Occupational, Public and Environmental Radiological Impact Caused by the Phosphoric Acid Industry: The Case of Huelva (Spain)

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Additional information is available at the end of the chapter

Abstract

The production of phosphate fertilizers usually uses as raw material sedimentary phosphate rock, which contains enhanced concentrations from U-series radionuclides about 10–100 times higher than unperturbed soils. This fact implies the need for evaluating the radiological implications of this activity. In our case, the study has been performed in a large fertilizer industrial complex located at Huelva town (SW of Spain), where sedimentary phosphate rock has been processed since 1965 to 2010, generating annually an average of about 2.5 million tons of a by-product called phosphogypsum (PG), which has been stored in big stacks 1 km away from Huelva city, covering 1000 ha. The fluxes of the radionuclides of interest along the production process and the effective doses received by the workers have been determined. In addition, the radioecological impact associated to the waste management strategy followed has been evaluated.

Keywords: NORM, radiation doses, phosphogypsum, radioecological impact

1. Introduction

The production of phosphoric acid (PA) from phosphate ore deposits is essential because phosphorus is an essential element to all living systems, and especially for the plants. The phosphate fertilizers and animal feeds (among others) are manufactured by using the PA as

raw material. The bioavailable phosphorus is usually present in very low quantity in most agricultural soils, and for this reason, it is necessary to add it as soluble phosphate.

Total global phosphate reserves are estimated to be around 1.6×10^9 tons. Most of these deposits are from sedimentary origin, with as little as 4% being of igneous origin [1]. Phosphatic materials are usually characterized in terms of their P_2O_5 concentration in percentage. This is done as a convenience and not as a strict chemical description. Phosphate ores generally have P_2O_5 concentrations ranging from 4 to 40%.

In simplified form, phosphate ore is converted into commercial products using the following three main process steps:

i) After being mined, phosphate ore is beneficiated to produce a concentrate known as phosphate rock (PR).

ii) According to International Fertilizer Industry Association [2], as much as 85% of the phosphate rock produced in step (i) is converted into intermediate or final products using a process of acid digestion known as the "wet process." A relatively small amount of PR is converted directly into elemental phosphorus by reduction in an electric arc furnace in a process known as the"thermal process," in order to obtain a more pure PA. It is estimated that 71% of all PR produced is processed into phosphoric acid, with the generation of a by-product called "phosphogypsum" (PG). In addition, the 24% of PR is processed directly into fertilizer without the generation of PG, whereas the remaining 5% is converted directly into various other products. The annual production of P_2O_5 in the form of PA is more than 30 million tons.

iii) Most of the phosphoric acid produced in step (ii) (75–90%) is subjected to further chemical processing to convert it into fertilizer. The fertilizer products so derived from PA thus account for some 55–60% of total phosphate rock production. Of the remaining 10–25% of PA produced in step (ii), about one-half is processed into animal feed supplements and the other half into a variety of other products.

The production of PA for the manufacture of phosphate fertilizers usually use sedimentary phosphate rock as raw material, which contains generally enhanced concentrations from U-series radionuclides; about two orders of magnitude in relation to unperturbed soils. This implies huge fluxes of radionuclides along the production process, and the generation of wastes and by-products enriched in natural radionuclides. For that reason, the evaluation of the occupational, public and environmental radiological implications of this industrial activity is needed.

This evaluation has been performed for the authors in a large fertilizer chemical industrial complex, located at Huelva town (SW of Spain), where sedimentary phosphate rock has been processed since 1965 to December 31, 2010, generating annually about 2.5 million tons of phosphogypsum waste (PG), which has been stored in big stacks (around 1000 ha and 100 million tons of PG are stored at this repository). The fluxes of the radionuclides of interest along the production process and the effective doses received by the workers have been determined. In addition, the radioecological environmental impact associated to the waste management strategy has been also evaluated.

2. Phosphoric acid production at Huelva

2.1. Description of the PA production

At Huelva five phosphoric acid plants were working, consuming annually around 1.5 million tons of phosphate rock, and producing 0.5 million tons of PA (expressed as P_2O_5), and 2.5 million tons of PG. PG is an unavoidable by-product in the production of PA by the sulphuric "wet-acid" method, where 5.5 tons of PG per ton of P_2O_5 are produced.

The process for obtaining the phosphoric acid from the phosphate rock can be described schematically by the following chemical reaction [3]:

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 2H_3PO_4 + 3CaSO_4 + 48.9 \text{ kcal} \qquad (1)$$

In the Huelva phosphoric acid plants the fluorapatite was mainly used as raw material, which in the process conditions induce the production of the phosphogypsum in the di-hydrate form, according to the following general reaction [3]:

$$Ca_{10}(PO_4)_6F_2CO_3Ca + 11H_2SO_4 + 21H_2O \rightarrow 6H_3PO_4 + 11CaSO_4 \cdot 2H_2O + 2FH + CO_2 \quad (2)$$
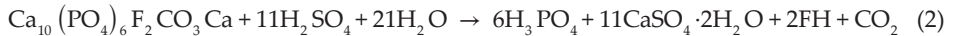
The industrial process can be divided into four different steps (**Figure 1**): (1) grinding and conditioning of the phosphate rock, (2) dissolution of the phosphate rock with diluted sulphuric acid (60%), (3) filtration, or PG separation from phosphoric acid (liquid fraction), and (4) washing of PG by water.

The grinded PR is introduced into the digesters where the phosphate rock is attacked (dissolved), and a pulp is obtained containing mainly PA in solution, and solid PG. This pulp is filtered and PA (24% P_2O_5) and PG are separately obtained. Then, three successive backwashes are done in order to extract the remaining PA still contained in the phosphogypsum. The first washing is carried out with PA at 12% P_2O_5 where phosphoric acid with 27% P_2O_5 is obtained. The second washing is done with 5% P_2O_5 to produce 12% P_2O_5 which is used in the first washing. Thirdly,
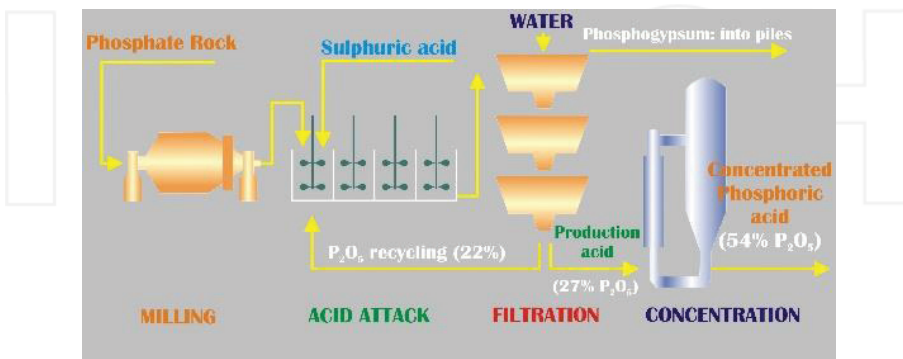

Figure 1. Industrial process of PA production.

a final washing is performed with hot water to produce 5% P_2O_5, which is used in the second washing.

Finally, the 27% P_2O_5 (production acid) is concentrated by evaporation for obtaining commercial acid (54% P_2O_5), since it is the normal concentration needed for the fabrication of the most demanded phosphate fertilizers: monoamonium phosphate (MAP), diamonium phosphate (DAP), and complex fertilizers (NPK).

2.2. Description of PG piles

Although during the last years research and attempts have been done for valorization of the PG, the use of the generated one in the Huelva factories has been until now quite limited and mostly in agriculture as a soil amendment [4]. Consequently, due to the lack of any market for this compound, the great majority of the generated PG in Huelva has historically been considered as a waste with the following management policy: (a) During the first 30 years of production (until December 1997), 20% of the PG generated was released directly into the Odiel Channel of the Huelva estuary, whereas the remaining 80% was transported from the phosphoric acid production plants in suspension with sea water to a neighboring marshland area (2 km away from the plants and located in the confluence of the mouths of the Odiel and Tinto rivers), where it was disposed of by means of decantation with the transporting waters draining directly into the estuary [5, 6]; (b) since beginning 1998, all the PG produced in Huelva has been stored in the PG piles following the OSPAR convention [7, 8]. The PG was transported to the disposal area with fresh water, which was reintroduced in the industrial process following a closed cycle, in order to prevent any impact on the estuarine ecosystem [9].

Since December 31, 2010, the production plants of phosphoric acid have been closed, and, as a consequence, the production of PG has been halted. The legacy from these plants involves a major area where millions of tons of PG have been accumulated, and can be considered as formed by four different areas called Zone 1, Zone 2, Zone 3 and Zone 4, as it is shown in **Figure 2**.

Zone 1 is a 450 ha sector and it was the first area submitted to regeneration work. It is calculated that about 12×10^6 tons of PG, including unknown amounts of urban wastes and mining wastes, were released in this sector. Restoration tasks were performed during 1990 by the Andalusia Regional Government in order to minimize both the visual and the environmental impact associated to the different wastes that were released there. To do that, a soil cover of about 30 cm average thickness and a vegetal coverage were added above the naked PG surface. Furthermore, several tenths of soil hills (1.5 m high) were scattered above the soil cover layer in order to allow small tree species to grow.

In Zone 2 (270 ha), the wastes were released until 2010 inside the water recirculation system. In this zone, the gypsum stacks reached 15 m in height above the natural ground, and it continued to grow following a pyramid shape. As the height increases, the sides of the pyramid are covered with a soil layer and a vegetal coverage, in order to minimize the visual impact.

Zone 3 (180 ha) is close to Zone 2. It is only conformed by PG, without any soil coverage.

Figure 2. Aerial photograph of the area of the Tinto river marshes. (1) Settling ponds, dumping area of FY; (2) regulating reservoir, (3) perimeter channel, and (4) pumping station.

Zone 4 was submitted to a similar restoration process than Zone 1. More detailed, different kinds of industrial and urban wastes were added above the PG: in the first place, a building debris layer was added; thereafter, different kinds of industrial wastes were added and finally, a soil layer like that of zone 1 for different vegetable species can grow on this cover. The total thickness of the coverage (including the three layers: wastes, debris, and soil) is more than 1 m.

Furthermore, one of the sectors contained within the PG stacks was contaminated some years ago by the radioactive ashes produced during the Acerinox Steel factory accident in 1998. An industrial ^{137}Cs radioactive source was accidentally melted with iron wastes in the steel factory. These wastes were treated in a purifier plant in the industrial complex of Huelva. Finally, the wastes and a certain amount of their ashes were released in Zone 4 and mixed with the PG. As a consequence of the releases, the Spanish National Wastes Enterprise (ENRESA) sealed the sector and restoration works were developed consisting in a cover with a layer of clay to minimize permeability and migration of radioactive cesium. Finally, different vegetal species were planted in the sector, and a vigilance program was established.

Besides, from Zone 3, it has been possible to observe liquid leakages (filtrations), mostly with a certain flow, into the Tinto River and adjacent marshlands, while from Zone 2, these leakages are clearly minor in number and diffused after overflowing the perimeter channel barrier.

Currently, there is an environmental plan under study in order to restore Zones 2 and 3; for the total application of which, a duration of 10 years has been estimated. It is expected that the planned restoration should solve the environmental impact on the neighboring areas.

2.3. Samplings

2.3.1. Phosphoric acid plants

In relation to the studies made inside the fertilizer plants, several sampling campaigns have been developed in the phosphoric acid factory located at Huelva (Spain), with the aim of analyzing the distribution [10–12] and levels of radionuclides in the materials involved in its production and evaluating the occupational, public and environmental radiological impact of this factory. Solid, liquid and air-filter samples were collected in: (a) the four steps of the PA process: (1) milling and grinding, (2) acid attack or digestion, (3) filtration and washing, and (4) PA concentration; and in (b) the plants devoted to the production of monoamonium phosphate (MAP) and diamonium phosphate (DAP) fertilizers. The solid samples included several matrices, from the phosphate rock until commercial phosphoric acid (54% P_2O_5).

The water samples were collected at the regulating reservoir associated to the big active pile where the PG was finally stored until 2010. This water is used for the phosphogypsum pumping into the ponds, and it was collected over a year at a rate of one sample per 2 months, in order to evaluate the possible temporal evolution in its radionuclide contents.

In order to estimate the committed effective doses received by the workers of the PA, MAP and DAP plants due to inhalation, aerosol filters were collected from different representative places of the plants. The aerosol collections were performed with Andersen PM10 high-volume samplers. The external radiological effective doses were measured by using a radiation monitor Universal Monitor (UMo) model LB 123. The "Universal Monitor" (UMo), manufactured by Berthold, is a monitor designed specifically for low dose rates. It is equipped with a probe which works on proportional mode and allows the measurement of both dose rate and integrated dose.

2.3.2. Phosphogypsum stacks

The research groups involved in the writing of this chapter have been performing research and monitoring studies associated to the PG stacks and their neighboring environmental compartments since the end of the 1980s.

Several sampling campaigns have been done inside the PG stacks in order to characterize the material accumulated, to analyze the spatial degree of variation in the levels of the radionuclides associated [4, 13], and to evaluate its radiological impact through external radiation, inhalation of particle matter and radon emanation. And also a detailed sampling campaign was done after the halting of the PG production in order to evaluate the radioactive content of the liquid leakages of the piles and the associated formed efflorescences [14].

In addition, dozens of sampling campaigns have been performed in the PG neighboring environments as are summarized in the following paragraphs. In this sense, more than 10 sampling campaigns have been performed from the end of the 1980s until now in the estuaries of the Odiel and Tinto rivers to evaluate the temporal evolution of the environmental radioactive contamination generated by the PG piles and the effluents from fertilizer plants. The majority of these sampling have involved the collection of waters (dissolved and particulate matter fractions), and superficial sediments, although special sampling campaigns were performed, for example, for the collection of several sediment cores in the estuaries to evaluate its possible use as historical archives of the radioactive contamination in the area [15]. In addition, sediments were collected in order to perform speciation studies [16]. In all the cases, several actions were taken in order to preserve the integrity and quality of the samples for radionuclide determinations (acidification of the waters after filtration, drying at room temperature of the sediments in order to avoid changes in the forms of association of the radionuclides to their different phases, etc.).

On the other hand, in addition to the studies carried out in the estuaries mostly with surveillance purposes, other sampling campaigns were performed in order to carry out more pure radioecological studies. In this sense, several sampling campaigns were performed for the collection of vegetation in the marshes surrounding the PG piles (halophytes plants) and the determination of natural radionuclide transfer factors (TFs) [17–19], and the collection and analysis of other biota samples (shellfish, shrimps, etc.).

2.4. Measuring techniques

The radioactive characterization of the great majority of the samples collected either in the production plants, in the PG stacks or in the neighboring environmental compartments (PG, waters, sediments, soils, efflorescences, vegetation, biota, etc.) have been performed by applying two independent techniques: both gamma-ray and alpha-particle spectrometry.

Gamma measurements in solid samples (PG, soils, sediments, biota, etc.) were carried out using along the time several gamma spectrometry systems, most of them based in High-Purity Germanium (HPGe) detectors, although in some specific cases when the amount of material was limited a well-Ge detector was used. The calibration of the gamma systems were performed following procedures as the described in Ref. [20], applying when was needed corrections due to self-absorption effects.

In the same solid samples, as well as in waters, Th-isotopes, U-isotopes and ^{210}Po activity concentrations were determined by alpha-particle spectrometry after the application of validated radiochemical methods, such as the described in Ref. [21], for the sequential isolation of the elements of interest. Alpha-spectrometric systems formed by independent chambers working in parallel and equipped with 450 mm^2 PIPS detectors were used for the measurements. After U and Th were isolated from the matrix under analysis, they were independently adapted for measurement by electrodepositing them onto stainless steel discs by applying the method of Hallstadius [22], whereas Po was self-deposited onto silver discs of 1 inch diameter using Flynn's (1968) method.

Along the 35 years of measurements in the area, other techniques have been also used for specific radionuclide determinations: U and Th elemental determinations, for example, have been performed in waters, PG and sediment samples by ICP-MS. ^{226}Ra and ^{210}Pb determinations in waters have been performed after radiochemical isolation by using the Liquid Scintillation Counting (LSC) technique or low-background gas-flow proportional counters; ^{222}Rn determinations have been carried out on the PG stacks using Rn monitors, etc.

All the procedures used for radionuclide determination have been periodically validated through the regular participation in intercomparison exercises organized at national (Spanish Security Council) and international (IAEA) level. Additionally, different quality control (QC) procedures were routinely applied: performance of replicate analysis, measurement of blank samples, measurement of certified reference materials, regular control of system's background, etc.

2.5. Radioactive characterization

2.5.1. Phosphoric acid plants

The sedimentary phosphate rock treated for the production of phosphoric acid is clearly enriched in radionuclides from the uranium series. They are at least 50 times higher than in representative unperturbed soils worldwide [23]. In addition, in the PR all members of the uranium series are in secular equilibrium (**Table 1**), as expected due to the fact that the material does not experiment any radionuclide enrichment during the physical processes applied before its digestion. On the other hand, the activity concentrations of the radionuclides belonging to the ^{232}Th chain in the treated phosphate rock are quite reduced.

During the digestion step, the first clear evidence of different behavior that the analyzed radionuclides from the U series show in the process is observed. A clear fractionation of the radionuclides contained in the mineral is produced between the liquid and solid fractions from the pulp samples collected from the digesters. The liquid fractions, corresponding mainly to the phosphoric acid formed at this step, are clearly enriched in uranium, whereas the concentrations of ^{230}Th, ^{226}Ra, and ^{210}Pb are very much lower or even negligible (this is the case of ^{226}Ra). On the contrary, solid samples contain the major proportion of the ^{230}Th, ^{226}Ra, and ^{210}Pb originally present in the phosphate rock, whereas the uranium isotopes concentrations are slightly lower. This solid fraction is mostly composed of the PG formed in reaction to the phosphate rock with sulphuric acid. However, it may also contain a proportion of non-attacked phosphate rock and some phosphoric acid occluded between the PG grains and not separated from the liquid samples.

The results obtained in the analysis of the samples collected in the filtration step allowed the confirmation of the different behavior of the uranium isotopes and their daughters previously drawn. By observing the data shown in **Table 1**, we can affirm that most of the uranium tends to be associated to the phosphoric acid fraction, whereas the majority of ^{230}Th, ^{226}Ra, and ^{210}Pb tends to be associated to PG. These conclusions are evident by observing the obtained activity concentrations measured in the phosphoric acid in relation to the P_2O_5 concentration.

The U concentration decreases in the PG samples according to their successive washings, which indicates that the remaining P_2O_5 of the PG is sequentially removed from the different

	^{238}U	^{234}U	^{230}Th	^{226}Ra	^{210}Pb	^{232}Th	^{228}Th	^{228}Ra
PR	1653 ± 21	1405 ± 504	1600 ± 87	1565 ± 124	1578 ± 95	26 ± 5	20 ± 3	21 ± 1
22% P$_2$O$_5$	870 ± 50	870 ± 50	95 ± 4	3.0 ± 0.4	74 ± 14	53 ± 11	1.7 ± 0.4	<1.8
Cake dig. L	1213 ± 186	1197 ± 189	305 ± 104	5 ± 1	73 ± 11	4 ± 2	5 ± 2	4 ± 4
Cake dig. S	490 ± 61	490 ± 61	650 ±125	607 ± 146	660 ± 185	15 ± 1	11 ± 2	12 ± 3
Pulp cake Solid	1340 ± 90	1330 ± 90	425 ± 78	4.0± 0.4	60 ± 12	6.5 ± 1.4	4 ± 0.5	<1. 0
Pulp cake liquid	150 ± 30	450 ± 30	750 ± 30	590 ± 25	590 ± 120	16 ± 2	11 ± 2	9. 4 ± 1.1
27% P$_2$O$_5$	1070 ± 110	1090 ± 110	230 ± 30	5,6 ± 0.5	78 ± 15	9.8 ± 1.8	3.9 ± 0.5	<1.8
22% P$_2$O$_5$	870 ± 50	870 ± 50	95 ± 4	3.0 ± 0.4	74 ± 14	53 ± 11	1.7 ± 0.4	<1.8
12% P$_2$O$_5$	470 ± 40	470 ± 40	80 ± 10	6,1 ± 0.5	<225	6.0 ± 1.5	<1.7	<1.9
5% P$_2$O$_5$	290 ± 20	290 ± 20	4,2 ± 0.3	1,8 ± 0.3	<135	0,17± 0.06	<1.0	<1.5
Gypsum	425 ± 152	439 ± 143	775 ± 47	635 ± 39	620 ± 16	26 ± 8	10 ± 3	10 ± 1
Sludges L	1675 ± 587	1670±608	750 ± 707	6 ± 2	65 ± 27	14 ± 12	11 ± 7	1.7 ± 0.1
Sludges S	1070 ± 226	1065±233	1455±771	2805±2114	1660±339	20 ± 11	21 ± 15	41 ± 33
32% P$_2$O$_5$	1300 ± 70	1320 ± 70	NM	3.6 ± 0.3	<135	NM	6.5 ± 0.4	<0.9
54% P$_2$O$_5$	1830 ± 180	1810 ± 180	NM	7.9 ± 0.5	109 ± 14	NM	13.2 ± 1.4	<1.0

Note: Uncertainty = standard deviation, L = liquid fraction, S = solid fraction, NM = not measured.

Table 1. Activity concentrations (mean values in Bq kg^{-1}) obtained for the samples collected along the milling, digestion, filtration, washing, and acid concentration steps.

washings. On the contrary, the concentrations of ^{230}Th, ^{226}Ra, and ^{210}Pb remain practically constant along the successive washings, showing this fact that this type of radionuclides are very hard bound on the PG fraction.

A clear linear correlation between both U and P$_2$O$_5$ concentrations was obtained by using the different materials involved in the phosphate fertilizer production process, with a slope of 35 ± 2 Bq kg^{-1} ^{238}U/% P$_2$O$_5$. This result demonstrate that the uranium follows the same route that the PA along the full fertilizer production process.

Another conclusion of these studies was that a high fraction of the uranium series radionuclides (mainly U and ^{230}Th) input in the P$_2$O$_5$ manufacturing arrives finally into the environment by the use of phosphate fertilizers in the agriculture.

2.5.2. Phosphogypsum stacks

The activity concentrations measured in the materials stored in the PG piles reflect the radionuclides fractionation in the PA manufacturing, being found for PG that the levels are in the sequence: ^{226}Ra ≈ ^{210}Pb ≈ ^{210}Po > ^{230}Th > ^{234}U = ^{238}U. Activity concentrations of 500–700 Bq kg^{-1} for both ^{226}Ra and ^{210}Pb, and 80–200 Bq kg^{-1} for ^{234}U and ^{238}U have been determined along the PG

stacks [9]. However, the activity ratios found in the PG stacks are something different than the determined ones in the fresh PG obtained immediately after its formation, reflecting this facto the different behavior of the radionuclides analyzed along the time in the deposits. In this sense, the PG stored in the stacks is depleted in U in comparison with fresh PG, which indicates that U is weekly bounded to the PG, incorporating it either to the waters used for the transport of the PG from the factories to the piles, or to the waters interacting with the piles (rain waters, tidal waters from the estuary, etc.). On the contrary, the ^{226}Ra levels in the PG stacks are similar to the found ones in fresh PG, in correspondence with its low solubility.

Supporting the previous comments, to point out that the average activity concentration of ^{210}Pb and ^{226}Ra in the PG are similar in both Zones 2 and 3 of the PG stacks (**Figure 1**), while the average concentration of ^{238}U in PG of Zone 3 (95 ± 15 Bq kg^{-1}) is lower than that in the Zone 2 (220 ± 85 Bq kg^{-1}). This fact is due to the PG from Zone 3 has over time, lost a fraction of U higher than Zone 2 (the PG in zone 3 was stored earlier).

The high solubility of the U contained in the fresh PG is reflected in the extremely high concentrations of this element in the leaching waters from zone 2. High activity concentrations, although in minor extent than for U, were also found in these waters for other uranium-series radionuclides such as ^{210}Po and ^{230}Th. The levels of uranium in these leaching waters are 4 orders of magnitude higher than those obtained in the sea water [24], and even reach the value of 300 Bq L^{-1} for ^{238}U, while the levels found for ^{210}Po and ^{230}Th were 3 and 2 orders higher, respectively, than in sea water. These waters present extremely low pH (pH < 2), which makes it clear that, in the planned process of restoration, these internal PG waters should be carefully treated and neutralized before their release into the estuary. The ^{230}Th/^{238}U, ^{210}Po/^{238}U, and ^{210}Po/^{230}Th activity ratios in these leaching waters are clearly at lower levels than in the PG, reflecting the different way of bounding these radionuclides to the PG and their different solubility in acidic waters.

The uranium activity concentrations determined in leakage waters percolating from Zone 3 to the neighboring salt marshes are also high in comparison with the activity concentrations usually found in seawater, but remain lower than those found in the waters from the perimeter channel (at least three to five times lower), a fact that can be associated with the possibility of a mixture of contaminated waters coming from the PG pile with waters from the estuary of markedly lower activity concentrations. The leaking waters from Zone 3 are also characterized by their very high concentrations of radionuclides from the uranium series analyzed although the relative abundance of these radionuclides in them is different than those in the waters leaking from Zone 2, because since its formation (more than 15 years ago), uranium series radionuclides have been leaking from this zone, and today only a fraction of the radionuclides remains out of those originally present in the pile. This fraction is lower for the radionuclides less bounded to the PG structure, i.e., those more easily dissolved. This fact explains why the U-isotope activity concentrations found in these waters, being very high and relatively uniform, are at the same time one order of magnitude lower than the concentrations determined in the perimeter channel of Zone 2, and lower than the highest values found in some waters percolating into the surroundings of Zone 2.

On the other hand, a big range of activity concentrations were found for different radionuclides of the uranium series in efflorescences collected in the surroundings of Zone 3 and 2 of the PG piles was found, with U-isotope activity concentrations up to 8.7 kBq kg^{-1}, ^{226}Ra activity concentrations up to 2.2 kBq kg^{-1}, and ^{210}Pb activity concentration up to 70 kBq kg^{-1} [14]. These results in efflorescences can be explained by taking into account the fact that they are formed by the evaporation of the diffused waters escaping from the piles that, in the situation of near dryness, induce the precipitation of a big proportion of the associated metals and radionuclides. The formation mechanism of these efflorescences explains in fact why the activity concentrations of ^{210}Pb are higher than the ^{238}U and ^{226}Ra activity concentrations in most of the samples analyzed, as is reflected in the ^{210}Pb/^{238}U and ^{210}Pb/^{226}Ra activity ratios which are generally higher than 1, because it is well known that the precipitation trend of Pb is different than that for Ra and U [25].

The activity concentrations of ^{226}Ra in the great majority of efflorescence samples analyzed are clearly lower than the activity concentrations of ^{238}U, ^{210}Pb, and ^{210}Po, and only in a very limited number of cases exceed the average concentrations found in the PG disposed of in both the analyzed zones, allowing the rejection of the hypothesis that the efflorescences in the surroundings of Zone 2 and 3 are formed by particles of PG with the smallest grain size transported by the leakage waters; it is well documented that the ^{226}Ra activity concentrations in the PG finest fractions are clearly higher than the found ones in the bulk PG.

Finally, it is worth to mention that the impact of the PG stacks in the atmospheric compartment has been also evaluated through radionuclide determinations performed in aerosol samples collected over the piles and through ^{222}Rn determinations. The obtained results indicate small enhanced concentrations from the uranium series radionuclides in the aerosols collected over the piles, although this fact is not reflected in significant either occupational or public doses, due to the very low aerosol concentrations generated in the area. The main reason is that the PG produces a hard crust on the surface of the piles that avoid the resuspension of material.

On the other hand, the concentration levels of ^{222}Rn over the piles are not statistically different to the values found in background reference areas, indicating that the generated ^{222}Rn in the piles as a daughter element of ^{226}Ra, when escapes from the piles, quickly experiments its dilution in the atmosphere, process that is favored by the breezes that usually affected the coastal area where the piles are disposed. A high spatial variability for ^{222}Rn exhalation was found in the PG piles, although the average values are one order of magnitude higher than the found ones in neighboring background areas [26]. This result confirms the importance of the commented dilution effects in the ^{222}Rn concentrations found.

3. Occupational radiological impact

The magnitude and behavior of the radionuclides involved in the PA production process revealed the need to determine its dosimetric impact on workers. Besides, a detailed dosimetric evaluation was carried out in the MAP and in the DAP plants located in the Huelva fertilizer facilities.

3.1. PA plants

Relatively small increments of the instantaneous external exposure were determined in the milling area during the processing of Moroccan phosphate rock. Only relatively higher values were found at or inside the silos used for the storage of the PR (0.25–0.37 mSv h^{-1}), due to the presence of large amounts of Moroccan phosphorite containing high activity concentrations of ^{238}U (around 1 kBq g^{-1}). It is worthy to note that lower values were also measured inside the rest room, room where the workers spend the majority of the time in the area.

Relatively high instantaneous external exposures over background were determined in some locations of the acid storage facilities and the concentration areas. However, the PA acids contain negligible amounts of ^{226}Ra and daughters, which are the main gamma emitter radionuclides inside the process.

The highest total effective external dose rates were measured inside the filtration facility (reaching 1.1–1.4 μSv h^{-1}), around the third washing stage, being 0.1 μSv h^{-1} the natural background of Huelva province. The measurements carried out above the filter itself, being a zone with very low occupation factors, show high external dose rate. The remaining measures were performed along the perimeter of the filter, and lower values were obtained due to radiation attenuation by the metallic lateral walls of the filtration system. The values obtained over the filter are clearly higher than expected in most cases. It is necessary to take into consideration that the values registered at 1 m over a semi-infinite extension of PG hardly surpass 0.3 μSv h^{-1} [13]. Consequently, an additional source of gamma radiation must be present in the filtering area, being a major contributor to the effective dose rate and, additionally, it should be present regardless of the PR rock treated in the process. Therefore, the existence of a permanent radioactive contamination in some parts of the filtering equipment (scales) can be derived. Quite high ^{226}Ra activities were determined in these scales, supporting the previous statement. We can then conclude from the external dose rate measurement campaigns that, with the exception of the milling area where only PR is involved, the values obtained for the external exposures cannot be correlated to the amount of radioactivity fluxing by them. Thus, the major fraction of the external exposure rates measured is produced by a permanent radioactive contamination fixed on the pipes, deposits and filtering systems in the plant.

The particulate matter concentration in outdoor surface air inside the factories (average = 370 ± 10 μg m^{-3}), and its natural alpha emitter radionuclides concentrations were measured. Based on these data, the additional committed effective doses due to aerosols inhalation received by workers were estimated, founding that the increases of the committed doses ranged 10–100 times lower than the limit value fixed for the public (1 mSv yr^{-1}).

3.2. MAP and DAP plants

External radiation and inhalation of particulate matter were considered the main routes by which increments in the exposure of the workers can be produced, whereas ^{222}Rn determinations were also performed in both plants in order to evaluate the possible additional risks associated with the presence of this radionuclide in enhanced amounts.

Regarding the eternal gamma radiation, the values were low and always in the range 0–0.08 $\mu Sv\ h^{-1}$ over background (which is 0.09 $\mu Sv\ h^{-1}$). These low values are to be expected when it is considered that the raw materials and final products are only enriched in radionuclides which are mainly alpha-emitters, and therefore they are depleted particularly in ^{226}Ra and daughters, as well as in radionuclides from the thorium series, and ^{40}K, which in NORM facilities represent the main contributors to the external gamma radiation.

With the external gamma dose rate determinations performed, it was possible to carry out a detailed assessment of the occupational exposures due to external radiation received by the workers carrying out their activities in the MAP and DAP plants.

The occupational exposures due to external radiation for different working categories were determined. The external exposures associated with the various kind of workers are relatively uniform (maximum of 0.1 mSv yr^{-1}), independent of the activities performed by each worker inside the plants, and are clearly below 1 mSv yr^{-1}.

The low external occupational exposures could be considered representative of the found ones for other plants devoted to the production of ammonium phosphate fertilizers that use phosphoric acid as a raw material. However, higher values can be expected in plants devoted to the production of NPK fertilizers that use MAP as a raw material, due to the contribution arising mainly from the ^{40}K intrinsically present in the natural potassium used for their generation.

The radiometric determinations performed in the aerosol filters collected in the plants show enhanced (and variable in time) mass activity concentrations of the radionuclides belonging to the uranium series in relation to the concentrations determined in the background area (El Arenosillo). However, no enhancements were observed for the radionuclides from the thorium series or for ^{40}K. In all cases these committed effective doses are moderate and remain below 0.12 mSv yr^{-1}.

The radiological study allowed us to conclude that the occupational doses received by the various worker categories in the plants do not reach the value of 0.3 mSv yr^{-1} when considering the worst scenarios and all the possible pathways of exposure. The dose increments due to the external radiation and inhalation of particulate matter are the main routes of exposure. No single action or adoption of any radiation protection measure needs to be taken in order to protect the health of the workers.

Furthermore, the ^{222}Rn concentrations inside the two analyzed plants are also of no concern since they were around the 20 Bq m^{-3}, which is one order of magnitude lower than the established limit that would trigger the adoption of remediation actions.

4. Public and environmental radiological impact

Very high levels of different radionuclides from the uranium series were observed in waters (dissolution and suspended matter) and superficial sediments before the beginning of the close

circuit of the pumping PG waters (1998), finding the highest ones in the Odiel river due to the direct releases of PG in this zone, since about 20% of the total PG production was directly released into Odiel Channel [27].

The sampling campaigns carried out before the change in the PG management policy (1998 year), the ^{226}Ra activity concentrations in the estuarine waters collected in the surroundings of the PA factories were around 10^2 Bq L^{-1} (two orders of magnitude higher than natural seawaters), diminishing clearly after 1998 to values near to the expected background ones.

The historical radioactive impact caused by the operation of the phosphoric acid plants in the neighboring estuaries have been found in selected sediment cores collected in the area. As an example, in the **Figure 3** is shown the ^{226}Ra profile obtained in one sediment core collected in the year 2000 in the Odiel estuary, together with the profile obtained simultaneously for ^{137}Cs. Assigning the maximum of the ^{137}Cs to the year 1963, it is possible to observe how the ^{226}Ra activity concentrations start to increase in layers with an age compatible with the starting of the operations of the factories in 1968, and how the levels of ^{226}Ra in different layers are clearly enhanced since 1968 until the surface layer of the sediment core [15].
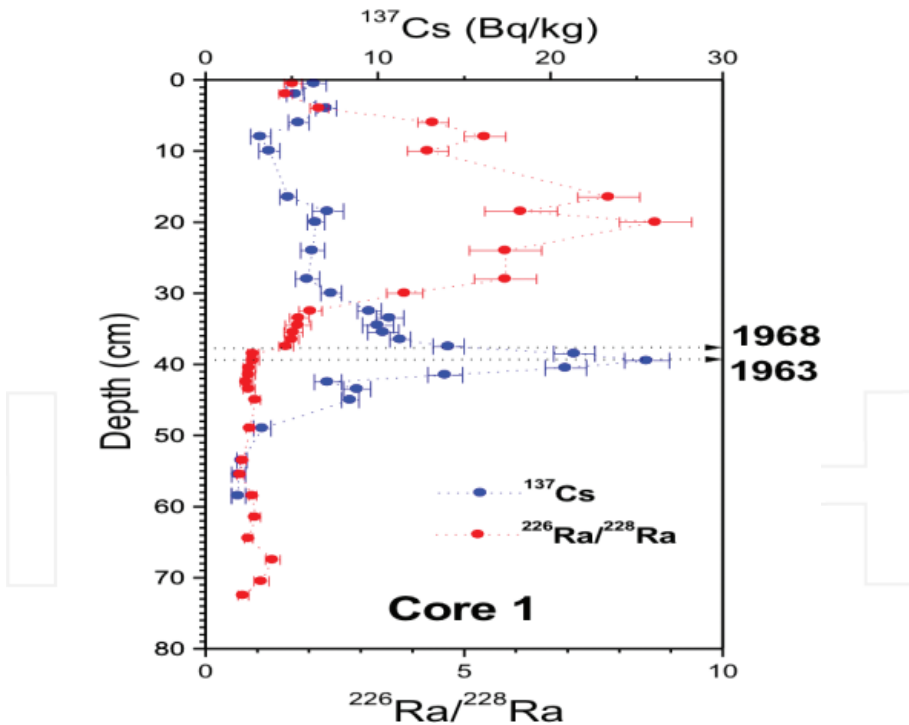

Figure 3. ^{226}Ra/^{228}Ra and ^{137}Cs activity profiles in one sediment core collected in the Odiel estuary. The results of ^{226}Ra are normalized to ^{228}Ra in order to discard the influence of possible changes in the composition of the sediments.

The decreases observed for ^{226}Ra in the waters of the Odiel estuary after 1998 where found also in the Tinto estuary waters and for other radionuclides of the uranium series, indicating that after the adoption of the new management policy for the PG disposal in 1998, the leakage waters coming from the zone A of the PG piles, and the diffused escapes from zone B have a quite limited impact on the neighboring environment. These leakage and diffuse waters contain enhanced levels of radionuclides from the uranium series, but its volumetric magnitude is very low comparable with the water fluxes discharging from the rivers in the estuary.

Since 1998, only some sporadic increments were observed in the levels of ^{226}Ra in waters of the Odiel river, mostly due to the resuspension of the oldest sediments contaminated before 1998 [24]. In the waters and superficial sediments of the whole estuary, since 1998 a clear decrease in the levels of radionuclides such as ^{226}Ra and ^{210}Pb has been observed that nowadays are approaching natural background references [28].

After 1998, only one exception was found in relation with the general trend of lower activity concentrations in the different environmental compartments of the estuary. This exception corresponds to the Uranium. The temporal evolution of the U activity concentrations determined in several sampling points of the Tinto estuary was studied, founding that the levels of U in the waters after 1998 were similar or even higher than in the sampling campaigns carried out before.

The particular U results are mainly reflected in the waters and sediments of the Tinto estuary and can be explained by the existence of an additional source of this element reaching the estuaries. The Odiel and Tinto rivers have been historically, since the Roman Empire, mining rivers affected by the activities performed by the extraction of metals such as Cu in their margins. Both rivers are along their course affected by acid mining drainage, showing its waters pH values clearly acidic. The mining drainage waters provoke the preferential dissolution of the uranium from the mine substratum, these being drainage waters incorporated to river water flow and transported to the estuary where the associated U in dissolution experiment and its precipitation being associated to the change of pH provoked by the mixing of the acid waters transported by the river with the sea water. In relation specifically with U, its activity concentration in the Odiel and Tinto river estuaries, with independence of the restoration plan applied to the area, will not reach background values due to this additional historical source.

The importance of the mining activities in the upper margin of the rivers, and the influence of the acid mining drainage effect in the U levels in the studied estuaries is clearly reflected in the U profile obtained in one sediment core collected during 1998 in the Tinto estuary just in front of zone A of the PG piles. A modified version of the ^{210}Pb-dating method was applied for dating this sediment core. The U profile obtained reflects clearly the history of the mining activities in the area: start to increase sharply in the middle of the nineteenth century (when the mining activities started in great extent), approaching the maximum levels in the first century of the twentieth century when the mining activities in the area reach the maximum levels. Just after the Spanish civil war in the 1930s, the mining activities decrease as it is reflected in the decrease of the U levels found in the sediment layers formed during this time, suffering only a modest final increase since 1968 due to the influence of the phosphoric acid plants.

The peculiarities of the estuary formed by the confluence of the Tinto and Odiel rivers from the radioactive point of view, with relatively well-defined sources of several radionuclides from the uranium series, has converted the area in a natural laboratory where different radioecological studies have been and can be performed. In this sense, determinations of distribution coefficient factors (k_d), and of transfer factors soil to plants (TF), have been performed. In addition, this estuarine ecosystem and the huge amount of radioactive data generated in it, has served for the historical development of numerical hydrodynamic models to explain and predict the dispersion of the radioactive pollution and to gain in this way a lot of information about the environmental behavior of different radionuclides in estuarine compartments [29]. These models solve water circulation due to tides and river stream flows, include uptake/release reactions of radionuclides between the dissolved phase and bed sediments in a dynamic way (using kinetic transfer coefficients) and allow to evaluate the relative significance of the different radionuclides sources into the estuary as well as the independent effect of the two components of water circulation (tides are river flows) on radionuclide dispersion patterns.

Quite recently [19], a detailed study has been performed analyzing natural radionuclide concentrations in three species of halophytes plants growing in salt marshes from the Tinto estuary. The results of this work have shown that, (a) natural radionuclide concentrations (specially the U-isotopes) in the Tinto salt-marsh sediments are one order of magnitude higher than those determined in unpolluted salt marshes taken as a reference, and (b) these radionuclide enhancements are reflected in the different organs of the plants having increased concentration of these radionuclides. The transfer factor (TF) of the most polluted radionuclides (U-isotopes and ^{210}Po) in the Tinto salt marshes are one order of magnitude higher than in the unpolluted reference site indicating that the fraction of each radionuclide in the sediment originating from the pollution is more available for the plants than the indigenous fraction. This last conclusion allows indicating that the plants of the salt marshes are unhelpful as bioindicators or for the phytoremediation of radionuclides. In this work additional information was obtained by analyzing the internal distribution of the natural radionuclides in the plants, by distinguishing among its main organs (roots, stems, and leaves).

In representative aliquots of living biota that can be found in the Huelva estuary, natural radionuclide determinations have been also performed. In particular, shrimps and different shellfish species collected in the Huelva estuary have been analyzed after 1998, and it is found that the levels of ^{210}Po, ^{210}Pb, U-isotopes, and ^{230}Th are similar to the determined ones for the same species in aliquots collected in an unperturbed estuary located nearby, and to the determined ones for the same species in unperturbed estuarine ecosystems distributed over the world. This fact indicates that the radioactive pollution existing in the Huelva estuary, which is diminishing since 1998 to levels near to background nowadays, have a quite or very limited impact in the upper levels of the trophic chain.

If in addition, we have in consideration that (a) the possible interaction of the radioactive pollution existing in the estuary with continental waters is limited to a possible interaction with an aquifer located below the phosphogypsum piles that is saline and consequently its waters have no use in agriculture and as a source of drinking water, and (b) no detectable increments in particulate matter and ^{222}Rn activity concentrations have been observed in the vicinity of the PG piles, we can conclude indicating that the public radiological impact associated to the radioactive

pollution of the Huelva estuary and to the presence of the PG piles is extremely limited—lower than 20 μSv yr^{-1}, being adopted for this estimation as extremely conservative assumptions.

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