

²¹⁰Pb Distribution in Riverwaters and Sediments Near Phosphate Fertilizer Factories

A. MARTÍNEZ-AGUIRRE and M. GARCÍA-LEÓN
Facultad de Física, Universidad de Sevilla, Apdo 1065,
41080 Sevilla, Spain

Two fertilizer factories operate at the estuary formed by the Odiel and Tinto rivers in Southwestern Spain. In previous work the authors have shown that such operation enhances the natural radionuclide background of the sea. Thus, fairly high levels of U, Th and Ra-isotopes were found in water and sediment samples taken from the estuary. In this paper, we have extended the study to investigate the presence of ²¹⁰Pb in the dissolved aqueous phase of the river and in bottom sediments. Significant enhancement of ²¹⁰Pb concentrations have been detected confirming the previously reported results.

Introduction

For geological reasons phosphatic rock, compared to other rocks, contains large amounts of U, ranging from 50 to 300 ppm, depending on the origin. As a consequence, the operation of phosphate fertilizer factories contributes to the enhancement of the natural radiation background, at least, in their close environment. This was demonstrated recently (Martínez-Aguirre and García-León, 1991; Martínez-Aguirre *et al.*, 1994) for two factories located at the estuary formed by the Odiel and Tinto rivers in Southwestern Spain (see Fig. 1). Significantly high levels of U-, Th- and Ra-isotopes were found in solution, in suspended matter and in sediments in both rivers. This was attributed to the activities of the factories which directly release their wastes into the Odiel river or store them in uncovered piles near the Tinto river channel (see Fig. 1).

In this work we have extended these studies to ²¹⁰Pb, so as to investigate the environmental relevance of this radionuclide in this kind of scenario (Ivanovich and Harmon, 1982).

Furthermore, we try to contribute a little more to the knowledge of the environmental behaviour of ²¹⁰Pb, specially in estuaries where experimental observations are scarce.

Samples and Experimental Methods

Samples of water and bottom sediments were taken from the ten stations in the estuary, which are displayed in Fig. 1. The sampling campaigns were performed in July 1988 and 1990 (dry season) and in February 1991 (wet season). The suspended matter was separated as soon as possible from the water sample by filtration through Nuclepore filters 0.45 µm pore size. The remaining aqueous phase was acidified to pH ~ 2 with concentrated HNO₃ and stored until analysed. Additional information was also gathered for the sampling campaigns of 1990 and 1991, such as the temperature, pH and salinity of the water samples. Bottom sedi-

ments were separated in four different grain size fractions and the organic content was determined in each sediment sample. For separation of the fractions, three different sieves with hole sizes of 1483, 355 and 62.5 µm, respectively, were used in a vertical column. Known amounts of sediment were introduced in distilled water and stirred before passing through the system. Each fraction was collected and weighed wet. Then, they were dried and powdered for analysis.

²¹⁰Pb measurements were performed at the end of 1993, through its daughter ²¹⁰Po. This time interval, between sampling and analysis, was considered to be long enough to allow unsupported ²¹⁰Po disappear from the sample and to let supported ²¹⁰Po grow into secular equilibrium. Water samples were evaporated to a small volume and transferred and evaporated to dryness in polyethylene bakets. There, they were digested with nitric acid and aqua regia and finally, the residue was redissolved in 8 M HNO₃. Sediment samples were also acid digested with HNO₃ and aqua regia and redissolved in 8 M HNO₃. Previous to the above procedures, the samples (water and sediment fractions) were spiked with well known amounts of ²⁰⁸Po for recovery determinations.

A solvent extraction technique with TBP (tributylphosphate) was used to extract ²¹⁰Po from the HNO₃ solution. The final solution was self-deposited onto silver planchets 2.2 cm in diameter. The method is fully described in Morón *et al.*, 1988. ²¹⁰Po was, finally determined by α-spectrometry with ion-implanted Si detector.

Results and Discussion

To simplify the discussion we will present separately the results for water and sediment samples. Samples O represent those taken in the Odiel river, T those from the Tinto river and OT from the confluence of both rivers. The index represents the sampling station along each river (see Fig. 1).

Water

In Table 1 the results obtained for ²¹⁰Pb in water samples collected during the low tide in 1988 (dry season), 1990 (dry season) and 1991 (wet season) are presented.

For the Odiel river, the distribution pattern of ²¹⁰Pb radioactive concentration clearly reveals the existence of a local source of radioactivity, obviously originating from the phosphoric acid industrial complex. This has been already shown for other natural radionuclides (Martínez-Aguirre and García-León, 1991 and Martínez-Aguirre *et al.*, 1994). The additional relative maxima at location O6 could be related to tidal displacements of the radioactive bag emitted from the source (Periáñez and García-León, 1993 and Periáñez *et al.*, 1994).

The height of the activity peaks at stations O3-O4 changes depending on the sampling campaign. This is related to the time distribution pattern of inputs from the source term. It also could explain the fact that levels during the summer 1990 are systematically higher than in winter 1991. However, the influence of a systematic lower water flow during summer, which helps to enhance the levels, should not be neglected.

As for the Tinto river it can be said that the distribution pattern is also similar for the three sampling campaigns. The differences among the radioactive concentrations are not so acute as in the case of the Odiel river, but it is clear that higher activities are always found at station T1. This station

is located close to an artificial stream (see Fig. 1) that comes from the phosphogypsum piles and, in fact, crosses it and can transport radioactivity from the piles to the river. It is interesting also to note the similarity of radioactive concentrations at stations O6 and T3. It could support the idea of tidal intrusion of the Odiel river waters into the Tinto channel. That is, the source located at the Odiel river could provide the Tinto river with radioactive material as well.

Levels of radioactivity in both rivers are always well above those accepted as general background in non perturbed rivers (Koster *et al.*, 1991). Consequently, it seems clear that the Odiel and Tinto riverwaters are clearly enhanced by the phosphoric acid production process.

In Table 1, the $^{210}\text{Pb}/^{226}\text{Ra}$ activity ratios for both rivers and the sampling campaigns of 1990 and 1991 are presented. The ^{226}Ra radioactive concentrations were taken from Periañez and Garcia-León, 1993. These authors measured

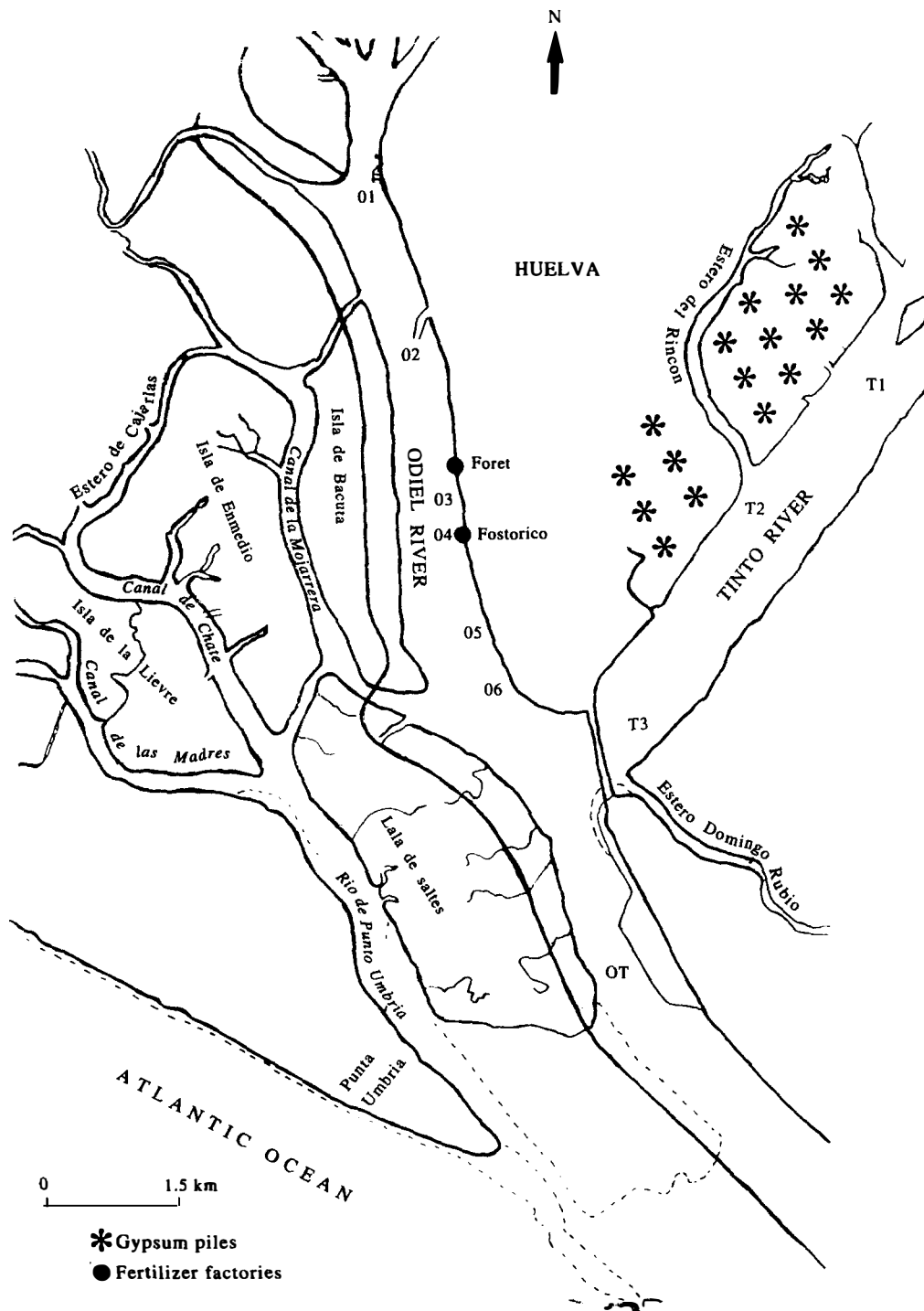


Fig. 1. Map of the Odiel and Tinto river channels. Sampling stations along both river channel, fertilizer factories and phosphogypsum storage area emplacements are shown.

Table 1. ^{210}Pb in mBq/L in water taken along the Odiel and Tinto rivers in different sampling campaigns. $^{210}\text{Pb}/^{226}\text{Ra}$ activity ratios for the 1990 and 1991 campaigns are also presented. ^{226}Ra data were taken from Periañez and García-León, 1993

Code	1988	1990		1991	
	^{210}Pb	^{210}Pb	$^{210}\text{Pb}/^{226}\text{Ra}$	^{210}Pb	$^{210}\text{Pb}/^{226}\text{Ra}$
O1	30.1 ± 2.3	7.9 ± 1.0	0.09 ± 0.01	7.8 ± 0.7	0.37 ± 0.04
O2	32.6 ± 2.9	10.2 ± 3.4	0.10 ± 0.03	3.7 ± 0.5	0.15 ± 0.02
O3	601 ± 43	289 ± 22	0.43 ± 0.03	36.4 ± 2.6	0.69 ± 0.06
O4	599 ± 27	34.4 ± 2.2	0.33 ± 0.02	8.4 ± 0.8	0.18 ± 0.02
O5	156 ± 8	12.2 ± 1.4		7.4 ± 1.1	
O6	36.3 ± 3.5	14.0 ± 1.0	0.17 ± 0.01	50.6 ± 3.9	1.09 ± 0.09
OT	18.9 ± 2.4	11.7 ± 1.0	0.17 ± 0.02	10.5 ± 1.2	0.19 ± 0.02
T1	38.6 ± 2.8	26.6 ± 3.0	0.40 ± 0.05	45.6 ± 2.7	0.70 ± 0.05
T2	11.3 ± 2.4	19.5 ± 1.5	0.28 ± 0.02	15.3 ± 3.1	0.43 ± 0.09
T3	13.3 ± 1.3	17.0 ± 1.5	0.27 ± 0.03	30.7 ± 5.7	0.91 ± 0.17

Ra-isotopes in solution from the same water samples as we did. In general, the $^{210}\text{Pb}/^{226}\text{Ra}$ activity ratio is below unity as expected and agrees with the data found in the current literature for other uncontaminated rivers. The ratio at locations O3 and T1, identified as local sources for the Odiel and Tinto rivers, is higher than in other stations. This, of course, could be related to the presence of direct inputs of both radionuclides. For samples O6 and O3 taken in 1991, the ratio is also higher than at the rest of the locations and is close to unity, a typical value for open ocean waters. It is very difficult to interpret this effect with only two values. The estuarine environmental dynamics are very complex and, consequently, a number of natural conditions could influence the value of this activity ratio. However, the influence of salinity in the behaviour of ^{210}Pb deserves some research. In fact, it is possible to guess some certain correlations between high salinity values and high activity ratios. It is, on the other hand, a well known fact that ^{226}Ra redissolves from the solid phase in the presence of high salinities (Martínez-Aguirre and García-León, 1994).

Sediments

Bottom sediments were collected at the same stations as water samples, and those from the campaigns of 1990 and 1991 were separated in four different grain size fractions. The fine grain size ($\leq 63 \mu\text{m}$) was analysed for ^{210}Pb in both sets of samples. Additionally another grain size (fine sand particles with diameter ranging from 63 to 355 μm) and total sediment sample were analysed for ^{210}Pb in the 1991 set of samples. For comparison, ^{210}Pb in the total sample was determined for those collected in 1988.

The data of ^{210}Pb in mBq/g dry weight for each sediment sample analysed are presented in Table 2. First, we will discuss the results obtained in the total sediment samples collected in 1988 and 1991.

In the Odiel river the ^{210}Pb radioactivity concentrations are fairly high both for the 1988 and 1991 campaigns and are well above the average background level found for unperturbed rivers. This means that river sediments are receiving and storing ^{210}Pb from the factories as has been

found for other natural radionuclides (Martínez-Aguirre and García-León, 1991; Martínez-Aguirre *et al.*, 1994).

As for the Tinto river it is clear that the phosphogypsum piles discharge radioactivity into the Tinto river bed. The levels found for sample T2 reveals that particle borne radioactivity is being transported from the gypsum piles to the river.

Similar conclusions can be deduced from the concentrations found in the fine grain fractions of the sediments, for 1990 and 1991, with values similar among them and well above those found for other non-perturbed rivers (Koster *et al.*, 1991).

Finally, in order to study the association between the enhanced levels of ^{210}Pb and the size of the particles contained in the sediments, we have also determined the concentration of such radionuclides in the fraction of particles with diameter ranging from 63 to 355 μm in sediments collected in 1991 (see Table 2). The levels are quite similar in both particle fractions and slightly lower than in the total sediment, with the only exception of sample OT. It seems that the contamination from the factories affects most of the particles contained in the sediment, either by release of particles or by contamination of particles from ^{210}Pb in solution.

In the Tinto river the level in the fine fraction range from 33 to 233 mBq/g for both campaigns. Again, no clear differences between grain sizes were found and the levels were slightly lower in both fractions than in the total sediment.

Conclusions

^{210}Pb has been analysed in water and bottom sediment samples collected in three sampling campaigns during low tide along the Odiel and Tinto river channels. The results show that most stations have concentrations of ^{210}Pb in solution and in sediments higher than the typical concentrations in unperturbed rivers. This is due to the existence of a local source of radioactivity, related to the operation

Table 2. ^{210}Pb concentrations in mBq/g in bottom sediments from the Odiel and Tinto rivers in three different campaigns. N.M. means not measured

Code	1988	1990	1991	1991	1991
	total	fine	total	fine sand	fine
O1	N.M.	13.9 ± 1.3	63.4 ± 3.7	69.6 ± 8.3	8.0 ± 0.7
O2	N.M.	27.2 ± 1.5	60.0 ± 3.5	57.3 ± 3.1	40.9 ± 2.7
O3	615 ± 28	212 ± 10	624 ± 49	465 ± 40	284 ± 14
O4	821 ± 50	438 ± 21	580 ± 24	419 ± 38	420 ± 31
O5	41.6 ± 2.7	799 ± 49	851 ± 39	598 ± 43	534 ± 25
O6	1195 ± 112	78.6 ± 3.7	554 ± 25	380 ± 32	411 ± 24
OT	339 ± 13	149 ± 11	208 ± 10	34.4 ± 2.0	204 ± 16
T1	N.M.	96.7 ± 6.1	42.6 ± 3.1	37.7 ± 2.2	33.1 ± 3.3
T2	252 ± 10	39.8 ± 1.9	442 ± 18	288 ± 13	233 ± 9
T3	341 ± 12	74.4 ± 4.8	76.1 ± 3.8	38.3 ± 3.6	47.9 ± 2.5

of the fertilizer factories located in the area. The same conclusions are obtained by studying different grain size fractions of bottom sediments. Thus, the contamination seems not to be restricted to specific particle size.

Acknowledgement—This work was supported under EU contract F13P-CT920035.

References

- Ivanovich M. and Harmon R. S. (Eds) (1982) *Uranium Series Disequilibrium: Applications to Environmental Problems*. Clarenton Press, Oxford.
- Koster H. W., Marwitz P. A., Berger G. W., Weers A. W., van Hegel P. and Niewuenwize J. (1991) ^{210}Po , ^{210}Pb and ^{226}Ra in aquatic ecosystems and polders: anthropogenic sources, distribution and enhanced radiation in The Netherlands. In *V International Symposium on the Natural Radiation Environment*. Salzburg, Austria, September 1991.
- Martinez-Aguirre A. and García-León M. (1991) Natural radioactivity enhancements by human activities in rivers of southwest Spain. *J. Radioanal. Nucl. Chem., Lett.* **155**, 97–106.
- Martinez-Aguirre A., Garcia-León M. and Ivanovich M. (1994) The distribution of U, Th and ^{226}Ra derived from the phosphate fertilizer industries on an estuarine system in Southwest Spain. *J. Environ. Radioactivity* **22**, 155–177.
- Martinez-Aguirre A. and Garcia-León M. (1994) Natural radioactivity in the Guadalquivir river at the south of Spain. *J. Radioanal. Nucl. Chem. Artic.* **178**, 337–350.
- Morón M. C., Martinez-Aguirre A. and García-León M. (1988) Determination and levels of U, Th and ^{210}Po in different environmental samples. In *International Conference on Environmental Radioactivity in the Mediterranean Area*, p. 111. SNE-ENS, Barcelona.
- Periañez R. and García-León M. (1993) Ra-isotopes around a phosphate fertilizer complex in an estuarine system at the south of Spain. *J. Radioanal. Nucl. Chem., Artic.* **72**, 71–79.
- Periañez R., Abril J. M. and García-León M. (1994) A modelling study of ^{226}Ra dispersion in an estuarine system in South-West Spain. *J. Environ. Radioact.* **24**, 159–179.