

Heavy Metals in Intertidal Surface Sediments from the Patagonian Coast, Argentina

M. N. Gil,¹M. A. Harvey,²J. L. Esteves¹

¹National Patagonic Center (CONICET), Bv. Brown 3000, (9120) Puerto Madryn, Chubut, Argentina

²Patagonian National University, Belgrano 504, (9100) Trelew, Chubut, Argentina

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The Patagonian coastal area of Argentina is nearly 3000 km long. It is a growing, developing region and is a highly biologically productive ecosystem. Human population is distributed among 13 towns, ranging from less than 1,000 inhabitants in Bahía Camarones to nearly 126,000 in Comodoro Rivadavia. The main pollution problems are related to sewage effluents with deficient or without treatment, agricultural runoff from the Negro and Colorado rivers, petroleum extraction and transportation and heavy metals wastes located near ports.

Previous studies of metal concentrations in Patagonian marine sediments are scarce and restricted to Nuevo and San Jose Gulfs (Harvey and Gil 1968). The aim of the present work, is to determine the content of total mercury and 0.5 N HCl leachable zinc, copper, lead and cadmium in intertidal surface sediments from 17 stations along Patagonian coast, between Colorado and Gallegos rivers.

MATERIALS AND METHODS

Sampling was carried out during 1994 and 1995. Intertidal surface sediments from the upper 9 cm were removed employing plexiglass cores. No less than four cores were collected at nearly 10 m intervals at each station, in order to reduce localized variability. After collection, they were dried at no more than 40°C in an oven, to avoid Hg and Cd losses (Camacho et al. 1992, Evans and Hanson 1993). After drying, sediments from each station were placed into a plastic container and thoroughly mixed to form an homogeneous composite.

Heavy metals were analyzed in the fine fraction (< 63 µm), to reduce grain size effects (Baudo and Muntau 1990). For Hg analysis, 1 g of sediment was digested in concentrated HCl and HNO₃ (1+9) at 50°C for 1 hr in Kjeldahl tubes and analyzed by the cold vapor AAS technique.

Zn, Cu, Pb and Cd were extracted with cold 0.5 N HCl (1g in 25 ml) overnight at room temperature (Agemian and Chau 1976). The

suspensions were then centrifuged for 15 min at 16,000 rpm in a SORVALL RC-5C automatic superspeed refrigerated centrifuge. Measurements were immediately carried out on the supernatant by flame air-acetylene AAS, employing an IL 457 Spectrophotometer. It is considered that cold 0.5 HCl allows extraction of the most bioavailable metal fraction (Luoma and Bryan 1981) and has been suggested as capable of identifying “anthropogenic fingerprints” (Chester and Voutsinou 1981). Organic carbon was also determined in the fine fraction by wet combustion (Walkley 1947).

All chemical determinations were run by duplicate and reagent blanks were processed with each batch of samples. Metal concentrations are expressed in ppm of dry weight (dw) of the fine fraction.

Detection limits for the analyzed elements were: Zn 0.47 ppm, Cu 0.64 ppm, Pb 1.8 ppm, Cd 0.03 ppm and Hg 0.05 ppm. Precision was determined by treating 10 replicates of one sample; the following coefficients of variation were found (mean values in parenthesis): Zn 0.77% (20.1 ppm); Cu 2.89% (7.4 ppm); Pb 1.88% (32 ppm); Cd 3.58% (2.51 ppm) and Hg (spiked sample) 2.9% (0.125 ppm). NIST SRM 1646a - Estuarine Sediment was analyzed employing the same metal extraction methods as for the samples (table 1).

Table 1. Metal concentrations in NIST SRM (1646a - Estuarine Sediment).

Element	Certified values* (ppm, dw)	Our results** (ppm, dw)	Recovery (%)
Zn	48.9±1.6	27.7±1.6	56.6
Cu	10.01±0.34	6.36±0.29	63.5
Pb	11.7±1.2	7.0±0.1	59.8
Cd	0.148±0.007	0.05±0.02	33.8
Hg	0.04 [#]	<0.05	-

* Total concentrations.

** Zn, Cu, Pb and Cd: extractable concentrations. Hg: total concentration.

[#]Informed value, noncertified.

RESULTS AND DISCUSSION

Metal results for stations 1 to 16 are shown in fig 2, while results for station 17 (Bahía San Antonio) are shown separately (fig 3), since this place presents a completely different situation.

Stations 1 to 16 (fig. 2): Hg and Cd levels were below their detection limits in all samples. Maximum and minimum concentrations measured for the other elements were: Zn 160 - 6.8 ppm, Cu 20.1 - 2.4 ppm and Pb 33

ppm - not detected. Station 11 (Bahía Camarones), located in an open bay with scarce human and industrial influence, showed the lowest values. The highest metal levels were found in areas characterized by high anthropogenic activities: stations 7 (Comodoro Rivadavia port), station 9 (Caleta Córdova), station 12 (Bahía Engaño) and stations 13 and 14 (Bahía Nueva). At the the remaining stations, Zn and Cu showed medium values and Pb was only detected at stations 3, 10, 15 and 16 (range: 9 - 15 ppm).

In general all samples were characterized by low to moderate content of organic matter (fig. 4a) and no correlations were observed with metals.

Station 17 (substations a to f – fig. 3): station 17 (Bahía San Antonio) showed the highest metal values of this study, with extremely high concentrations at substations e (Zn 7,300 ppm, Cu 4,750 ppm, Pb 14,500 ppm and Cd 7.5 ppm) and f (Zn: 8,690 ppm, and Cd 11.2 ppm). Organic matter contents were low to moderate (fig. 4b) and no correlations were found with metal levels.

Increased metal values from substations a to e (fig 3) as well as concentrations in soil samples collected near the coastal area (substation g -Table 2, data provided by the Chemical Service of the Centro Nacional Patagónico), proved the existence of an important source of contamination.

Table 2. Bahía San Antonio (Substation g). Extractable metal concentrations in soil samples (ppm, dw)*.

Depth (cm)	Zn	Cu	Pb	Cd
0-5	10,500	1,575	24,150	180
5-10	22,150	11,574	10,850	342

* Total Hg: not detected.

Lixiviation processes caused by extremely high tides, rainfalls and wind, as well as soil infiltration, are supposed to have been carrying metals towards the bay. Furthermore, water inflowing in from San Matías Gulf at flood-tide and leaving the system at ebb tide, may cause metals to spread along the west side of the bay. (Esteves et al. 1996). The high concentrations of Zn and Cd registered in substation f, would also be attributed to this general contamination process. Substation a (Caleta Falsa) is scarcely influenced by the bay hydrodynamics and presents the lowest metal contents in Bahía San Antonio.

Regarding the obtained results and literature data where similar mild acid techniques have been used (Dassenakis et al. 1996), the studied sites may be divided into three groups: unpolluted (stations 1, 2, 4, 5, 6, 8, 11,

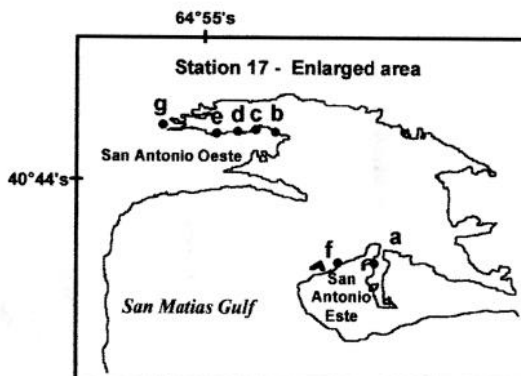
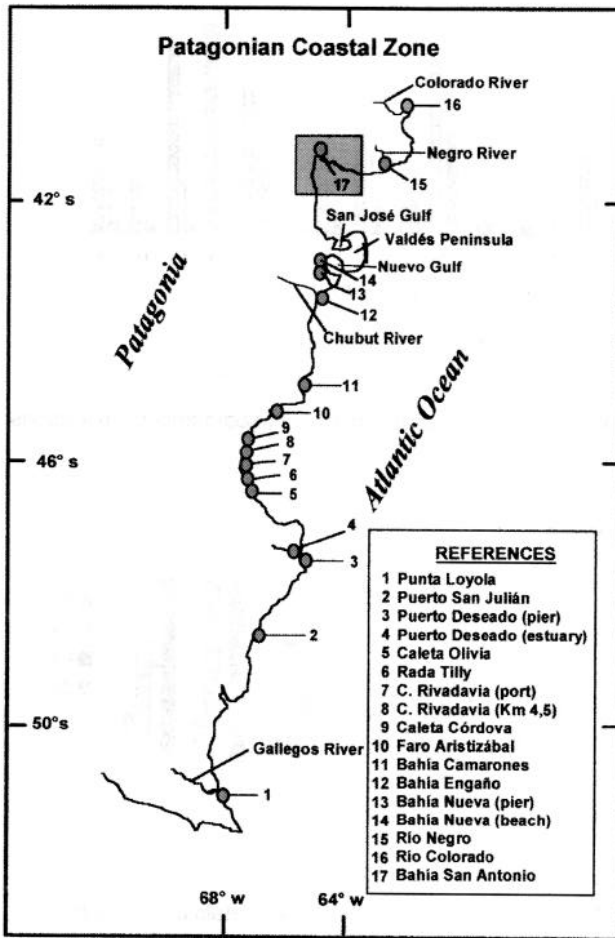


Figure 1: Sampling stations

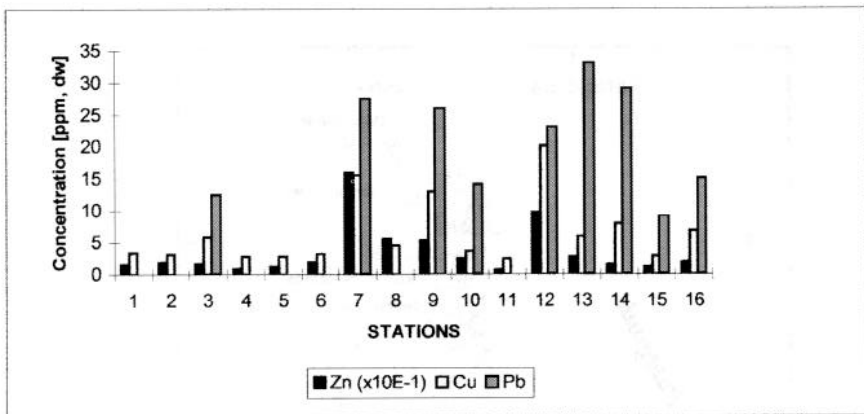


Figure 2. Concentrations of extractable metals in sediments from stations 1 to 16.

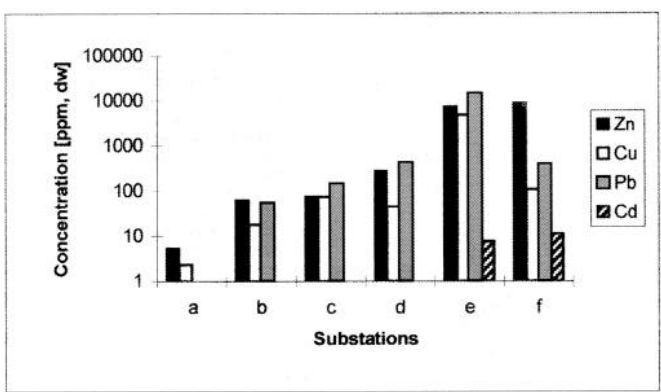


Figure 3. Concentrations of extractable metals in sediments from station 17 (Bahía San Antonio).

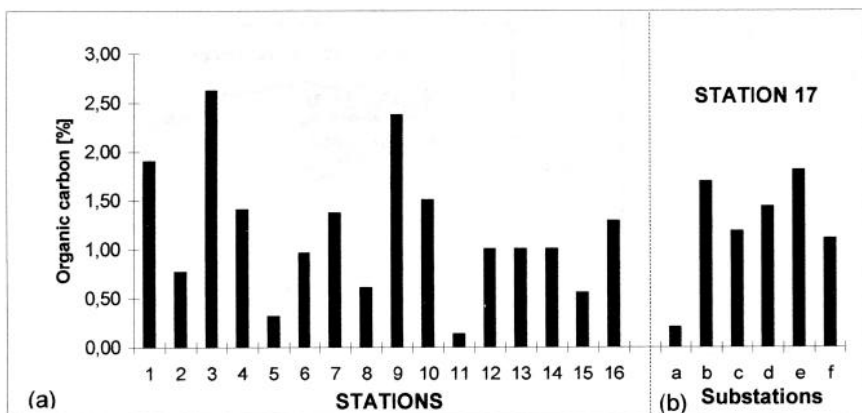


Figure 4. Organic carbon content of sediments.

slightly polluted (stations 3, 7, 9, 10, 12, 13, 14, 15, 16, particularly C. Rivadavia, C. Córdova, B. Engaño and B. Nueva) and heavily polluted (station 17: Bahía San Antonio, except for Caleta Falsa).

The Patagonian coastal area is in a stage of rapid development and new mining and chemical activities are being incorporated. Therefore, changes in pH, salinity, redox conditions of the sediment and degradation of organic complexes are expected. These processes could mobilize these metals (Burguess and Scott 1992) and expose the biota to a chronic contamination, representing a serious threat, especially in Bahía San Antonio. The possible present and future impacts upon the marine environment in this location, as well as the public health and economical hazards, should be assessed.

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