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Levels of ^{137}Cs in muddy sediments of the seabed of the Bay of Cádiz, Spain. Part I. Vertical and spatial distribution of activities

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Abstract

This is the first of a two-part paper. This first part describes a detailed study conducted of the spatial and vertical distribution of the concentration of the radionuclide ^{137}Cs, utilising columns of sediment extracted from the seabed of the Bay of Cádiz (Spain) as specimens. The activity concentrations have been measured by means of gamma spectrometry using a HPGe detector and ^{137}Cs is used as an indicator of the sedimentation and contamination processes in the zone. At the same time the relationship between the levels of activity found and other hydrodynamic and sedimentological variables characteristic of the zone have been studied. The experimental results obtained will also serve to develop a model of the distribution of ^{137}Cs, which will be presented in the second part of this paper.

Keywords: Environmental pollution; Radionuclide; Sediment column; Seabed sediment; ^{137}Cs

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1. Introduction

The Bay of Cádiz (Fig. 1) is situated to the south of the Iberian Peninsula, some 100 km to the northeast of the Straits of Gibraltar. The Bay is approximately 30 km in length, with an average width of 15 km, and is bounded by broad areas of salt marshes separated from the sea by littoral strips of sand. This geographic area constitutes a zone of considerable importance in terms of ecology, economics, tourism, and general social and cultural significance. Its configuration is the result of a natural evolution determined by geological agents, principally the littoral dynamics, the mouth of the river Guadalete and the aeolian regime characteristic of the zone, and by biological factors such as the vegetation and fauna, to which must be added the profound alteration of the environment caused by man, by the exploitation of salt lagoons and fish farms in particular and by the development of the surrounding metropolitan area in general. In fact we are dealing with a singular set of surroundings in which autochthonous elements co-exist including the marine medium itself, the salt marshes, the beaches and pine forests with urban nuclei and a variety of infrastructure installations like ports and marinas, roads and tourist facilities.

Situated to south the Inner Bay is delimited by emerged wet zones and by the sandy strip that separates it from the a beach; it is surrounded by the municipalities of Cádiz, San Fernando and Puerto Real. The Inner Bay has a maximum length and width of 9.3 km and 5.25 km, respectively, giving it a total area of 33.6 km^2; the

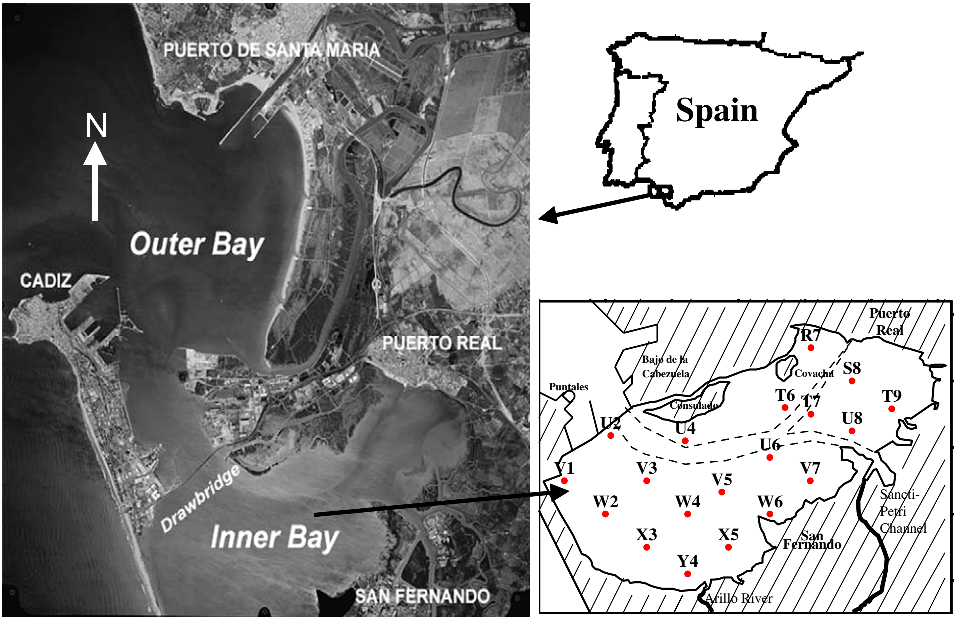

Fig. 1. Bay of Cádiz and locations of the sampling stations.

volume of water contained at low tide is approximately 30 Hm^3 (Muñoz and Sánchez, 1994). It is drained by the main channel that runs from the Puntales strait, continues along the creek of La Carraca, and flows into the open sea through the tidal channel of Sancti Petri. Its bottom is relatively shallow, with a depth of less than 3 m, apart from the navigation channel where it exceeds 15 m. It is sheltered from the worst of the weather and surf, and this has permitted the accumulation of muddy sediments on its bottom. The hydrodynamics of this zone are controlled by the tides, with the winds also being an important influence; the tidal action stirs up the bottom sediments and generates a swell that can produce intense wave action in the western zone when there are strong winds from the east.

Despite the acknowledged value of its natural environment, to date no detailed study has been made of the dynamics and sedimentary contamination in the Inner Bay; because of its location, sheltered from the ocean currents and storms, it has great importance as a zone of transition between the sandy beaches of the Outer Bay and the large tract of muddy sediments comprising the salt marshes to the south and east.

The central objective of the present work is to study the sedimentary dynamics in the Inner Bay of Cádiz, by means of the measurement of the artificial radionuclide ^{137}Cs; this is present in the sediments as a consequence of the nuclear weapon tests carried out in the 1950s and 1960s. The activity of ^{137}Cs reached its maximum values in the years 1962–63 when there was a significant increase in nuclear tests, and in more recent episodes, particularly the Chernobyl nuclear power station disaster in 1986. Therefore, the profile of ^{137}Cs in the columns of sediment should demonstrate the incorporation of this radionuclide in the medium, and the peaks of its concentration just mentioned can be employed as a method of dating, for recent sediments laid down less than 50 years ago (Pinglot and Pourchet, 1995; Callaway et al., 1996). However, this technique has serious limitations, due to the behaviour of ^{137}Cs in aquatic systems: on the one hand, this element has a long residence time in the marine medium, which may delay its incorporation in the sediment, resulting in the peaks in the concentration profile being displaced to more superficial levels; and on the other hand, its high degree of mobility in the sediment column causes the radio element to be diffused towards deeper levels.

2. Experimental

To study the zone adequately, 19 sampling stations were distributed uniformly over the area of the Inner Bay, located at the nodes of a grid, with sides approximately 1 km long, the axes of which are orientated in the northeast and northwest directions. Following this arrangement strictly, some stations would be located in the navigation channel, where there is a reduced or disturbed presence of radionuclides due to the currents and the periodic dredging. In these cases, the positioning of the station in question was moved towards the outer edge of the channel. In Table 1 the geographical coordinates of the stations are given, and in Fig. 1 their locations are indicated on a map of the bay.

Table 1
Geographical coordinates of the stations

Station	Longitude	Latitude
R7	6°11′55″W	36°31′30″N
S8	6°11′18″W	36°31′00″N
T6	6°12′18″W	36°30′36″N
T7	6°11′55″W	36°30′30″N
T9	6°10′42″W	36°30′35″N
U2	6°14′55″W	36°30′11″N
U4	6°13′48″W	36°30′06″N
U6	6°12′32″W	36°29′51″N
U8	6°11′18″W	36°30′15″N
V1	6°15′37″W	36°29′30″N
V3	6°14′23″W	36°29′30″N
V5	6°13′15″W	36°29′20″N
V7	6°11′55″W	36°29′30″N
W2	6°15′00″W	36°29′00″N
W4	6°13′46″W	36°29′00″N
W6	6°12′32″W	36°29′00″N
X3	6°14′23″W	36°28′30″N
X5	6°13′09″W	36°28′30″N
Y4	6°13′46″W	36°28′06″N

The columns of sediment were extracted in cylindrical tubes of aluminium of 1 m length and 6 cm diameter, by means of a Lanesky type vibrocore system that allows the complete column to be obtained without altering the structure of the sediment. The sampling campaigns were conducted during the first half of 1998. The sediment cores were taken to the laboratory where they were kept at a temperature of −5 °C to ensure that the interstitial water remained at its corresponding level in the sediment column. Later, the columns of sediment were sectioned into slices of 2 cm thickness, and each sample obtained was dried at 60 °C, to determine its porosity, and milled using an agate mortar to a grain size of less than 0.5 mm, to ensure its homogeneity for the spectrometry measurements.

The water content, w, was obtained from the wet and dry weights of each sample. This parameter is associated with the degree of compaction of the sediment, this being indicative of the energy levels prevailing in the environment, and of the granulometry of the sediment.

The organic carbon content, OC, was determined by applying a modification of the technique of Gaudette et al. (1974) developed by El-Rayis (1985); this consists of the oxidation of the sediment sample with potassium dichromate in a strongly acid medium at a temperature of 135 °C. The OC content is obtained by measuring the surplus dichromate remaining after the oxidation, with ferrous ammonium sulphate. The percentage of OC detected by this method depends on the type of sediment, but is between 80 and 95% of the true total. In this technique, the elemental carbon remains unaltered and the carbonates do not present interference problems.

The rest of the sediment was put into cylindrical plastic containers of 4.6 cm diameter for analysis by gamma spectrometry.

The sample bulk density was determined, after dried, by gravimetric procedures, and was found to be in the range of 0.8–1.7 g/cm^3.

The ^{137}Cs was measured by gamma spectrometry, employing a coaxial HP Ge detector with an active volume of 90 cm^3, with a relative efficiency of 20% (in comparison with a NaI (Tl) detector of 3×3 inches) and a resolution of 2 keV, at 1332 keV. This detector is sensitive in the 50 keV–10 MeV energy range. The sample holder of the measuring equipment utilises lead shielding 10 cm thick, with internal sheets of Cu and Cd 1 mm thick, to reduce external radiation. The determination of the ^{137}Cs was performed using detection of 662 keV emission and 85% intensity, emitted by its descendent, ^{137}Ba^{m}, with which it is in secular equilibrium.

The efficiency was obtained experimentally by means of the measurement of a sediment standard of variable height H with emissions in the energy range E usually found in environmental measurements (Ramos-Lerate et al., 1998). Applying a correction factor that takes into account the density dependent self-absorption of the samples (Cutshall et al., 1983), the efficiency function $\epsilon(E, H, \rho)$ was obtained. This efficiency is applicable in the range of measurement of the sediment samples, $E=100$–2000 keV, $H=1$–5 cm, $\rho=0.8$–1.7 g/cm^3, and its uncertainty is 5%.

Given that ^{137}Cs accumulates in superficial sediments and is below detection limit beyond a certain depth, in function of different variables that depend on the location of each sampling station, the number of layers analysed in each column was varied from one station to another. In general terms, a maximum depth of 50 cm was reached, although in some columns this was increased 70 cm in order to widen the profile of ^{137}Cs with depth.

3. Results

3.1. Vertical distribution

To describe the sedimentary conditions characterising each station, the profiles of porosity and organic carbon were studied. This provides a qualitative description of the basic characteristics of the sediment, such as the grain size or the capacity for adsorption of substances. The content of organic matter in the sediments plays a fundamental role in the fixing or capture of the elements, and the sediment porosity is directly related to grain size, this also being indicative of the absorption capacity of the sediment. In addition, the porosity profile allows us to evaluate the effect of compaction, since this has to be taken into account for the determination of the rates of sedimentation.

To analyse the results obtained, we shall designate as the *joint profile* of a parameter in respect of depth, the representation of the values found for that parameter in all the sampling stations, and as the *mean profile* of a parameter in respect of depth, the average of all the experimental values of that parameter found. Although both profiles contain similar information, the joint profile enables the range of variability of the parameter to be identified better, and the mean profile is more useful for identifying the trend of the parameter.

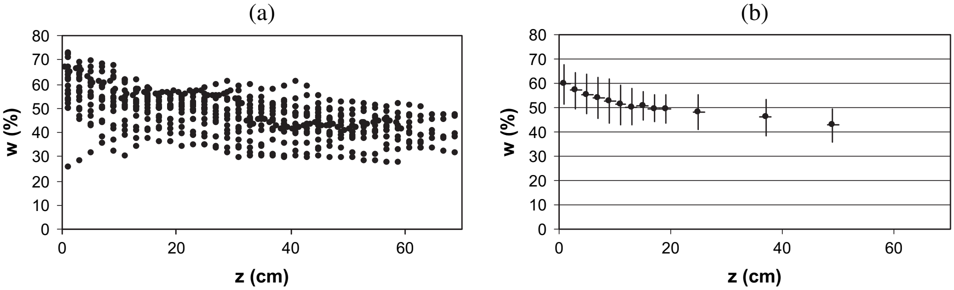

Fig. 2. Joint and mean profiles for the porosity of the sediments.

In Fig. 2 the joint and mean profiles of the porosity are represented. The value of this magnitude falls within the range 70% to 25%, and shows an overall trend of decrease with depth. In the mean profile of *w*,a decrease from 60% to 50% can be observed in the first 20 cm of superficial sediment, and beyond this depth the decrease is more gradual, reaching a value of 43% at 50 cm below the surface. This behaviour is characteristic of the fine sediments (muds and clays) that are the predominant sediment materials in the Inner Bay. The decrease of interstitial water with depth is controlled by the compaction of the sediment from the increased pressure on the deeper layers.

Fig. 3 shows the profiles, as already defined, for the content of organic carbon in the sediments. The value of OC falls within the range of 0.8–5%, and a trend of decrease with depth can be seen. In mean terms, the OC remains constant, at a value of about 2.9% in the first 10 cm of superficial sediment. Below this depth it decreases steadily, with the mean value falling to 1.8%, at a depth of 50 cm. It is interesting to observe that the spatial variation of this parameter is much greater in the surface sediments than at the deeper levels. This is because the supply of organic matter takes place in the aquatic medium, and the microbial action occurs over a longer period of time in the deeper sediments, degrading and reducing the content of organic matter.

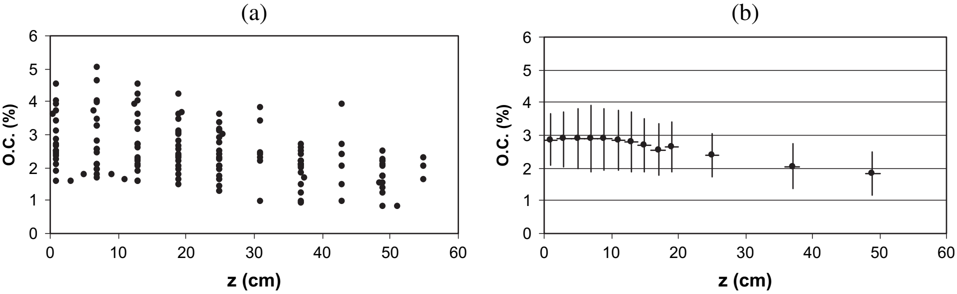

Fig. 3. Joint and mean profiles for the organic carbon content of the sediments.

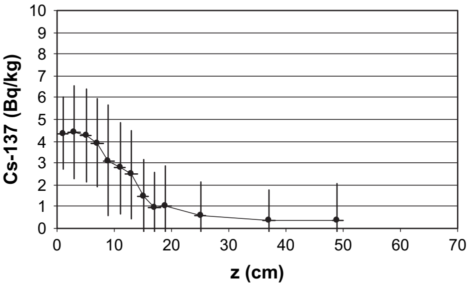

Fig. 4. Mean profile for the concentration of ^{137}Cs activity.

The values of concentration activity found for ^{137}Cs in the sediments of the Bay of Cádiz are typical of coastal sediments that received radioactive fallout in the 1950s and 1960s (UNSCEAR, 2000). Fig. 4 shows the mean profile for the concentrations of ^{137}Cs activity, which presents a range of variation between 0 and 9 Bq/kg. The mean profile shows a surface layer of 5 cm thickness where the activity remains constant, at around 4.4 Bq/kg. Below this layer, the mean activity decreases rapidly, reaching the value of 1 Bq/kg at a depth of 20 cm, and thereafter it decreases more gradually to the minimum value detectable (0.5 Bq/kg), at a depth of 50 cm. The behaviour described is analogous at all the stations studied, consequently we can state that three regions of the activity profile of this radionuclide can be appreciated: (A) high activity; (B) rapid decrease of activity; and (C) low activity.

The activity of ^{137}Cs in region (A) of the various stations is found in the relatively narrow range of 3–6 Bq/kg, due to the homogeneity of the sedimentological conditions of the Inner Bay; these give rise to very little variation in the parameters on which the incorporation of ^{137}Cs in the sediment depends (granulometry, mineralogy and organic matter content).

An important observation is that it is not possible to date directly the different strata from the activity profiles of ^{137}Cs in the sediment column. This is because variations in the residence time of the radio element in the water lamina and its mobility in the sediment column itself (through processes of diffusion in the interstitial water and of biological activity) prevent these profiles from reflecting the element's incorporation from the atmosphere at specific times. In fact, it is not even possible to detect unequivocally the peaks of activity corresponding to the years 1961 and 1962.

However, from the activity profiles of ^{137}Cs, it is possible to determine the inventory associated with a station, I, defined as the total activity of the column by unit of surface area. Designating N as the number of layers of sediment that contain ^{137}Cs, a_i as the specific activity, and m_i as the mass of sediment of a layer $i(1 \leq i\ 0\ 1 \leq N)$, the inventory of each station can be calculated by means of

$$I = \frac{1}{S} \sum_{i=1}^{N} a_i m_i$$

Table 2
Inventories calculated for the stations of the Inner Bay

Station	Z_M (cm)	I (Bq/m^2)
R7	19	319±22
S8	11	192±17
T6	13	165±22
T7	9	166±16
T9	21	369±23
U2	15	195±21
U4	13	220±19
U6	21	481±24
U8	61	2141±56
V1	15	304±19
V3	35	816±34
V5	13	231±23
V7	13	560±25
W2	37	575±46
W4	26	567±32
W6	11	376±38
X3	17	507±30
X5	13	328±19
Y4	19	220±20
Range	9–61	165–2141
Average	20.1	460±5

where S is the surface area of the specimen utilised. Table 2 gives the inventories calculated for the stations of the Inner Bay.

The mean inventory of ^{137}Cs in the Inner Bay is below the value estimated, of 2×10^3 Bq/m^2, for the integrated deposition of this element in the belt of 30–40° latitude in the northern hemisphere (UNSCEAR, 2000). This reduced value indicates that, after the radioactive fallout, some of the ^{137}Cs is removed from the Bay. The very high solubility of ^{137}Cs in the marine medium results in the greater part of the element deposited escaping from the Bay, swept out by tidal currents. Only a fraction of the ^{137}Cs, less than 25%, becomes incorporated into the sediment at the interface, and contributes to the inventory of the sediment column.

3.2. Spatial distribution

The pattern of sampling stations established in the Inner Bay enables a detailed study of the spatial distribution of the parameters considered. For this the interpolation method of Kriging (Cressie, 1991; Davis, 1986) has been utilised; this method finds an interpolation function from a discrete pattern of experimental values that provides the continuous spatial distribution of the variables considered. The analysis of the sediment interface, corresponding to the first layer of 0–2 cm at each station, is especially interesting, since it is here that the processes of exchange between the aquatic medium and the sediment take place, in consequence of the

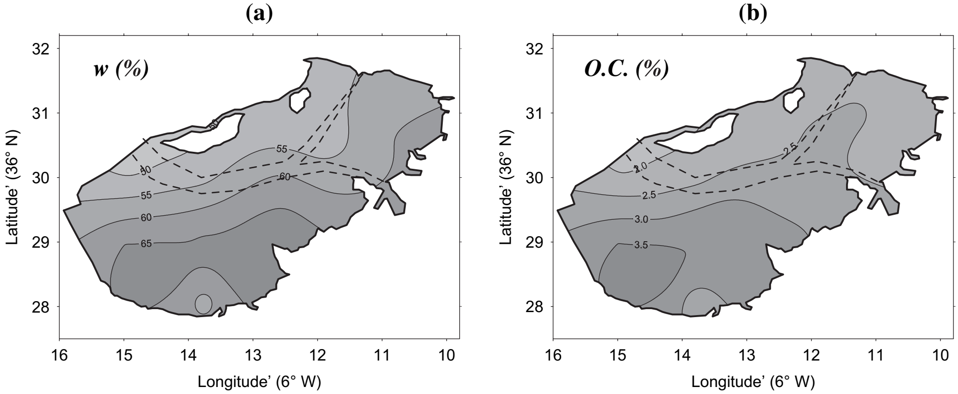

Fig. 5. Contour lines for *w* and OC.

processes of transport and accumulation of the elements associated with the tidal currents and the sedimentation.

Moreover, given that the inventory *I* is linked to the behaviour of the sediment in the medium term, its spatial distribution identifies the zones of accumulation of ^{137}Cs; this in turn is linked to the accumulation of sediment that had previously incorporated this radionuclide.

To analyse the spatial distribution of the porosity, the values of *w* determined at the sediment - water interface (0–2 cm) are considered. Fig. 5a shows the isoline map drawn for this parameter; from this some interesting conclusions can be reached. Firstly, it is observed that porosity increases towards the southern zone of the Inner Bay, where tidal currents are less strong and, for this reason, the predominant sediment here is of small particle size. In the zones with a very strong dynamic, such as the navigation channel (that is outlined in the figure with a broken line), minimum porosity values are found since the sediments in such zones are predominantly sands. We can also observe that the porosity isolines run at right angles to the direction of the stronger currents, as in the proximity of the bridge; hence the gradient of the porosity indicates the dominant currents in the zone. This pattern of behaviour changes in the intertidal zones where, despite the existence of clay-type granulometry, the value of *w* is relatively low, due to the loss of the interstitial water at low tide, as can be appreciated in the riverside zone in the south of the Bay.

Fig. 5b represents the spatial distribution of the content in organic carbon of the sediments; this coincides with the description provided by other authors (Muñoz and Sánchez, 1994), and here it can be appreciated that the behaviour of this parameter is very similar to that of the porosity, due to its analogous dependence on the grain size of the sediment, and therefore also on tidal currents.

In Fig. 6 are shown the spatial distributions obtained for the ^{137}Cs activity at different depths. The distribution of ^{137}Cs at the interface is similar to the distribution of the interstitial water *w* and of organic carbon OC, which indicates that the ^{137}Cs activity at the interface is linked to the tidal dynamic. The element

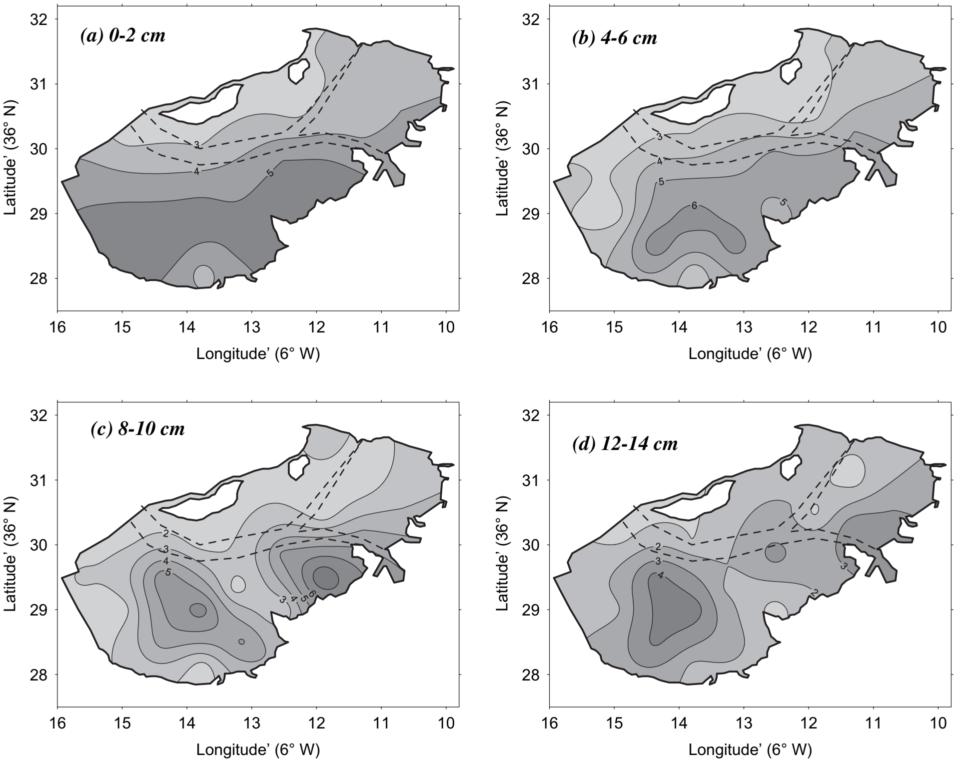

Fig. 6. Contour lines for ^{137}Cs activity at different depths.

accumulates preferentially in zones of calm hydrodynamics, where the sediments are mainly of clay and rich in organic matter, thus presenting a high capacity of absorption. The strong currents that exist in the proximity of the Puntales strait do not favour the accumulation of fine sediment and organic matter, nor of ^{137}Cs. The reduced ^{137}Cs activity in the intertidal sediments of the southern part of the bay and of the zone between the Consulado and Covacha islands is due also to the reduced time of contact between the interface of these sediments and the aquatic medium. The concentration of ^{137}Cs in deeper layers depends both on the activity taking place at the interface and on the mobility of the radionuclide in the sediment column, and although one of these two effects may prevail over the other, in general both take place simultaneously.

From these spatial representations, we can appreciate that in the first layers of sediment are a larger uniformity for the activity concentration of ^{137}Cs. However, below a depth of 10 cm, a considerable decrease of this latter variable is recorded; this decrease had already been detected in the vertical profiles analysed in the preceding section. We may also note that not in all the places with a high concentration of ^{137}Cs in surface sediment are high values of depth maintained; this

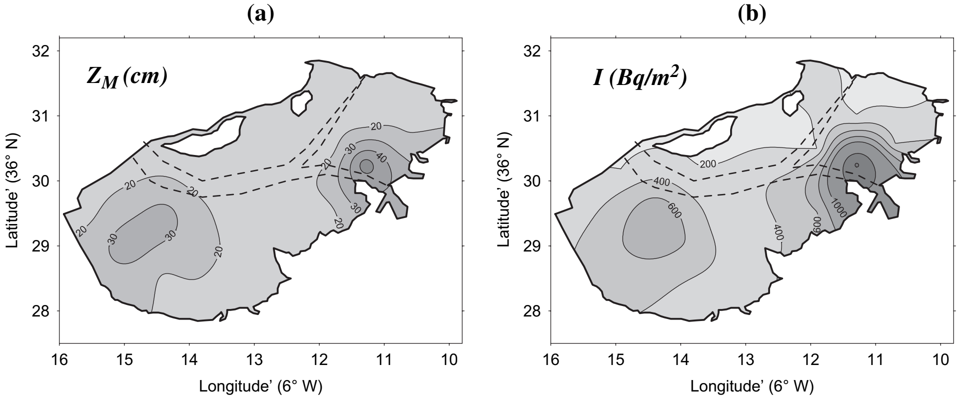

Fig. 7. Concentration of ^{137}Cs activity at the maximum depth, and its inventory, in the Inner Bay.

finding allows us to identify zones in which the mechanism of migration within the column appears to predominate over that of concentration in the interface. To demonstrate this fact, Fig. 7 presents the values of Z_M, the maximum depth reached by the ^{137}Cs, and of its inventory, utilising the same interpolation method previously cited. Both isoline maps reveal the same two well-defined zones where the penetration is maximum, and that do not coincide exactly with the maximum concentrations of this radio element in the surface; this indicates that other factors contribute to the process of migration of ^{137}Cs in the sediment column, and these will have to be considered to establish the corresponding model of vertical diffusion.

4. Conclusions

As a consequence of its recent incorporation into the natural environment, ^{137}Cs is only found in the more superficial layers of submarine sediments and, due to the influence of its varying residence time in the water lamina and the complex phenomena of redistribution in the sediment column, the profiles of activity against depth do not directly reflect the temporal evolution of the ^{137}Cs in the atmosphere.

The principal agent that governs the spatial dispersion of ^{137}Cs activity in the Inner Bay is the dynamic of tidal currents. In the zones with strong currents, fine sediment, rich in organic matter, does not accumulate; therefore the sediment there shows little capacity for absorption of the ^{137}Cs. In contrast, the zone presenting a relatively calm hydrodynamic does allow the deposition of fine sediment and organic matter, and thus becomes the main area for accumulation of the ^{137}Cs.

However, the picture is rather different with the vertical distribution of ^{137}Cs, since the association between the specific activity and the grain size of the sediment disappears in the layers of sediment situated below the interface. The inventory of ^{137}Cs, which measures the total accumulation of the radionuclide in the column, is not related to the grain size of the sediment, nor is the maximum depth of penetration. Both parameters seem to indicate that the accumulation of ^{137}Cs takes place as a consequence of the sedimentation of material that had previously incorporated the radionuclide in its place of origin.

Two basic factors influence the mobility of ^{137}Cs in the sediment column: the concentration of the element available at the interface and its capacity for migration in the column. This fact is fundamental for the development of a model capable of explaining the behaviour of ^{137}Cs in sediments of the seabed.

Acknowledgements

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References

Callaway, J.C., DeLaune, R.D., Patrick, W.H., 1996. Chernobyl ^{137}Cs used to determine sediment accretion rates at selected northern European coastal wetlands. Limnol. Oceanogr. 41 (3), 444–450.

Cressie, N.A.C., 1991. Statistics for Spatial Data. Wiley, New York.

Cutshall, N.H., Larsen, I.L., Olsen, C.R., 1983. Direct analysis of ^{210}Pb in sediment samples: self-absorption correction. Nucl. Intstrum. Methods B 206, 309–312.

Davis, J.C., 1986. Statistics and Data Analysis in Geology. Wiley, New York.

El-Rayis, O.A., 1985. Re-assessment of the titration method for determination of organic carbon in recent sediments. Rap. Commun. Int. Mer. Médit. 29, 45–47.

Gaudette, H.E., Flight, W.R., Toner, L., Folger, D.W., 1974. An inexpensive titration method for the determination of organic carbon in recent sediments. J. Sediment. Petrol. 44, 249–253.

Muñoz, P.J.L., y Sánchez, A., 1994. El medio físico y biológico en la Bahía de Cádiz: Saco Interior. Informaciones Técnicas 28/94. Consejería de Agricultura y Pesca, Junta de Andalucía.

Pinglot, J.F., Pourchet, M., 1995. Radioactivity measurements applied to glaciers and lake sediments. Sci. Total Environ. 173, 211–223.

Ramos-Lerate, I., Barrera, M., Ligero, R.A., Casas-Ruiz, M., 1998. A new method for gamma-efficiency calibration of voluminal samples in cylindrical geometry. J. Environ. Radioact. 38, 47–57.

UNSCEAR, 2000. Sources. In: Sources and Effects of Ionizing Radiation, vol. I. United Nations Scientific Committee on the Effects of Atomic Radiation, New York.