Bull. Environ. Contam. Toxicol. (1985) 35:348–353


Bulletin of Environmental Contamination and Toxicology

# Superficial Accumulation of Heavy Metals in Near Shore Marine Sediments: an Objective Index of Environmental Pollution

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Accumulation of heavy metals in marine sediments provide an excellent indicator of pollution, particularly in densely populated coastal zones or close to the outlets of heavily industrialized rivers. In order to assess the degree of heavy metal pollution in the sediments of a shoreline zone, the analysis of a large number of samples is required. In those cases in which the establishment of a relationship between heavy metal contents in sediments and their origins (natural or anthropogenic) is desired, different layers of each core of sediment should be chronologically labelled. In general, these dating-techniques become highly laborious.

In this study the effect of civilization has been evaluated in the Bay of Cádiz (SW Spain). This area represents a densely populated and relatively enclosed coastal zone having a special interest due to the use of its salt-ponds as fish-farms. The vertical evolution of six heavy metals and other complementary parameters have been studied in a few sampling-stations, chosen as representative sedimentary environments of this zone. By means of the concentrations of metals found at different depths, according to Rapin (1981) a Superficial Enrichment Factor was established. This methodology is based on a careful selection of the sampling-stations, which requires a previous knowledge of sedimentary development of the studied area. So that, metal concentrations in the more superficial layers can be compared to those found in deeper ones, deposited in times when urban and industrial wastes were negligible.

## MATERIALS AND METHODS

Figure 1 shows the sampling sites. Sites 1 to 5 were chosen as representative of the different sedimentary environments found in the Bay of Cádiz. They were selected taking into account both granulometry of the sediment and the different degree of influence of the urban and industrial wastes. Sites 6 to 9 were selected in the salt-ponds dedicated to the extensive culture of marine fish.

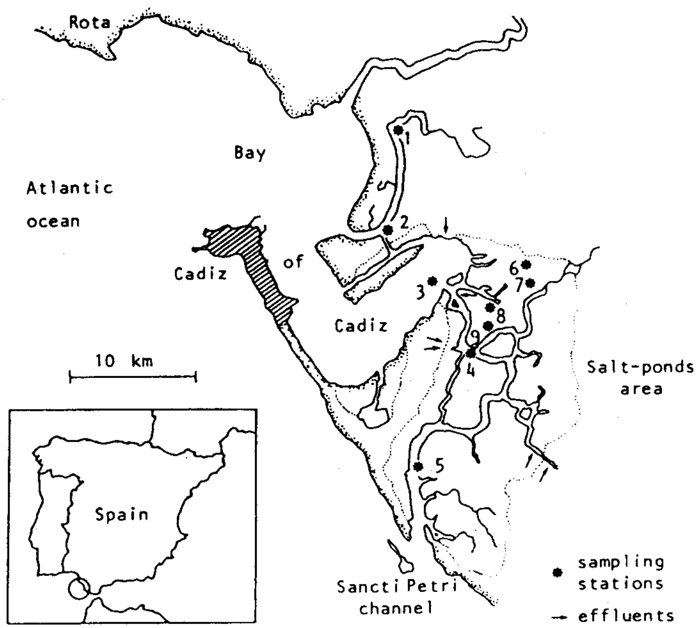


Figure 1. Map of the zone studied showing the locations of the different samplig-stations established.

Samples were collected with a PVC cylinder 40 mm in diameter, cut lengthwise. The two halves were joined firmly together with adhesive tape prior to use. Given the shallowness of the sampling-stations, the PVC cylinder was manipulated from a small boat with a PVC rod about 3.5 m long. The cores were frozen to -20°C in less than 3 hours and cut into pieces of 0-3, 5-10, 10-15, 15-20, 20-25 and 50-55 cm. Sediments were dried to constant weight at 110°C and after separating off mollusc shells and foreign solids, were ground to a size of less than 200 μ. These ground samples were kept in PVC containers until analyzed.

Each fraction was analyzed for the solid content (S.C., loss of weight at 110°C of the original wet samples), organic carbon (O.C.) according to Gaudette et al. (1974), and the concentration of six heavy metals (Fe, Mn, Zn, Cu, Pb and Cd). The metals were determined by atomic absorption spectrometry in the filtrate resulting from acid digestion of the samples. Three consecutive leachings (Gómez-Parra 1983) of each 3 g sample with a mixture of $HCl/HNO_3$ 10:1 V/V (Katz et al. 1977) were carried out.

## RESULTS AND DISCUSSION

Table 1 shows the results obtained from the different sedimentary layers. Large differences in the mean values of the analyzed elements were observed between one site and another. In general, the content of organic carbon and heavy metals in the sediments of this zone appeared to be determined by the granulometry of the

Table 1. Solids, organic carbon and heavy metals content in the different sedimentary layers considered in 9 sampling-stations in the Bay of Cadiz and in its salt-ponds.

| Sampling station | Depth cm | S.C. % | C.O. % | Fe % | Mn ppm | Zn ppm | Cu ppm | Pb ppm | Cd ppm |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 0-3 | 52.87 | 1.29 | 3.02 | 376 | 201 | 32 | 51 | 1.48 |
| | 5-10 | 53.81 | 1.06 | 2.90 | 377 | 210 | 28 | 55 | 1.65 |
| | 10-15 | 54.23 | 1.12 | 3.41 | 418 | 227 | 33 | 54 | 1.72 |
| | 15-20 | 61.36 | 0.97 | 2.64 | 396 | 276 | 26 | 48 | 1.95 |
| | 20-25 | 60.64 | 1.02 | 2.97 | 437 | 274 | 28 | 48 | 1.70 |
| | 50-55 | 64.51 | 1.03 | 2.70 | 302 | 171 | 27 | 42 | 0.60 |
| 2 | 0-3 | 58.94 | 0.92 | 1.70 | 413 | 133 | 15 | 42 | 1.86 |
| | 5-10 | 64.38 | 1.23 | 1.87 | 415 | 137 | 17 | 37 | 1.66 |
| | 10-15 | 60.84 | 1.50 | 2.54 | 452 | 201 | 22 | 44 | 1.91 |
| | 15-20 | 60.29 | 1.23 | 2.47 | 419 | 325 | 21 | 41 | 1.78 |
| | 20-25 | n.d. | 1.58 | 2.57 | 418 | 132 | 26 | 43 | 0.92 |
| | 50-55 | 58.32 | 1.16 | 2.50 | 386 | 204 | 18 | 38 | 0.58 |
| 3 | 0-3 | 45.07 | 2.06 | 2.73 | 356 | 250 | 41 | 74 | 1.98 |
| | 5-10 | 50.97 | 2.04 | 3.12 | 551 | 342 | 26 | 81 | 2.15 |
| | 10-15 | 47.86 | 2.68 | 3.84 | 392 | 316 | 29 | 83 | 2.13 |
| | 15-20 | 48.67 | 2.14 | 2.92 | 403 | 361 | 36 | 64 | 1.62 |
| | 20-25 | 49.37 | 2.15 | 3.02 | 387 | 358 | 32 | 58 | 1.92 |
| | 40-45* | n.d. | 1.14 | 2.56 | 315 | 196 | 23 | 20 | 0.64 |
| 4 | 0-3 | 53.93 | 1.88 | 3.70 | 291 | 294 | 49 | 86 | 2.29 |
| | 5-10 | 50.52 | 2.35 | 3.07 | 316 | 315 | 51 | 115 | 2.64 |
| | 10-15 | 48.18 | 2.29 | 3.62 | 360 | 362 | 58 | 92 | 2.52 |
| | 15-20 | 48.71 | 2.14 | 3.10 | 284 | 384 | 47 | 80 | 1.86 |
| | 20-25 | 49.91 | 1.95 | 2.86 | 293 | 326 | 46 | 54 | 1.92 |
| | 50-55 | 56.14 | 1.64 | 3.78 | 290 | 236 | 22 | 21 | 0.82 |
| 5 | 0-3 | 51.38 | 1.38 | 2.86 | 260 | 341 | 25 | 39 | 1.25 |
| | 5-10 | 51.78 | 1.32 | 3.12 | 413 | 361 | 27 | 57 | 1.42 |
| | 10-15 | 52.01 | 1.20 | 3.16 | 281 | 350 | 31 | 51 | 1.31 |
| | 15-20 | 52.69 | 1.46 | 2.60 | 315 | 215 | 24 | 32 | 1.12 |
| | 20-25 | 54.61 | 1.54 | 2.50 | 306 | 282 | 32 | 46 | 1.28 |
| | 50-55 | 61.88 | 0.92 | 2.10 | 242 | 148 | 19 | 19 | 0.36 |
| 6 | 0-3 | 49.57 | 1.42 | 3.43 | 466 | 167 | 25 | 43 | 1.45 |
| | 5-10 | 49.37 | 1.30 | 3.81 | 503 | 420 | 28 | 51 | 1.80 |
| | 10-15 | 46.44 | 1.93 | 3.32 | 492 | 106 | 37 | 57 | 1.94 |
| | 15-20 | 47.56 | 1.78 | 3.63 | 516 | 97 | 26 | 55 | 1.87 |
| | 20-25 | 48.11 | 1.54 | 3.41 | 506 | 122 | 24 | 40 | 1.61 |
| | 50-55 | 68.84 | 1.02 | 3.42 | 498 | 110 | 21 | 26 | 0.62 |
| 7 | 0-3 | 46.58 | 1.76 | 2.76 | 412 | 96 | 23 | 44 | 1.62 |
| | 5-10 | 51.05 | 1.27 | 2.71 | 391 | 142 | 31 | 54 | 1.63 |
| | 10-15 | 47.16 | 1.40 | 3.02 | 456 | 315 | 34 | 56 | 1.71 |
| | 15-20 | 41.39 | 1.93 | 2.63 | 390 | 263 | 27 | 48 | 1.48 |
| | 20-25 | 48.49 | 1.19 | 2.36 | 394 | 166 | 26 | 41 | 1.37 |
| | 50-55 | 61.17 | 0.90 | 2.20 | 312 | 106 | 18 | 28 | 0.48 |
| 8 | 0-3 | 36.81 | 2.28 | 4.52 | 329 | 308 | 41 | 64 | 1.13 |
| | 5-10 | 41.23 | n.d. | 4.04 | 278 | 138 | 25 | 52 | 1.28 |
| | 10-15 | 43.89 | 2.11 | 5.20 | 387 | 197 | 36 | 72 | 1.74 |
| | 15-20 | 43.88 | 1.80 | 4.09 | 339 | 139 | 26 | 47 | 1.37 |
| | 20-25 | 43.77 | 1.80 | 4.25 | 353 | 148 | 27 | 64 | 1.31 |
| | 50-55 | 62.60 | 0.97 | 4.19 | 342 | 135 | 26 | 31 | 0.74 |
| 9 | 0-3 | 22.47 | 4.71 | 3.84 | 473 | 163 | 30 | 68 | 1.37 |
| | 5-10 | 26.88 | 3.58 | 3.42 | 551 | 305 | 51 | 64 | 1.50 |
| | 10-15 | 40.52 | 3.16 | 3.94 | 422 | 121 | 27 | 69 | 1.79 |
| | 15-20 | 44.64 | 2.03 | 3.89 | 482 | 413 | 28 | 43 | 1.28 |
| | 20-25 | n.d. | 3.13 | 3.89 | 533 | 270 | 31 | 49 | 1.46 |
| | 50-55 | 66.40 | 1.41 | 3.40 | 471 | 143 | 24 | 23 | 0.59 |

(*) maximun depth available in the core
n.d.: not determined

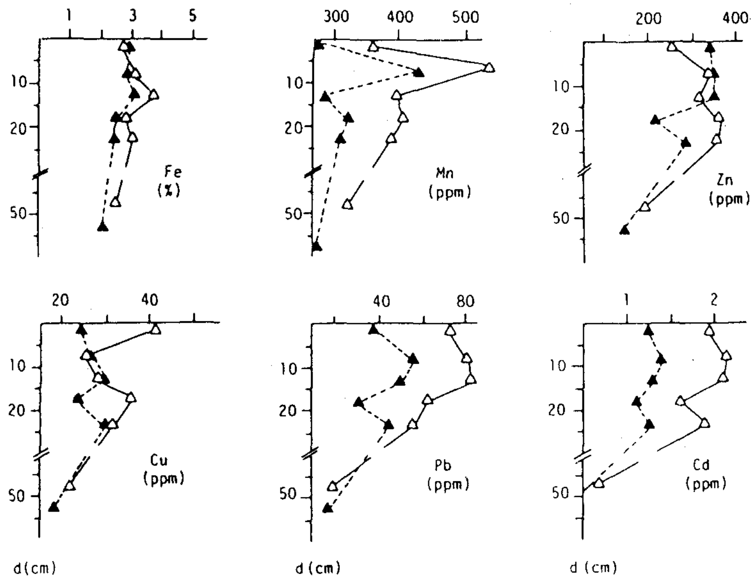


Figure 2. Evolution of Fe, Mn, Zn, Cu, Pb and Cd concentrations in the sedimentary column of station 3 (Δ) and 5 (▲).

bottom, although the vertical trend of these parameters is conditioned by the proximity of the sampling-stations to the outlets of the urban and industrial effluents of the area (Figure 1). This dependence is shown in Figure 2, in which the results obtained from sites 3 and 5, located in the two outlets of the Sancti Petri channel, are represented. This channel is the main artery of a complex system of secondary channels. They supply sea water to the majority of salt-ponds lying to the South of the Bay Cadiz, and receive the discharges of the residuals wastewaters of nearby towns and industries. It is observed that the most pronounced concentration gradients of metals correspond to the northern area, where the greater number of effluents are located.

The progressive reduction with depth of typically polluting metals (fundamentally Cu, Pb and Cd) occurs to a greater or lesser extent in all the sampling-stations, and an extremely complex situation was found in the more superficial layer (above 15-20 cm). This situation is frecuently found in shoreline marine sediments, mainly due to changes in the redox conditions of the environment. It is provoked by the consumption of oxygen required by bacterial decomposition of organic matter. There also exists an appreciable biological alteration as a result of the excavating activities of the great number of benthonic organisms (Petr 1977).

The anthropogenic contribution to the metal fluxes accesing to this area has been calculated as a Superficial Enrichment Factor (SEF), in accordance with Rapin (1981), given by:

Table 2. Superficial Enrichment Factor values that have been defined for the different sampling stations established.

| Station | C.O. | Fe | Mn | Zn | Cu | Pb | Cd |
|---|---|---|---|---|---|---|---|
| 1 | 1.08 | 1.11 | 1.30 | 1.34 | 1.10 | 1.24 | 2.83 |
| 2 | 1.05 | 0.86 | 1.10 | 0.98 | 1.04 | 1.08 | 3.11 |
| 3 | 1.96 | 1.23 | 1.35 | 1.62 | 1.43 | 3.78 | 3.08 |
| 4 | 1.32 | 0.89 | 1.08 | 1.44 | 2.33 | 4.40 | 2.84 |
| 5 | 1.46 | 1.40 | 1.31 | 2.14 | 1.41 | 2.36 | 3.54 |
| 6 | 1.58 | 1.04 | 0.99 | 1.80 | 1.38 | 1.98 | 3.39 |
| 7 | 1.77 | 1.26 | 1.32 | 1.92 | 1.60 | 1.80 | 3.35 |
| 8 | 2.13 | 1.07 | 0.97 | 1.45 | 1.23 | 1.90 | 1.86 |
| 9 | 2.39 | 1.11 | 1.02 | 1.75 | 1.42 | 2.52 | 2.52 |
| average | 1.64 | 1.11 | 1.16 | 1.60 | 1.44 | 2.34 | 2.95 |

$$SEF = \frac{MC_s}{MC_p}$$

where $MC_s$ represents the mean concentration of the element considered in the more superficial 20 cm, and $MC_p$ stands for the mean value of the deepest layer of sediment studied. This later one (50-55 cm) yields information about the metals levels in an impolluted environment (Warren 1979).

The Superficial Enrichment Factors for the different stations are shown in Table 2. This value is quite variable depending on the metal and the sampling-station considered. The quantities of iron and manganese have not increased greatly in recent years. On the other hand, in the superficial sediments, concentrations of lead and cadmium of 350 and 400% compared to baseline levels were found. The relatively high value of the Superficial Enrichment Factor of lead in station 3 must be attributed to its proximity to a naval construction center. This is due to the use of this metal in the manufacture of anticorrosive paints intensively employed in ship-building.

In the salt-ponds (stations 6 to 9) the influence of anthropogenic activity was found to be similar to other places where the movement of the water is not restricted. This result becomes specially important considering the present use of these salt-ponds. The progressive increase in the levels of heavy metals as a consequence of the residual effluents could endanger the future production of these fish-farms in the area.

According to the area Superficial Enrichment Factor mean values (Table 2), the order in which the metals studied have increased their concentration in this area becomes:

$$Cd > Pb > Zn > Cu > Mn > Fe$$

This sequence is typical for an environment polluted by urban and industrial effluents and agrees with other studies in the Mediterranean (Rapin 1981) and American Atlantic coasts (Goldberg et al. 1977).

It may be concluded that an important increase in heavy metals entering the Bay of Cadiz has been produced. These metals are generated in the same area as a result of the industrial and demographic growth that has taken place in recent years. Accumulation in the superficial sediments of typically polluting metals results especially intense near the effluents. However the complex hydrodynamics of the area, that also affects the granulometry of the sediments, may give rise to anomalous distributions for some heavy metals (Gómez-Parra et al. 1984).

The methodology applied in this study provides an objective pollution index. It may be used in other shoreline areas, but it is always neccesary to consider all the outstanding sedimentary environments. Moreover, the sediment layer to be used to compare with more recent sediments, must be taken at an adequate depth as to supply the baseline of heavy metals of the area.

Acknowledgments. The authors wish to thank A.M. Gómez and M.D. Frutos for their help in sampling and sample preparation.

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Received October 15, 1984; accepted October 21, 1984