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Mercury in a Marine Trophic Chain

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The mud of the northern zone of the Gulf of Arauco is considered an area of sediments rich in organic matter, due to the current regime and to the geomorphology of the gulf. The possible accumulation of heavy metals derived from industrial and human activities could occur. Mercury levels were researched in suspended particulate matter (organic and inorganic), sediment (using total and partial digestion from 26 sampling stations) and living organisms: *Pleuroncodes monodon* ("squat lobster") a crustacean that feeds on sediment organic matter, and *Genypterus maculatus* ("black ling"), a benthodemersal fish which feeds ca. 24% on *P. monodon*.

Our working hypothesis was that sediments in the northern part of the Arauco Gulf become a temporary reserve for the potential or actual pollutants generated upriver by human activities in the Biobío basin. As an open system, it receives -in the northern sector of the gulf- all the contributions of the basin, mainly in the area of the Biobío canyon and in the immediate continental platform. In a previous report we informed about cadmium and lead behaviour in this trophic marine chain (González *et al.* 1998).

MATERIALS AND METHODS

The methylmercury determination was carried out according to Hight (1987) and Hight & Corcorán (1987) modified by González (1994). Methylmercury was obtained after treatment with acetone and toluene followed by hydrolysis with HCl and subsequent toluene extraction from lyophilised sediments. Identification and quantification was carried out by Gas liquid chromatography using a known concentration of methylmercury Merck as standard.

The certified recovery value for crustacean hepatopancreas, (TORT-1) was 109% mercury, and 98% methylmercury; 156% mercury for spring dogfish liver (DOLT-1); 109% mercury for spring dogfish muscle (DORM-1). The recovery for certified marine sediments PACSS-1 was 94% for Hg concentration (Table 1). In addition, Hg reproducibility level determination in a "squat lobster" sample (*Pleuroncodes monodon*) was carried out from 1 kg of "squat lobsters", lyophilised and ground with Titanium knife blender. The mean mercury level was 0.2 µg/g ± 0.02 (n=7; variation coefficient 10%). According to these results the instrumental methods used proved adequate. All glass and plastic material used was pre-cleaned according to UNEP (1984).

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Table 1. Hg and CH_3Hg laboratory determination in certified standard (NRCC).

National Research Council Canada (NRCC) Standards	Mercury		Methylmercury	
	Certified µg/g	Laboratory µg/g	Certified µg/g	Laboratory µg/g
Marine Sediments Pacss-1	4.57 ± 0.16	4.3 ± 0.1		
Lobster Hepatopancreas (Crustacea)Tort-1	0.33 ± 0.06	0.36 ± 0.01	0.128 ± 0.014	0.125 ± 0.004
Spring Dogfish Liver(Shark) Dolt-1	0.225 ± 0.037	0.35 ±0.04		
Spring Dogfish Muscle (Shark) Dorm-1	0.798 ± 0.074	0.73 ± 0.10		

The areas studied were: **i)** Arauco Gulf between Punta Cullinto (36°47'S, 72°60'W) and Punta Lavapié (37° 09'S, 73° 10'W), and for reference areas **ii)** Cobquecura (36° 07'S, 72° 57'W), for *P. monodon*, and **iii)** Lebu (36° 55'S, 73°39'W), for *G. maculatus*.

Water samples containing suspended particulate matter (5 m above sediment), and sediment samples were collected and treated as suggested by González *et al.* (1998). For total attack of sediment an extraction procedure with HNO_3 (4 mL, 120°C, 1 h, in acid digestion Parr bomb) was carried out.

A representative sample of adults of *Genypterus maculatus* (standard length 49.4 ± 5.8 cm) was captured in the Gulf of Arauco near the mouth of the Biobío River (González *et al*, 1998). In Lebu, the control area, 13 specimens of *G. maculatus* were sampled. All the specimens (105 individuals, obtained in 5 sampling periods) were dissected by surgical steel knife: liver, kidneys, gill, stomach content and muscles (below pectoral fins) of *G. maculatus* was taken, then stored at –80°C in a deep freezer, and then analysed each organ from each fish separately.

Specimens of *P. monodon* were identified according to Gallardo *et al.* (1993). A minimum sample size, 10 individuals of 10 cm long of cephalothorax were used. A sample unit of 20 individuals of "squat lobster" was collected each time during February and May 1992, using a trawl net at 100 to 150 m deep during 15 min.. Both samples were taken in Cobquecura, the control area for *P. monodon* and unaffected by human activity of the Biobío Basin, and Arauco Gulf.

All samples were lyophilised for 72 h to reach constant weight, and packed in plastic bags (pre-cleaned with nitric acid 10%, and bi-distilled water) in a deep freezer, up to the moment of analysis. Moisture content of tissues was calculated. Between 0.5-1 g of this lyophilised material was then soaked during 8 h in HNO_3, in a refrigerated system, and then heated during 1 h at 40°C, filtered through a MFS N° 11 filter paper and the filtrate raised up to volume (20 mL) with Milli-Q bidistilled water (Capelli 1983, UNEP 1982, González 1994).

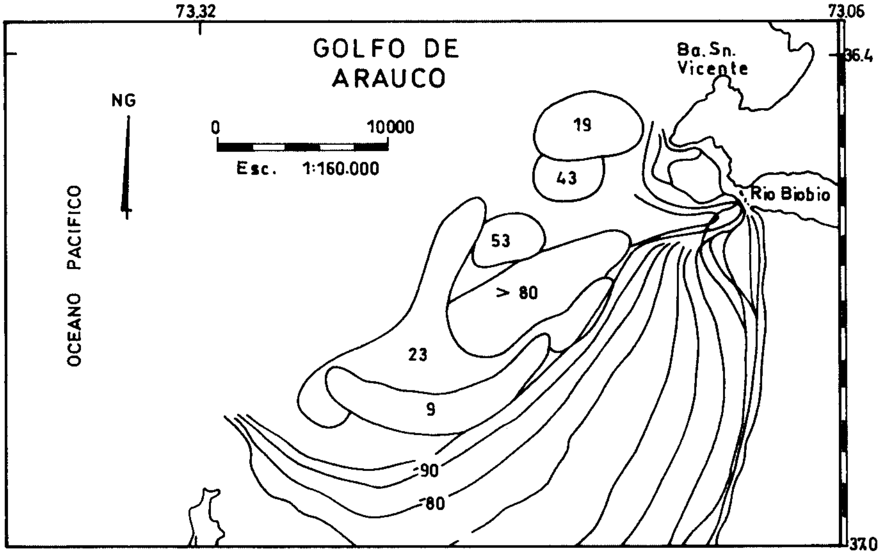

Figure 1. Distribution of mercury content in the water mass above the sediment, of sampling stations grouping by UPGMA. The mercury content is expressed as ng of mercury/g sediment. In water surface the Hg content was 61 ng/g d.w. in the mouth of the Biobío River.

RESULTS AND DISCUSSION

Oceanographic and meteorological conditions allowed sampling at about 120 m deep during February, April and May (in 1992 and 1993). The water temperature was of 11°C at about 100 m deep with a increasing dissolved oxygen content from February to May, due to up-welling event of autumn. Total suspended matter (TSM) in waters above the bottom (5 m above the sediment) was obtained and its Hg content determined. The mercury content in different sampling station grouping by UPGMA (Wilkinson 1989) is showed in Figure 1, and the monthly mean in Table 2. Mean concentrations of Hg 0.4 ± 0.2 μg/g in sediments. Methylmercury has a mean concentration of 24 ng/g d.w.± 6. Mercury distribution on sediments sampling station grouping by UPGMA (Wilkinson 1989) is shown in Fig. 2.

Hg content in "squat lobster" and in different "black ling" organs is shown in Table 3. As shown in the table, the metal content in the Lebu "black ling" control specimens was higher than the one found in the Gulf of Arauco specimens.

Table 2. Monthly Hg average in total suspended matter (TSM).

Month	Hg content in TSM(μg/g)
February	0.01±0.01
April	0.02±0.01
May	0.05±0.02

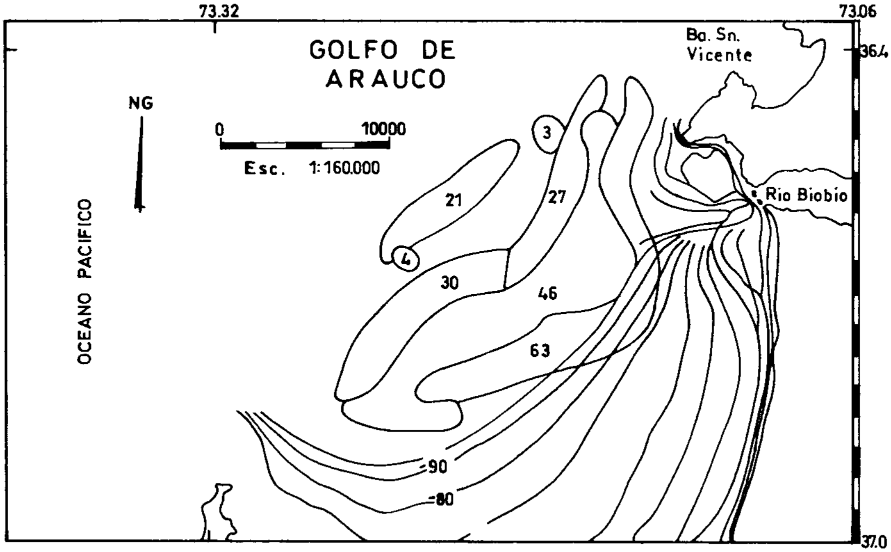

Figure 2. Distribution of mercury content in the sediment, grouping by UPGMA. Hg content is expressed as $\mu g/g \times 10^{-2}$ d.w.

The organic matter content in sediments is the main energy source for the benthodemersal fauna of the Gulf of Arauco and it is possibly the main source of heavy metal accumulation (Louma 1990). Higher mercury concentration in the sediments in the mouth of the river, and higher concentrations in the suspended sediment in the surface water at the same geographic point after a long time of heavy rain during the rainy season (May) would indicate that suspension sediments that flow out of the river from basin to the gulf are adsorbed by organic matter or phaeopigments (Table 4) as suggested by some authors (González *et al* 1991).

This fact, in addition to high mud in sediments, makes possible a transitional high content in Hg in some stations that decrease in May due to the fact that the Hg adsorbed is dissolved during aerobic degradation of organic matter. This would occur in May, because of changes from anoxic environmental conditions to less anoxic ones (from April to May: 0.65 to 3.6 mL O_2/L) (González 1994).

It could be possible that Hg has accumulated in the Biobio basin as a consequence of ore washing plant of Quilacoya, located in the middle of the basin during 16 century (Pacheco 1991), and recently by contributing from industrial effluents of cellulose plant (Cepal/Pnuma/CPPS, 1984) in the Gulf of Arauco. In the Gulf of Arauco as well as in Lebu, coal extraction processes could increase the Hg content. Some research in coal suggests of Hg content levels associated to inorganic fraction of coal from 15-1000 ppb (Grieve & Goddarzi 1993), associated with sulphide minerals. Higher levels (0.2 to 2.25 μg/g) were found by Sager (1993) in coal, slag and ash samples. Römer *et al.* (1992) showed that fly ash emission from a coal power plant increased the Hg content in soils next to the power plant.

Table 3. Average Hg content in biological matrixes studied (μg/g dry weight basis).

Matrix	Mercury Arauco μg/g	Mercury Lebu (L)or Cobquecura (C) μg/g
TSM	0.01	---
Sediment • Hg • MeHg	 0.4 0.02	 --- ---
Pleuroncodes monodon ("squat lobster") Total	0.3± 0.3	0.6± 0.4 (C)
Genypterus maculatus ("black ling") Total	0.3	-----
Genypterus maculatus Liver	0.2± 0.2	0.2± 0.1(L)
Genypterus maculatus Gill	0.4± 0.4	0.2± 0.1(L)
Genypterus maculatus Kidneys	0.5± 0.6	0.4± 0.4(L)
Genypterus maculatus Stomach Contents	0.4± 0.3	0.2± 0.4(L)
Genypterus maculatus Muscles	0.3± 0.2	0.3± 0.1 (L)

Like all crustaceans, *P. monodon*, feeds on detritus through the re-suspension of sediments followed by suction and filtration (Gallardo *et al.* 1993). Thus, "squat lobster" is the first link in the sediment based on trophic chain. The second concentration factor level estimated by the "black ling" metal content/ "squat lobster" metal content ratio was found to be 1 for Hg. The ratio of total metal in "black ling" vs. total metal in sediment was 12.5 for Hg in relation to methylmercury content in sediments. The same ratio is observed in Hg squat lobster/MeHg sediments.

The bio-available metal content of sediments, expressed as wet weight for mercury were the following: the total concentration of metal is 0.36 μg/g, and 6.7% of mercury as methylmercury content in sediments is bio-available. In "squat lobster" the average mercury concentration is 0.31 μg/g and in "black ling" 0.34 μg/g. No biomagnification was found, probably due to environmental availability of "squat lobster"; because *G. maculatus* is a carnivore that feeds on several benthic fish and crustaceans besides *P. monodon*. The Hg levels in *P. monodon* are in the range of those found for other Crustacea such as shrimps: *Pandalopsis dispar*, *Pandalus borealis*, and lobster *Scyllarus thirouxi* (Kureishy 1993) and above levels reported for prawns *Pandalus platyceros* (Harding & Goyette (1989), *Penaeus semisulcatus* (Kureishy 1993). Levels reported for some authors about fishes that feed on species associated on bottom-dweling species are in the same level of *Genypterus maculatus* (Harding & Goyette, 1989; Jorgensen & Pedersen 1994; Kureishy 1993; Pellegrini & Barghigiani 1989).

Table 4. Mud percentage, phaeophytin content, organic matter content and mercury content in each group of sediment stations in the Gulf of Arauco.

Mud in sediments (%)	Phaeophytins (µg/g)	Organic matter content (%)	Hg (µg/g) dw
77	10	25	0.03
20	39	25	0.04
50	38	43	0.27
50	64	57	0.21
95	37	75	0.63
93	87	75	0.46
93	63	144	0.30

Hg enrichment factors in the gulf sediments in relation to their concentration in the earth crust, were 1.5. This means that the Hg in the Gulf of Arauco sediments do not have a natural origin (Salamanca *et al.* 1988).

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