Heavy metals content in sediments of the continental shelf of Cadiz (SW of Spain)

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The greater part of trace elements found in marine waters are in low or very low concentrations. In many cases their levels are governed by the type of sediments and the direct or indirect action of organisms, while in others they come from the industrial activity, constituting in this last case a clear indication of pollution. In this work we analyze the heavy metals content of the superficial sediments of the northern continental shelf of the Gulf of Cadiz, among Chipiona (near the estuary of the Guadalquivir river) and the Cape of Trafalgar, in the proximities of the Straits of Gibraltar. The study area is extended to the limit of the continental shelf and beginning of the slope, some 50 Km from the coast.

The superficial sediments in this area are characterized by the siliceous nature of their components. Quartz is the most abundant mineral in sandy sediments and illite prevails in the argillaceous formations. However, the carbonates, mainly of bioclastic origin, reach proportions higher than 20%. These materials are also very poor in non-bioclastic organic elements, such as organic matter, nitrogen, phosphorus, etc. (Gutiérrez Mas, 1992).

Methodology

The sample extraction was accomplished with a piston corer. The mineralogical analysis were carried out by means of X-ray diffraction (powder method for bulk and heavy fractions and orientated aggregates treated with ethylene glycol, dimethyl-sulphoxide and heating to 550°C for the clay fraction). The determination of carbonates has been accomplished by volumetric valuation and organic matter (OM) by the 'method of the organic carbon' (Gaudette et al., 1974). The Cu, Cd, Zn, Ni, Co, Fe, Mn and Pb contents were determined by Atomic Absorption Spectroscopy (AAS), using a Philips PU 9200 X equipment and by Inductively Coupled Plasma (ICP Leemans PS1000).

Geochemical data and statistic results

The distribution of heavy metals in the continental shelf shows the general tendency of these elements to be concentrated in muddy facies (silt and clay), with some focus of high values. The greater concentrations are reached in a sector located in front of the Bay of Cadiz, at 40 and 100 m depth. Pb, Zn and Cu present their maximum contents in adjacent areas. The majority of the studied heavy elements show a discrete negative correlation with depth, sand and gravel, and positive correlation with small sizes, especially with silt.

Copper. It present a average of 18 ppm, with high concentrations (43–46 ppm) to the W and SW of the Bay of Cadiz. Smaller contents appear in distal areas of the continental shelf and beginning of the slope (< 10 ppm).

Cadmium. The average is less than 1 ppm. To the southern of Cadiz the concentrations are low and it does not appear near Conil, while the highest value (2.8 ppm) are found in front of the Bay of Cadiz and isolated points of the continental shelf.

Zinc. It has a average concentration of 67 ppm. The maximum (150 ppm) is found in the internal continental shelf, to the NW of the Bay of Cadiz, associated with muddy facies. The concentrations decrease toward the S and sea inside, reaching the minimum (30 ppm) in distal areas of the external continental shelf.

Nickel. It shows concentrations around 26 ppm and maximum of 84 ppm in front of the Bay of Cadiz, decreasing toward the S.

Cobalt. The mean is 17 ppm, while the topmost is found in front of the Bay of Cadiz. The lowest concentrations are reached to the southern of the study area, in internal continental shelf or infralitoral areas.

Iron. The maximum concentrations are found in middle and inner continental shelf areas, with values of 65000 ppm. The decrease of its concentration takes place far away from the
coast and toward the S of the study area, being more stressed in this last direction, reaching the lowest concentrations near Cape Roche (11000 ppm), while in the external continental shelf the data oscillate around 30000 ppm.

Manganese. It exhibits a mean of 276 ppm, with maximum around 500 ppm to the NW of the Bay of Cadiz and minimal (225 ppm) in the external continental shelf.

Lead. It shows an average of 30 ppm and a homogeneous distribution. The highest contents are found in the NW of the Bay of Cadiz (89 ppm), and the minimum in the external continental shelf (< 30 ppm).

**Factorial analysis**

Two factors explain the 83% of the variance of the whole. Factor 1 associates Co, Cd, Ni and Fe. It is focused in two sectors of the continental shelf, one in front the Bay of Cadiz with high values and other to the NW, near a submarine canyon aligned with the estuary of the Guadalquivir river, with lower values but meaningful. Factor 2 associates Zn, Cu, Pb and Mn and it is distributed widely by nearly all the continental shelf, mainly to the southern of the parallel of Cadiz and it seems to be more influenced for the inputs of the Guadalete river, showing a certain flow or dispersion from the Bay of Cadiz.

**Discussion and conclusions**

The mineralogical composition of the studied sediments reveals the inherited character of the greater part of their components, except for carbonates. The inputs come from several source areas drained by the Guadalquivir and other fluvial courses. At the same time, sediments show a great scarcity in organic components, which are found associated with small sizes (cf. Gutiérrez Mas, 1992). The distribution of the heavy metals in the continental shelf shows some focus with very high concentrations, mainly in front of the Bay of Cadiz and the estuary of the Guadalquivir river, coinciding with the presence of submarine canyons. On the other hand the correlation of many of the heavy metals with the mineralogy of the heavy fraction leads us to think that a part of these metals may come from andalucite, chloritoid, sillimanite, turmaline, etc. and, also, the possibility of a certain alteration of the measures of the heavy metals contents by breaking of the crystal lattices of these heavy minerals during the chemical attack in the laboratory. Nevertheless the lack of a direct correlation with the majority of terrigenous components seems to indicate that accumulation processes and/or fixing of heavy metals in these sediments should be fundamentally of marine origin, except for areas where spillage points have been detected.

Results of the factorial analysis reveal three heavy metal associations: 1) Ni, Co, Fe, Cd and Pb, well correlated with silt; 2) Mn and Zn, with clay; and 3) Pb, Cu and Zn, with the organic matter. The lack of correlation among Cd and Zn and its inclusion in different factors evidence the presence of spillage points due to the industrial activity in neighbouring continental areas. The distance of these points to the coast evidences that waste disposal are made from ships and not directly from the continent.

**References**


This investigation was partially supported by Group 4065 of the Junta de Andalucía and project AMB93-0794 (CICYT).