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

G. Manjón
Departamento de Física Aplicada 2, E.T.S. Arquitectura, Universidad de Sevilla, Av. Reina Mercedes 2, 41012 – Sevilla, Spain.

Recibido el 2 de marzo de 2006; aceptado el 18 de agosto de 2006

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.


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 (Bolivar et al., 1996). The high amounts of treated mineral, about $2 \times 10^6$ 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 $3 \times 10^6$ 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-cleansing 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 (226Ra, U-isotopes and 210Po). These techniques were well-established by previous works (Martínez-Aguirre et al., 1996; Perea, 2002; Moreno et al., 2000; Martínez-Aguirre and García-León, 1994). However, the experimental techniques corresponding to determinations of 210Pb 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 Ba²⁺ and 30 mg of Pb²⁺ were added to ev ery sediment aliquot. Samples were burnt at 550°C for 24 h. Ashes were diluted with aqua regia for 4 h and then oxidized (with HNO₃ and H₂O₂) overnight. The supernatant is separated by filtration. The dissolution is neutralized. Then, Ba-Pb SO₄ is precipitated with H₂SO₄ 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 ²²⁶Ra. Finally, PbSO₄ is precipitated with H₂SO₄ at pH=3 (Al-Masri et al., 1997).

The PbSO₄ precipitate is dissolved with 2 ml of EDTA 0.2 M and 8 ml of NH₄OH 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 ²¹₀Bi will be present.

2.2. Activity concentration measurement

The measurement of ²¹₀Pb 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 ²¹₀Pb measurements (Villa et al., 2003).

Activity concentration of ²¹₀Pb 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 ²¹₀Pb source (without ²¹₀Bi), \( R_b \) is the beta-counting rate in a blank source, \( \varepsilon \) is the counting efficiency corresponding to a ²¹₀Pb-²¹₀Bi 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 ²¹₀Bi of the beta-counting rate of the calibration source.

2.3. Counting efficiency

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

A so-called ²¹₀Pb-window (low-energy channels) is selected for counting in the beta-spectrum. However, the low-energy tail of ²¹₀Bi is also counted in these conditions. For that the ²¹₀Bi contribution must be corrected for the evaluation of the ²¹₀Pb activity concentration of the sediment samples. Anyway, the value of the counting efficiency was 0.749 ± 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 (\( m_i \)) of Pb in every precipitate and \( y \)-values where the result of the equation

\[ y = \frac{R_s - R_b}{60 \cdot \varepsilon \cdot A \cdot m_i} \]

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.
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 % ($1\sigma$). 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 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 $^{210}\text{Pb}$ and $^{226}\text{Ra}$ 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) $^{226}\text{Ra}$; b) $^{210}\text{Po}$; c) $^{238}\text{U}$; in sediments collected in the Odiel River.

Figure 7. Activity concentration of a) $^{226}\text{Ra}$; b) $^{210}\text{Po}$; c) $^{238}\text{U}$; 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 $^{226}\text{Ra}$, $^{210}\text{Po}$-$^{210}\text{Pb}$ and $^{238}\text{U}$ in the samples collected in the estuary since 1988 until 2002.

Figure 6 show the activity concentration in the Odiel River sediments of $^{226}\text{Ra}$, $^{210}\text{Po}$-$^{210}\text{Pb}$ and $^{238}\text{U}$, respectively. A similar pattern of activity concentration of $^{226}\text{Ra}$ and $^{210}\text{Po}$-$^{210}\text{Pb}$ 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 $^{238}\text{U}$ 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 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 $^{210}$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. Conclusions

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.

Acknowledgements

This work was partially supported by ENRESA (Spanish Nuclear Waste Management Enterprise) and Consejo de Seguridad Nuclear (Spanish Nuclear Safety Regulatory Administration). Logistic help for sampling campaigns was done by Junta de Andalucía (Regional Government of Andalusia, South of Spain). Physicists, from Universidad de Huelva, have partially contributed to obtain experimental data.

Collaboration and assistance of R. García-Tenorio, J. M. Abril, J. Díaz, M. Villa, S. Hurtado, A. Absi, H. F. Moreno and R. Periáñez are deeply acknowledged. This program is alive today and two new young researchers, J. Mantero and A. Calleja, have already obtained important results. The twenty-year old research program, devoted to the radioactive control of estuary, has been developed under the supervision of Professor M. García-León.