

# 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)  $\text{CH}_3\text{COONH}_4$  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)  $\text{HNO}_3$ - $\text{HClO}_4$  (4:1) acid mixture. Samples were digested for 4 h at 90°C in Sovirel bottles with screw caps.
- 4) an acid mixture of  $\text{HF}$ - $\text{HNO}_3$ - $\text{HClO}_4$  (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 ( $\text{mg}/\text{m}^2/\text{year}$ ) 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  $\text{CH}_3\text{COONH}_4$  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  $\text{CH}_3\text{COONH}_4$  1M. In general the greatest differences between upper and lower section for the metal extraction with both  $\text{CH}_3\text{COONH}_4$  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  $\text{CH}_3\text{COONH}_4$  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.

## REFERENCES

- BRYAN, W., 1984. "Pollution due to heavy metals and their compounds". In: *Marine Ecology*, John Wiley & Sons, 1289-1431.
- CAMPBELL, P.G.C. and TESSIER, A., 1989. 'Biological availability of metals in sediments: analytical approaches', *Heavy Metals in the Environment*, 7th International Conference, Vol. 5, pp. 516-525.
- CONTU A., FLORE C., SCHINTU M., SPIGA G., 1986. Piombo e cadmio nel suolo e nei vegetali di un'area industrializzata della Sardegna. *Inquinamento*, XXVIII, 3, 2-6.
- DEGETTO S., SBRIGNADELLO G., SCHINTU M., 1993. Stratigraphic radiochemical analysis of short-core sediments from Portovesme (Sardinia) as a record of environmental pollution. *Atti XXII Congresso Nazionale di Chimica Inorganica*, Villasimius (Cagliari), Settembre 1993, p. 85. D.P.R. 23/4/93. Piano di disinquinamento per il risanamento del territorio del Sulcis-Iglesiente. *Gazzetta Ufficiale della Repubblica Italiana*, 14/8/93.
- KERSTNER M. and FORSTNER U., 1990. Speciation of trace metals in sediments. In "Trace metal speciation: analytical methods and problems", G. E. Batley Ed., CRC Press.
- LUOMA S. N., 1983. Bioavailability of trace metals to aquatic organisms- A review, *The Science of Total Environment*, 28, 1-22.