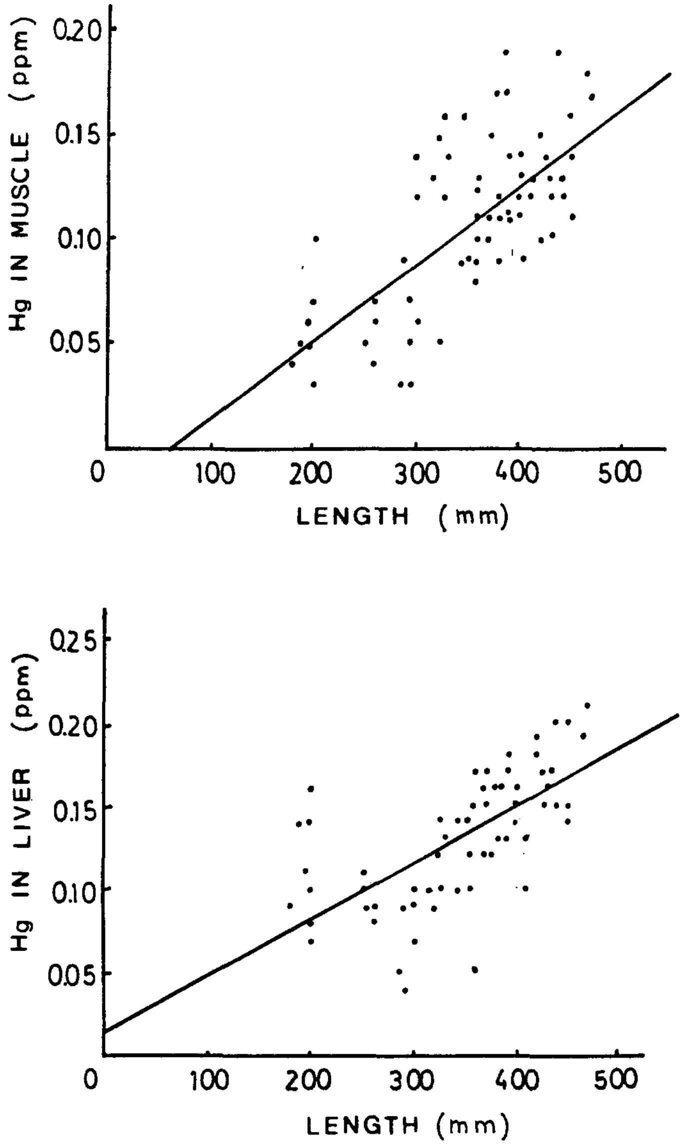

Fig. 2. Total mercury level vs. total length relationship in tissues of *Micropogonias furnieri*. Muscle (above), Liver (below).

characteristics in order to be suitable for use as bioindicator; i.e., they should be abundant and easily collectable; they should be non-migratory; and they should have an homogeneous distribution throughout the year in the environment under

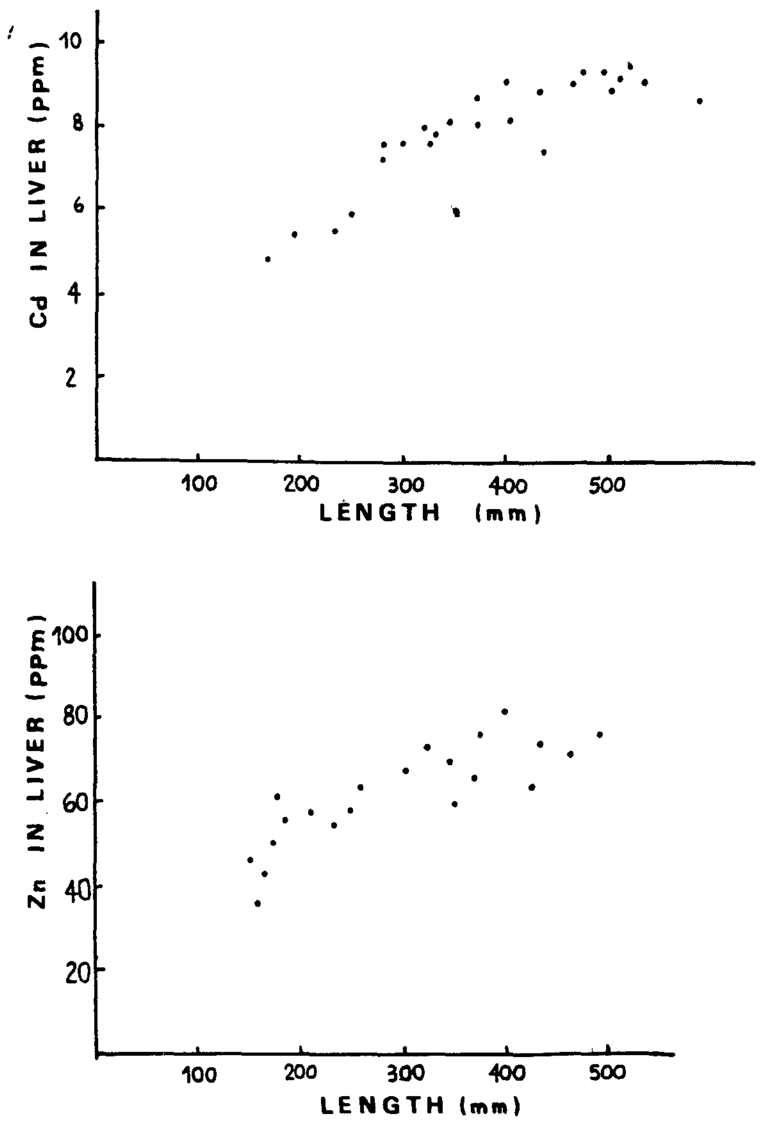

Fig. 3. Cadmium and zinc levels vs. total length relationship in the liver of *Parona signata*.

study (Dix *et al.*, 1975; Essink, 1985). With these requirements in mind, *Micropogonias furnieri*, and then *Mugil liza* and *Macrodon ancylodon* turned out to be the most appropriate species for this goal.

Finally, considering these results, the very low metal levels of the fish species

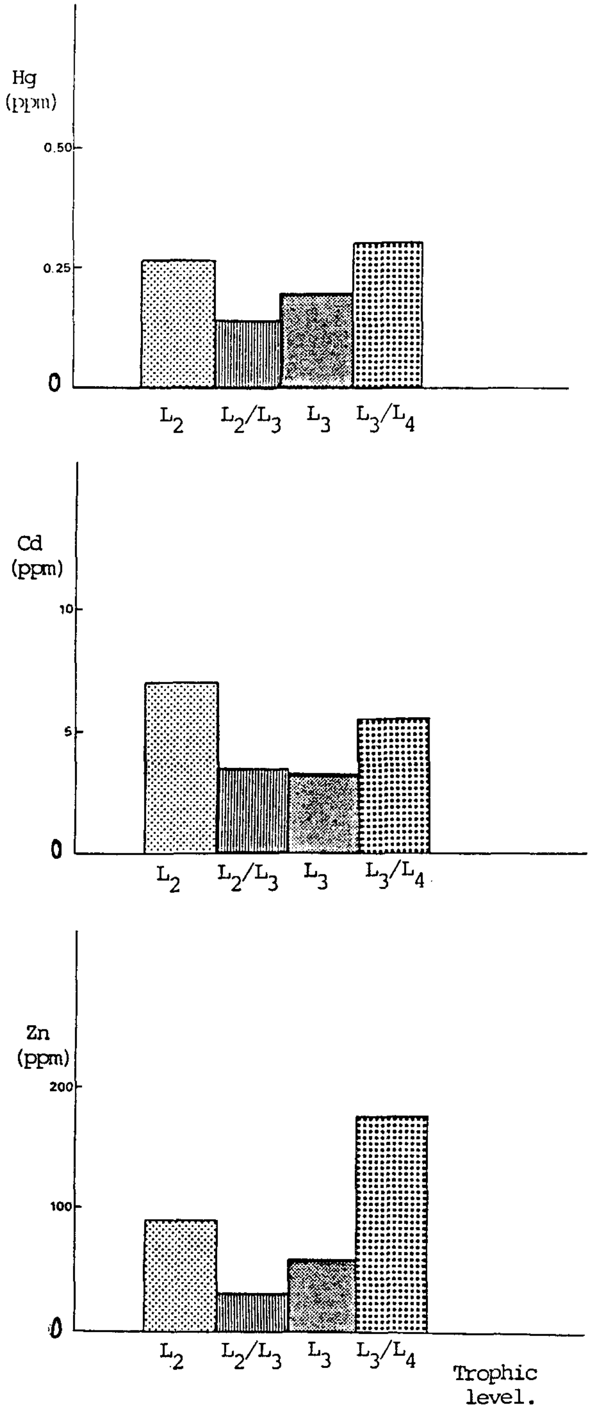

Fig. 4. Heavy metals distribution in the tropic web of Samborombón Bay. $L_2 \rightarrow L_4$: Considered trophic levels.

from Samborombón Bay – in La Plate river estuary – deserve to be underlined. This fact allows us to conclude that only a scarce bioavailability of heavy metals exists in this environment. On the other hand, considering future monitoring programmes for heavy metal pollution in Samborombón Bay, the use of the selected bioindicator species is recommended.

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