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Mercury distribution in estuarine environments from Argentina: the detoxification and recovery of salt marshes after 15 years

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Abstract

Total Hg contents from abiotic (surface sediments and suspended particulate matter) and biological (crabs, fishes and halophytes) compartments from Bahía Blanca estuary and Mar Chiquita Coastal Lagoon, Argentina, have been monitored since the 1980′s. At Bahía Blanca estuary, high Hg concentrations were recorded during the early 1980′s in surface sediments (0.34 ± 0.22 μg/g) and suspended particulate matter (0.19 ± 0.10 μg/g). Fish species, *Mustelus schmitti* (0.89 ± 0.29 μg/g), *Paralichthys brasiliensis* (0.85 ± 0.18 μg/g) and *Micropogonias furnieri* (0.37 ± 0.11 μg/g) also presented high Hg concentrations. The large industrial nucleus located within the estuary has been identified as the main metal source for this environment. Hg contents from the same area during 1996–1998 were significantly lower: surface sediments (0.164 ± 0.023 μg/g), suspended particulate matter (0.048 ± 0.0017 μg/g), fish *Micropogonias furnieri* (0.13 ± 0.02 μg/g) and crab *Chasmagnathus granulata* (0.334 ± 0.071 μg/g). This trend of environmental detoxification is probably related with *(i)* the technological changes incorporated by the local industry, *(ii)* a most adequate management of industrial effluents, and *(iii)* the removal of great sediment volume by dredging and refill.

During the 1980′s Mar Chiquita Lagoon Hg concentrations reached 0.08 ± 0.01 μg/g in surface sediments and 0.09 ± 0.025 μg/g in suspended particulate matter, and 0.14 ± 0.04 μg/g in the fish *Basilichthys bonariensis* and 0.22 ± 0.08 μg/g in*Paralichthys brasiliensis*, and 0.08 ± 0.01 μg/g in the crab *C. granulata*, Hg concentrations were lower than at Bahía Blanca. Remote Hg sources for this Coastal Lagoon and atmospheric and stream transport of Hg is proposed as major Hg sources, since no Hg point sources exists nearby. Mercury concentrations recorded in the 1996–1998 period were lower than those recorded in the previous decade: surface sediments (0.019 ± 0.004 μg/g), suspended particulate matter (0.030 ± 0.008 μg/g), halophyte *Spartina densiflora* (0.013 ± 0.008 μg/g) or crab *C. granulata* (0.011 ± 0.009 μg/g).

Both Hg bioaccumulation and biomagnification processes were verified in Bahía Blanca estuary and in Mar Chiquita Coastal Lagoon. This apparent recovery of both estuarine environments deserves to be carefully analyzed, in order to fully understand the foundations of these processes.

Introduction

Mercury has been fully recognized as a severe environmental pollutant, not only because of its high toxicity, even at low concentrations, but also considering its ability to enter into biological systems (Clarkson, 1992). It is well known that aquatic systems are particularly vulnerable to Hg pollution and wetlands, in particular, have been pointed out as very

Figure 1. Location of the studied environments along the Argentine coast.

sensitive to this kind of pollution (Legret and Pagotto, 1999; Horvat et al., 1999). In this sense a large number of reports on Hg occurrence, concentration and/or distribution in sediments, suspended particulate matter or different organisms from estuaries and salt-marshes have been reported for many environments (Barcellos et al., 1997; Marins et al., 1997).

Even though many papers on Hg pollution in salt-marsh environments, either in abiotic or in biological compartments (Lacerda et al., 1997; Marcovecchio et al., 1988a; Law et al., 1992), have been previously reported, information is scarce in relation with detoxification processes after this type of pollution has occurred.

In the present paper, historical data of the last 15 years of Hg, concentration and accumulation into both biological and abiotic compartments of two estuarine environments of Argentina (Bahía Blanca estuary and Mar Chiquita Coastal Lagoon) have been analyzed, looking for modifications of their distribution trends and environmental status.

Materials and methods

Description of the studied environments

Both studied environments – Bahía Blanca estuary and Mar Chiquita coastal lagoon – are located in the south-eastern Buenos Aires Province coast, on the Argentine Atlantic littoral (Figure 1). Each of these systems has particular attributes and environmental characteristics, which conditionals the bio-geochemical processes occurring within them.

Bahía Blanca estuary is located between 38°45′ and 39°40′S, and 61°45′ and 62°30′W, in the south-eastern area of Buenos Aires Province, in Argentina. Water interchange within the bay is influenced by a semidiurnal tidal regime. The bay encompasses an area of 400 km^2, and at high tide the total area is nearly 1,300 km^2 (Villa and Pucci, 1987). The hydrography of the estuary is strongly influenced by climatic conditions (Freije et al., 1981). Several streams and channels flow into the bay, most of them affected by anthropogenic activities. The freshwater contribution is approximately 4,000 $m^3.day^{-1}$. Tidal oscillations of 3 m and predominant northwesterly winds create strong tidal currents, which facilitate water mixture, leading to a uniform vertical distribution of the principal oceanographic parameters.

At the northern boundaries of the estuary various ports, towns (with a population exceeding 300,000 inhabitants) and industries are located, and several streams discharge into the area. Oil refineries and terminals, petrochemical industries, meat factories, leather plants, fish factories, textile plants, wool washing plants, silos and cereal mills discharge their processing residues into the streams or directly into the estuary. Nearly 10 $m^3.day^{-1}$ of raw sewage are discharged into the study area. This estuary is extensively used by fishing boats, oil tankers and cargo vessels and therefore requires regular dredging. In this way, this coastal marine system receives contaminant inputs from municipal wastewater, direct industrial discharges, harbor-related operations, runoff water, which carries materials from land development areas and aerial fallout from atmospheric pollutants. Six sample stations have been monitored along the estuary, including different areas influenced by the mentioned potential sources of pollution.

Mar Chiquita Coastal Lagoon is located between 37°33′ and 37°43′ S, and 57°15′ and 57°30′ W, on the Atlantic coast of Buenos Aires Province, 32 km northeastwards Mar del Plata city, in Argentina. This

coastal lagoon has an area of approximately 60 km^2, and with a tributary basin of 10,000 km^2. It is irregular in shape, but its bottom topography is very smooth with a maximum water depth of 1.50 m (Lanfredi et al., 1981). The lagoon is connected to the sea by an elongated inlet channel, with approximately 6 km long and more than 200 m wide. Freshwater influence is more important than the seawater one. Thus, the main freshwater input is the continental drainage that collects rainwater from a large basin including the Tandilia orographic system. Moreover, the average rainfall for this area is approximately 800 mm.year^{-1}, with an homogeneous distribution along the year; even though, torrential rainfalls have been usually recorded during winter and spring (from June to October) (Olivier et al., 1972). In addition, the role of the freatic reservoir regulating not only the lagoon water level but also the standard meteorological conditions of the area has been recognized (Fasano et al., 1982).

Six (6) sampling stations have been monitored along the coastal lagoon, where selected sites were representative of this environment.

Sampling and analytical methods

Evaluated environments, Bahía Blanca estuary and Mar Chiquita coastal lagoon, has been monitored since 1982. Mercury distributions and concentrations in the present paper were recorded along two periods: 1982–1988 and 1994–1998. Corresponding results have been reported, and in the present overview a comparative analysis is developed, looking for possible variation in each environment's trends. Details of methods and procedures have been previously published (Marcovecchio, 1988; Marcovecchio et al., 1986a, b, 1988)

Sampling cruises, in a monthly basis, were carried out in both studied environments in order to obtain the necessary samples (sediments, suspended particulate matter, estuarine water and biological samples.

Estuarine water was sampled using acid washed polycarbonate Van Dorn bottles. Water samples were vacuum filtered through 0.45μ mesh cellulose acetate filters, to obtain suspended particulate matter samples. After, they were carefully store at –20 °C until analytical treatment at the laboratory.

Surface sediment samples were obtained with an acid washed PVC sampler, put into polyethylene bags, and store at –20 °C.

Biological samples were obtained using different techniques. Fish samples (white croaker *Micropogonias furnieri,* flat fish *Paralichthys brasiliensis,* shark *Mustelus schmitti* and/or 'pejerrey' *Basilichthys bonariensis*) were got through traditional fishing arts. Crabs (*Chasmagnathus granulata*) and marginal halophyte vegetation (*Spartina densiflora*) samples were handily collected in both environments.

Total Hg in abiotic and biological samples was determined through cold vapor atomic absorption spectrophotometry (CVAAS). Analysis were performed with an AA-2380 Perkin Elmer atomic absorption spectrophotometer, and analytical grade reagents were used to calibration curves and blanks build up. The AQ was checked against 'reference materials' provided by The National Institute for Environmental Studies (NIES), Tsukuba (Japan).

Results and discussion

1982–1988 period

During this period, Hg contents in surface sediments, suspended particulate matter and organisms tissues have been determined in both studied environments. In the case of Bahía Blanca estuary Hg concentrations in surface sediments have ranged between 0.11 and 2.78 μg/g, with average values of 0.34 $\pm$ 0.22 μg/g in a dry weight basis (Marcovecchio et al., 1986a). The levels determined in suspended particulate matter varied between 0.05 and 1.76 μg/g, with a mean value of 0.19 $\pm$ 0.10 μg/g dry wt. (Marcovecchio, 1988). These Hg levels were significantly higher than those found in sediments of the adjacent marine coastal system. Location of the samples with higher Hg contents in both surface sediments and suspended particulate matter has always agreed not only with the dumping area for industrial effluents, but also to the proximity of the landfill zone of Bahía Blanca city (Marcovecchio et al., 1986a).

Hg concentrations in organisms from Bahía Blanca estuary, mainly edible ones, were also higher than those found in species from the marine coastal zone (Marcovecchio, 1988; Marcovecchio et al., 1988). Fish and shellfish species, representing five different trophic levels of Bahía Blanca estuary were analyzed, and increasing Hg concentrations were observed from species of trophic level 2 (primary consumers) up to those of trophic level 4–5 (top predators) (Marcovecchio et al., 1988), characterizing a typical biomagnification processes. Highest Hg values reported for fish species from Bahía Blanca estuary during this period

Table 1. Mercury concentrations (μg/g ww) recorded in fish species from Bahia Blanca estuary during the 1980′s (after Marcovecchio et al., 1998a).

Species	Hg in muscle	Hg in liver
'White croaker' *Micropogonias furnieri*	0.37 ± 0.11	0.32 ± 0.11
'Flat fish' *Paralichthys* sp.	0.85 ± 0.18	0.73 ± 0.18
'Gatuzo shark' *Mustelus schmitti*	0.89 ± 0.29	0.88 ± 0.35

are presented in Table 1. The large industrial nucleus located close to the bay has been identified as the main Hg source for the system, which effluents were dumped directly into the estuarine waters.

During the same period a similar study has been done within Mar Chiquita coastal lagoon, always obtaining lower concentrations than in Bahía Blanca, not only in abiotic compartments (surface sediments and suspended particulate matter) but also in biological ones. Mercury levels in Mar Chiquita sediments varied from <0.002 to 0.29 μg/g, with a mean value of 0.08 ± 0.01 μg/g, in a dry weight basis. Also those of suspended particulate matter ranged from 0.03 to 0.33 μg/g, with an average concentration of 0.09 ± 0.025 μg/g, in a dry weight basis. Mercury concentrations determined in Mar Chiquita biota were also low, indicating that punctual sources of this pollutant did not exist within the system (Marcovecchio et al., 1986b). Hg concentrations in selected aquatic species from Mar Chiquita are presented in Table 2.

Notwithstanding the low Hg concentrations, biomagnification of this pollutant through the food web has been observed, which suggests that this process does not need high concentrations to occur. Keeping in mind that neither industrial factories nor large urban centers are located close to Mar Chiquita coastal lagoon, the occurrence of remote Hg sources together with the presumable atmospheric and stream transport of this metal has been proposed as responsible for the levels of Hg found within this ecosystem (Marcovecchio et al., 1986b)

1994–1998 period

During this period a similar study scheme was applied in order to evaluate mercury distribution in both scenarios. In the case of Bahía Blanca, all of the analyzed compartments have shown significantly lower Hg concentrations than those corresponding to the previous study stage. Average Hg concentrations in surface sediments were $0.164 \pm 0.023\mu$g/g, ranging

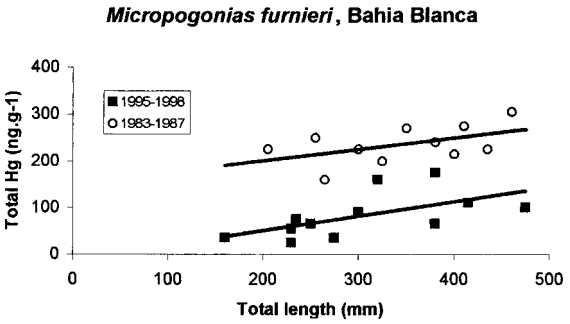

Figure 2. Comparison of Hg concentrations in *Micropogonias furnieri* at Bahia Blanca estuary in both studied periods.

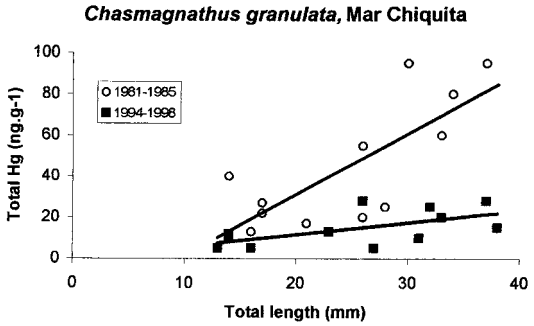

Figure 3. Comparison of Hg concentrations in *Chasmagnathus granulata* at Mar Chiquita coastal lagoon in both studied periods.

from 0.03 μg/g to 0.21 μg/g (in a dry wt. basis). Average Hg concentrations in suspended particles of the estuary were 0.048 ± 0.0017 μg/g (in a dry wt. basis), ranging from 0.002 μg/g to 0.12 μg/g. For the study of Hg in the biota the fish *M. furnieri* were used as indicator organism, and the mean value of Hg recorded in its muscle were 0.13 ± 0.02 μg/g (in a wet wt. basis), ranging from 0.06 μg/g to 0.20 μg/g. Figure 3 shows a comparison between Hg concentrations in *M. furnieri* in the two periods studied.

These results seem to indicate that such a kind of *'environmental detoxification process'* is occurring within the Bahía Blanca estuary, probably related with: i) the technological improvement incorporated

Table 2. Average, maximum and minimum Hg concentrations (μg/g ww) recorded in fish muscle from Mar Chiquita lagoon during the 1980's (after Marcovecchio et al., 1998b).

Species	mean Hg level	Minimum	Maximum
'Flat fish' *Paralichthys* sp.	0.22	0.17	0.25
'Pejerrey' *Basilichthys bonariensis*	0.20	0.08	0.44
'Lisa' *Mugil brasiliensis*	0.11	0.05	0.18

by the industrial factories of the region; ii) the most adequate management of industrial and urban effluents within the region, and iii) the remove of a great volume of sediments because of the dredging and refill of the main navigation channel.

Mar Chiquita coastal lagoon environment has shown the same trend of Bahía Blanca, but with significantly lower Hg concentrations. Surface sediments of Mar Chiquita presented an average concentration of 0.019 $\pm$ 0.0004 μg/g, with extreme values from 0.002 μg/g to 0.11 μg/g (in a dry wt. basis). Although, levels in suspended particulate matter have reached 0.09 $\pm$ 0.025 μg/g (dry wt.). For the analysis of Hg content in the biota, the crab *C. granulata* has been selected, not only because it is on the basis of the trophic web of the system, but also because Hg data from the previous period existed. The average value as found in the crab tissues were 0.08 $\pm$ 0.01 μg/g, in a wet wt. Basis. Figure 4 shows a comparison between Hg concentrations in *C. granulata* in the two studied periods.

In conclusion, the analysis of the results from the comparative study of Bahía Blanca estuary and Mar Chiquita coastal lagoon along 15 years has allowed to sustain the following comments: 1) both studied environments have presented detectable concentrations of Hg in most of the analyzed samples, 2) in the case of Bahía Blanca estuary, Hg contents recorded in the 1983–1988 period in abiotic and biological compartments showed to be higher than the corresponding ones for the 1995–1998 period. 3) the obtained results for Mar Chiquita coastal lagoon during the period 1982–1986 were higher than those of 1994–1998, even though all the determined values were very low. 4) the observed decrease in Hg concentrations in Bahía Blanca estuary was assumed to be related with: *(i)* The technological changes as incorporated by industrial factories; *(ii)* A most adequate management of industrial effluents; and, *(iii)* The remove of large sediment volume because of dredging and refill. 5) both atmospheric and stream transport seem presumably to be the main remote Hg sources for Mar Chiquita coastal lagoon, keeping in mind that there are no punctual ones nearby.

Even though the results have shown to be significantly clear and presented a marked trend distribution, this apparent recovery of both estuarine environments deserves to be carefully analyzed, in order to assure a full understand of the process which regulates their functioning.

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