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RADIONUCLIDES IN THE ENVIRONMENT OF THE BAY OF CÁDIZ

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Abstract — Commercial activities in the Bay of Cádiz (south-western Spain), together with the erosion and transport of sediments through the Guadalete and San Pedro rivers and the natural contribution of the salt pans, suggest that this region is altered from a radiological point of view. Alterations in radioactivity levels produced by such processes are here studied, making use of analysis by gamma spectrometry of ^{226}Ra, ^{40}K and ^{137}Cs activities in seabed sediments. After the analysis of the samples, it can be said that the distribution of ^{226}Ra follows the sea-bottom current pattern, and simply reflects the geomorphological features of the zone. The incorporation of ^{40}K can be observed through the Guadalete river and contact with the Interior Bay, producing a bigger concentration in stagnation zones or regions where ^{40}K coming from salt pans is transported by currents. The increase in the concentration of ^{137}Cs is linked to spillages caused by ship loading and unloading operations, which bring to the natural environment materials coming from opencast mining, so that they incorporate fallout activities of the original region.

INTRODUCTION

The Bay of Cádiz (south-western Spain) has not been greatly studied from an environmental or radiological point of view in spite of its strategic geographical situation (the Atlantic side of the Straits of Gibraltar area). It is possible to distinguish three zones inside what is frequently termed the 'Bay of Cádiz': the Maritime Bay, the Terrestrial Bay and the Amphibian Bay[1], shown in Figure 1. The Amphibian Bay shows one of the most singular and original morphological aspects of the Bay of Cádiz: the inter-tidal regions or maritime–terrestrial influence zones. Part of this area is still virgin (natural salt-marshes, 4373 ha), another part has been transformed to salt pans (5513 ha) and a last fraction has been dried (5824 ha). In 1989, the two first zones were declared Protected Natural Space (Bay of Cádiz Natural Park).

The Terrestrial Bay (1312 ha) can be identified with the Urbanised Bay, which appears like a coastal belt in the north, and in the most consolidated lands in the south it is distributed more discontinuously. Five cites are situated on this Bay and constitute the metropolitan area or 'Bay City': El Puerto de Santa Maŕa, Puerto Real, Cádiz, San Fernando and Chiclana de la Frontera.

The Maritime Bay, at the same time, can be divided into two areas:

(1) The Exterior Bay (8032 ha) which extends from the north of José León de Carranza Bridge, which joins Cabezuela Quay and the eastern part of the city of Cádiz, to Rota. It is the most affected by tide, wind and swell, and its seabed is composed of sand and mud sediments over a pliocene rock substratum.
(2) The Interior Bay (1313 ha), which is situated to the south of the Bridge. It is less affected by the eroding elements, and its seabed is formed mainly by clay and silt sediments, usually not very compact and turned into mud. This has allowed the development of an exceptional biotope.

It is almost impossible that the 400,000 persons living in the five cities of the Bay of Cádiz can develop their lives without any alteration of the environment, in particular because the productive functions linked to the marine medium have marked the economical structure

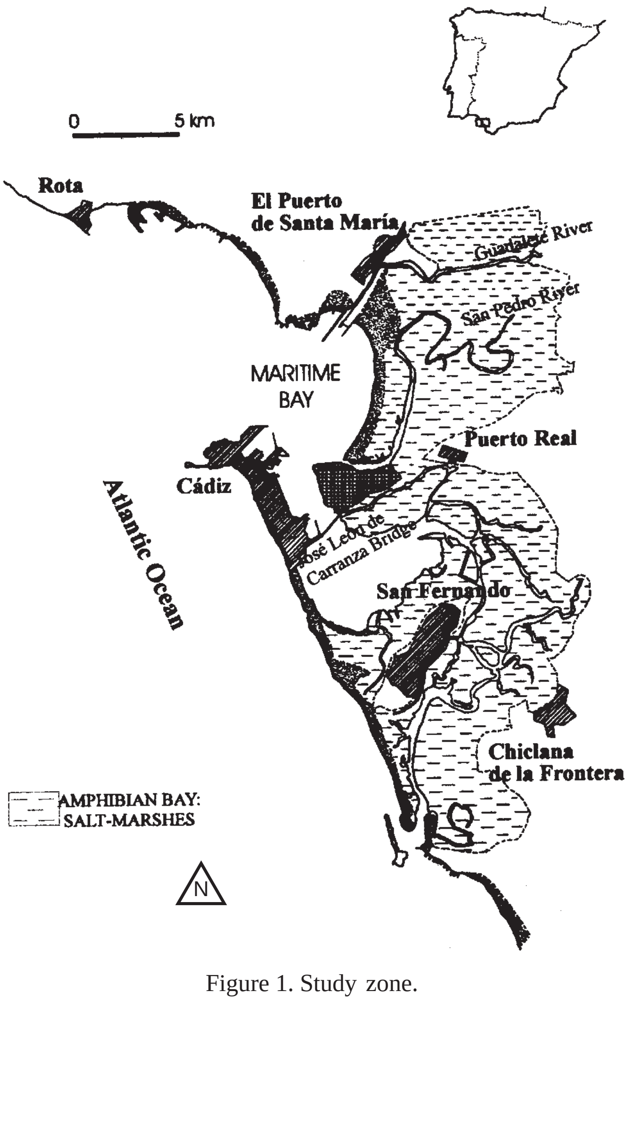

Figure 1. Study zone.

of this zone. Human interventions can be shown through a wide variety of possibilities: from the simple morphological transformation to the most radical denaturalisation.

The major environmental impacts produced by man in this zone are due to the following: the building of the Bridge crossing the Bay, the thermal power station at Puntales (now not working), the fish farms, the traditional exploitation of the salt pans, the recent yachting harbour and, especially, the harbour traffic together with the sediment transport and erosion through the Guadlete river which flows into the Bay. One of the most important points is the harbour traffic[(2–4)], especially the oil, concrete and clinker transport (250000 t.y^{-1}, 169000 t.y^{-1} and 180000 t.y^{-1} respectively), and special clays (attapulguitas-sepiolitas, 60000 t.y^{-1}) from the

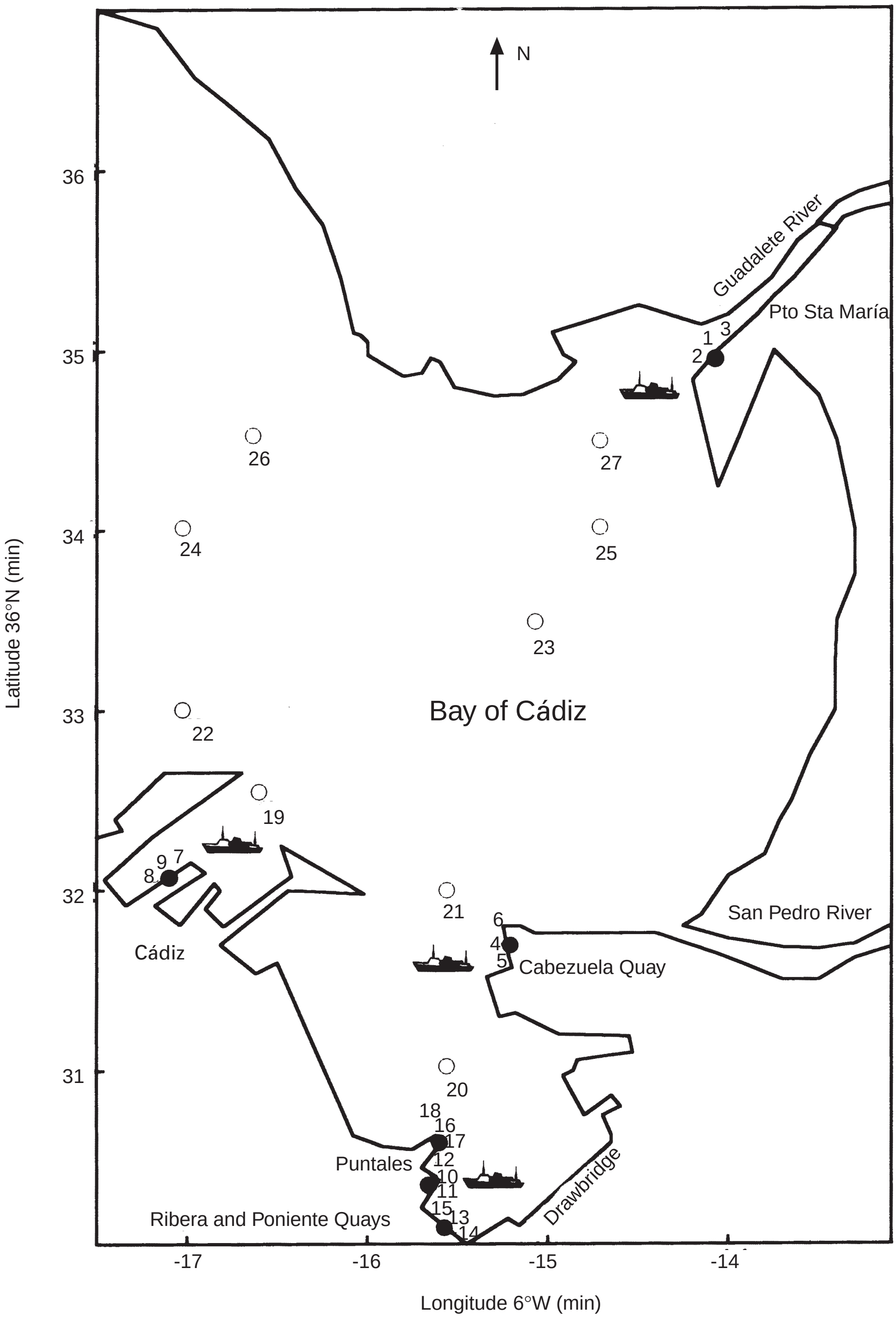

Figure 2. Sampling stations.

mines of El Cuervo (Cádiz-Sevilla), which can only be found in three other places in Spain (Toledo, Madrid and Cáceres).

Systematic studies of the radiation levels are necessary as a database in case of future industrial installations, as well as to throw light on the radionuclide transport in the environment and its subsequent influence on man.

METHODOLOGY

Sampling and pretreatment

Initial research has been focused on the Exterior Bay bordered on the 6°17.5′W Meridian at the west, the 36°30′N Parallel at the south and the coast. In this region, 17 square nautical miles approximately, two important features can be found: the Guadalete and San Pedro mouths, and the maximum industrial activity, whose influence in the environment was studied(2–4).

In 1995, a sampling campaign was carried out, and seabed sediments were collected in 18 stations where a special anthropogenic influence was assumed (six locations and three samples in every location: one at the point of maximum contamination and the other two up-stream and down-stream of this point) and in nine more stations, distributed in the study region, used for reference and whose locations can be seen in Figure 2.

The seabed sediments were taken with a Van Veen dredge and, after determining organic matter and moisture content, were dried at 105°C for 24 h, powdered, and passed through a 0.5 mm sieve in order to obtain homogeneity. The apparent densities were determined and the samples were stored in sealed polyethylene cylindrical containers of 64 mm inner diameter filled to 5.5 cm height. The spectrometric measurements were performed a month after sealing, so that secular equilibrium between ^{222}Rn and ^{226}Ra was assured.

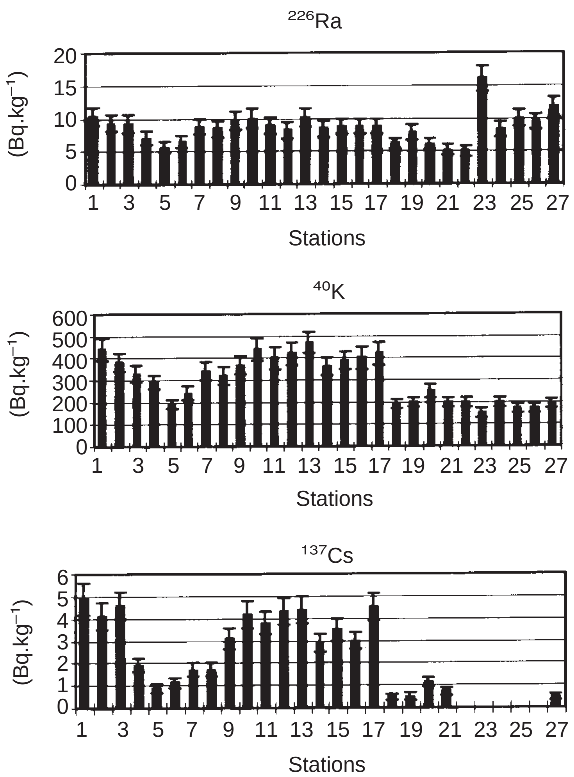

Figure 3. Histograms with the measured activities.

Gamma analysis

Gamma spectrometry provides a fast and simple method to measure dispersion and concentration of natural and anthropogenic radionuclides in the environment. Although the radiochemical procedures are more precise, they are too specific and require a longer time. The multi-elemental and non-destructive character of the gamma spectrometry makes it more useful in most environmental problems.

For the present study, ^{226}Ra, ^{40}K and ^{137}Cs have been measured. The last two of these were measured directly through their respective emissions at 1460.8 and 661.66 keV, while ^{226}Ra was measured through the emissions of the daughters: ^{214}Bi (609.3 keV, 46%) and ^{214}Pb (351.99 keV, 37.1%). In no sample was ^{211}Bi detected, whose emission at 351.1 keV (12.2%) could interfere with the one in ^{214}Pb. The 186 keV line of ^{226}Ra was not used due to interferences with the 185.7 keV line of ^{235}U.

The measurements were performed with an integral pre-amplifier Canberra GC2020-7500SL p-type coaxial HPGe detector system. The useful energy range of this detector is from 50 keV to above 10 MeV. The Peak/Compton ratio is 46 for the 1332 keV ^{60}Co photon. The relative efficiency to a 3 in × 3 in NaI(Tl) detector is 20% and resolutions at 122 and 1332 keV of 1.1 and 2 keV, respectively, are given.

The spectrometer is shielded by a 10 cm cubic geometry box of low-background lead (smelted more than 500 years ago), with an inner 1 mm Cd + 1 mm Cu layer, and is connected to a standard set-up: Canberra Model 2020 Amplifier and a PC-based 8 K multichannel analyser. It is situated in a laboratory where temperature and humidity are maintained constant using an Airwell SLM 7/9 air-conditioning system. The laboratory temperature and humidity are (22 ± 2)°C and (60 ± 5)% respectively, and are checked with a maximum–minimum thermometer and a psychrometer.

The samples were always measured in the same geometry, with the bottom of the cylindrical container at 3 mm from the detector window. The efficiency, with summing corrections, was determined(5,6), obtaining a function depending on the apparent density of the sediment and the energy of the emission with an uncertainty of 10% for a confidence level of 95%. The background was measured using an empty polyethylene container in the same measuring conditions as the rest of the samples.

RESULTS AND DISCUSSION

The ^{226}Ra, ^{137}Cs and ^{40}K activities, as well as the minimum detectable activity are shown in Table 1. The first 18 stations correspond to points where a special anthropogenic influence is believed to exist, and the last 9 correspond to reference stations. These same activities are shown in the histograms of Figure 3.

The ^{226}Ra activity has a constant value at stations 1 to 18, with some exceptions in Cabezuela (stations 4, 5 and 6) due to the dredging made in the zone some months before samples were taken. Therefore, it can be said that the concentration of ^{226}Ra is constant all over the coast.

None of the reference stations showed a substantial variation in the concentration of this radionuclide, with the only exception being station 23, where an important increase can be observed. The explanation can be found in the morphology of the seabed, as the station is over a mud island, in contrast to the rest of the reference stations, where the seabed consists of sand[(7)]. The fine mud particles favour the fixing of the radionuclide to the sediment.

The ^{226}Ra activity can be considered constant and equal to (8.5 ± 3.5) $Bq.kg^{-1}$, a value consistent with those found in other places in the world[(8)], where the usual range found in soils is 2.96–141 $Bq.kg^{-1}$ although there are regions with a high radioactive background where values of 1011[(8)] and 2100 $Bq.kg^{-1}$[(9)] have been measured.

The ^{40}K activity histograms are much more interesting as they allow us to distinguish clearly the anthropogenic influence in the region. In fact, radionuclide concentrations at stations 1 to 18, with the only exceptions at the Cabezuela stations, already mentioned, are much higher than in the reference stations. This observation suggests that the reference stations reflect the geomorphological features in the zone whilst the first 18 stations reflect the effect of intense harbour activity (concretes, clinkers, attapulguitas-sepiolitas, special clays and petrol products) as well as the deposits from the Guadalete river, which crosses the ‘La Tapa’ salt pans, the most important in the region and other influences of the salt pans in the south, through the currents.

The value of ^{40}K activity at the reference stations can be considered uniform and equal to (200 ± 50) $Bq.kg^{-1}$, increasing up to 470 $Bq.kg^{-1}$ at the rest of the stations

Table 1. Activities and minimum detectable activities.

Station number	Activity ($Bq.kg^{-1}$)			MDA $(Bq.kg)^{-1}$		
	^{226}Ra	^{137}Cs	^{40}K	^{226}Ra	^{137}Cs	^{40}K
1	10.4 ± 1.4	4.9 ± 0.7	440 ± 50	1.09	0.55	10.50
2	9.3 ± 1.3	4.1 ± 0.6	380 ± 40	1.03	0.51	9.39
3	9.2 ± 1.3	4.6 ± 0.6	330 ± 40	0.94	0.46	10.39
4	7.0 ± 1.0	1.9 ± 0.3	290 ± 30	0.86	0.43	8.12
5	5.6 ± 0.8	0.87 ± 0.19	190 ± 20	0.74	0.37	7.38
6	6.4 ± 0.9	1.14 ± 0.23	240 ± 30	0.82	0.41	7.61
7	8.8 ± 1.2	1.7 ± 0.3	340 ± 40	0.92	0.46	8.70
8	8.4 ± 1.2	1.7 ± 0.3	320 ± 40	0.94	0.47	8.97
9	9.7 ± 1.4	3.1 ± 0.5	370 ± 40	1.11	0.55	10.66
10	10.0 ± 1.4	4.2 ± 0.6	440 ± 50	1.01	0.51	9.42
11	8.9 ± 1.2	3.8 ± 0.5	400 ± 50	0.90	0.46	8.33
12	8.2 ± 1.2	4.3 ± 0.6	420 ± 50	0.94	0.46	8.61
13	10.2 ± 1.4	4.4 ± 0.6	470 ± 50	1.08	0.57	10.51
14	8.4 ± 1.2	2.9 ± 0.4	360 ± 40	0.89	0.44	8.19
15	8.8 ± 1.2	3.5 ± 0.5	390 ± 40	0.90	0.45	8.33
16	8.8 ± 1.2	3.0 ± 0.4	400 ± 50	0.90	0.46	8.60
17	8.8 ± 1.2	4.5 ± 0.6	420 ± 50	0.90	0.46	8.22
18	6.1 ± 0.9	0.50 ± 0.14	190 ± 20	0.71	0.35	6.59
19	7.8 ± 1.1	0.49 ± 0.16	200 ± 20	0.89	0.44	8.75
20	6.0 ± 0.8	1.16 ± 0.22	250 ± 30	0.80	0.41	7.91
21	5.1 ± 0.8	0.73 ± 0.18	200 ± 20	0.89	0.43	8,90
22	5.0 ± 0.8	*	200 ± 20	0.82	0.40	7.97
23	16.0 ± 2.0	*	150 ± 20	0.86	0.45	8.19
24	8.3 ± 1.1	*	200 ± 20	0.86	0.44	8.48
25	10.0 ± 1.3	*	170 ± 20	0.85	0.43	8.31
26	9.4 ± 1.2	*	170 ± 20	0.78	0.40	7.55
27	11.7 ± 1.5	0.48 ± 0.16	190 ± 20	0.93	0.47	9.11

*Asterisks indicate that the activity is below the minimum detectable level.

because of the influence of the salt pans, which are rich in ^{40}K. This is inside the world range (100–700) $Bq.kg^{-1}$[10], and below the value in ‘high radioactive background zones’, up to 1362 $Bq.kg^{-1}$ in Kerala, India[8].

With regard to ^{137}Cs, and considering that in the Bay of Cádiz there are neither nuclear power plants nor other direct sources, its concentration is only due to the fallout directly over the zone or over regions further away and brought in various ways to this zone.

The activity histogram also shows an accumulation of this radionuclide in the stations linked to the harbour activities, with some exceptions explained later. On the other hand, the concentration of ^{137}Cs in the reference stations is negligible, and in most of them is below the minimum detectable activity.

As was said before, in every place linked to harbour activities, three stations were considered: one at the point of maximum contamination due to ship loading and unloading operations (stations 1, 4, 7, 10, 13 and 17), and the other two up-stream and down-stream of each point. The ^{137}Cs histogram reveals that in the first stations relative activity maxima can be found, confirming that the increases in the ^{137}Cs concentration are directly linked to the spillages due to ship loading and unloading operations. As most of these materials are cements and clays, coming from opencast mining, they have incorporated the ^{137}Cs activity corresponding to the fallout in their original regions.

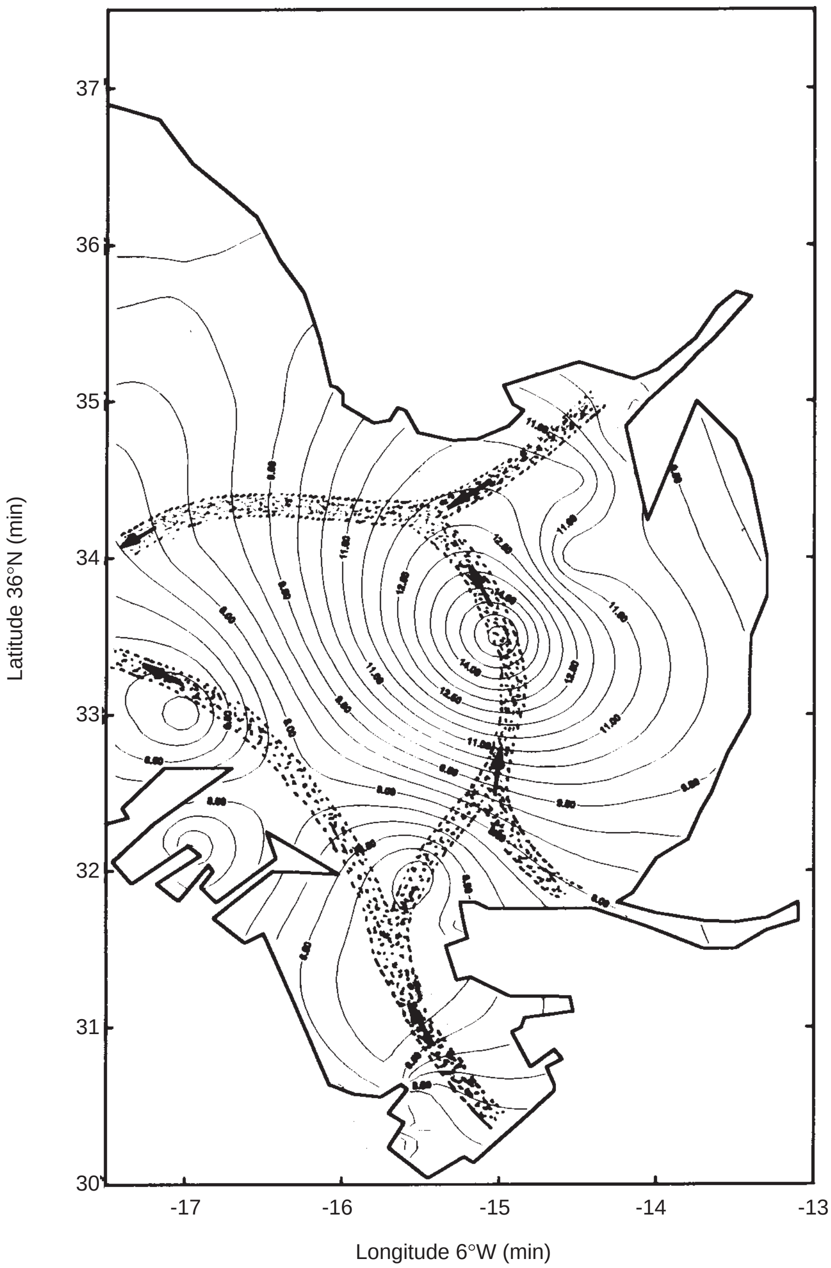

Figure 4. ^{226}Ra activity isolines map. The sea-bottom current pattern (ebb tide) has be superimposed.

The stations located in El Puerto de Santa Maria register the maximum ^{137}Cs activity because of the harbour traffic together with the contribution of the mouth of the Guadalete river which deposits the fallout coming from all its route. The minimum activities at stations 4 to 9 correspond to the aforementioned dredging of Cabezuela Quay and to the reduced traffic of materials at Cadiz Quay.

In both hemispheres the ^{137}Cs concentrations due to fallout are maximum at medium latitudes and minimum at the equator and the poles. In seabed sediments coming from all the Spanish Mediterranean Platform, activities of (0.5 ± 0.3) Bq.kg^{-1}[(11)] have been measured, similar to the values found in the middle of the Bay of Cádiz. For comparison, on the western coast of the Irish Sea, activities of two orders of magnitude greater than the ones found in Spain have been measured.

It is possible to do a more detailed study of the distribution of radionuclides in the zone, building a map of activity isolines based on the grid of stations used. An interpolation method allows us to calculate activity values in a regularly distributed grid, to represent the corresponding activity fields.

This process has been done employing the Krigging interpolation method and the results are shown in Figures 4, 5 and 6, where the sea-bottom current pattern

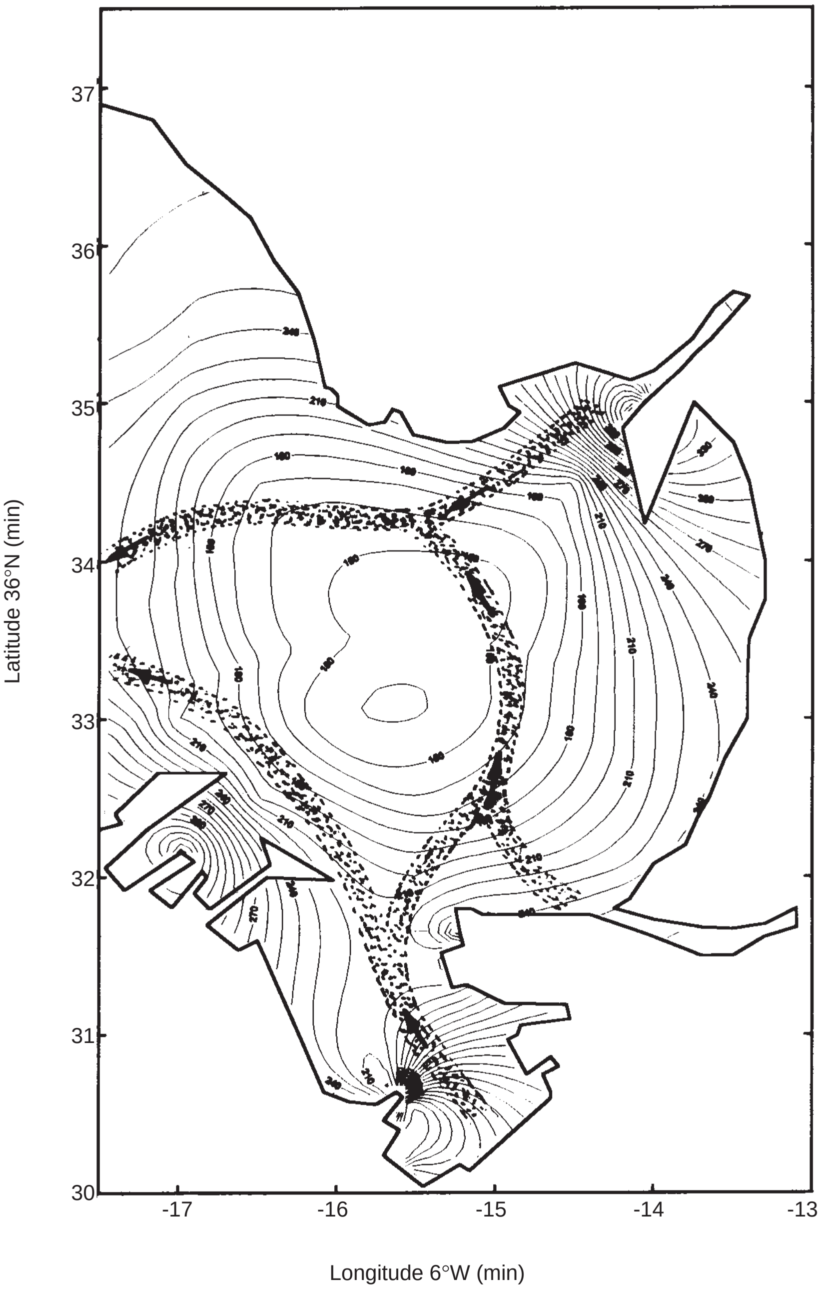

Figure 5. ^{40}K activity isolines map. The sea-bottom current pattern (ebb tide) has been superimposed.

has been superimposed[7]: this knowledge will be very important in interpreting some of the results found in this study.

As can be seen from Figure 4 the ^{226}Ra distribution in the zone is governed by the marine dynamics, represented through the orientation of the sea-bottom currents, as these currents coincide with the gradients of the radionuclide activity field. The map also shows the maximum activity round station 23, for which an explanation has already been given. In addition, both the activity values and the relative orientation of isolines and currents make clear that the contribution from the Guadalete river is much more important than the one from the San Pedro river. These results are in line with the fact that ^{226}Ra is a natural radionuclide coming from ^{238}U and with a long residence time in the region, so that it has been incorporated in the sediments due to slow and gradual erosion and transport.

Although it is not the aim of this study, it can be emphasized that the distribution of long residence time radionuclides in seabed sediments could constitute an indirect method of estimating the granulometry of the zone. So, for a given compostion, equal density of activity isolines is a consequence of a similar grain size[12,13].

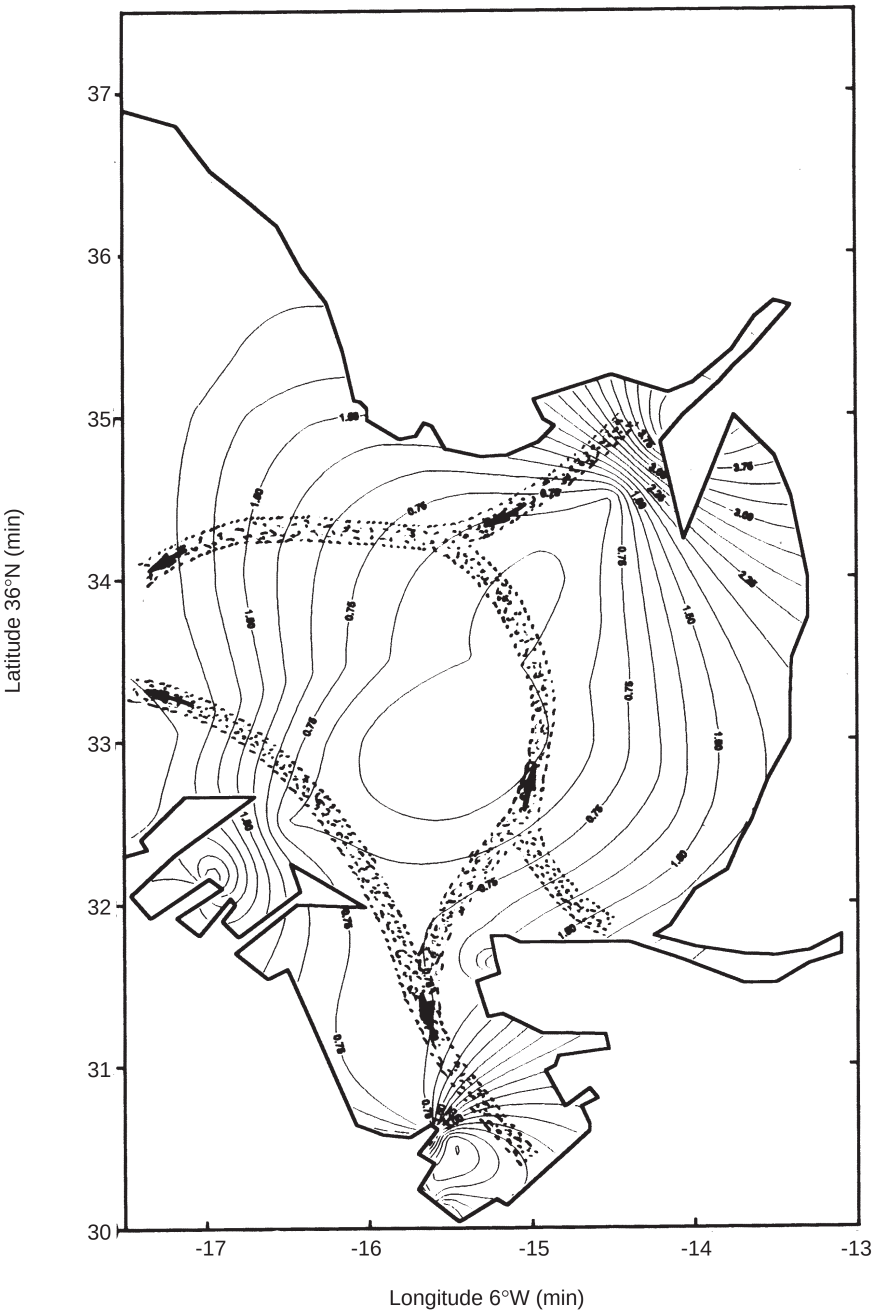

Figure 6. ^{137}Cs activity isolines map. The sea-bottom current pattern (ebb tide) has been superimposed.

The maps of activity isolines for ^{137}Cs and ^{40}K have some analogies, as in both cases two access canals are the Guadalete river, at the north-east, and the contact with the Interior Bay, at the south. With regard to the ^{40}K activity, the result was predictable, as both canals bring materials coming from the salt pans and therefore rich in ^{40}K. It can be observed that, as a consequence of the currents, a stagnation zone is found in the east of the Bay where an increase in the radionuclides concentration as well as in the salinity are found. Also in Ribera, Poniente and Cádiz Quays the detected activity increases because the harbour structures operated like walls opposite to currents, so that the deposits to the windward are favoured. Stations 18 and 19, corresponding to Puntales, are subject more directly to the sea-bottom currents, and this can explain the minimum values for ^{40}K and ^{137}Cs activities. In both cases, the minimum activities detected in the centre of the Bay reflect the non-indigenous character of both radionuclides in the region.

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REFERENCES

1. Barragán, J. M. *Estudios para la Ordenación, Planificación y Gestión Integradas de las Zonas Húmedas de la Baha de Cádiz*. Barcelona: Oikos-Tau S.L. (1996).
2. Barragán, J. M. *Puerto, Ciudad y Espacio Litoral en la Bahia de Cádiz*. (Salamanca: Varona) ISBN 84-606-2663-6 (1995).
3. Ministerio de Obras Públicas y Transportes, Puertos del Estado. *Nemoria Anual* (1993).
4. Consejeŕa de Economía y Hacieda de la Junta de Andaluća. *Memoria e Inventarios de las Actividades Extractivas de la Provincia de Cádiz*. Informe elaborado por la empresa consultora G3 (1991).
5. Ramos-Lerate, I., Barrera, M., Ligero, R. A. and Casas-Ruiz., M. *A New Method for Gamma-Efficiency Calibration of Voluminal Samples in Cylindrical Geometry*. J. Environ. Radioact. **38**, 47–57 (1998).
6. Ramos-Lerate, I., Barrera, M., Ligero, R. A. and Casas-Ruiz., M. *A New Summing-Correction Method for Gamma-Efficiency Calibration with Multi-Gamma-Ray Radionuclides*. Nucl. Instrum. Meth. A**395**, 202–206 (1997).
7. Parrado Román, J. M., Gutiérrez Mas, J. M. and Achab, M. *Determinación de Direcciones de Corrientes Mediante el Análisis de "Formas de Fondo" en la Baha de Cádiz*. Geogacta **20**, 114–117 (1996).
8. Narayana, Y., Radhakrishna, A. P., Somashekarappa, H. M., Karunakara, N., Balakrishna, K. M. and Siddappa, K. *Distribution of some Natural and Artificial Radionuclides in the Environment of Coastal Karnataka of South India*. J. Environ. Radioact. **28**, 113–139 (1995).
9. Malaca, A., Repetti, M. and Gazzola, A. *A Radiological Investigation of the Monazite Sands of the Atlantic Brazilian Shore*. Nucl. Geophys. **9**, 453–459 (1995).
10. UNSCEAR. *United Nations Scientific Committee on the Effects of Atomic Radiation. Report to the General Assembly* (New York: United Nations) (1982).
11. Molero, J. *Comportamiento y Distribución de los Radionúclidos de Vida Larga en Ecosistemas marinos, Estudio relativo a Radiocesio y a los Transuránidos Plutonio y Americio en el Entorno Ambienital de la Costa Mediterránea Española*. PhD thesis, Universitat Autonoma de Barcelona (1992).
12. He, Q. and Waling, D. E. *Interpreting Particle Size Effects in the Adsoprtion of ^{137}Cs and Unsupported ^{210}Pb by Mineral Soils and Sediments* J. Environ. Radioact. **30**, 117–137 (1996).
13. Meijer, R. J., Tánczos, I. C. and Stapel, C. *Radiometry as a Technique for Use in Coastal Research*. In: Geology of Siliciclastic Shelf Seas, Geological Society Special Publication **117**, pp. 289–297 (1996).