Available online at www.sciencedirect.com
SCIENCE DIRECT®
Environment International 30 (2004) 99–104
ENVIRONMENT INTERNATIONAL
www.elsevier.com/locate/envint

Environmental impact of unleaded gasolines in the bay of Cádiz (Spain)

R.A. Ligero[a,*], M. Casas-Ruiz[a], M. Barrera[a], F. López-Aguayo[b], D. Sales[c], D. García[d]

[a] *Departamento de Física Aplicada, Centro Andaluz Superior de Estudios Marinos, Universidad de Cádiz. Campus Rio San Pedro, 11510, Puerto Real, Cádiz, Spain*
[b] *Departamento de Geología, CASEM. Universidad de Cádiz. 11510, Puerto Real, Cádiz, Spain*
[c] *Departamento de Tecnología del Medio Ambiente, CASEM. Universidad de Cádiz. 11510, Puerto Real, Cádiz, Spain*
[d] *Departamento Ciencias y Técnicas de la Navegación, CASEM. Universidad de Cádiz. 11510, Puerto Real, Cádiz, Spain*

Received 12 April 2003; accepted 27 May 2003

Abstract

Given the strategic situation of the José León de Carranza bridge, which spans the Bay of Cádiz (in the SW of Spain) and carries very heavy motor traffic, together with knowledge of the currents and tidal flows in the zone, we have used a technique of radioactive dating of sediments to study the temporal evolution presented by contamination from lead in the sediment column.

This has allowed us to observe the environmental impact, in terms of the concentration of Pb in the sea bed sediments, that has been produced in the zone by the introduction of unleaded gasolines as substitutes for traditional automobile fuels that employ organic forms of tetra methyl lead as an antidetonant agent in the fuel.

Keywords: Environmental impact; Lead pollution; Dating; Sediment column; Radionuclides; Motor traffic

1. Introduction

The city of Cádiz, a provincial capital, is situated at the tip of an isthmus, in the SW of the Iberian Peninsula. It is the administrative centre of a relatively large region containing several important nuclei of population, such as Rota, Sanlúcar de Barrameda, Jerez de la Frontera, Puerto de Santa María, Puerto Real, San Fernando and Chiclana de la Frontera, with a total of some 800,000 inhabitants. During the months of summer, this number is duplicated, generating an enormous amount of road traffic between the capital and these nearby towns (Fig. 1).

In 1969, the José León of Carranza bridge linking the city of Cádiz with the municipal town of Puerto Real was opened, with the aim of shortening the communication by road, by avoiding the need to drive around the perimeter of the entire Bay, as was previously required. The bridge is situated on the Puntales strait, and spans the Bay, effectively dividing it in two parts, the so-called Outer Bay (80 km^2), directly open to the Atlantic, and the Inner Bay (13 km^2) that is joined to the Atlantic further to the south, through intertidal channels and salt marshes of important ecological value. Since then, the bridge has carried the greater part of the local vehicle traffic and has become the main communication artery in the region. Therefore, it can also be considered a source of contamination from automobile emissions, and in particular of lead contamination, which will be the subject of this study.

Together with the rest of the solid-contaminating elements emitted, lead falls onto the surrounding seawater, and after a short residence time in the liquid lamina, subjected to the hydrodynamic effects characteristic of the Bay, it is finally deposited in the submarine sediments that thus become the destination and reservoir of this contamination.

The introduction of the unleaded gasoline is seen as an important event from environmental quality, as has happened in other places of the planet (Simmons and Knap, 1993). The assessment of the environmental impact in the described area is the purpose of this work.

The development of radiological mapping (Ramos-Lerate et al., 1998) and knowledge of the principal currents in

* Corresponding author. Tel.: +34-956-016068; fax: +34-956-016079.
E-mail address: rufino.ligero@uca.es (R.A. Ligero).

0160-4120/$ - see front matter
doi:10.1016/S0160-4120(03)00152-1

Fig. 1. Bay of Cádiz.

the bay (Parrado Román et al., 1996) enables the localisation and study of zones of preferential accumulation where concentrations of lead have been gradually deposited over the course of time.

2. Marine dynamic

The zone of study, relatively sheltered from the wave action, both deep and wind-generated, originating from the Atlantic Ocean, is dominated by tidal currents in respect of sediment transportation. The tides are of the semi-diurnal type, with two high and two low tides every day, with a small time dysphase and a certain asymmetric character. Waves of tidal origin are propagated towards the east, with a gradual decrease of the tidal range (the dysphase between Tarifa and Ayamonte is of 35 min and the maximum amplitudes of the waves are 1.58 and 3.70 m, respectively).

Recent studies (Alvarez et al., 1999; Alvarez, 2000), using a bidimensional numerical model, have demonstrated that dissipative effects and the influence of contours (basically those of the Puntales strait), cause the propagation of the tidal wave to be retarded by some 12 min between the Outer and Inner Bay. The tidal currents produce a transport of materials during the flow (incoming) and the ebb (outgoing) tides that have been determined and are illustrated in Fig. 2.

In the Inner Bay, from the Sancti Petri Creek (close to San Fernando) up to the Puntales strait, and following the navigation channel towards the naval dockyards of La Carraca, there is a dominant current that, in its final stretch, runs parallel to the bridge and gives rise to a broad eddy stream. This stream, on the one hand, feeds the body of water flowing towards the Outer Bay, and on the other hand, diverts the bulk of the sediments in suspension towards the southwestern zone of the Inner Bay. Since the Inner Bay is characterised by a reduced hydrodynamic activity and its sediments are of the clay type, ideal conditions are produced for the matter in suspension and transported by the water to be deposited, gradually and progressively, on the seabed and to be thus incorporated into the sedimentary matrix. Any of the deposits formed in this way can be considered a faithful witness of the lead

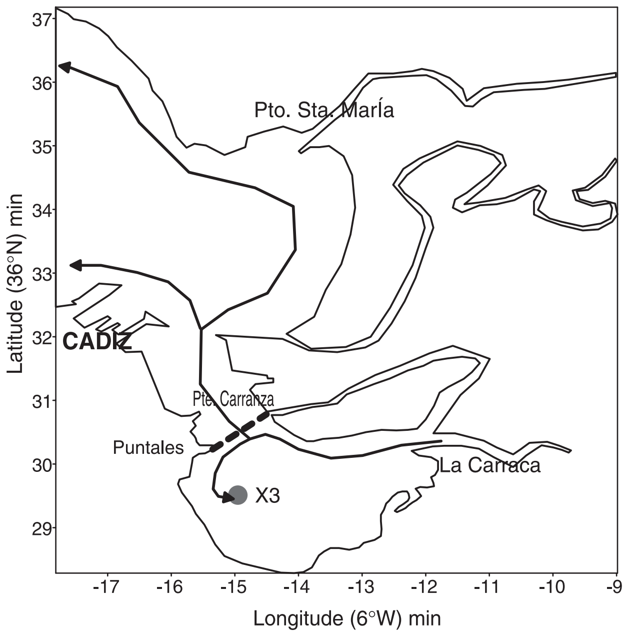

Fig. 2. Main tidal streams and sedimentary samples station (X3).

contamination that has taken place in the region in recent decades.

3. Experimental

Previous works (Ramos-Lerate et al., 1998; Ligero et al., 2001) has demonstrated the utility of radioactive measurements in sediments in order to establish a net of sampling stations for pollution control. It is possible to do a detailed study of the distribution of radionuclides in the zone, building a map of activity isolines based on the grid of stations used. The Krigging interpolation method (Burgess and Webster, 1980; Davies, 1986; Cressie, 1991) allows us to calculate activity values in a regularly distributed grid, to represent the corresponding activity field by contour lines.

Accordingly and utilising radiological mapping of the region, the sedimentation zone X3, indicated in Fig. 2, was identified. It is important to state that, in studies of contamination by heavy metals (Gomez-Parra et al., 1984), anomalous high levels in the concentrations of Pb had already been found, and it was suggested that these anomalies could to be due to contamination originating from automobiles.

The procedure used was the extraction, using a Lanesky type vibrator system, of several sediment cores; these were contained in aluminium tubes of 60 mm diameter and up to 1 m length. This core length was considered a sufficient depth for this purpose, taking account of the sedimentation rates characteristic of this region. The cores were kept at − 5 °C, so as to freeze the interstitial water in each stratum of the column, since data on this water is relevant to the study. Later, the columns were sectioned in slices of 2-cm thickness and subtracting dry weight to moist weight, the porosity of each slice was measured. The representation of the moisture content with respect to depth provides an indication of the suitability of the sampling station chosen: if this parameter decreases steadily with the depth, until a practically constant value is reached, and no sharp singularities are presented, it can be stated that the process of sedimentation undergone by the column has not been disturbed by accidental phenomena and that the column is representative of the sedimentation processes occurring in the zone. This criterion was utilised to select the particular column to be submitted for analysis.

The sediment samples obtained from the column selected were milled using an agate mortar, to a grain size of less than 500 μm to ensure their homogeneity. By a gravimetric method, the apparent density was determined, which is necessary for obtaining the correct efficiency curve in gamma spectrometry, the milled samples were separated into three aliquots: first to determine the organic carbon content, second to determine the content of Pb, and the third was deposited in a cylindrical receptacle, where it remained sealed for a minimum of 1 month (in order to ensure the secular equilibrium between the ^{226}Ra and the ^{222}Rn) before proceeding to the stage of analysis by gamma spectrometry.

The gamma emitters ^{137}Cs, ^{40}K and ^{226}Ra measurements were performed with a coaxial detector HPGe of 90 cm^3 active volume, with a relative efficiency of 20% (with respect to a NaI(Tl) detector 3×3 in.) and a resolution of 2 keV, for 1332 keV. This detector is sensitive in the energetic range 50 keV–10 MeV. The samples were packed in cylindrical containers of 4.6-cm diameter. The determination of the ^{40}K has been performed through the detection of the 1461 keV and the ^{137}Cs from the 662 keV photon and intensity 85%, emitted by its descendent in secular equilibrium, ^{137}Ba^{m}. The measurement of the ^{226}Ra has been performed by the detection of the 352 keV photon, and intensity 35%, emitted by ^{214}Pb, which is in secular equilibrium with ^{222}Rn and consequently with ^{226}Ra. The measurement system uses a 10-cm thick lead shielding, with interior 1-mm plates made of Cu and Cd, to minimise the external radiation. It has been necessary to apply interference corrections for the 352 keV photon (^{226}Ra), but not for the 662 keV photon (^{137}Cs). The measurement of the environmental radiation background has been performed periodically. The efficiency of the equipment, which is a function of the gamma radiation energy, the sample height and the sediment density (Ramos-Lerate et al., 1998; Barrera et al., 1999) was calibrated. To obtain meaningful statistics in the measurements, the time of spectrometry for each sample was 72 h.

The content of organic carbon was measured using the technique described by Gaudette et al. (1974), modified by El-Rayis (1985), which consists of the oxidation of the sediment sample with potassium dichromate in a strongly acid medium at a temperature of 135 °C. The organic carbon content is obtained by tritation of the ferrous ammonium sulphate from the surplus dichromate remaining after the oxidation. The percentage of organic carbon detected by this method depends on the type of sediment, and is situated at between 80% and 95%. In this technique, the elemental carbon remains unaltered and the carbonates do not present interference problems.

The dating of the sediments is performed employing the profile of the radioelement ^{137}Cs originating from the radioactive fallout that originally fell after the nuclear tests and the accident of the Chernobyl nuclear power station. This dating specifically involves locating the layers of sediment presenting maximum activity of this radioelement, and that correspond to the events producing its maximum concentration in the natural environment generally. These events occurred in 1963 (massive testing of nuclear weapons carried out by the great powers) and in 1986 (the Chernobyl accident). However, the high mobility of ^{137}Cs in the sediment column, as a consequence of molecular diffusion in the interstitial water and of bioturbation caused by benthic organisms, generates a continuous profile in which the maximum levels are masked or disappear. Therefore, a model is required that interprets the relevant physical phenomena in the incorporation and subsequent evolution of the radioelement in the column. The model employed to describe this profile in the sediments of the Bay of Cádiz was developed in a previous study (Barrera, 2002). This model sets out the corresponding transport equation; its resolution by means of finite differences, and the fit with the experimental profile, provides the rate of sedimentation, and from this, the chronology of the successive sediment layers is derived. Although the method is only strictly applicable to the more superficial layers (with ages of around 60 years), under the hypothesis of a constant rate of sedimentation (applicable to the zone under study), it is possible to extrapolate to longer periods of time.

The measurement of the concentrations of Pb was performed by Atomic Absorption Flame Spectrophotometer (FAAS) using a UNICAM mod. 939 instrument, with a slotted tube atom trap (STAT), acetylene-air flame, incident radiation with a wavelength of 217.0 nm, a slit of 0.5 nm and a limit of detection of 0.04 mg/l. Before the acid digestion of the sediment samples, particles less than 200 μm were separated with a nylon fibre sieve. Following digestion in a strongly acidic medium (Sturgeon et al., 1982; Conde, 1993), lead concentration levels were determined.

4. Results and discussion

Table 1 gives the values obtained for the porosity (*w*,%), organic carbon (oc, %), lead (Pb, mg/kg) and attributed date of sedimentation, for the different depths (*z*, cm) of the samples analysed.

From this, we can observe that the limit of dating by the method utilized, which is of the order of 125 years, is reached at a depth of 43 cm. Although not relevant for the study conducted, the values of the other parameters measured at greater depths have been listed, so as to provide a better perspective of the behaviour of porosity and organic carbon content in the sediment column. In Fig. 3, the porosity against depth is represented, and we can observe that this shows a behaviour in accordance with what one would expect in a zone of regular sedimentation, free from accidental interactions and other factors outside the process of natural sedimentation (Establier et al., 1984; Jahnke et al., 1986; Santschi et al., 2001). This observed behaviour confirms the suitability of the particular sediment column chosen for this study, as referred to in the preceding section.

Table 1
Values obtained for porosity (*w*), organic content (oc), lead concentration (Pb_{st}) and corresponding date for each depth

z (cm)	*w* (%)	oc (%)	Pb_{st} (ppm)	Date
1	72.67	4.53	35.29	1996
3	69.05	4.72	44.89	1993
5	69.66	4.93	46.95	1990
7	66.61	5.05	44.54	1987
9	64.72	4.94	43.12	1984
11	61.51	4.72	–	1980
13	57.28	4.54	40.00	1975
15	55.53	4.42	–	1970
17	54.37	4.32	–	1965
19	55.13	4.2	29.27	1960
21	54.76	4.01	–	1954
23	56.42	3.93	–	1949
25	52.18	3.62	19.62	1944
27	50.53	3.41	–	1938
29	45.32	3.25	–	1932
31	41.81	3.01	18.50	1924
33	44.54	2.8	–	1916
35	44.93	2.76	–	1910
37	44.98	2.69	21.37	1903
39	44.82	2.75	–	1896
41	46.45	2.77	–	1890
43	46.4	2.72	18.24	1884
45	43.46	2.53		
47	39.56	2.33		
49	37.67	2.13		
51	37.56	2.14		
53	39.87	2.08		
55	40.03	2.05		
57	40.71	2.07		

In the same figure, the content of organic carbon measured in the column is represented; this shows behaviour analogous to that of the moisture content of the strata, in other words, it tends to decrease progressively until a noticeably constant value is reached. This is intimately related to the concentrations of lead that follow the progressive degradation of the organic matter produced by the action of the benthic microorganisms.

Fig. 4 shows the concentrations determined for the lead, and in this figure, we can appreciate the following:

- The presence of lead in the sediments is due not only to the contamination originating from automobile engines because appreciable quantities of this element are

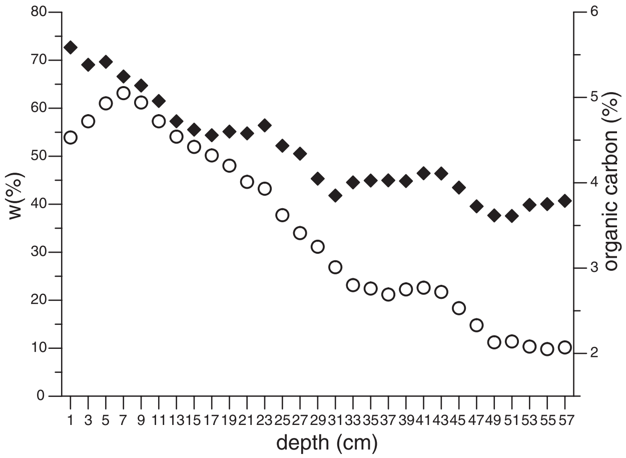

Fig. 3. Porosity (◆) and organic carbon content (○) versus depth in the sedimentary column.

recorded in strata corresponding to the end of the 19th and beginning of the 20th centuries, forming a base level of lead concentration in the sediments.

- From the 1940s up to well into the 1980s, a significant and progressive increase of the lead concentration in the bay was produced, and not all of this can be imputed to motor traffic, since the use of the automobile in Spain did not become popular until the 1960s, as a consequence of the relatively slow rate of economic development of the country.
- At the end of the 1980s, a sudden decrease is recorded in the concentration of lead in the submarine medium. Considering that the bridge over the bay was opened in 1969, and that unleaded gasolines were introduced from 1986, the decrease of lead contamination observed seems likely, in principle, to be associated with the introduction of unleaded gasolines.

To confirm this last hypothesis, data have been obtained of the consumption of such fuels provided by the Spanish Organisations Association of Petroleum Refining Companies (ASERPETROL), Association of Petroleum Operators

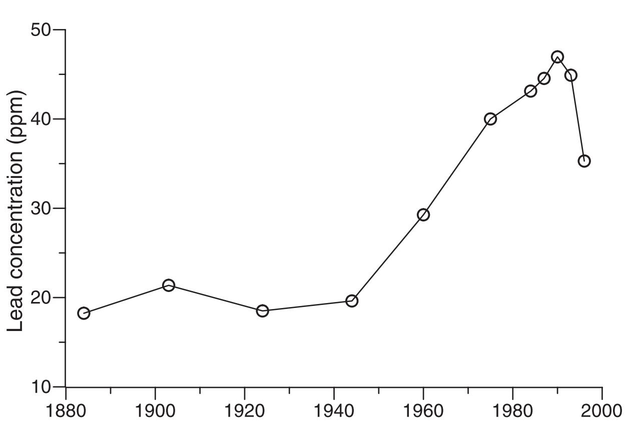

Fig. 4. Time evolution of the Pb pollution in the sediment column.

Table 2
Annual consumption of leaded gasolines

Year	Consumption (Mkg)
1987	6853
1988	7361
1989	7845
1990	8215
1991	7992
1992	8204
1993	7649
1994	7067
1995	6514
1996	5947
1997	5318
1998	4717
1999	4097
2000	3108

(AOP) and Corporation of Strategic Reserves of Petroliferous Products (CORES). According to these sources, the marketing of unleaded gasolines first took place in 1986, and Table 2 presents the evolution over time of the consumption of fuels containing lead, up to the year 2000, although the experimental data in this study on sediment only run to the year 1996. Although such data do not allow precise quantitative conclusions to be drawn, they can be considered representative; they are the most reliable that it is possible to obtain, and enable a close enough approximation to be made for some qualitative conclusions on this subject.

Thus, in Fig. 5, the sales curve of gasolines with lead from 1987 to 1999 and the concentrations of Pb determined for the sediment strata corresponding to the same dates are superimposed. To allow comparison, both graphs have been normalised to their respective amplitudes, and it can be appreciated that the trend of the concentration of Pb is concordant with the trend of annual sales of gasolines with lead. Furthermore, the deviation between the two data series from 1987 to 1990 reflects the progressive rejuvenation of Spain's total stock of vehicles and the substitution of older vehicles by others adapted to use the new unleaded fuel.

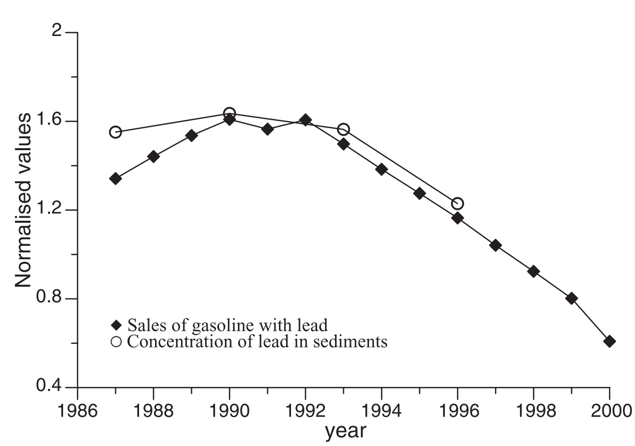

Fig. 5. Evolution of sales of gasoline with lead, and concentration of lead in littoral sediments.

With this result, it is not reckless to state that the introduction of the unleaded gasolines is correcting the impact of contamination by Pb due to the motor traffic in the zone, given that the current levels of contamination have dropped back to those occurring in the 1960s, when the incidence of the internal combustion engine in environmental contamination began to be noticeable.

Extrapolating these results, it can reasonably be expected that the total disappearance of gasolines with lead may lead to the return to base level values (some 20 ppm) characteristic of the beginning of the 20th century, when insignificant amounts of gasolines with lead were used in internal combustion engines.

5. Conclusions

The José León de Carranza bridge, spanning the Bay of Cádiz and carrying a huge volume of motor traffic, is a focal point of contamination from the residual products of the internal combustion engine that are deposited on the seabed under the influence of the prevailing hydrodynamics of the Bay.

The radio nuclide techniques employed, both for locating the sedimentary deposits and for the dating by layers of the sediment column, have once more been shown to be very useful in oceanographic and environmental disciplines, providing greater accuracy and a notable saving of resources and time, compared with other traditional techniques.

The sediment deposits on the seabed, located with radionuclide techniques and on the basis of knowledge of the local currents, are ideal for providing evidence of the temporal evolution of contamination and for evaluating its impact in this region.

Lead contamination in the Bay of Cádiz has been controlled fundamentally by the use of gasolines that contained organic compounds of tetra methyl lead as an anti-knock agent.

The introduction of unleaded gasolines has notably diminished the concentration of this metal in sediment, and its trend appears to be towards the total recovery of the previous levels of lead concentration, before the intensive motor traffic pollution in the bay.

Acknowledgements

This study has been possible through the financing obtained from the Ministerio de Ciencia y Tecnología (Project MAR2000-1261) and the Agencia del Medio Ambiente de la Junta de Andalucía (Project OT-126/96).

References

Alvarez O. Simulación numérica de la dinámica de marea en la Bahía de Cádiz: análisis de los constituyentes principales, interacción marea-brisa e influencia del sedimento en suspensión. PhD Thesis. Universidad de Cádiz; 2000.

Alvarez O, Izquierdo A, Tejedor B, Mañanes R, Tejedor L, Kagan BA. The influence of sediment load on tidal dynamics, a case study: Cádiz Bay. Estuar Coast Shelf Sci 1999;48:439–50.

Barrera I. Aplicaciones de técnicas de espectrometría nuclear a sedimentos en la Bahía de Cádiz. PhD Thesis. Universidad de Cádiz; 2002.

Barrera M, Ramos-Lerate I, Ligero R-A, Casas-Ruiz M. Optimization of sample height in cylindrical geometry for gamma spectrometry measurements. Nucl Instr Meth Phys Res A 1999;421:163–75.

Burgess TM, Webster R. Optimal interpolation and isarithmic mapping of soil properties. I. J Soil Sci 1980;31:315–31.

Conde B. Metales pesados en los sedimentos de la zona intermareal de la Ría del Tinto. Thesis Doctoral. Universidad de Sevilla; 1993.

Cressie NAC. Statistics for spatial data. New York: Wiley; 1991.

Davies JC. Statistic and data analysis in geology. New York: Wiley; 1986.

El-Rayis OA. Re-assessment of the titration method for determination of organic carbon in recent sediments. Rapp Comm Int Mer Médit 1985; 29:45–7.

Establier R, Blasco J, Gómez A, Escolar D. Materia orgánica en los sedimentos de la bahía de Cádiz y sus zonas de marismas y salinas. Inv Pesq 1984;48(2):285–301.

Gaudette HE, Flight WR, Toner L, Folger D. An inexpensive titration method for the determination of organic carbon in recent sediments. J Sediment Petrol 1974;44:249–53.

Gomez-Parra A, Establier R, Escolar D. Heavy metals in recent sediments from the Bay of Cadiz, Spain. Mar Pollut Bull 1984;15:307–10.

Jahnke RA, Steven R, Emerson SR, Cochran JK, Hirschberg DJ. Fine scale distributions of porosity and particulate excess ^{210}Pb, organic carbon and $CaCO_3$ in surface sediments of the deep equatorial Pacific. Earth Planet Sci Lett 1986;77:59–69.

Ligero R-A, Ramos-Lerate I, Barrera M, Casas-Ruiz M. Relationships between seabed radionuclide activities and some sedimentological variables. J Environ Radioact 2001;57:7–19.

Parrado Román JM, Gutiérrez-Mas JM, Achab M. Determinación de direcciones de corrientes marinas mediante el análisis de "formas de fondo" en la bahía de Cádiz. Geogacta 1996;20:114–7.

Ramos-Lerate I, Barrera M, Ligero R-A, Casas-Ruiz M. Radionuclides in the environment of the Bay of Cadiz. Rad Prot Dosimetry 1998; 75(1–4):41–8.

Santschi PH, Laodong G, Liang-Saw W. Box coring artifacts in sediments affected by a waste water outfall. Mar Pollut Bull 2001;42(4):267–72.

Simmons JAK, Knap AH. The impact of leaded to unleaded gasoline conversion on the oceanic island of Bermuda. Atmos Environ, A Gen Topics 1993;27(11):1729–33.

Sturgeon RE, Desaulniers JAH, Berman SS, Russell DS. Determination of trace metals in estuarine sediments by graphite-furnace atomic absorption spectrometry. Anal Chim Acta 1982;134:283–91.