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RADIOACTIVE ENVIRONMENTAL IMPACT DURING THE PHOSPHORIC ACID PRODUCTION

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ABSTRACT

In this work results are presented on the radioactive environmental impact produced by two phosphoric acid plants located at Huelva, SW Spain. Concentrations of several natural radionuclides are reported for a wide variety of samples (water, suspended matter, sediments, soils and plants). The study has provided with a very valuable information on the environmental impact of this kind of non-nuclear industries as well as on the behaviour of natural radionuclides in estuarine systems.

INTRODUCTION

Phosphate rocks contain large amounts of natural radioactivity, mainly, although not only, U. Indeed, depending on the geological origin of the rock the concentration of U in it can range from 50 to 300 ppm. Consequently, the mining and the industrial processing of such material lead to the redistribution into the environment of significant quantities of natural radionuclides.

The phosphoric acid, used for fertiliser production, is obtained from phosphate ore rocks. Roughly speaking, during the so called wet process, the phosphate ore is treated with sulphuric acid and phosphoric acid is produced together with phosphogypsum, a waste by-product, formed mainly by impure Ca sulphates. Such gypsum is normally stored into open air piles or directly discharged into surface waters. It is also known that about 86% of U and 70% of Th present in the phosphate rock appear in the phosphoric acid, while 80% of its Ra content comes to the gypsum *(Köster et al. 1992)*. Taking into account the large annual amount of raw material used in a typical phosphoric acid factory is easily understood that its operation will enhance the natural radioactivity content, at least, of its close environment.

In this paper our experience on the determination of the radioactive environmental impact which have been produced by two phosphoric acid factories located at Huelva, SW Spain, is summarised. The industrial plants are located in a estuarine area (see Fig. 1) and processes annually around $2x10^6$ Tm of phosphate rock which produces $3x10^6$ of gypsum. So far, usually about 80% of this by-product has been currently stored in a 1000 Ha open air piles area near the factories, on the bank of the Tinto river, while the remaining 20% has been directly released into the Odiel river. The huge amount of raw material used in a year makes that some 2.2 TBq of ^{226}Ra, 2.3 TBq of ^{238}U and 1.4 TBq of ^{232}Th are involved in the production process. Part of these activities have obviously been reintroduced into the environment.

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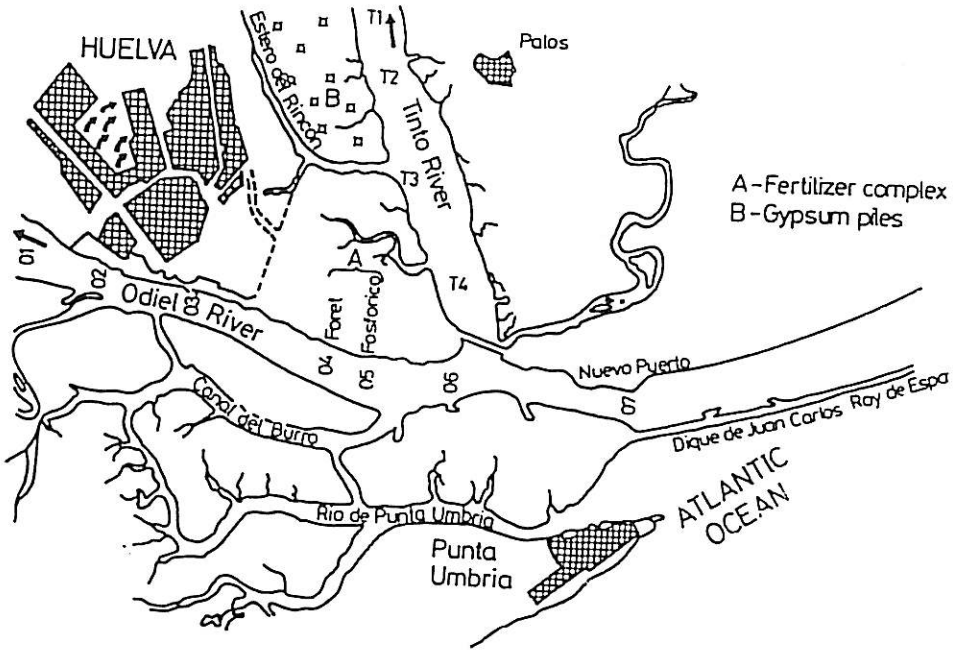

Figure 1.- Map of the studied area. The location of the phosphoric acid factories is shown as well as that of the phosphogypsum piles.

TABLE 1

Natural radionuclide concentrations (mBq/g) measured in the phosphate rocks used at the phosphoric acid factories located at Huelva, SW Spain, as well in the produced phosphoric acid and phosphogypsum. The rock usually comes from the three African countries listed in the Table.

Sample	^{238}U	^{210}Po	^{226}Ra
Phosphate rocks from Senegal			
Phosphate rock	705	984	1025
Phosphoric acid	620	35	149
Phosphogypsum	16	529	518
Phosphate rocks from Morocco			
Phosphate rock	1005	1303	1310
Phosphoric acid	680	16	40
Phosphogypsum	225	779	618
Phosphate rocks from Togo			
Phosphate rock	1040	931	1207

SAMPLES AND METHODS

The study has been done with samples of river water, suspended matter, sediments, soils and plants collected along several sampling campaigns from 1988 to 1996. The sampling stations are also depicted in Fig. 1.

Alpha- and γ-spectrometry as well as gas counting have been used for the determination of radionuclides in the different samples. A complete account of such procedures, together with the radiochemical methodology for radionuclide separation can be found, for instance in *Martínez-Aguirre et al. 1994, Bolívar et al. 1996b and 1996c.*

RESULTS

Phosphate rocks and phosphogypsum

In Table 1 we present some estimations on the presence and distribution of U- and Ra-isotopes, ^{210}Po, and ^{40}K in the different phosphate rocks used at the above mentioned factories, as well as in the produced phosphoric acid and gypsum *(Bolívar et al. 1995)*. The results agree fairly well with previously obtained data *(Van der Heidje et al. 1988)* and show that the rock used at Huelva is very much enriched in U and daughters with concentrations 50 times higher than in typical soils *(Roessler et al. 1979)*. Taking into account that around 1.5 g of phosphogypsum is produced from each 1 g of phosphate rock, it can be found that, depending on the origin of the rock, some 87% to 94% of the ^{226}Ra and ^{210}Po originally present in the rock come into the phosphogypsum, the rest remaining in the phosphoric acid. The opposite happens with U. Now, from 74% to 98% of the U originally present in the rock come into the phosphoric acid, while the rest appear in the phosphogypsum.

The Odiel river

As commented before part of the wastes are directly incorporated into the Odiel river. And, of course, the results obtained so far reveal an important radioactive impact on the Odiel river from the phosphoric acid factories *(Martínez-Aguirre et al. 1994, Martínez-Aguirre and García-León 1996, Martínez-Aguirre et al. 1996a, Periáñez and García-León 1993, Periáñez et al. 1994 and 1996)*.

In Table 2 we summarise our results on the concentrations of different radionuclides in waters (dissolved phase), sediments and suspended matter obtained along the different sampling campaigns. We give minimum, maximum and average levels together with typical data from presumably unaffected rivers, for the sake of comparison.

We have shown in many previous works that there exists a local source of natural radioactivity around the phosphoric acid factories area. This is consistent with the fact of the direct release of wastes into the Odiel river and explain the high radionuclide concentrations observed either in water, sediments or suspended matter Odiel river samples.

Certainly the concentrations in waters can change depending on several factors: time pattern dependence of the source term, tidal conditions, water stream, etc. However, it seems very clear that important amounts of natural radioactivity is being accumulated in the Odiel river bed. Consequently, although the wasting practices will change in the future, and no more radionuclides will be directly deposited in the river bed, likely the Odiel river sediments will have to be considered as a source of radioactivity.

TABLE 2

Minimum, maximum and average mass concentration for U and Th and radioactivity concentrations for ^{226}Ra, ^{210}Pb and ^{210}Po in different samples from the Odiel river. When it has been possible levels for similar samples obtained by exploring current literature are given on the line "other" for the sake of comparison. Data has been obtained by averaging results from several sampling campaigns (see text). Units for mass concentration are mg/l (water) and mg/g dry weight for solid samples. As for radioactivity concentration we give the results in mBq/l and mBq/g dry weight respectively.

ODIEL RIVER	U	Th	^{226}Ra	^{210}Pb	^{210}Po	References
Waters						
minimum	2.7	0.15	71	7.9		
maximum	10.7	1.2	670	286		
average	4.6	0.56	187	61.3		
others	≤2	$\sim 10^{-2}$	≤3	≤3		a
Sediments						
minimum	6.3	2.4	40.3	8.0		
maximum	89.0	61.7	1377	799		
average	57.4	30.2	489.5	272		
others	≤5	≤14	≤60	≤100		b
Suspended matter						
minimum			18.6			
maximum			2494			
average			600			
others			≤70			c
Marsh sediments						
minimum	2.4	1.2		15.4	16.2	
maximum	58.2	25.2		820	778	
average	17.2	9.1		255	226	
Spartina densif.						
minimum	0.2	0.07			5.6	
maximum	3.4	0.74			45.2	
average	0.9	0.32			15	
Spartina maritima						
minimum	0.2				5.1	
maximum	4.0				43.4	
average	1.7				21	

References a : *Scott 1992, Plater et al. 1992.*
References b : *Köster et al. 1992, Osmond and Ivanovich 1992, Scott 1992.*
References c : *Moore 1981.*

The Tinto river

The industrial activities affect te Tinto river in a different manner. Indeed, the phosphogypsum is not directly released into the river but dumped into the piles shown in Fig. 1. There exist several mechanisms of radioactivity transport from the gypsum piles to the Tinto river *(Bolívar et al. 1995)* which give place to radionuclide contamination also of the Tinto river *(Martínez-Aguirre et al. 1994, Martínez-Aguirre and García-León 1996, Martínez-Aguirre et al. 1996a, Periáñez and García-León 1993, Periáñez et al. 1994 and 1996).*

The summary of our results is presented in Table 3. As before we give minimum, maximum and average concentrations for different radionuclides. Such a levels are compared with those concentrations found in non perturbed rivers.

In the case of waters the levels found are systematically smaller than those measured at the Odiel river. However with the exception of U, it can be said that the concentrations for the rest of radionuclides are still higher than in non perturbed environments.

As for the sediments they are also observed concentrations smaller than in the case of the Odiel river. The levels of Th are similar to those found in the current literature. Nevertheless, it seems apparent that U and daughters are being accumulated into the Tinto river bed, leading us to the same conclusion as before.

The ^{226}Ra concentrations in suspended matter are smaller than those in the Odiel river but still higher enough to confirm the transport of radioactivity from the gypsum piles into the Tinto river.

TABLE 3

Same as Table 2 but for the Tinto river.

TINTO RIVER	U	Th	^{226}Ra	^{210}Pb		References
Waters						
minimum	2.8	0.02	64	11.7		
maximum	4.0	11.8	69.3	26.6		
average	3.5	2.5	66.8	18.7		
others	≤ 2	$\leq 10^{-2}$	≤ 3	≤ 3		a
Sediments						
minimum	6.0	6.2	33.2	33.1		
maximum	41.6	13.2	149.9	233		
average	20.9	9.8	79.2	87.5		
others	≤ 5	≤ 14	≤ 60	≤ 100		b
Suspended matter						
minimum			95			
maximum			268			
average			153			
others			≤ 70			
						c
Marsh sediments						
minimum			8,4			
maximum			587			
average			153		27.7	
					1242	
					352	

Salt marshes

As seen in Fig. 1 an important marsh area surrounds both rivers, Tinto and Odiel. Some research has also been done on the radioactive impact in the marsh located at the right bank of the Odiel river and the marsh located at the left bank of the Tinto river. For that samples of sediments from both marshes were analysed. Data on Spartina densiflora and Spartina maritima, two typical marsh plants, from the Odiel marsh area are also given.

The results are presented in Tables 2 and 3. Both for the Tinto and Odiel marsh areas an unambiguous radioactive impact has been shown *(Bolívar et al. 1995, Martínez-Aguirre et al. 1996b and 1997, Martínez-Aguirre and García-León 1997)*.

In the case of the Tinto marsh the impact is produced by the deposition and accumulation of radionuclides from the U series that previously had been leached or dissolved from the gypsum piles by waters that temporally can cross them. A careful analysis of the data reveals that atmospheric transport as a way of carrying radionuclides from the piles to the surrounding areas should be discarded.

As for the Odiel marsh it seems clear that the impact is produced through tidal movements. Thus, the incoming Odiel river waters, which directly receive wastes from the phosphoric acid plants, enhance certain zones of the studied marsh. In fact, the radioactivity concentration in soils really trace the tidal movements in the marsh area. The study of radionuclide concentration in Spartina densiflora and maritima also is conclusive. These marsh plants are affected by the operation of both factories. Indeed, high concentration of activities in plants are coincident with high concentrations in the corresponding soil substrate. This has permitted an extensive study on the plant-soil concentration factors for these plant species *(Martínez-Aguirre et al. 1997)*.

CONCLUSIONS AND FUTURE DEVELOPMENTS

Our results confirm that during the operation of phosphoric acid factories a non-negligible radioactive environmental impact is produced. A clear intrusion of natural radioactivity into the different environmental compartments of the studied areas has been observed in our case. This being attributed to the phosphoric acid factories present in Huelva, SW Spain.

Indeed, higher natural radionuclide concentrations than typical have been found for waters, sediments and supended matter taken from the estuarine area formed at the common mouth into the Atlantic Ocean of the Odiel and Tinto river. Furthermore, the natural radioactivity enhancement is observed also in the marsh soils that surround the area under research, as well as in marsh plants which confirms the input of natural radioactivity into the biosphere.

As a consequence the developed research has permitted to gaining a very interesting and fundamental knowledge on the behaviour, dissemination and behaviour of natural radionuclides *in situ* conditions.

Nevertheless, it is also true that all the presented results suggest the need of changes in the wasting practices and the affording of urgent rehabilitation works. And it seems that during the next months the phosphogypsum management will change.

The studied system will answer to the new situation by a self-restoration process which invites us to meet new challenges. Indeed, now the accumulated radioactivity in the sediments and marsh soils will be the source term for a new radioactivity transport cycle in the studied system. How will this process take place or how long will it take are new questions whose answer will help very much to understand, for instance, how radionuclides migrate along the environment or under which natural conditions a radioactive deposit is cleaned.

Acknowledgements
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