Time Evolution of Activity Concentration of Natural Emitters in a Scenario Affected By Previous Phosphogypsum Contamination

Cite as: AIP Conference Proceedings **1034**, 291 (2008); https://doi.org/10.1063/1.2991229
Published Online: 10 September 2008

M. Villa, J. Mantero, F. Mosqueda, S. Hurtado, G. Manjón, F. Vaca, and R. García-Tenorio

Time Evolution of Activity Concentration of Natural Emitters in a Scenario Affected By Previous Phosphogypsum Contamination

M. Villa[(*)a], J. Mantero[b], F. Mosqueda[c], S. Hurtado[a], G. Manjón[b], F. Vaca[c], R. García-Tenorio[b]

[(*)] *Corresponding author. Tel: +34-95-4559750; fax: +34-95-455 97 53*
E-mail address: mvilla@us.es
[a] *Centro de Investigación, Tecnología e Innovación. CITIUS. Universidad de Sevilla. Av. Reina Mercedes 4B. 41012-Sevilla, Spain*
[b] *E. T. S. Arquitectura. Dpto. de Física Aplicada II. Universidad de Sevilla. Av. Reina Mercedes, 2. 41012-Sevilla, Spain*
[c] *Dpto. de Física Aplicada. Facultad de Ciencias Experimentales. Universidad de Huelva. Campus de El Carmen. 21007-Huelva, Spain*

Abstract. The estuary formed by the confluence of Tinto and Odiel river-mouths is located in the South of Spain, close to Huelva town. This estuary has been deeply studied through the years because it has a double particularity. On one hand, since the beginning of the 1960s, the estuary has been affected by direct and indirect phosphogypsum (pg.) releases from two phosphoric acid and fertilizers factories that are working in the area. On the other hand, the pyrite mining operations upstream the Odiel and Tinto rivers has caused historically the formation of H_2SO_4, through oxidation of the natural sulphur deposits, the acidification of the waters and the consequent mobilisation of heavy metals from the mining area to the Huelva estuary. As a consequence, enhancement contamination levels in natural emitters from the ^{238}U series were found in the surroundings of the factories in the previous years to 1998. However, in 1998 the management policy of waste releases drastically changed in the area, and direct discharges to Tinto and Odiel River had to be ceased.

A thorough study of the affected zone is being carried out. Riverbed sediments and water samples have been analyzed from four different sampling campaigns in the estuary during the years 1999, 2001, 2002 and 2005. Different radioanalytical techniques have been employed to obtain the activity concentrations of U-isotopes, Th-isotopes, ^{226}Ra, ^{210}Pb and ^{210}Po. Furthermore, the results for the rates of de-contamination of the area are presented. This data will be discussed in order to establish the present status of the contamination in the area, and moreover, to predict the time-evolution of the self-cleaning

Keywords: Estuary, phosphogypsum, contamination, ^{226}Ra, ^{210}Pb, ^{238}U
PACS: 91.50.Cw, 92.40.Aa, 92.40.Qk

INTRODUCTION

The study of the natural evolution of the contamination in an environmental compartment affected by enhanced levels of natural radioactivity becomes relevant. It has been proved that the activity concentrations in the Huelva estuary, formerly affected by phosphogypsum (pg.) releases, have been decreasing since the phosphogypsum discharges have stopped [1]. From a radio-ecological point of view, it is important to make a study of the activity levels through the years, in order to know if a self regeneration of the estuary is taking place, once the contamination due to the primary

CP1034, *The Natural Radiation Environment—8th International Symposium,* edited by A. S. Paschoa

source have disappeared. Moreover, it is possible to use the data of the self cleaning in the estuary, to infer the more relevant mechanisms that rule the behaviour of the estuary.

SAMPLING AND METHODS

Four sampling campaigns were performed in 1999, 2001, 2002 and 2005. Samples of surface water and surface sediment were taken in every sampling station in low-tide periods. Sampling stations are shown in Figure 1. The estuary is divided in three areas, Odiel River, Tinto River and the area of the confluence of Odiel and Tinto River.

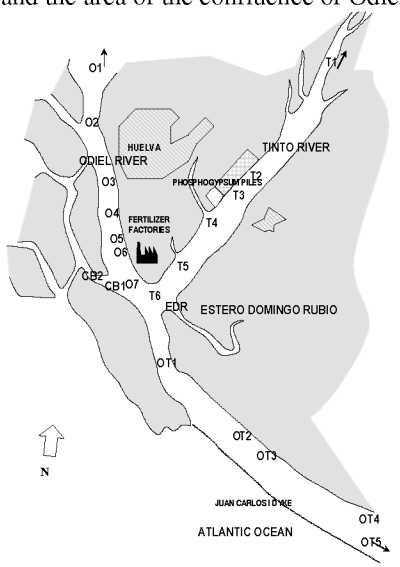

FIGURE 1. Sampling stations in the estuary of the Odiel River (Huelva, Spain). Same sampling stations were used in the different sampling campaigns since 1988

Different radiochemical treatments were applied. ^{226}Ra was determined using liquid scintillation counting (LSC) through co-precipitation of the Ra isotopes with $BaSO_4$ [2]. $PbSO_4$ co-precipitation procedure has been also used for the determination of ^{210}Pb trough LSC [3]. ^{210}Pb has in some cases been evaluated through gamma spectrometry using a Canberra (REGe) detector [4]. ^{238}U evaluation has been measured by alpha spectrometry after the solvent extraction method described in [5].

RESULTS

Activity concentrations in water and sediments for ^{226}Ra, ^{210}Pb and ^{238}U are shown in figure 2. The values in Tinto, Odiel and Confluence correspond to the average values in the corresponding sampling points.

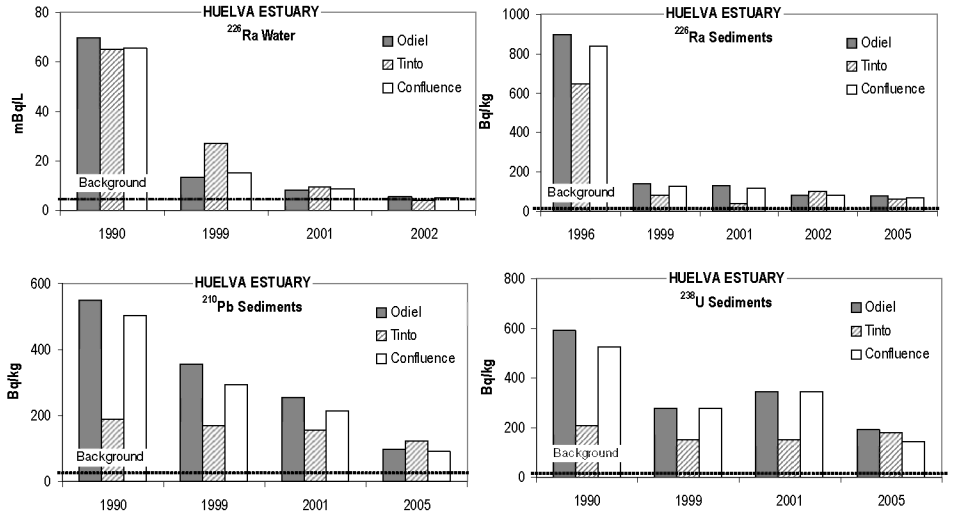

FIGURE 2. Activity concentrations in water for ^{226}Ra and sediments in Tinto and Odiel rivers and in the Confluence, for ^{226}Ra, ^{210}Pb and ^{238}U. Mean background it is included. Data from 1990 are obtained from [1], [5] and [6]

The cleaning in the river waters can be clearly seen for ^{226}Ra since the activity concentration in the year 2002 had already reached the expected natural values. Activity concentration in the Odiel River had been higher along the years due to the direct pg. discharges to that river from the factories. Nowadays, discharges are forbidden and activity concentrations have drastically decreased.

Activity concentration for ^{226}Ra, ^{210}Pb and ^{238}U is also decreasing in the bottom sediments of the estuary; however background levels are not reached yet. Besides, this cleaning takes place in different ways, depending on the radionuclide and on the area. The activity decreasing seems to be higher for ^{210}Pb than for ^{226}Ra and ^{238}U. Initially, radioactivity values in the Tinto River were lower than in the Odiel River, due to the absence of direct releases. Nowadays direct released to the Odiel has ceased, but activity concentration in Tinto river is lowering more slowly than in the rest of the estuary, the reason is that there is still lixiviation of the former open air piles located next to the Tinto river and the radionuclides flow to the river through the rivulets.

DISCUSSION

It is possible to evaluate the rate of decontamination in Odiel and Tinto Rivers for ^{226}Ra, ^{210}Pb and ^{238}U. Average activity concentrations in the three areas of the estuary can be drawn versus the sampling date. If the data are fitted to an exponential, it is possible to know the cleaning half-time in the different areas. In Figure 3 are presented these data for ^{210}Pb and ^{238}U in sediments form Odiel River. The results differ for both radionuclides, on one hand data from ^{210}Pb are fitted to an exponential curve, with excellent regression coefficients, similar result can be obtained from ^{226}Ra decay. On the other hand ^{238}U decay in the sediments is not easily fitted to an exponential. The reason is the continuous flowing of ^{238}U from the acid mine drainage upstream Tinto and Odiel rivers.

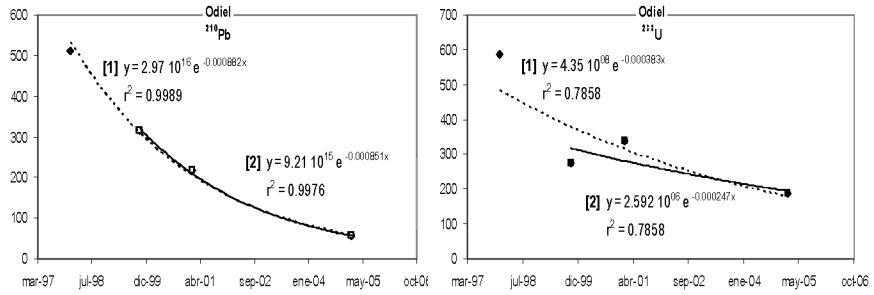

FIGURE 3. Decay of the activity concentration versus sampling time in Odiel River sediments for ^{210}Pb and ^{238}U

The data of the half-life decay obtained are shown in Table 1. The different behavior of ^{226}Ra and ^{210}Pb in Odiel and Tinto river shows the complexity of the mechanism that rule the river, these mechanisms will be studied in further studies. Besides, the higher half-time in Tinto River shows that there is an extra input of radionuclides that comes from the lixiviation of the not isolated old piles, in close contact with Tinto River, due to the surrounding streams.

TABLE a). Rates of de-contamination for ^{226}Ra and ^{210}Pb. Effective half-lives

Column Header Goes Here	**$T_{1/2}$ (^{226}Ra) years**	**$T_{1/2}$ (^{210}Pb) years**
ODIEL RIVER	5.35	1.79
TINTO RIVER	No exponential fitting	5.43
ODIEL & CONFLUENCE	4.82	1.86

REFERENCES

1. A. Absi, M. Villa, H. P. Moreno, G. Manjón, R. Periañez. *Sci. Total Environ.* **329**, 183-195 (2004)
2. M. Villa, H.P. Moreno and G. Manjón. *Rad. Measurem.* **39**, 543-550 (2005).
3. M. Villa, S. Hurtado, G. Manjón and R. García-Tenorio Villa. *Rad. Measurem.* In Press, Corrected Proof, Available online 24 May 2007.
4. S. Hurtado, M. Villa, G. Manjón and R. García-Tenorio. *Nucl. Instr. and Meth. A* **580**, 234-237 (2007)
5. A. Martínez-Aguirre and R. Periañez. *J Environ Radioact.* **45**, 67-80 (1999).
6. Martínez-Aguirre, A. y García-León, M. ^{210}Pb distribution in riverwaters and sediments near phosphate fertilizer factories. *Appl. Radiat. and Isot.* **54** (1996) 599-602.