

HEAVY METAL SPECIATION IN COASTAL SEDIMENTS NEAR AN INDUSTRIAL AREA (SARDINIA, ITALY).

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The industrial area of Portovesme, in the south-western coast of Sardinia (Italy) has been mainly based on aluminium production, lead-zinc smelting and coal-fired power generation, since the early 1970's. The area is located in a mineralised region (mainly lead and zinc deposits) with past and present mining activity. Although a substantial direct atmospheric fallout of metals was identified as the main source of land pollution around the industrial area (CONTU *et al.*, 1986; D.P.R. 23/4/1993), there are several other possible mechanisms of contamination of the marine environment in the surrounding area:

- 1) the direct discharge of liquid effluents from a smelter and a coal-fired power plant into the harbour at Portovesme
- 2) continuous losses of coal, ores or concentrates during loading/unloading of ships and handling
- 3) the run-off from mining and smelting areas.

To investigate the heavy metal content of the sediments, cores up to about 40 cm were collected from 4 sampling stations in the harbour of Portovesme in January 1993. Samples were taken by scuba divers using Plexiglas liners with a diameter of 6 cm. Sediment cores were immediately frozen and cut into 2 cm layers in the laboratory. Radiochronological and chemical analyses were carried out. The depth distribution of the activity of Pb-210 and Cs-137 revealed different sediment accumulation rates in the sampling stations in the harbour and procured the pollution history of the area up to beginning of this century. Details of these procedure have been given elsewhere (DEGETTO *et al.*, 1993).

In an attempt to determine the distribution of Pb, Zn, Cd and Hg among the major sediment components and to assess a possible remobilisation of contaminants, metals were extracted from wet samples by a series of reagents of increasing reactivity:

- 1) CH₃COONH₄ 1 M (at a solid/solution ratio of 1/20) at pH 7.0 in centrifuge tubes for 2 h, at room temperature.
- 2) HCl 0.5 N (24 h at room temperature).
- 3) HNO₃-HClO₄ (4:1) acid mixture. Samples were digested for 4 h at 90°C in Sovirel bottles with screw caps.
- 4) an acid mixture of HF-HNO₃-HClO₄ (total attack) in Teflon lined acid bombs.

Lead, Zn, Cd, and Hg were measured by atomic absorption spectrometry with background correction using the standard addition method. Mercury was determined with the cold vapour method. Grain size distribution, Al, and organic substances were also determined.

Metal accumulation in the sediments proved to be strongly affected both by the grain-size and by the presence of extremely high concentrations of Al of anthropogenic origin in the upper layers of the cores. Very high total concentration of Cd, Hg, Pb and Zn were measured in the upper layers of all cores in the sediment accumulated after the industrial development of the area (1965). The highest metal concentration (Hg 109 mg/kg d.w.; Cd 118 mg/kg d.w.; Pb 2520 mg/kg; Zn 13400 mg/kg d.w.) as well as the highest fluxes of the metal (mg/m²/year) were found near the liquid effluent outlet of the plants, where a point source of contamination were detected. The level of all metals were increased substantially above background. Metal enrichment factors defined as the ratio between the average of the metal concentration in the layers deposited after 1965 and the lowest layer, ranged from 4 to 7 for Hg and from 4 to 6 for Cd. However background values are quite high, considering the geochemical characteristics of the area.

Percentages of Cd ranging from 51 to 89% of the total metal were extracted with HCl 0.5 N from the superficial layer (0-2 cm) of the cores, while in the lowest layers these percentages ranged from 14 to 26%. A similar pattern was found for Pb and Zn while lower percentages of the total were extracted. Mercury was recovered with both HCl 0.5 M and CH₃COONH₄ 1M only from the superficial layers of the cores, in percentages ranging from 2.5 to 11.5% of the total Hg for the dilute HCl attack, and from 1.5 to 5% with the CH₃COONH₄ 1M. In general the greatest differences between upper and lower section for the metal extraction with both CH₃COONH₄ 1M and dilute HCl were found in the area most exposed to the industrial waste effluent.

The results suggest that most of Cd, Hg, Pb, and Zn accumulated in the sediments after the settlement of the industries are of anthropogenic origin and in exchangeable or adsorbed forms. Several authors (LUOMA, 1983; BRYAN, 1984; CAMPBELL *et al.*, 1988; KERSTNER and FORSTNER, 1990) considered the metals extracted by HCl 0.5 M or CH₃COONH₄ as a measure of their bioavailability. These results point out the risk of remobilisation of high quantities of toxic metals from the sediments in the harbour.

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IODINE SPECIATION IN THE WATER COLUMN OF THE ROGOZNICA LAKE (EASTERN ADRIATIC COAST)

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Iodine occurs in sea water predominantly as iodate and iodide, although some quantities of organic iodine may also be present. Total iodine concentration in sea water is approximately 500 nM. The calculated concentration ratio of iodate to iodide under redox equilibrium conditions (pH = 8.1, pO₂ = 0.21) is 10^{13.5}, and it is assumed to be controlled by O₂/H₂O couple which strongly favours iodate. Measurable concentrations of iodide and nutrient-like behavior of iodine suggest that biological and photochemical processes may promote a reduced form of iodine (LUTHER and WU, 1992).

Due to redox sensitive and biophilic nature of iodine it is of special interest to study the distribution of iodide, iodate and organically bound iodine in the water column of a basin where both oxic and anoxic conditions occur (LUTHER and CAMPBELL, 1991; LUTHER *et al.*, 1991). Such conditions have been found in the Rogoznica lake (Dragon's eye). It is a small, salt lake, surrounded with vertical carbonate rocks. The existence of mediolittoral zone suggest the connection between the lake and nearby sea. Due to oxygen content the water column of the lake can be divided into the upper oxic and the lower anoxic zone, during the stratification period (April-October).

To ascertain the depth and seasonal variations in speciation of iodine, samples were collected in September and November 1993, and April 1994. Temperature, salinity and oxygen content were determined immediately after collection. Iodide has been determined directly in water samples by cathodic stripping square wave voltammetry. Differential pulse voltammetry has been used to determine iodate, total iodine (by hypochlorite oxidation of the lake water sample to iodate) and indirectly organo-iodine (by UV irradiation followed by hypochlorite treatment).

Depth	September, 1993			November, 1993			April, 1994		
	O ₂ /mg l ⁻¹	S/‰	t/°C	O ₂ /mg l ⁻¹	S/‰	t/°C	O ₂ /mg l ⁻¹	S/‰	t/°C
0.5	6.62	33	23.9	7.97	37	17.8	8.95	27	15
2.0	6.63	36	23.1	8.46	37	17.6	8.48	27	15
5.0	5.36	36.5	22.9	4.89	39	19.2	7.69	35.5	17
7.0	4.46	37	22.9	4.62	40	19.5	4.12	38	19
8.0	4.38	38	22.9	4.46	39	19.5	2.96	38	19
8.5	4.32	38	22.9	4.09	40	19.5	3.93	39	19
9.	4.22	38	22.7	4.19	40	19.5	1.09	39	19
9.5	3.77	38	22.7	3.99	40	19.5	0.07	39	19
10.0	2.71	38	22.6	3.62	40	19.5	0.09	39	19
10.5	3.74	38	22.6	3.73	39.5	19.5	ND	39	19
11.0	2.52	38	22.5	3.02	38	19.5	ND	39.5	18
12.0	ND	38	22.5	1.45	40	19.5	ND	39.5	18

Table 1. Salinity, temperature and oxygen content from the Rogoznica Lake, September and November 1993, and April 1994.

The depth of the oxic-anoxic interface varies upon the season and strongly affects the vertical distribution of iodine species.

Iodate concentrations in the upper layers are similar to those observed in sea water. Only reduced forms of iodine are found to be present in the bottom layers. The difference between the total iodine and the sum of iodide and iodate was significant in April and can be attributed to organic compounds which can react with hypochlorite. No difference was found in November. The contribution of other organo-iodine species (determined as species decomposed by UV-irradiation) was also the lowest in November, and can be connected with negligible biological activity during this period of year.

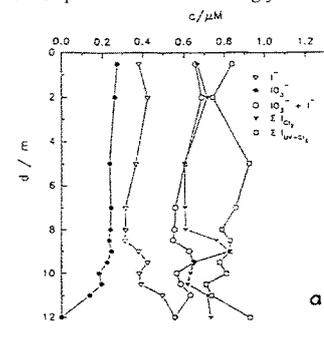
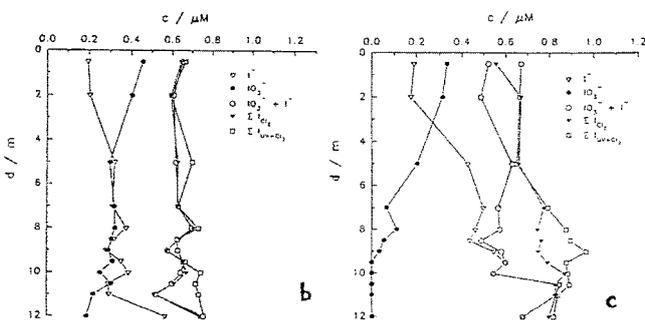


Figure 1. Vertical distribution of iodine species in the Rogoznica Lake a) September 1993. b) November 1993. c) April 1994.



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