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HEAVY METALS DISTRIBUTION IN THE SEDIMENTS OF THE GULF OF CADIZ, SPAIN

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by

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ABSTRACT

A four year study has been conducted on the Cadiz Gulf. The primary objetives of this investigation were: (1) to provide a baseline information on the concentration and distribution of heavy metals in the bottom sediments of the Gulf and (2) to determine the effect of the wastes discharged in the study area. For these purposes, the following determinations were carried out: granulometric composition, organic matter, calcium carbonate, iron, manganese, zinc, copper, lead, chromium and nickel. The data indicate that the concentration of the most of the metals considered show marcked differences in the sediments of coastal and offshore stations, with the values increasing toward the coast. Sediments of the northern position of the area generally contain high concentrations originating from metal pollutants discharged into the water from permanent antropogenic sources of pollution.

INTRODUCTION

The sediments constitute a receptacle for trace metals in the sea. In many regions, specially in those adjacent to large industrial and urban areas, these are the largest deposits and the greatest potential source of metalic pollutants in the aquatic environment. The presence of concentrations of heavy metals in the sediments, in quantities wich are several times higher than natural levels, has been a source of great concern in the past several decades and the analysis of sediments has been the most common method of studying marine pollution and its control.

In 1986, a systematic study was begun on the pollution in the Spanish South-Atlantic region where due to a series of anthropogenic sources, specially from industry and mining, a high concentration of metals could accumulate in the marine environment and particularly in the sediments. The purpose of the study was to provide basic information on the concentration and distribution of heavy metals in the area, detect any increase in pollution levels due to these elements and determine the effects that the waste materials has on the Gulf of Cadiz, an important fishing ground.

The elements that have been studied are iron, manganese, zinc, lead, copper, nickel and chromium. The granulometry of the sediments, their content of organic material and calcium carbonate were also determined, for the purpose of complementary information.

MATERIALS AND METHODS

A total of 60 sampling stations were selected for the study as shown in figure 1. The sediment samples were collected during 4 cruises made in july, 1986; july, 1987; november, 1988 and november 1989 on board R.V. "Cornide de Saavedra" and R.V. "F.P. Navarro".

The sediments of the first cruise were obtained using a modified box corer (Papucci et al., 1985), and after the collection, the sediment cores were cut on board in 1 cm sections. In successive cruises the sampling was carried out by means of a

200 kg stainless steel box corer, taking only the surface layer of the sediment (1-3 cm), avoiding the part that was in contact with the metal box. The samples were frozen and transported to the laboratory in plastic containers.

Once in the laboratory, the sediment was sieved with a 63 um nylon mesh. After the sieving, the collected fine fraction was freeze-dried and finely ground. The trace metals concentrations were determined from the dried sample following the procedures given by Loring and Rantala (1977), using a Perkin-Elmer 2380 Atomic Absorption Spectrophotometer equipped with a Graphite Furnace HGA 400. To ensure the accuracy and precision of the methodology, replicate blanks and samples were routinely analyzed, and in no case were variation coeficients of more than 8% found in the metals analized. The quality of the data was contrasted by the participation in the intercalibration exercises organized by the I.C.E.S. (1/TM/MS), (Loring, 1987) and the I.A.E.A. (Fukai, 1986) and with the analysis of N.I.E.S. Certified Reference Material No. 2 "Pond Sediment" with each batch of sediments to assess daily performance.

The granulometric description of the sediments of the area was made following the methodology proposed by Buchanan (1971), and the content of organic matter and carbonates was determined according to weight loss by calcination over 24 hour period at 450 C and 1050 C respectively.

RESULTS AND DISCUSSION

In the area of the Gulf of Cadiz in wich samples were taken, the grain size of the sediments varied according to the location of the stations, generally decreasing as the depth increased. The finer grained sediments, referred to as mud (containing >70-95% of material <63 um), along with those that contain >50-70% of material <63 um (sandy mud) comprise most of the data collected in the central and southern area. The coarse sediments with a lower material content <63 um (sand and muddy sand) were foun in the coastal area and in the southeastern part of the sampling area. Figure 2 shows the nature of the seabeds of the area according to this classification.

The organic content ranged between 0.12% and 3.38%. The maximum values corresponding to the coastal stations. The sandy sediments contain more organic matter than the finer fraction, this could be attribute to remains of organism originally living in the sediments.

Figures 3-9 show the results an a dry weight basis of the metals content found in the fraction <63 um of the surface sediment of the area. Each value represents the mean of the replicate analysis.

The concentration of iron varied between 22 mg/g and 65 mg/g, with the higher value being found in the station A located at the mouth of the Ria of Huelva. In general the highest values are found in the coastal area and in the rest of the areas the values vary between 22.0 and 40.0 mg/g.

Lead ranged between 20 ug/g and 1013 ug/g. The maximum value corresponds to the sediments taken at station A. In figure 4 it can be observed that the highest values are found around the coastal areas, from 100 to 240 ug/g. In the rest of the area the concentrations vary between 20 and 70 ug/g, increasing the nearer we are to the coast.

The copper content of the sediments in the area ranged from 23-30 ug/g in the southwestern part of the sampling area up to values of between 500 and 1300 ug/g in the area nearest the mouth of the Ria of Huelva (the latter corresponding to the station A). A negative gradient can be observed in the copper concentrations as we get further away from the coast.

Chromium varied from 26 ug/g in the east-central part up to 63 ug/g in the north and south. It can be observed that the maximum levels of this metal are found near the coast, decreasing as we get further away from the shoreline and increasing again in the southern part, until they reach concentrations similar to those of the coastal area.

In the case of nickel, the maximum values, around 100 ug/g were found in the southern part of the sampling area. Generally, the values vary between 30 and 40 ug/g with an increase in the coastal area of up to concentrations of 60 ug/g.

Manganese concentrations ranged between 250 and 770 ug/g. The samples that showed the highest values, over 500 ug/g, were found around the deepest areas in wich fine grain sediments predominate. In the rest of the area similar values were found, most of them between 250-350 ug/g.

As for zinc, again a clearly negative gradient can be observed from around the mouth of the Ria of Huelva (1647 ug/g) to the deepest and furthest area from the coast (68 ug/g). On rest of the continental shelf the values are greater than 150 ug/g. At greater depths they are <100 ug/g.

The abundance and distribution of trace metals in the sediments is usually controlled by the textural characteristics of the sediments, the composition of the materials supplied in the medium and the physical-chemical modifications of the material during and afterwards deposition.

As shown in the figures, the averages values of Fe, Pb, Cu, and Zn, obtained along the coast area were markedly higher than the averages corresponding to the open sea area. In general, it can be observed that the concentrations of these metals decrease as distance from the coast is increased, with the highest levels being found in the surface sediments of the station located at the mouth of the Ria of Huelva where values are found to be several times higher than in the other areas of the coastal shelf.

This illustrates that this area is exposed to more pollution than the rest of the area. The sharp increase in the concentration of metals in the coastal sediments, and specially in those corresponding to the area near of the Ria of Huelva, reflect the marked anthropogenic influence on the area, originating mainly from the dumping of industrial wastes and/or from mining, not to mention the discharge from dredging materials coming from the port of Huelva and other inputs from the rivers draining into the area, although for most coastal areas natural trace metals concentrations can range over 2 orders magnitude causing confusion in data interpretation regarding anthropogenic loading. (Windom et al., 1989).

The distribution for the rest of the metals studied follows a different pattern, since for Cr two maximum levels can be observed, one in the area near of the Ria of Huelva and the other in the deepest part of tha area, with the other values being similar. The distribution of Ni and Mn also show maximum values in the southern part of the area studied where the authorized discharges of acid wastes from the production of TiO_2 are produced.

On the other hand, if we eliminate the values corresponding to the coastal most area, near of the Ria of Huelva, it can be observed that the high concentrations of Mn (>400 ug/g), Cr (>30 ug/g), Ni (>30 ug/g), Pb (>25 ug/g), Cu (>30 ug/g) and Zn (>100 ug/g), occur in fine grained sediments, in the central part of the area studied. In this area, it is obvious that the metal concentrations vary directly according to grain size and therefore a valid comparison can only be made between sediments that have similar textures. This is due generally to the increase in specific surface area and to the surface properties of clay minerals (Förstner et al., 1982).

Figure 10 gives a profile of the vertical distribution of Mn in the sediments taken from two stations located at 36 30′ N, 7 02′ W and 36 32′ N, 7 15′ W, respectively, where maximum concentrations have been detected. Likewise an enrichment in the upper layers of the core can be observed which might be due to the fact that the Mn concentration in the sediments is conditioned (1) by the redox potential of the sedimentary column that could produce a fixing of the element and therefore the Mn tends to be transformed into a dissolved species in deepest layers and migrates onto the surface layers, where it remains trapped, and (2) by the influence of the sedimentation rate. Aloisi (1986), in three cores taken off the mouth of the River Rhône, at 9, 18, and 32 Km, could observe that the differences in the thickness of the contaminated layer fit closely to the sedimentation rates measured in that area. Similar vertical distribution has been found by Fernandez (1984) at the Alboran Sea and Fernex et al. (1989) in the Sardignia Basin. The profiles of Cu, Pb and Zn differ from the profiles of Mn in that no large decreases in concentration can be observed in deeper parts of the sediments.

Comparing the data collected over these four years no particular tendency has been observed that would indicate an increase or decrease in the levels of these metals in the sediments studied.

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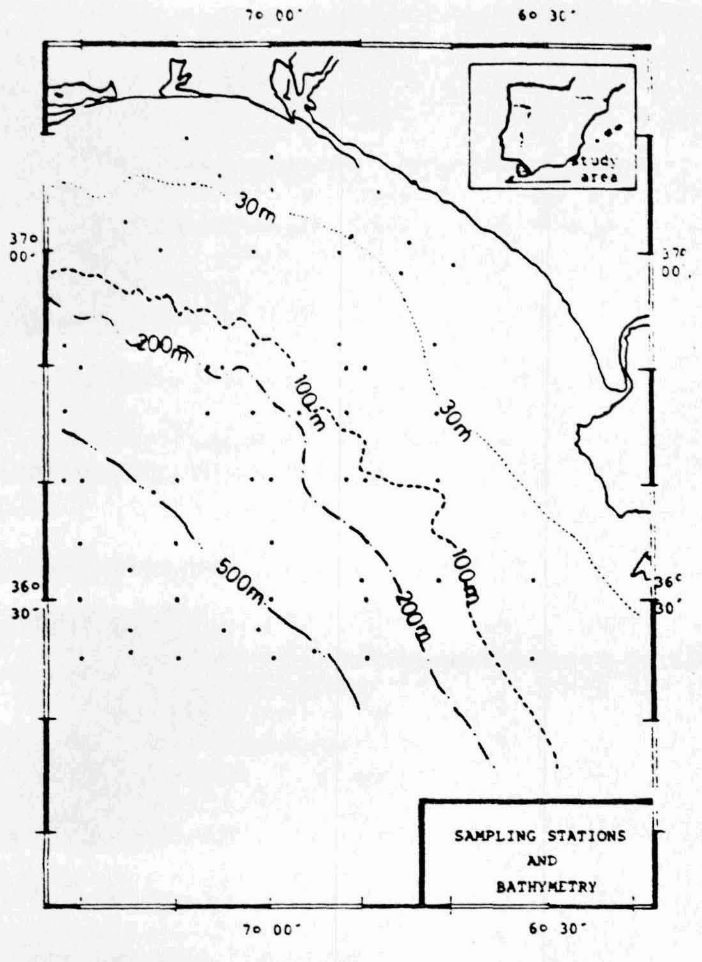
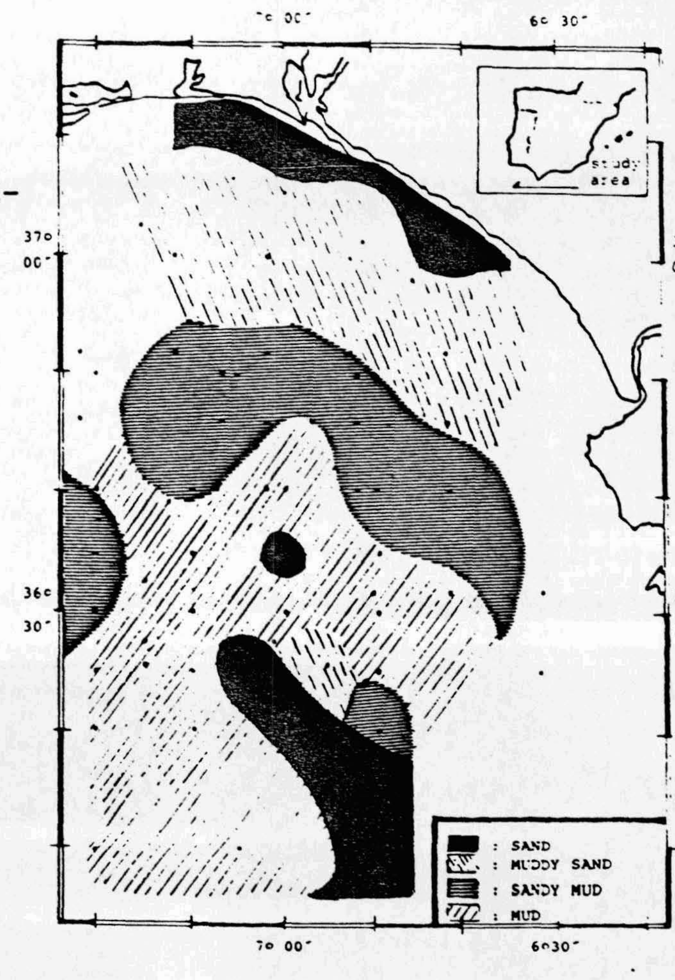


Fig. 1.- Sampling stations and bathymetry of the area.

Fig. 2.- Grain size distribution of sediments.



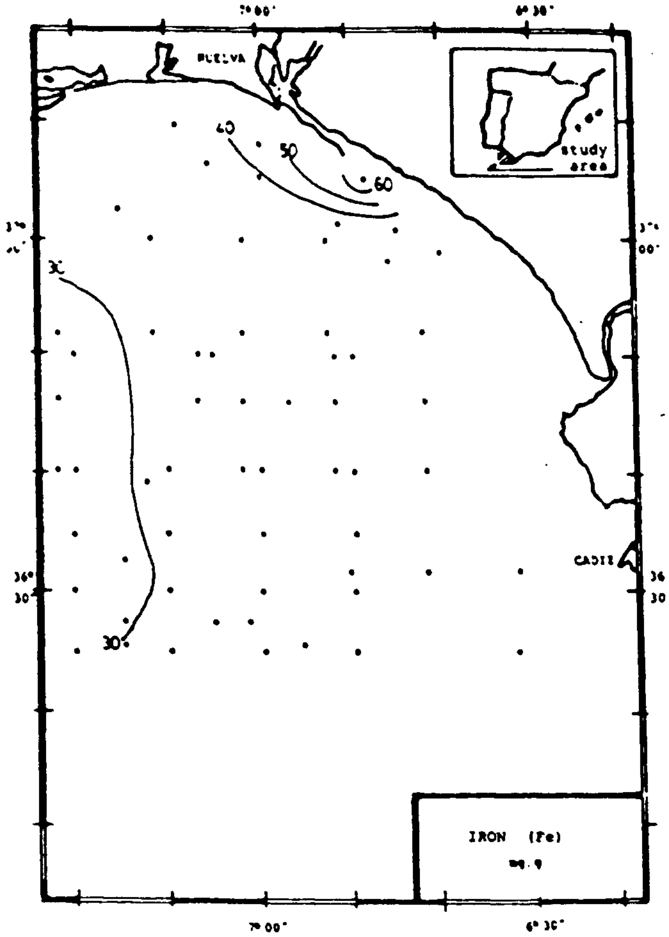
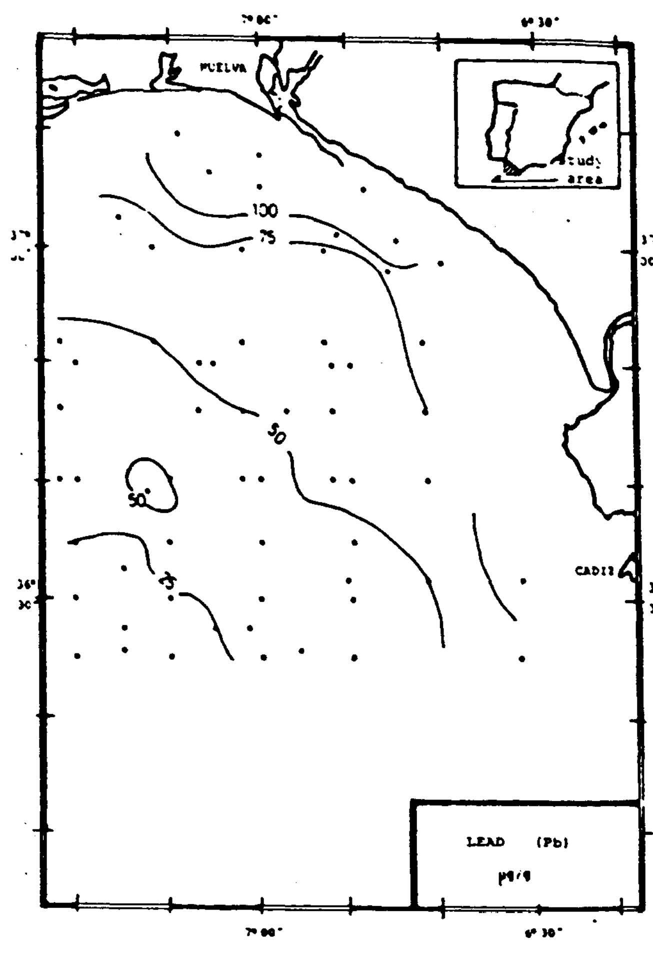


Fig. 3.- Distribution of Iron in surface sediments.

Fig. 4.- Distribution of Lead in surface sediments.



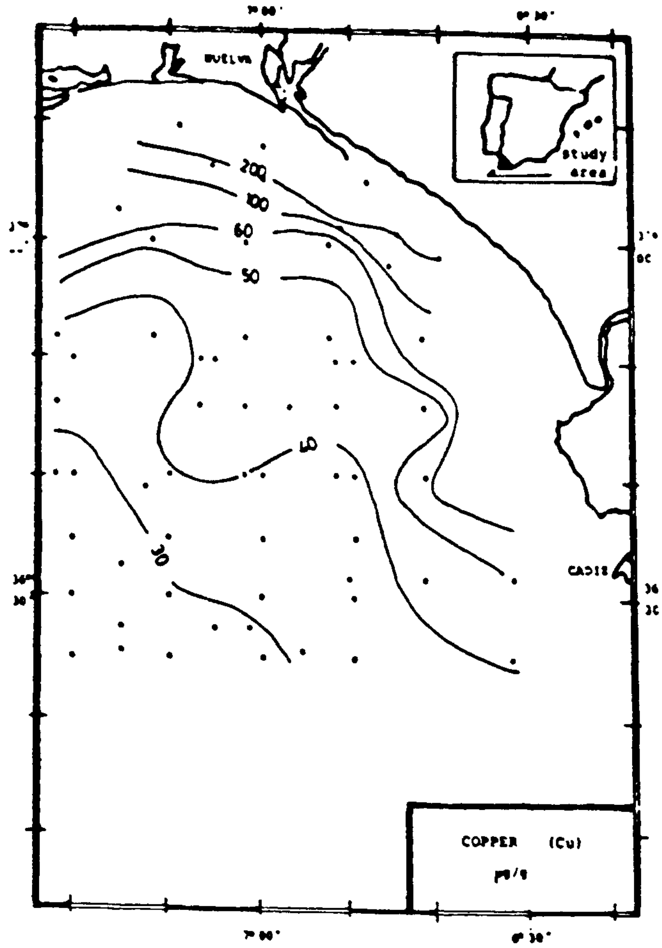


Fig. 5.- Distribution of Copper in surface sediments.

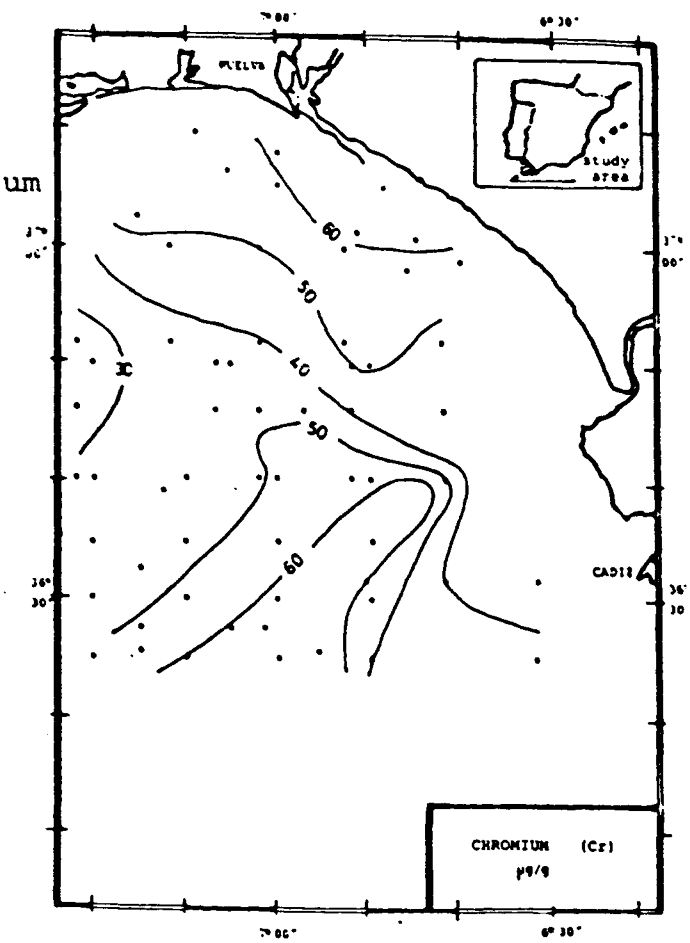


Fig. 6.- Distribution of Chromium in surface sediments.

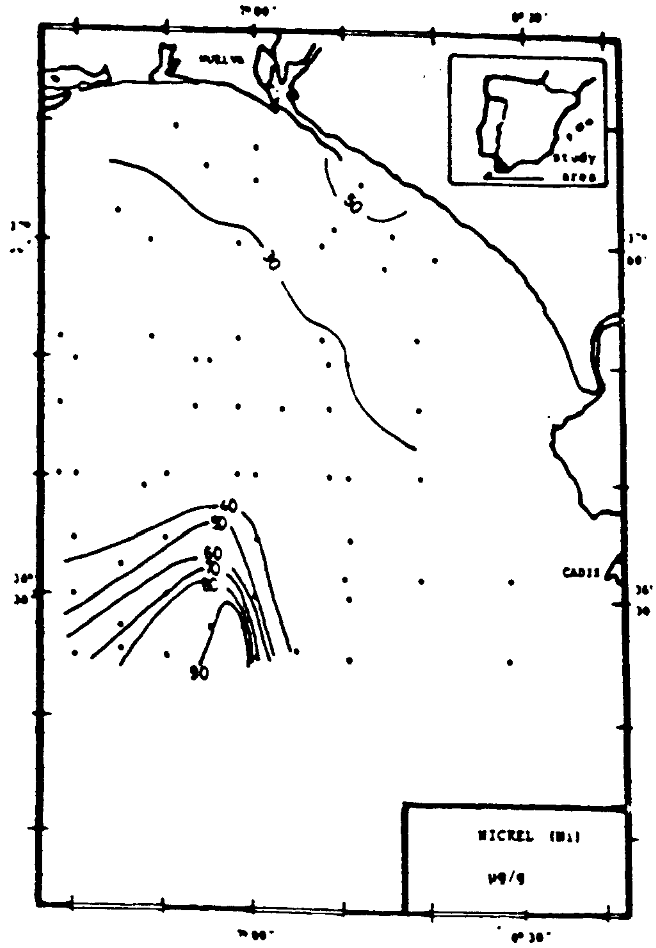
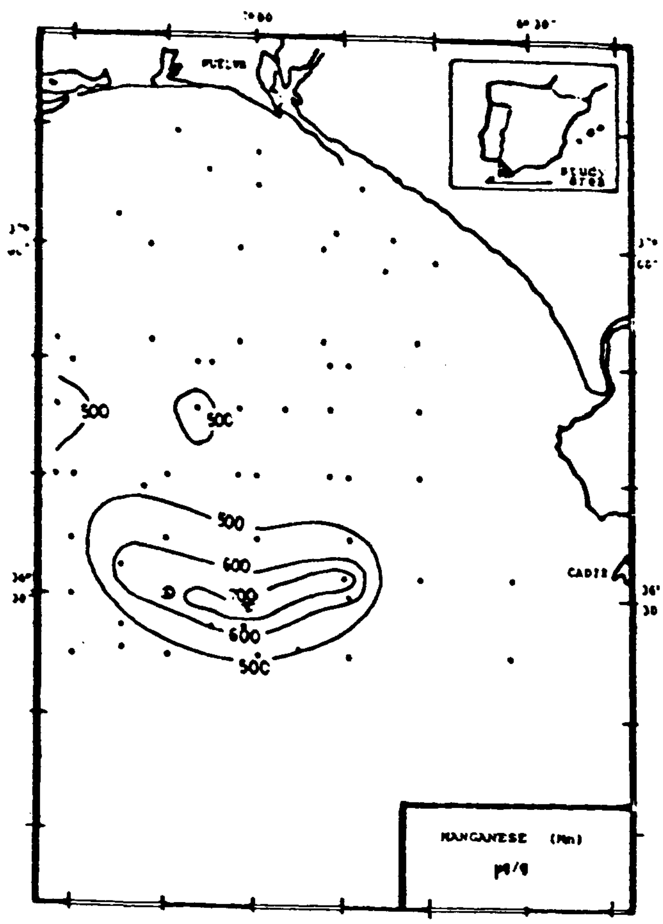


Fig. 7.- Distribution of Nickel in surface sediments.

Fig. 8.-Distribution of Manganese in surface sediments.



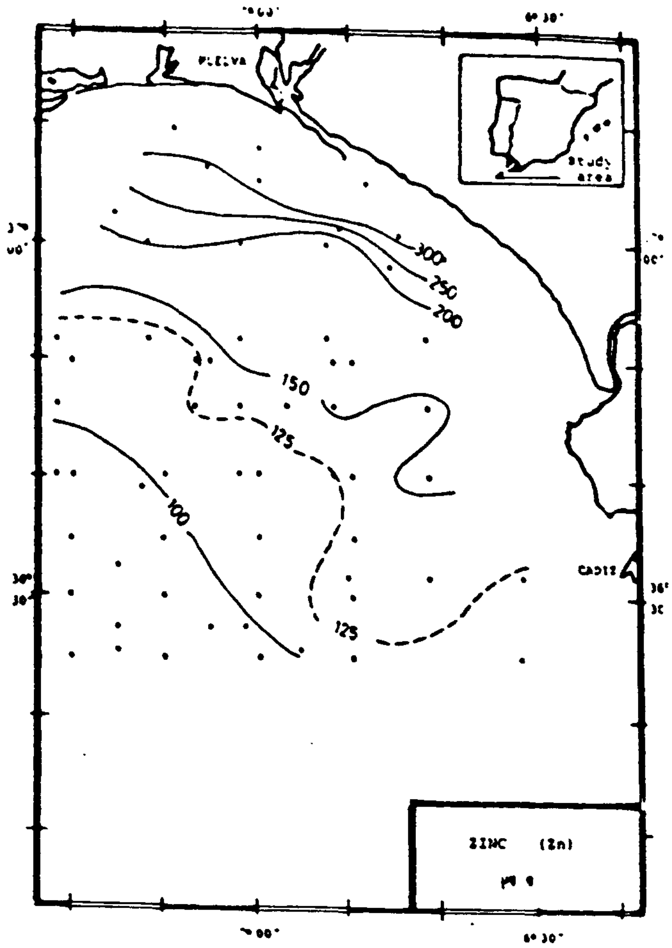


Fig. 9.

Distribution of Zinc in surface sediments.

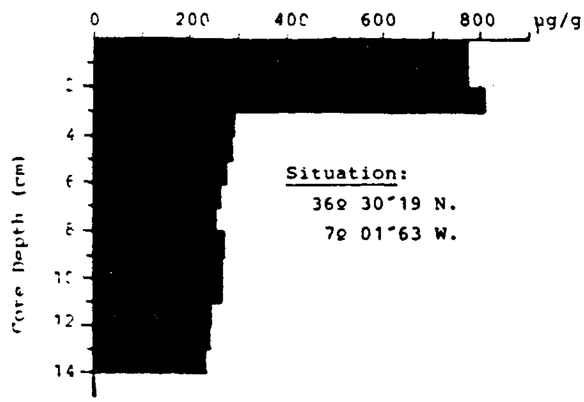


Fig. 10.

MANGANESE VERTICAL DISTRIBUTION IN TWO STATIONS OF THE AREA