Palabras clave: laguna, contaminacion, Argentina
Key words: lake, contamination, Argentina

Copper, zinc and chromium in water, sediments and biota in the pampean Chascomús Lake (Argentina)

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ABSTRACT

Contamination caused by heavy metals (copper, zinc and chromium) was studied in a Pampean lake and its biomagnification was considered. The samples were taken seasonally in different sites of the Chascomús lake during 1996 and 1997. The three elements were measured in water, sediments, fish muscle and viscerae, clam muscle, phytoplankton and zooplankton. The concentration was higher than the limits allowed for acuatic life by international and domestic legislation. Spatial and temporal differences were detected both in water and sediments. The average value of total copper observed in water was 1.78 mg/l. The average value of total zinc in water was 0.19 mg/l. A higher quantity of zinc than copper was accumulated in the sediments. Hexavalent chromium was of 0.12 mg/l in its average value. Accumulation was found in the viscerae and muscles of the ichthyofauna. In the benthic fauna, copper concentration in muscle decreases according to the species' swimming capabilities. In the limnetic fauna the concentration increases in higher trophic levels.

RESUMEN

Cobre, zinc y cromo en agua, sedimento y biota en la laguna Chascomús (Argentina).

Se analizó la contaminación por algunos metales pesados (cobre, zinc y cromo) en la laguna Chascomús y se consideró su biomagnificación. Los muestreos se realizaron estacionalmente en 1996 y 1997. Se midieron los elementos mencionados en agua, en sedimentos, en músculo y vísceras de peces, músculo de almejas, en fitoplancton y en zooplancton. Se encontraron altas concentraciones de los tres elementos analizados, superando el valor límite aconsejado para la vida acuática. Se comprobaron diferencias espaciales y temporales tanto en agua como en sedimentos. El valor promedio de cobre total observado en el agua fue 1,78 mg/l, el de zinc total en agua de 0,19 mg/l y el de cromo hexavalente de 0,12 mg/l. En el sedimento se determinó mayor concentración de zinc respecto a cobre. En la fauna íctica se encontró acumulación en vísceras y en músculo. En la fauna asociada a los sedimentos, cuanto más nadadora es la especie considerada, menor fue la concentración de cobre encontrada en músculo. En cuanto a la fauna relacionada a la zona limnética, la concentración aumentó a medida que avanzamos en el nivel trófico.

0329-2177/99/30 (1 y 2): 67-76 $2,00 © Asoc. Cienc. Nat. del Litoral

INTRODUCTION

Certain elements such as heavy metals resist treatment and can stay a long time in the environment. The heavier metals are not generally involved with the activities of living systems. When the biomass is consumed at higher trophic levels, the consumer can receive a large dose of absorved heavy metals (Waite, 1984). Copper, zinc, lead, cadmiun, and mercury are very toxic and relatively accesible and are the elements of greatest concern for water quality (Wood, 1974). Local disorders caused in natural water by heavy metals are less transitory in freshwater than in seawater (Margalef, 1983).

Limnological studies of pampean lakes began 60 years ago (Cordini, 1938). Probably, the best known lake in the area is Chascomús (Ringuelet, 1968, 1972). In this lake, the species composition of fish community (Barla, 1991a), the species trophic relationships (Destéfanis and Freyre, 1972) the biology and some species population studies (Ramírez, 1963; Sendra and Freyre, 1978; Rodrigues Capítulo and Freyre, 1979) and silverside feeding (Ringuelet, 1942, Ringuelet *et al.*, 1980) are known. Chemical composition of this lake and its affluents has been studied even though pollutants in the system were not analyzed (Conzonno, 1991; Conzonno and Claverie, 1990; Conzonno and Fernández Cirelli, 1987, 1988, 1995, 1996; Quirós, 1988). However, gill lesions in fishes produced by toxic pollutants were investigated (Romano and Cueva, 1988).

Abiotic conditions in pampean lakes are not stable

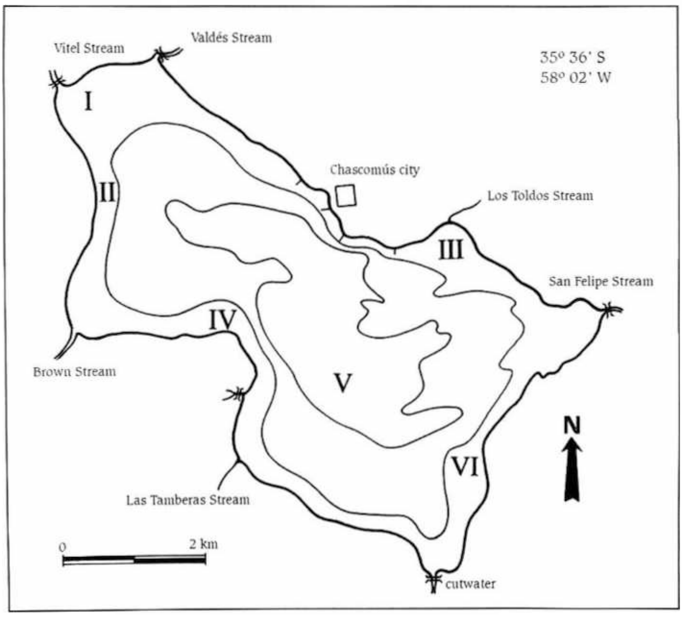


Figura 1

Sampled sites in the Chascomús Lake.

(Barla, 1991b). They are subject to cyclic and succesional changes, even excluding the human influence of activities such as agrarian and industrial developments. The purpose of this paper is to measure three heavy metals (copper, zinc and chromium) and to evaluate their effects on the environment and aquatic communities. We consider that the present paper is a starting point for the study of chemical contamination in pampean lakes.

MATERIAL AND METHODS

Six different sites (Fig. 1) were seasonaly sampled in Chascomus Lake, Argentina (35°36'S, 58°02'W) from May 1996 to February 1997. Water, sediments, phytoplankton, zooplankton, benthic fauna and fishes were considered. Plankton nets for phytoplankton and zooplankton, a dredge for sediments and benthic fauna, and trawls (Barla 1991a) and gillnets for fishes were used. Gillnets were 25 m long with 30, 32, 34, 36 and 50 mm square meshes. La Limpia lake (35°37'S, 57°48'W) considering water, sediments and fish, and Mar Chiquita coastal lagoon (37°40'S, 57°23'W) considering muscles of silverside, both unconnected to Chascomus Lake, were also sampled.

Quantification of metals was carried out by the following methods: Hach digesdahl system (Hach Company) was used for sample pretreatment. In this procedure the sample is oxidized by a mixture of sulfuric acid and hydrogen peroxide. Digestion with sulfuric acid of a dry sample requires 4 minutes at 440°C for sediments and 468°C for muscle. Charred sample was clarified with 10 ml 50% hydrogen peroxide and boiled off excess by heating for one more minute.

Digest is diluted to approximately 70 ml with deionized water and pH adjusted to 4 with 8 N potassium hydroxide when aliquots are taken for analysis using bicinchoninate method for total copper (Hach 1993) Zincon method for total zinc and 1,5-diphenylcarbohydrazide for hexavalente chromium (Greenberg *et al.*, 1992).

Simultaneously, oxygen (Ysi Meter mod. 50 oxymeter), pH (Orion pH sensor), water conductivity and temperature (Hatch conductimeter) and transparency (Secchi disk) were measured.

The metals were measured in the muscles and viscerae in the following fishes: 1) Two planktivorous fish, the silverside *Odonthestes bonariensis bonariensis* (Cuv and Val.) (of economic and sporting importance) and the bagarito *Parapimelodus valenciennesi* (Kroyer). 2) Three benthic zone species, the carp *Cyprinus carpio* L., the vieja *Hypostomus commersoni* (Cuv.and Val.) and the bagre sapo *Rhamdia sapo* (Valenciennes). 3) A piscivorous fish, the tararira *Hoplias malabaricus malabaricus* (Bloch) which diet consist of insects and fishes in the juveniles and fishes in the adults (Oliveros and Rossi, 1991). Metals were also measured in the muscles of a mollusc, the clam *Anodontites anodontites trapesialis* (Gray)(Bivalvia, Mycetopodidae), in phytoplankton and in zooplankton.

In the analysis, we considered: 1) the benthic fauna of mud-fedders and bottom dwelling organisms, which are associated with the sediments and the detritic chain; and 2) the producers and primary, secondary and tertiary consumers of the limnetic zone.

RESULTS AND DISCUSSION

The physico-chemical factors measured in the Chascomus Lake during the present period do not differ singificantly from those previously recognized (Barla, *op. cit.*; Conzonno, *op cit.*, Quiros, *op. cit.*; Table 1). During the sampled period the water-level rose 40 cm.

Table 1

Physical and chemical variables recorded in Chascomus Lake during the period 1996-1997. Maximum and minimum values of depth, air and water temperatures, transparency, dissolved oxigen (DO), pH and total dissolved solids (TSD).

	Min.	Max.
Depth (m)	0.25	1.4
Air temperature (°C)	19	28.7
Water temperature (°C)	20	24.1
Transparency (cm)	5	19
DO (mg/l)	6.5	11
pH	8.5	9.28
TDS (g/l)	0.4	1.21

Table 2

Concentration in parts per million (ppm) of copper,zinc and chromium in water, sediments, bottom and limnethic fauna in Chascomús Lake during the period 1996-1997. Size of sample (N), mean (x), standard deviation (SD), and range. (n.d.: not detected)

		Concentration (ppm)											
		Copper				Zinc				Chromium			
		N	x	SD	Range	N	x	SD	Range	N	x	SD	Range
Water													
Phytoplankton													
Zooplankton													
O.b.bonariensis	muscle	17	1.78	1.28	0.27-5.05	15	0.19	0.25	n.d.-1.02	17	0.13	0.17	0.02-0.61
	spleen	1	0.2			1	0.08			1	n.d.		
	liver	1	0.1			1	0.6			1	n.d.		
	gill	32	530.9	712.63	33-2510	32	296.5	399.26	14-1860	32	41.1	67.8	n.d.-297
	ovary	1	2633			1	546			1	193		
P.valenciennesi	muscle	1	800			1	386			1	84		
H.m.malabaricus	muscle	1	1133			1	310			1	910		
		1	200			1	263			1	567		
Sediment		11	359.4	659.71	10-2160	11	283.5	387.65	70-1380	11	71.4	111.79	12-350
A.a.trapesialis	muscle	1	1260			1	600			1	500		
H.commersoni	muscle												
	spleen	12	16950	7787.22	6530-34930	12	3697	1648.86	950-5530	12	438	480.45	80-1830
	liver	2	785	35.35	760-810	2	1705	516.19	1340-2070	2	173.5	9.19	167-180
	gill	14	1699.5	1666.28	50-5150	14	909.8	792.14	116-2640	14	73.4	91.77	8-330
	ovary	1	500			1	106			1	148		
R.sapo	muscle	1	233			1	158			1	105		
	spleen	1	533			1	160			1	404		
	liver	1	250			1	123			1	298		
	gill	3	629.3	641.4	258-1370	3	412	235.82	200-666	3	123.7	162.54	11-310
	ovary	1	2666			1	373			1	11		
C.carpio	muscle	1	1466			1	504			1	106		
	spleen	1	800			1	424			1	136		
	liver	1	700			1	626			1	325		
	gill	8	315.6	329.12	23-870	8	273	282.33	28-760	8	151.6	220.15	18-650
	ovary	1	1266			1	466			1	287		
		1	466			1	720			1	331		
		1	233			1	920			1	72		
		1	766			1	573			1	95		

The three elements, but especially copper, showed high concentrations in water, sediments and biota (Table 2). In samples from La Limpia Lake and Mar Chiquita Coastal Lagoon these metals were not detected. Nevertheless, mercury and lead were found in the biota at Mar Chiquita by Marcovecchio *et al.* (1986).

Copper. The concentration observed in the water was 890 times higher than the limit recommended for aquatic life (0.002 mg/l) by the current legislation and domestic and international standards and quality criteria for specific pollutants in natural waters, according to the Secretaría de Recursos Hídricos de la República Argentina. Concentration in sediments was even higher: 9,522 times higher than the limit considering the mean values.

Spatial and temporal variations in concentration were observed both in sediments and water. Higher concentrations in water were detected at the beginning of 1996, gradually diminishing afterwards. A large accumulation of copper in sediments was found even though concentration in water had diminished. The highest concentrations were measured in site II (Fig. 2 a, b). We consider that copper originated from human activities because very low concentrations of this metal (average 5 ppm, Csech, 1997) occur in soil in the río Salado basin.

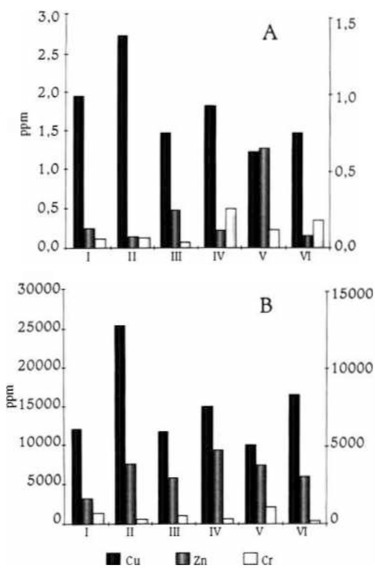


Figura 2

A: Copper, zinc and chromium concentration (ppm) in water. Average of the period sampled in each site (from 1996 to 1997). The left range for copper and the right for zinc and chromium. B: idem for sediments.

We analyzed muscle in fishes because of its importance for human consumption finding a remarkable accumulation of copper. However, metals can accumulate in different organs, with variations according to species (Reichenbach-Klinke, 1976). We detected that the highest concentration in fishes was in viscerae, mainly spleen, liver and gills. We also analyzed ovaries and found significant concentrations.

Pathological alterations in silverside gills from Chascomús Lake were described by Romano and Cueva (1988) who considered that the lesions were occasioned by toxic metals. Copper and zinc generate similar lesions (Llyod, 1960 *fide* Romano and Cueva, 1988).

Among the benthic fishes, the higher concentration occurs in the vieja *Hipostomus commersoni*, a bottom dweller, illiophagous fish (Ringuelet *et al.* 1967)(Fig. 3 a). The next decreasing concentration is found in the bagre sapo *Rhamdia sapo*, related with the bottom and vegetation; it is an omnivorous fish, that can even feed on mud. The lowest concentration occurs in the carp *Cyprinus carpio*, which feeds on mud and vegetables. None of these species preys on each other. According to their morphology, some are better swimmers than others (Webb, 1984).

In the limnethic zone, copper becomes more concentrated in the tissues of organisms at successively higher trophic levels in food chains (Tyler Miller, 1990) and could indicate biological amplification (Fig. 3b).

Zinc. Concentration observed in water surpasses the recommended limit for aquatic life (0.03 mg/l) but not that for recreational activities (5 mg/l). The mean value found in water is 6.33 times the recommended limit, but the mean value in sediments is 19,458 times that found in water. Zinc reaches a much higher concentration in sediments than copper, perhaps due to a less concentrated but long lasting income.

Zinc and copper, both in water and sediments, showed the highest concentrations at the beginning of the study. High concentrations were observed in muscle, with the exception of *Cyprinus carpio*, which showed the highest concentration in gills. The contact of zinc with gill laminae provokes an increase of mucous cells, which

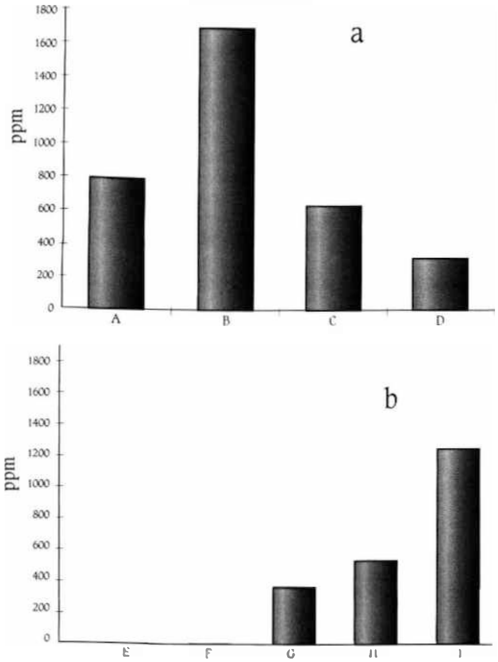
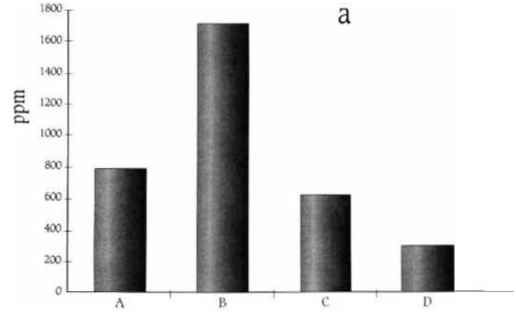


Figura 3
Copper mean concentration (ppm) in muscle. a: benthic zone: *Anodontites anodontites trapesialis* (A), *Hipostomus commersoni* (B), *Rhamdia sapo* (C), *Cyprinus carpio* (D). b: limnetic zone: phytoplancton (E), zooplancton (F), *Parapimelodus valenciennesi* (G), *Odonthestes bonariensis bonariensis* (H), *Hoplias malabaricus malabaricus* (I).

could cause breath distress with epithelium damage (Carpenter, 1927; Jones, 1939; Skidmore, 1970 *fide* Romano *op. cit.*).
Zinc concentration in benthic fauna has the same pattern than copper.
A similar pattern was observed in the limnetic zone, but with more overlapping standard deviations than in copper (Fig. 4 b).

Chromium. The concentration of hexavalent chromium in water (medium value: 0.12 mg/l was higher than the limit recommended for aquatic life (0.002 mg/l) and recreational activities (0.05 mg/l). The concentration is 3,369 higher in sediments than in water. Sites IV and VI showed the highest concentrations in water at the beginning of the period. In the Site V the highest accumulation in sediments was found at the end of the period.
In the biota, the highest accumulation was in gills and muscle (also in ovaries in *Rhamdia sapo*).
In the benthic fauna, the concentration pattern of chromium differs from that observed for copper and



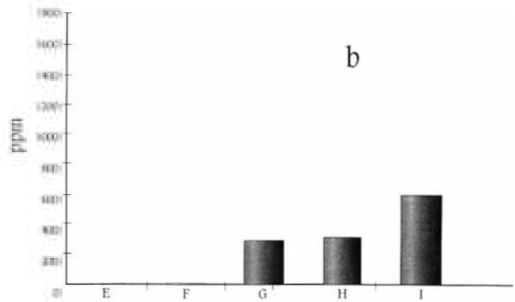


Figura 4.
Zinc mean concentration (ppm) in muscle. a: benthic zone: *Anodontites anodontites trapesialis* (A), *Hipostomus commersoni* (B), *Rhamdia sapo* (C), *Cyprinus carpio* (D). b: limnetic zone: phytoplankton (E), zooplankton (F), *Parapimelodus valenciennesi* (G), *Odonthestes bonariensis bonariensis* (H). *Hoplias malabaricus malabaricus* (I)

zinc. Besides, there are more value dispersion. The different pattern is probably due to the lower chromium concentration in sediments respect to the other metals. In the limnetic zone, accumulation was observed in the predatory species *Hoplias malabaricus malabaricus* (Fig 5 b).

We did not include those inhabitants of vegetated waters which are preyed by *Hoplias malabaricus malabaricus* (Ringuelet, 1975). During the period, we caught only one specimen of the tertiary consumer *Hoplias malabaricus malabaricus*. The scarcity of this fish could be due to overfishing but it could also indicate that the community structure is regulated by a «bottom up» control, where the prevailing factors are resource availability and environmental perturbations (Bechara, 1993; Brewer, 1994). Finally, we agree with the suggestion by Romano and Cueva (1988) that the Chascomús lake is contaminated with chemicals coming from sewers, plaguicides used in surrounding rural establishments and illegal industrial waste.
Finally, according to the present evidence,

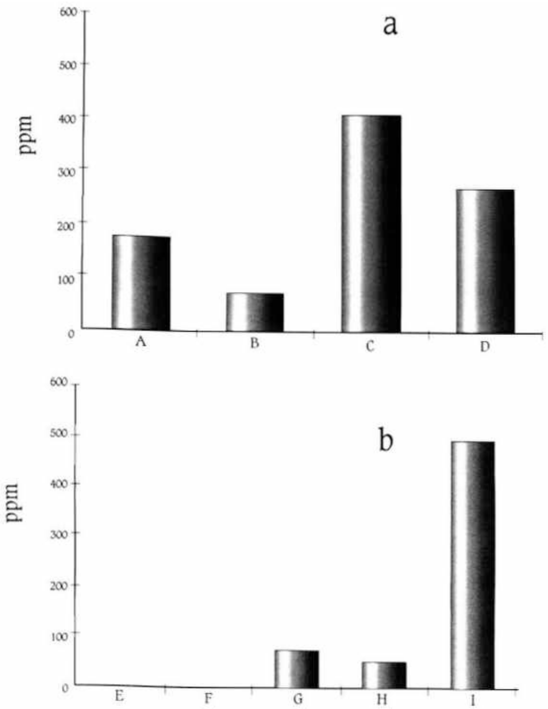


Figura 5
Chromium mean concentration (ppm) in muscle. a: benthic zone: *Anodontites anodontites trapesialis* (A), *Hipostomus commersoni* (B), *Rhamdia sapo* (C), *Cyprinus carpio* (D). b: limnetic zone: phytoplankton (E), zooplankton (F), *Parapimelodus valenciennesi* (G), *Odonthestes bonariensis bonariensis* (H), *Hoplias malabaricus malabaricus* (I)

contamination in the Chascomus Lake seems to have been originated from sewers, plaguicides used in surrounding rural establishments, and illegal industrial waste.

ACKNOWLEDGMENTS

To Bioq. Gomez Casati for advice in chemical analysis, Drs. E. Martín and M. P. Tassara for mollusc identification, M. Cerda Gilbert for samples from Mar Chiquita Lagoon, Lic. F. Pieckenstain for valuable information, Dr. V. Conzonno for comments on a former version of the manuscript.

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Recibido / Received: 28 diciembre 1998
Aceptado / Accepted: 30 octubre 1999

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Argentina: Hetty Bertoldi de Pomar, Victor Conzonno, Berta Cousseau, Norma Díaz, Esteban Labilla, Marta Loiácono, Jorge Marcovecchio, Amalia Miquelarena, Juan José Morrone, Jorge William.

Austria: W. Foissner

Brasil: Harold Fowler, Lionel Goncalvez

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Italia: Norberto Milani