Radionuclides in the environment in the south of Spain, anthropogenic enhancements due to industry

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Levels of natural radionuclides in the environment are affected by human activities in the South of Spain. Industry wastes, such as phosphogypsum, have been released to an estuary since sixties until 1997. Nowadays the wastes management is careful with environment protection, which can be clearly observed today in the radionuclides pattern. Different sources of radionuclides (industry wastes, tidal action and mining) can be distinguished in the estuary. Uranium isotopes, ^{226}Ra, ^{210}Pb and ^{210}Po were determined in water and sediment samples for this study. An iron recycling factory is working close to Seville (South of Spain). A ^{137}Cs source was accidentally burnt in a furnace of this factory in 2001. The environmental impact of this accident was immediately determined. Monitoring procedure and results are shown in this contribution. Radionuclides measurement involves difficult techniques. In this communication a procedure to determine the activity concentration of ^{210}Pb by liquid scintillation counting is presented. Two quality tests, using gamma- and alpha-spectrometry were applied to the ^{210}Pb results.

Keywords: Radioactivity; environment; phosphogypsum; norm.

Los niveles naturales de isótopos radioactivos en el ambiente son afectados por actividades humanas en el sur de España. Desechos industriales, tales como phosphogypsum, han sido depositados en un estuario desde los años sesenta hasta 1997. Actualmente el manejo de los desechos se realiza de manera a protejer el ambiente, lo que se observa claramente en la evolución de los patrones de los isótopos radioactivos. Las diferentes fuentes de radioisótopos (desechos industriales, mareas y minería) pueden distinguirse en el estuario. Isótopos de Uranio, ^{226}Ra, ^{210}Pb y ^{210}Po se midieron en muestras de agua y sedimento para este estudio. Una fábrica de reciclado de acero funciona cerca de Sevilla (Sur de España). Una fuente de ^{137}Cs fue accidentalmente quemada en uno de sus hornos en 2001. El impacto ambiental de este accidente fue inmediato. En este trabajo se presentan los procedimientos para el monitoreo así como los resultados obtenidos. La medida de radioisótopos involucra técnicas complejas. Aquí presentamos el procedimiento para determinar la concentración de ^{210}Pb por medio de conteo en centelleadores líquidos. Dos controles de calidad, espectrometría alfa y gama, confirman los resultados.

Descriptores: Radioactividad; ambiental; contaminación; España.

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1. Introduction

The interest on natural radionuclides related to conventional industry processes is clearly observed in the current literature (Oatway *et al.*, 2005). Although the study of naturally occurring radioactive materials (NORM) is applied to many industries (iron, zircon, coal, ...) the phosphoric acid factories are still the main objective of these research works (Beddow *et al.*, 2005).

Two factories manufacture phosphoric acid, fertilizers and detergents using phosphate rock from North Africa as raw material. Phosphate rock is the raw material of the phosphoric acid industry. Sedimentary rocks, such as mineral from Maroc used in the factories of Huelva (South of Spain), present high activity concentrations of natural radionuclides (U-isotopes, ^{226}Ra, ^{210}Pb and ^{210}Po), which are in secular equilibrium in the mineral (Bolívar *et al.*, 1996). The high amounts of treated mineral, about 2×10^9 kg per year in the case of the Huelva factories, become the acid phosphoric industry as the first objective of the NORM regulatory implementations.

Alternatively, an igneous rock, such as mineral from Kola Peninsula (Rutgers van der Loeff *et al.*, 2003), generally present lower levels of natural radioactivity, but relatively high amounts of Th-isotopes. The use of this raw material could decrease the levels of radionuclides in the products and wastes of phosphoric acid industries.

In the wet treatment of phosphate rock to produce phosphoric acid the secular equilibrium of the radionuclides, belonging the U-series, is broken. Thus, a high fraction of ^{226}Ra, ^{210}Pb and ^{210}Po is associated to phosphogypsum, a by-product that is released into the environment, whereas a high fraction of U-isotopes is associated to phosphoric acid, fertilizers and detergent.

Since 1960's until 1998 the 20% of phosphogypsum wastes was directly discharged into the Odiel River, just after high tidal events, and the rest (80%) was stored in air-opened piles. For that, phosphogypsum was pumped with seawater until the piles, then phosphogypsum was deposited and the supernatant drifted by drainage until the Tinto River. According to phosphoric acid factories data, the amount of phosphogypsum released was 3×10^9 kg per year.

In 1998 the waste management of industries located in the estuary of the Odiel and Tinto rivers was deeply changed. The direct releases to the Odiel River were stopped and the air opened piles were well-protected against any impact on the Tinto River environment.

The objective of this work was to compare the radioactive impact of the phosphate fertilizer industry in the estuary of the Odiel and Tinto rivers since 1998 until 1998, and the self-cleaning situation caused by the change of wastes management in the estuary.

2. Experimental

Different radiometric and radiochemical techniques were applied to environmental samples in order to obtain the activity concentrations of radionuclides (^{226}Ra, U-isotopes and ^{210}Po. These techniques were well-established by previous works (Martínez-Aguirre *et al.*, 1996; Periáñez, 2002; Moreno *et al.*, 2000; Martínez-Aguirre and García-León, 1994). However the experimental techniques corresponding to the determination of ^{210}Pb were developed by our group for the analysis of river sediments collected after 1998 in the estuary of Odiel and Tinto rivers. For that we only present the main characteristics of these experimental techniques in this paper.

2.1. Radiochemical procedure

Sediment samples were firstly dried. Once dried, 5 g of sediments were selected for every analysis. Next, 25 mg of Ba^{2+} and 30 mg of Pb^{2+} were added to every sediment aliquot. Samples were burnt at 550^{o}C for 24 h. Ashes where dilute with *aqua regia* for 4 h and then oxidized (with HNO_3 and H_2O_2) overnight. The supernatant is separated by filtration. The dissolution is neutralized. Then, Ba-Pb SO_4 is precipitated with H_2SO_4 10M. The precipitated is separated by filtration (Milipore 45 μm pore size) and dissolved again with EDTA at pH= 9. A second precipitation at pH= 4.5 is made to separate ^{226}Ra. Finally, PbSO4 is precipitated with H_2SO_4 at pH= 3 (Al-Masri *et al.*, 1997).

The $PbSO_4$ precipitate is dissolved with 2 ml of EDTA 0.2 M and 8 ml of NH_4OH 0.2 M, then is evaporated until 9 ml and mixed with a liquid scintillation cocktail (Optiphase Hisafe 3) in a liquid scintillation vial (low-potassium glass vial). The vial or radioactive source is immediately measured before ^{210}Bi will be present.

2.2. Activity concentration measurement

The measurement of ^{210}Pb was made with a liquid scintillation spectrometer Quantulus 1220. Two photomultiplier tubes were used to the beta counting, whereas other two photomultipliers (guard) were connected in anticoincidence to obtain an ultra-low background. Alpha- and beta- counts were analyzed in two different spectra using a pulse shape analyzer previously calibrated for ^{210}Pb measurements (Villa *et al.*, 2003).

Activity concentration of ^{210}Pb was calculated according to next equation:

$$A = \frac{R_s - R_b}{f \cdot \varepsilon \cdot m \cdot R_q \cdot 60}$$

where, R_s is the beta-counting rate determined in a ^{210}Pb source (without ^{210}Bi), R_b is the beta-counting rate in a blank source, ε is the counting efficiency corresponding to a ^{210}Pb-^{210}Bi calibration source, m is the mass of the environmental sample, and R_q is the radiochemical yield of every analysis. Finally, f is a correction factor, which must be used for taking into account the contribution of ^{210}Bi of the beta-counting rate of the calibration source.

2.3. Counting efficiency

The determination of the counting efficiency was made using sources of ^{210}Pb-^{210}Bi, both radionuclides in secular equilibrium. The contribution of ^{210}Po (decay daughter of ^{210}Pb) is avoided by the pulse shape analyzer because this is an alpha-emitter.

A so-called ^{210}Pb-window (low-energy chanels) is selected for counting in the beta-spectrum. However the low-energy tail of ^{210}Bi is also counted in these conditions. For that the ^{210}Bi contribution must be corrected for the evaluation of the ^{210}Pb activity concentration of the sediment samples. Anyway, the value of the counting efficiency was 0.749 $\pm$ 0.005, in our working conditions.

For determining the correction factor, f, a series of sediment samples were traced with known amounts of 210Pb. Once the radiochemical procedures presented above was applied, the correction factor was evaluated as the slope of a fitted line (Fig. 1), where x-values where mass (m_s) of Pb in every precipitate and y-values where the result of the equation

$$y = \frac{R_s - R_b}{60\,\varepsilon\,A}\, m_i$$

being m_i the mass of Pb of carrier, A the activity of tracer and the rest of parameters the same as defined above. According to our experiment the value of correction factor, f, was 0.622.

2.4. Radiochemical yield

The radiochemical yield of analyses were evaluated by a gravimetrically procedure. For that the mass of Pb obtained in the precipitate is compared to the mass of Pb of carrier

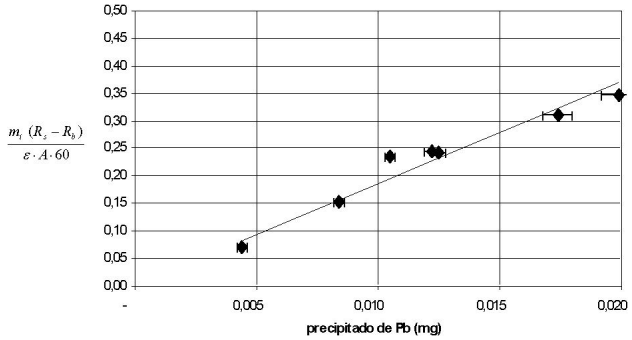

FIGURE 1. Results obtained using sediment samples traced with ^{210}Pb. Fitted line was used to the determination of correction factor, f, of the ^{210}Bi contribution. See text to a better comprehension.

added to the sediment aliquot at the starting step of the procedure. Then, an uncertainty due to a possible fraction of precipitate, which was not dissolved, must be assumed.

This method was applied to three aliquots of a same sample and the standard deviation of results was 1 % (1σ). Finally, activity concentration obtained in 12 sediment samples by liquid scintillation counting was compared with the results obtained by gamma-spectrometry (Hurtado *et al.*, 2004) and alpha-spectrometry, measuring ^{210}Po (Absi, 2005), in order to make sure de goodness of method.

3. Results and discussion

Samples of sediments were collected in the estuary of the Odiel and Tinto rivers (South of Spain). Sampling campaigns started in 1988 and they will be continued until 2001. The sampling stations were the same for every sampling campaign and can be located in the map of Fig. 2. The activity concentration of ^{220}Pb obtained in the sampling made in

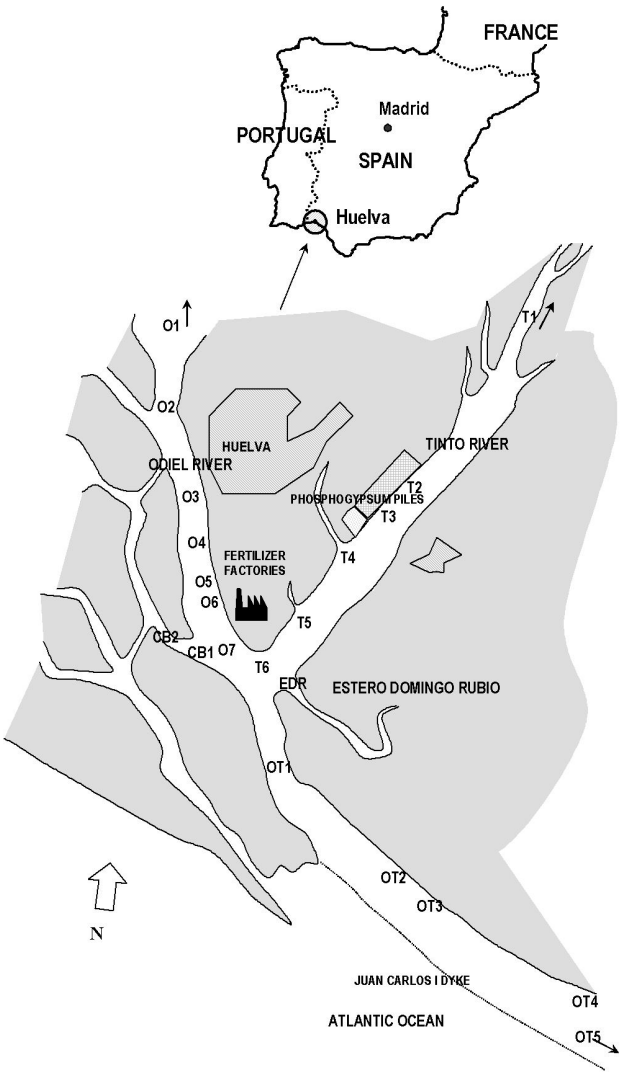

FIGURE 2. Map of the estuary of the Odiel and Tinto rivers (South of Spain).

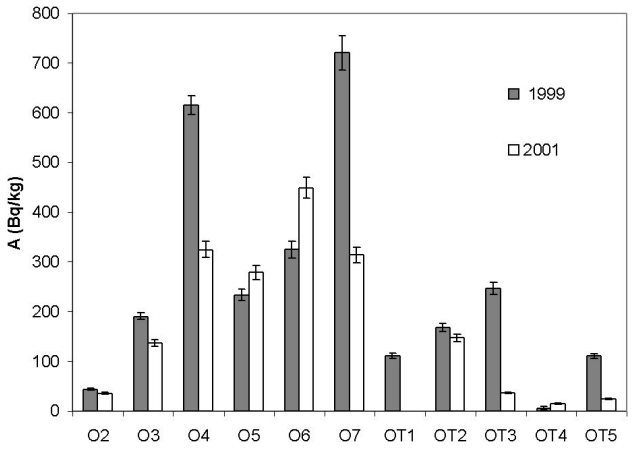

FIGURE 3. Activity concentration of ^{210}Pb in sediments collected in the Odiel River.

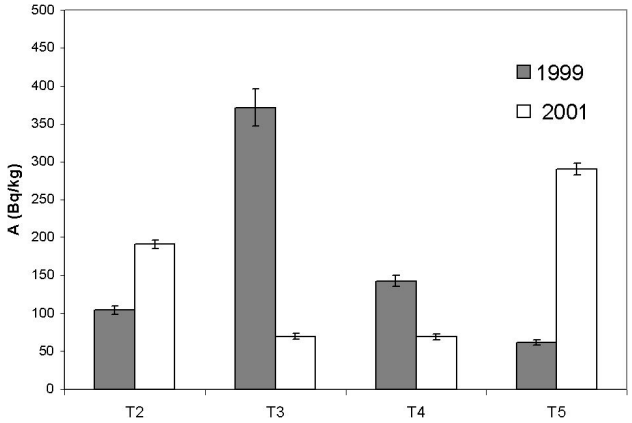

FIGURE 4. Activity concentration of ^{210}Pb in sediments collected in the Tinto River.

1999 and 2001 in every point are presented in Fig. 3 (the Odiel River) and Fig. 4 (the Tinto River).

The results obtained in the Odiel River in 1999 and 2001 show higher activity concentrations in the vicinity of the wastes discharges point (O4), which is consequent with the role of historic files of sediments (Ridgway and Shimmield, 2002). However a decreasing tendency can be inferred from the mean levels observed in 1999 and 2001, which is confirmed by the ^{226}Ra mean values observed in the same samples. An easy calculation can be used to evaluate a half-life of this decreasing of activity concentration or self-cleaning. For that we have fitted the mean values (Fig. 5) to an exponential curve. Then the half-life will be 630 days, which is similar to the half-life calculated by numerical models (Periáñez *et al.*, 2005).

The results of ^{210}Pb in the Tinto River (Fig. 4) show a homogenization in the range 50 – 200 Bq/kg. An anomalous high level observed in 1999 in T3 could be related to an accident of the phosphogypsum pile happened in 1998. Finally, the high activity concentration observed in T5 could be considered as a consequence of the role of sedimentation focus of the confluence of both rivers (Odiel and Tinto), which can

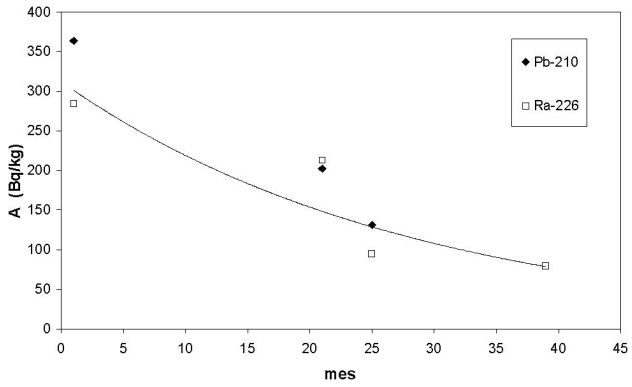

FIGURE 5. Average activity concentration of ^{210}Pb and ^{226}Ra calculated in the estuary of the Odiel and Tinto rivers fitted to the sampling time (month) counted since January 1998. Results were fitted to an exponential function in order to estimate a half-life corresponding to self-cleaning process.

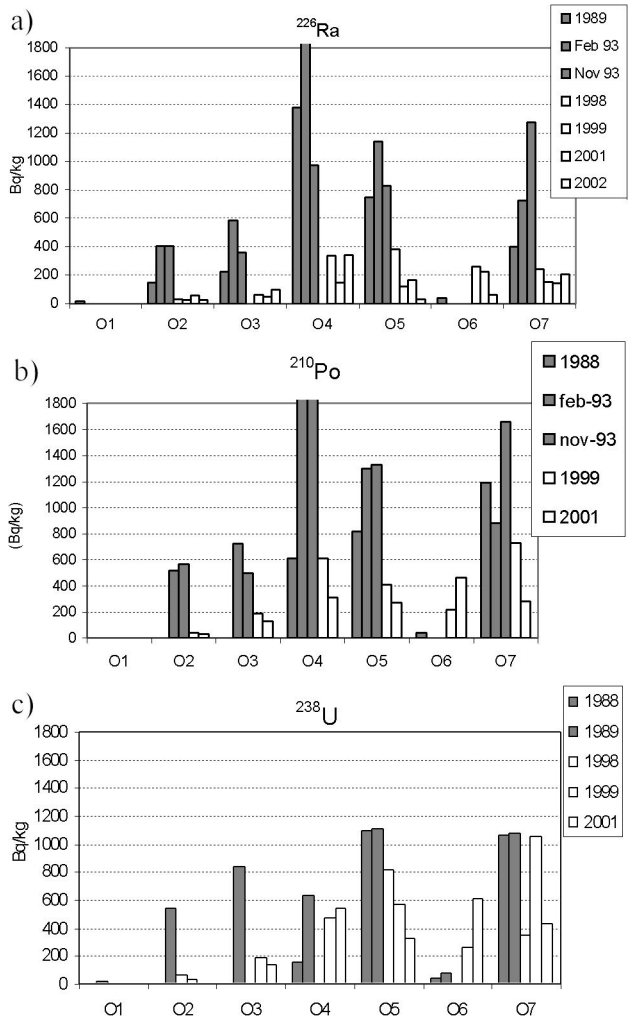

FIGURE 6. Activity concentration of a) ^{226}Ra; b) ^{210}Po; c) ^{238}U; in sediments collected in the Odiel River.

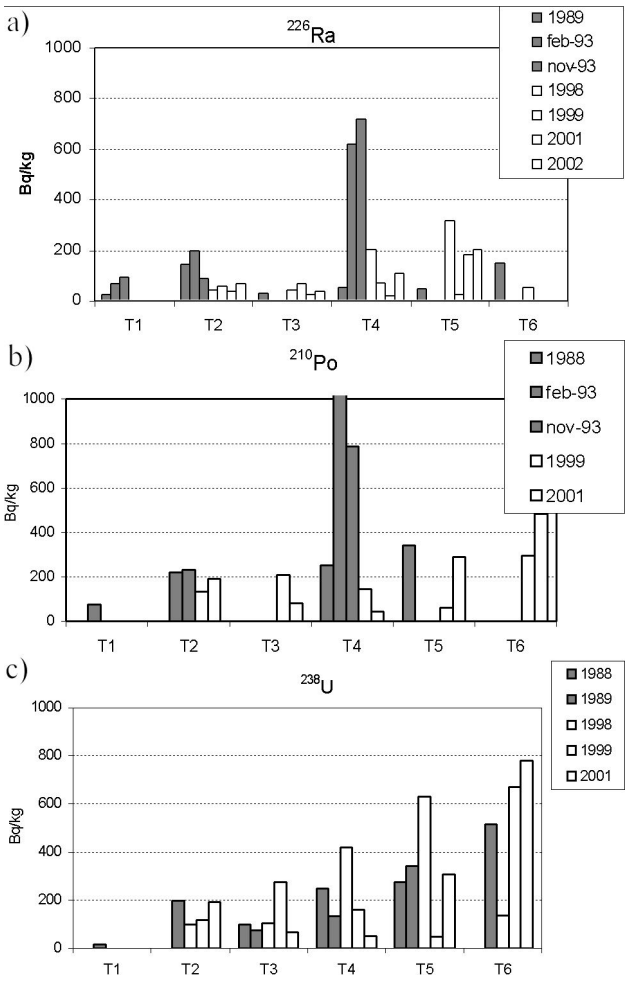

FIGURE 7. Activity concentration of a) ^{226}Ra; b) ^{210}Po; c) ^{238}U; in sediments collected in the Tinto River.

be confirmed by the activity concentration observed in O7 (in the Odiel River).

Although the decrease of the activity concentration in the sampling station directly affected by phosphogypsum discharges (O4 and T4) was easily observed since 1998 (Villa *et al.*, 2005); a more detailed discussion about the time evolution of the natural radionuclides levels in the estuary could be made if the rest of the estuary is also considered. For that, we present the activity concentration of ^{226}Ra, ^{210}Po-^{210}Pb and ^{238}U in the samples collected in the estuary since 1988 until 2002.

Figure 6 show the activity concentration in the Odiel River sediments of ^{226}Ra, ^{210}Po-^{210}Pb and ^{238}U, respectively. A similar pattern of activity concentration of ^{226}Ra and ^{210}Po-^{210}Pb is observed in these figures. These results are a consequence of the presence of these radionuclides in the phosphogypsum wastes. Thus, levels observed before 1998 are deeply affected by phosphogypsum wastes. However, levels observed after 1998 show a decrease until environmental levels observed in an unaffected estuary.

On the other hand, the activity concentration of ^{238}U in sediments (Fig. 6c) are similar in either the period before

1998 (stop of discharges) and after 1998. In this case we must noted the presence of three sources of radionuclide in the estuary: the phosphogypsum wastes, the tidal action and the uranium dissolved and driven from the river head to the estuary (Grande *et al.*, 2003; Sainz *et al.*, 2003). This last source could be the most important in both periods.

A similar presentation could be made for the results observed in the Tinto River. Activity concentration of natural radionuclides (^{226}Ra, ^{210}Po-^{210}Pb and ^{238}U) in sediment samples are presented in Fig. 7. Natural radionuclides present in the phosphogypsum piles could affected the Tinto River sediments in the vicinity of the piles (T4). That is clearly observed in Figs. 7a and 7b, where activity concentration of ^{226}Ra and ^{210}Po-^{210}Pb are presented. However, activity concentration of ^{238}U was similar in the samples collected before 1998 (close of not protected piles) and after 1998 (start of discharges in the well-protected pile). ^{238}U pattern is a typical of a not affected estuary, increasing the activity concentration as high as close to the sea.

4. Conclussions

The measurement of ^{210}Pb activity concentration in sediment samples collected in the estuary of Odiel and Tinto rivers have confirmed the environmental impact of phosphoric acid in the environment and the self-cleaning process started in 1998, when direct wastes discharges were stopped and a new well-protected air opened pile was used for phosphogypsum storage.

Natural radionuclides, such as ^{226}Ra, ^{210}Po and ^{210}Pb, have presented a different distribution in the estuary. Before 1998 the distribution shows a deep contamination event, however natural levels become typical of a not affected estuary after 1998.

The case of ^{238}U was clearly different. Although a fraction of the amount of uranium present in the raw material is processed with phosphogypsum, the impact on the river sediments could be negligible due to the presence of uranium leached from the river heads and deposited in the estuary.

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