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THE PHOSPHORIC ACID PRODUCTION AS A SOURCE OF ENVIRONMENTAL RADIOACTIVITY: THE SPANISH CASE

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ABSTRACT
In this paper results are summarised on the radioactive environmental impact produced by the wastes of two phosphoric acid plants located at Huelva, SW of Spain. Additionally, are evaluated the new actions that have been recently adopted to improve the management of these wastes, and are outlined some predictive conclusions, obtained through modelling studies, concerning the radioactive evolution of the close environment to the factories.

INTRODUCTION
In Huelva (SW of Spain) and in the estuary formed by the confluence of the Odiel and Tinto river mouths, it is placed a vast industrial complex which includes some phosphoric acid plants. In these factories, are treated phosphate rocks that have different origins and contain enhanced levels of natural radionuclides, mainly, although not only, from the Uranium series (1). In fact, the phosphate rocks processed in the Spanish factories, contain U concentrations of about 1 kBq/kg, with the daughters in near secular equilibrium. Consequently, in the industrial processing of such material significant quantities of natural radionuclides are involved.

In the process of phosphoric acid production are obtained huge amounts of phosphogypsum (PG), a by-product formed mainly by calcium sulphate. This PG, in the Spanish case, was until now either directly released into the Odiel river, or stored in a 1000 Ha open air piles area near the factories, on the bank of the Tinto river. As the PG contains a fraction of the natural radioactivity originally present in the ores (~15% of U-isotopes, ~40% of Th-isotopes and ≥80% of Ra-226 and Po-210) (2), it is obvious to deduce the clear radioactive environmental impact produced by the phosphoric acid plants in the neighbouring environment, as has been shown by our group in several works (examples are the references 3,4,5,6) and was summarised in the previous NORM conference (7).

Trying to decrease the environmental impact produced by these wastes, since few years ago and gradually have been taken several actions. In this paper, and together with the description of the actual "radioactive" situation of the close environment to the factories, these actions are summarised. In addition, the knowledge of the new wasting practices allowed us, through experimental and modelling work, to evaluate the expected clear change in the environmental radioactive impact produced by the phosphoric acid factories, and to do predictive studies concerning the evolution of the actual radioactive contamination in the estuary.

RESULTS AND DISCUSSION

Environmental Radioactive Impact
In the Figure 1 it is shown a map of the area where the phosphoric acid factories are located. Also, in this figure it is specially marked the zone on the bank of the Tinto river where in open piles a fraction of the PG is stored.

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The factories are producing phosphoric acid since the sixties, and during the last years its annual production of PG can be evaluated in 3.10^6 Tm. 20% of this amount has been released into the Odiel river (near code O4, Figure 1), while the remaining 80% is stored in the commented piles, being in both cases the PG previously mixed with sea water (20% of suspended matter). The waters used for the conduction of the PG to the piles, after the deposition of the solid material, drain to the Tinto river.

This way of waste management, has obviously distributed significant amounts of radionuclides in the close environment, mainly from the Uranium series. In fact, previous work summarised in (7) reveals:

a) The important radioactive impact on the Odiel river, with a clear source around the phosphoric acid factories and with important amounts of natural radioactivity being accumulated in the river bed.
b) The existence of a radioactive impact also in the Tinto river, but affecting the industrial activities in different way that in the Odiel, because the PG is no directly released on it. The impact is produced mainly through the waters used for the conduction of the PG to the piles, that drain finally into the Tinto river.
c) The important role that the tidal movements have in the extension and distribution of the radioactive contamination, and as a consequence, the extension of the radioactive impact to the important marsh areas that surrounds this estuary.

Only as an example of the clear radioactive impact produced by the operation of the phosphoric acid factories, and additionally, as a way to analyse the historical evolution of this contamination, we show in the Figure 2 the Th-230/Th-232 activity ratio profile determined in one sediment core (1 m length) collected in the marshes of the Odiel river, just in front of the factories (near code O5, figure 1). Knowing that the normal values for the commented ratio ranges from 0.8 to 1.5 in uncontaminated sediments (8,9), it is clear to conclude from the Figure 2, the existence of clear anthropogenic inputs of Th-230 (radionuclide from the U-serie) coming from the wastes of the fertiliser plants, in the upper centimetres of the core. In addition, knowing the high reactivity with the material of the Th-isotopes, and because it is known the date when the factories started its production, from the profile can be inferred information for the determination of an average sedimentation rate in the core.

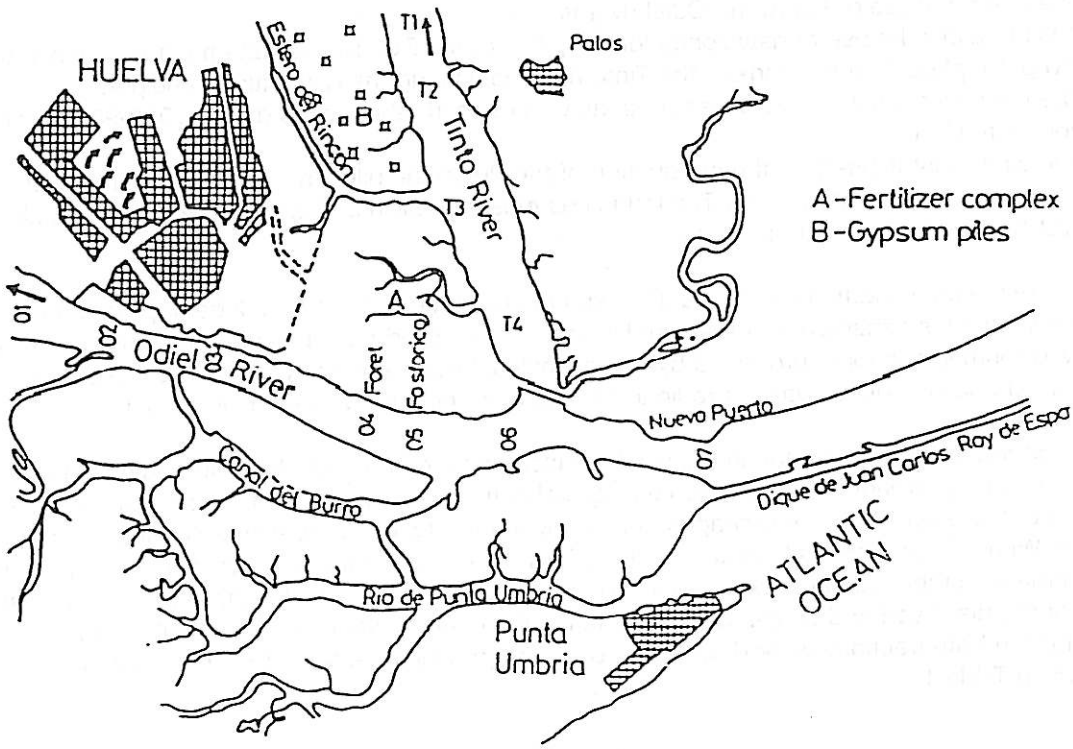

Figure 1: Map of the studied estuary. The locations of the phosphoric acid plants, as well as of the phosphogypsum piles are specially marked.

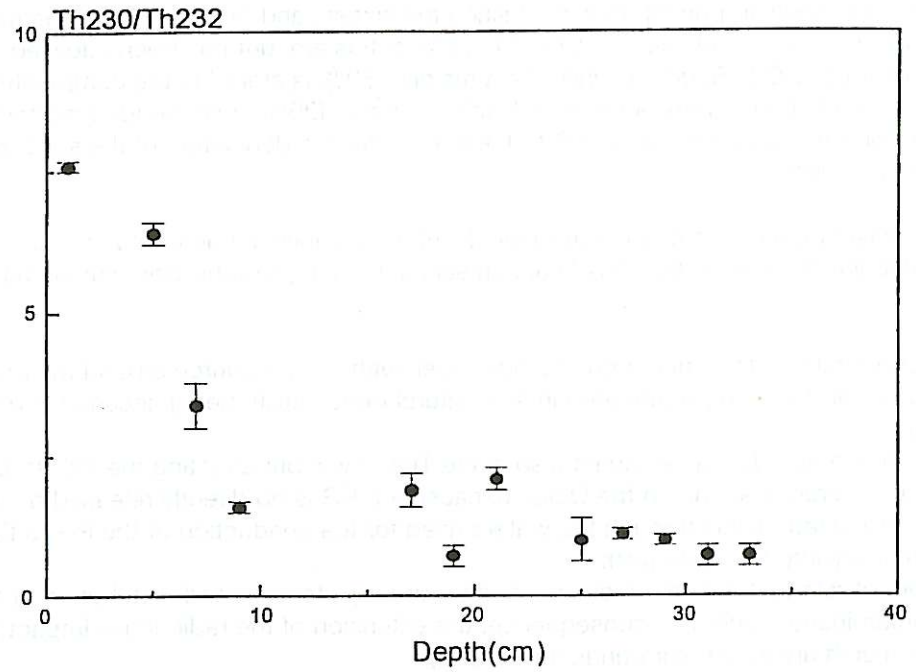

Figure 2: Th-230/Th-232 activity ratio profile obtained in a core collected from the salt-marshes placed just in front of the phosphoric acid plants (near code O5 in Figure 1)

Changes in the wasting practices

Trying to decrease the environmental impact produced by these wastes, during the last years have been taken several actions promoted by the regional government. In these sense, and during 1991-93, about 400 Ha of the open air PG piles have been restored, by its coverage with a layer of soil (30 cm thickness). In addition, just few months ago, has been elaborated a project revising/optimising the wasting practices in the studied zone. This project can be summarised in the following points:

a) The direct release of PG to the Odiel river is forbidden.
b) It is not allow the use of new zones for the piling of the PG. The storage must be done in the old piles, placed on the bank of the Tinto river, continuing the deposition in height.
c) The industries must restore these piles, as was done in other zones during 1991-93, after their complete filling.
d) The water that is used for the conduction of the PG to the piles must not drain directly into the Tinto river as occurred before. The industries must establish a closed circuit for the circulation and cleaning of the waters.

All these points are actually in application with the exception of d) that will be applied in few months, and it is expected that their implementation will produce a clear change/improvement in the environmental impact produced by these wastes, because theoretically disappears most of the direct and/or indirect ways of radioactive inputs to the surrounding environment.

The importance of this change in the waste management can be clearly evaluated (at least approximately) through the estimation for several natural radionuclides of the annual amounts that with the previous waste management has been introduced in the estuary during the last years. With this end, several aliquots of the effluents (mixture of the sea water and PG), just after its formation in the factories, were collected. In these effluents, and after the separation by filtration of the dissolved and suspended (PG) matter, the concentration of several natural radionuclides in both fractions were determined by alpha-particle spectrometry. The results are shown in Table 1.

Table 1: **U-isotopes and Po-210 specific activities, Bq/kg in suspended matter (SM) and Bq/l in dissolved material (DM), in the effluents of the phosphate fertiliser plants.**

SAMPLE	^{238}U	^{234}U	^{210}Po
FESA A (SM)	140 ± 9	138 ± 9	888 ± 71
FESA A (DM)	0.68 ± 0.04	0.70 ± 0.04	0.84 ±0.08
FESA B (SM)	115 ± 8	114 ± 8	1015 ± 63
FESA B (DM)	12 ± 1	12 ± 1	2.0 ± 0.2
FORET (SM)	129 ± 8	145 ± 9	540 ± 46
FORET (DM)	4.0 ± 0.2	4.1 ± 0.2	0.97 ± 0.08

From these results, knowing the annual amounts of effluents that previously were either released to the Odiel river, or conducted to the PG piles, and assuming that all the radioactivity in dissolved form transported to the piles drain finally to the Tinto river, the following annual amounts of U-isotopes and Po-210 can be estimated that were entering in the Odiel and Tinto river until the entrance of the new policy of PG management

Odiel River — 1 TBq of U-234 and U-238
0.4 TBq of Po-210

Tinto river — 0.1 TBq of U-234 and U-238
20-30 GBq of Po-210

However, the expected drastic decrease in the amount of radioactivity entering in the different compartments of the surrounding environment of the factories, does not imply the sudden disappearance of the radioactive impact in this zone. The sediments from the estuary and surrounding salt-marshes will be in the future the source term of radioactivity interacting with neighbouring compartments (waters, suspended matter, plants, ...) during several years, until its "cleaning" by physico-chemical exchanges and/or sedimentation. This fact open new perspectives in our studies for the better understanding of the behaviour of several radionuclides in the environment, and for the better knowledge of the influence of several natural conditions in the cleaning of a radioactive deposit. As a preliminary step for the future control of the evolution in different compartments of several radionuclide concentrations, and as basis for modelling work, a compilation of the most actual data produced for our group concerning surface sediments and soils from the estuary and salt-marshes has been done, being a summary shown in Table 2.

Table 2: **Average mass concentration for U and Th (μg/g) and radioactivity concentrations for Ra-226, Pb-210 and Po-210 (Bq/kg) in sediment and/or soil samples from the Tinto and Odiel riverbeds and surrounding salt-marshes. Between brackets are shown the maximum values found in some specific samples of every zone. In the paragraph Reference we show the expected levels for similar samples collected in uncontaminated places (8,9).**

PLACE	U	Th	^{226}Ra	^{210}Pb	^{210}Po
Odiel river	60 (90)	30	500 (1400)	280 (900)	
Odiel marsh	20 (60)	9	210 (800)	250 (800)	225 (800)
Tinto river	20 (40)	10	80 (150)		90
Tinto marsh			150 (600)		350 (1200)
Reference	≤ 5	≤ 14	≤ 60	≤ 100	≤ 100

Modelling Studies

By other hand, it is obvious that without the help of mathematical models is difficult the understanding of all the information that can be inferred from the experimental data collected in every

specific environment. For that reason, and since several years ago, our group has been involved in the mathematical modelling of the behaviour of several radionuclides in the environment, specially in aquatic systems (10).

In particular, we have developed a mathematical hydrodynamic model for non-conservative radionuclides that has been applied to our specific estuary (In the model, the description of the ionic exchanges between the different phases: water, suspended matter and sediments are done in terms of kinetic transfer coefficients). The agreement obtained between the experimental and model results confirm the goodness of the description of the processes included in the model (10, 11, 12, 13), and gives a very rich information about the behaviour and migration of several radionuclides in this specific place, that can not be obtained only from the experimental results. But in addition the model becomes a powerful tool for the performance of predictive studies, that are now extremely important after the change in the wasting practices of the fertiliser factories. In fact, the process of radioactive evolution of the estuary riverbeds and surrounding salt-marshes has been analysed, assuming that no new inputs of radioactivity from the wastes are going to affect these zones. The model results indicate that the cleaning process is relatively slow, remaining a considerable proportion of the radioactivity in the sediments after several years of no radioactivity inputs.

SUMMARY

Several studies done by our group indicates that during the last years the operation of two phosphoric acid plants have produced a clear input of natural radioactivity to the surrounding environmental compartments.

Due partially to this environmental radioactive impact, actually the wasting practices of these plants are changing. With these revisions, the direct intrusion of natural radioactivity to the estuary will stop, opening new perspectives in our research by the experimental study of the natural cleaning process that will be followed for the different compartments of our studied environment. In fact, and based in our wide experience in mathematical modelling of the behaviour of several radionuclides in aquatic systems, predicting studies in the estuary concerning the self-restoration processes has been done, that in addition can be very useful to judge the necessity of possible rehabilitation works.

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