Radioactivity levels in aerosol particles surrounding a large TENORM waste repository after application of preliminary restoration work

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Abstract

In this paper, ^{238}U-series radionuclides have been analysed in particulate matter samples collected at a phosphogypsum stack system located near the city of Huelva (SW Spain) during the course of 1 year. The results have been compared to those collected at a reference (background) site located a few km away, in order to establish if the stack system provokes an increase in radionuclide exposure due to inhalation with particulate matter. The ^{222}Rn progeny, which is considered a very important contributor to the internal dose rate received by the population, was collected for 6 months. The results indicate that for several types of radionuclides there is a significant increase in the radioactivity adsorbed by the aerosol particles collected at phosphogypsum stacks. The isotope analysis indicates that this increment could be affected by the water vapour emissions from the factory, which contain high concentrations of these radionuclides. However, the majority of these radionuclides could not be detected at the background location. The corresponding dose increment estimated at the sampling point is, however, negligible. This fact is a consequence of the very small radionuclide concentration increment, together with relatively conservative nature of the occupational factor applied. Regarding the Rn progeny, no significant differences between either the collecting sites has been registered due to of the dominant wind regime at the sampling locations.

Keywords: Natural radioactivity; TENORM; aerosol; resuspension

1. Introduction

It is estimated that more than a half of total radioactive dose rate received by world's population is associated to radioactivity inhalation via aerosol particles (UNSCEAR, 2000). At locations far from nuclear industrial activities, only radioactive fallout (related to atmospheric nuclear tests during the 1950s and 1960s) and natural radioactivity should be considered from the internal dose point of view. However, background levels of radionuclides in aerosol particles can be enhanced due to industrial processes involving NORM (Naturally Occurring Radioactive Material) work activities, one of these being the production of phosphoric acid using phosphate rock. This sedimentary raw material usually contains high concentrations of radionuclides belonging to the natural ^{238}U-series: ^{238}U-series activity concentrations ranging from 200 up to 2000 Bq/kg have been reported, where ^{238}U is in secular equilibrium with its

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daughters (Bolívar et al., 1996; Azouazi et al., 2001). These values are up to 100 times higher than those corresponding to an average soil which is around 20 Bq/kg for ^{238}U. This radionuclide is usually close to secular equilibrium with its daughters (UNSCEAR, 2000).

During the industrial process, the secular equilibrium conditions existing in the raw material are altered, and a by-product called phosphogypsum (PG, mainly $CaSO_4 \cdot 2H_2O$) is formed, which also contains a certain amount of phosphoric acid (about 1% contents in P_2O_5). Different fractions of the heavy metals and natural radionuclides contained in the phosphate rock are thus released with the PG. Hence, the different radioactive isotopes released from the raw ore are carried by either the phosphoric acid or the generated by-product, according to their respective elementary chemical behaviour.

In the previous studies performed for the plants located at Huelva, it has been found that a major fraction of Ra isotopes (more than 95%), Th isotopes (~70%) and a smaller fraction of U isotopes (~15%), follow the by-product (Bolívar et al., 1996; Pérez-Moreno, 2005). The presence of high concentrations of ^{226}Ra in the PG (average value of about 650 Bq/kg, Mas et al., 2006) is very important from the radiological point of view: ^{226}Ra is the parent radionuclide of the noble gas radioisotope ^{222}Rn, whose short-lived daughters are responsible for an important fraction of the total internal dose received by the population.

During the past 40 years, different facilities devoted to the production of phosphoric acid, and located in the surroundings of the city of Huelva (SW Spain), have released a PG total amount of about 8×10^7 tonnes. Until 1997, 80% of the PG generated by this fertilizer industrial complex was stored in nearby salt marshes. This disposal site presently covers about 1200 Ha, a situation considered by the scientific communities as a radiological anomaly.

Due to the proximity of the PG stacks to the city of Huelva (less than 2 km) and as consequence of the intensifying social alarm generated over the years, the regional authorities have been carrying out different restoration work from the beginning of the 1990s. Among these activities, more than 50% of the surface of the PG stacks has been covered with successive layers of different materials including natural soils, building by-products and neutralised industrial waste.

The principal concern of this work is to check the existence of an extra radioactivity supply through air from the phosphogypsum stacks, and, if found, to establish its environmental and radiological impact. According to the previously explained problem, target radionuclides are naturally occurring radionuclides associated to the gypsum stacks (^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{222}Rn and ^{210}Pb). Besides the fact that many papers have been devoted to the radiological impact on the aquatic system that surrounds the PG stacks (Bolívar et al., 1996, 1995; Mas et al., 2001), to the best of our knowledge there are no reference data for radioactivity contained in the aerosol particles in this study area. Hence, one of the major objectives of this work is to clarify the radiological impact (i.e., the dosimetric increment above the background level) on both local population and workers within through the inhalation of both ^{222}Rn progeny and long-lived natural radionuclides in aerosol particles. Workers could be exposed to an increase of inhaled radioactivity during their working time at the PG stacks. The population could be exposed as a consequence of the proximity of both the PG stacks and the factories to the city (see below for details).

2. Materials and methods

2.1. Air sampling

An extensive sampling campaign was carried out during the course of 1 year (24 May 2002 to 16 May 2003) at two different sampling locations. The first selected point is located over the PG stacks where the external exposure reaches its maximum value (Mas et al., 2006). The maximum occupational factor is also located at this point. The second sampling point is located 25 km away from the PG stacks (see Fig. 1). This location is selected in order to obtain a background reference level.

Total suspended particles (TSP) were collected in fiberglass filters using a high-volume pumping system CAV-A/HF (MCV, Barcelona, Spain), keeping sampling flow rate at a value of 30 m^3/h. Each sample was collected over a period of 3 weeks, with an effective collection time of 1 week. This is the time in which the filter tends to reach saturation and its aerosol particles collection efficiency becomes drastically reduced. Sampling was performed using cycles of 240 min during 3 weeks consisting of an 80-min sampling period followed by a stop period of about 160 min. Under these conditions, during a sampling period of 3 weeks, the pause episodes successively cover different periods until a whole day is scanned. This sampling scheme was selected as a compromise between the objectives of the study and several technical and operative requirements (see below for details).

Aerosol particles were retained onto 12-cm diameter Whatman A borosilicate fiberglass filters. The deposited mass was determined by a gravimetric method, i.e., the

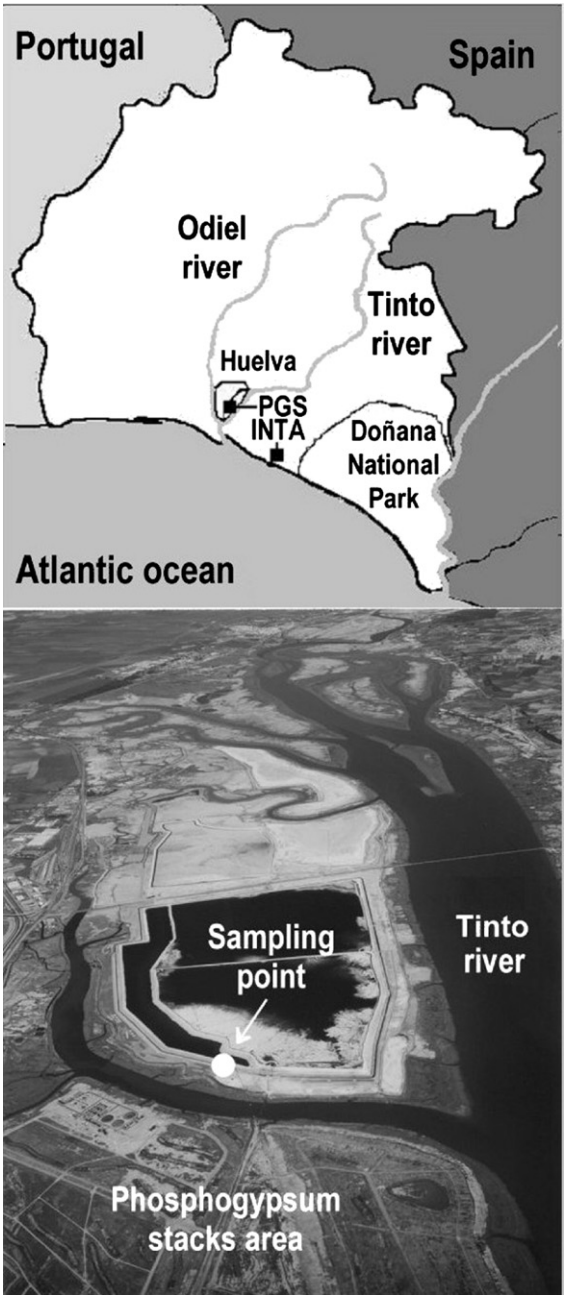

Fig. 1. Location of the two sampling points in Huelva province (SW Spain). One of location, PGS, is the phosphogypsum stack which are spread along the east border of Huelva town, whereas the other sampling point, INTA, is in a research centre located in a pine tree area near Doñana National Park.

aerosol particles mass was determined by subtracting the mass filter from the total mass after sampling (and after having desiccated to a constant weight). To this end, an electronic weighing machine with 0.1 mg precision was used. Sampled total mass was always within a range of 0.1–0.3 g.

Radionuclide activity concentrations were determined using either conventional alpha or gamma spectrometry, as described below. From these concentrations, only those long half-life radionuclides from ^{238}U-series have been finally used in this study. Cosmogenic radionuclides such as ^{7}Be are beyond its scope.

Total radon progeny content was registered by monitoring as described below at the same location as particulate matter, only over the course of 6 months; the background location was monitored for 1 month.

2.2. Radioactivity measurement

The ^{238}U, ^{234}U and ^{230}Th levels were measured by alpha particle spectrometry. The ^{210}Po was not determined due to the long decay time elapsed after the sampling. Besides the fact that analytical corrections are possible, there are several reasons for their avoidance in this work: (1) the magnitude of the relative uncertainties so introduced (i.e., after passing a long time between sampling and analysis) is so high the quality of the information so achieved is drastically reduced, and (2) this determination would require a replication of each analysis at different times, thereby provoking a drastic reduction of the filter mass available. At the present time, however, a new sampling methodology is being applied in order to facilitate an immediate analysis of filter samples, for example, the ^{210}Pb/^{210}Po disequilibrium is applied to obtain the calculation of air mass residence time. Alpha particle spectrometry was performed using an EG and G ORTEC SOLOIST-U0450 system, consisting of eight independent chambers, each with an implanted silicon barrier detector. Counting time per sample was about 3 days depending on the activity level. In this case, a radiochemical method was previously applied to each filter for separation and isolation of alpha emitter radionuclides.

The isolation of U and Th isotopes was carried out according to a chemical extraction method developed by Holm and Fukai (1977) and was conveniently adapted to our operational requirements (Bolívar et al., 1996). The chemical yields (which are within the range 40–70%) were calculated by using the internal standard technique after addition of about 40 mBq of ^{232}U and ^{229}Th.

It is necessary to consider the activity added by the fiberglass material (i.e., the blank levels) in order to correct the calculated concentrations, especially bearing in mind the relative mass difference between the filter itself and the TSP mass. To take this contribution into

account, both U and Th-isotopes were measured in three filters from each commercially available batch of 25 filters. The blank activities of these radionuclides were within a range of 1–4 Bq/kg.

The ^{226}Ra and ^{210}Pb were measured by gamma spectrometry using a coaxial germanium XtRa (Extended Range) detector (Canberra GX3519; 38% relative efficiency) which included passive shielding (a 15 cm-thick Fe layer). The ^{226}Ra was measured through the 352-keV emission of its daughter ^{214}Pb once secular equilibrium was reached in the sample (after 3 weeks). On the other hand, ^{210}Pb was analysed through its 46.5 keV gamma emission. Whereby each circular filter was folded 3 times to a 45° sector of a circle and wrapped with plastic paper before analysis. Counting time was 1 week. Efficiency calibration was performed according to a methodology developed in our laboratory in order to take into account the great thickness differences between filter samples and common, liquid/solid matrices (Martínez-Ruiz et al., 2006).

Finally, radon progeny was measured using a TN-WL-02 monitor (Thompson Nielsen electronics Ltd., Canada) ensemble that includes a pump for air sampling, working at a flow rate of 1 L/min. Sucked air is forced to pass through a 0.45-μm Millipore filter, where aerosol particles, including those with adsorbed Rn-progeny atoms, are retained. The filter is located opposite a semiconductor detector where alpha emissions produce the generation of pulses which are registered in a digital pulse recorder. This filter is changed every 2 days, and data for ^{222}Rn, in Bq/m^3, are produced every 15 min. Due to the sensitivity of the detector to alpha emissions from the short half-life Rn progeny, the physical magnitude determined is the equivalent equilibrium concentration (EEC), which is the magnitude of interest regarding dosimetric evaluations.

An estimation of the effective doses received through inhalation by people in the proximity of the gypsum stacks could be performed. To this end, the corresponding dose rate factors proposed in UNSCEAR (2000) should be applied. However, it is necessary to bear in mind that dose rate received through inhalation depends on many factors that have been not analysed in this work, such as grain size, radionuclide solubility, absorption rate in body fluids, etc. As these parameters are beyond the scope of this work, only a raw estimation could be made. This has been performed assuming that (1) Th absorption rate is slow (absorption type "S") and (2) the absorption rate of the remaining radionuclides is medium (absorption type "M"). The limitations of this methodology on the ability to predict the accurate dose rates are discussed in the next section.

3. Results and discussion

3.1. Total suspended particles (TSP)

Individual data for TSP at both sites are given in Fig. 2. A general correlation between the two data sets can be found here. It is observed that the highest values at both locations occur during the summer, reflecting that typical meteorological conditions in this season (less rainfall and humidity, higher temperatures, greater atmospheric stability) favour the aerosol formation. In the case of PG stacks, data imply an annual average value of 49.1 ± 19.0 μg/m^3. This value is in agreement with previously published values for the city of Huelva (50 μg/m^3, Querol et al., 2002). However, it is greater than that for INTA (33.1 ± 11.3 μg/m^3) since individual data at PG stacks are systematically higher than those taken at the background location. Indeed, when the ratio of TSP contents is performed for each sampling period, it is always greater than one, with an average ratio of 1.65 ± 0.22. This behaviour indicates that there exists a local source of aerosols that increases the TSP in this zone. Nevertheless, this increment is mainly due to the fact that the PG stacks are in more industrial and urban surroundings than INTA, and not due to a contribution from the PG stacks. They formed the east border of the city of Huelva and an important industrial complex is located in the south of the city in the confluence of the Odiel and Tinto rivers. The radionuclide activities (^{238}U, ^{230}Th and ^{226}Ra) should imply either support or contradiction of this hypothesis, by showing if the

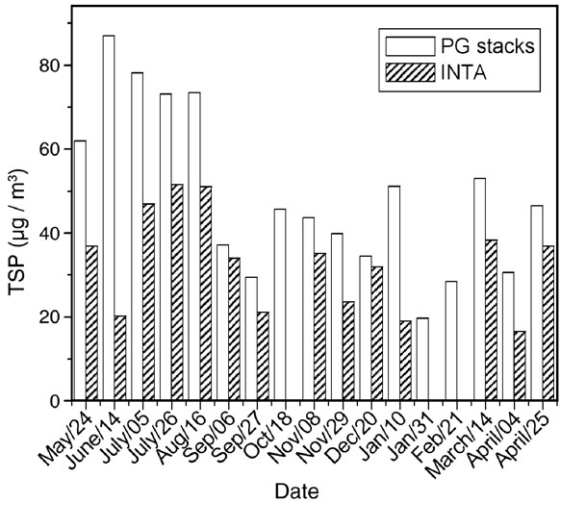

Fig. 2. TSP content, in μg/m^3, at the two sampling points from 24 May 2002 to 16 June 2003. Gaps in the data indicated reflect that the air sampler had broken down.

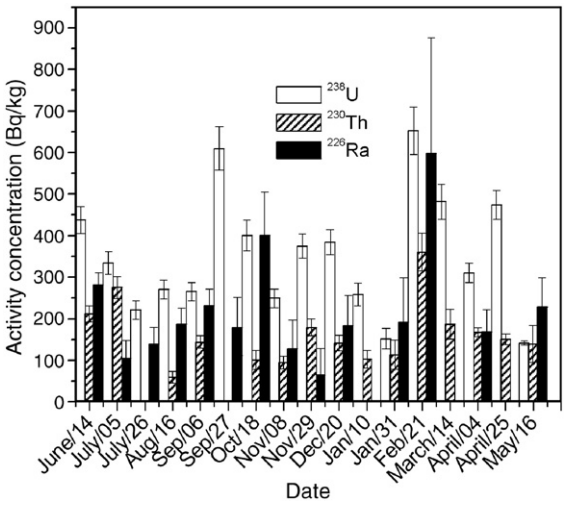

Fig. 3. The ^{238}U, ^{230}Th and ^{226}Ra activities, in Bq/kg, at the PG stacks. Gaps in the data reflect a level below our minimum detectable activity.

origin of such a possible TSP enhancement could be due to PG. This fact will be discussed in the following sections.

3.2. U isotopes

Fig. 3 shows the ^{238}U (and ^{230}Th and ^{226}Ra) content, in Bq/kg, in the aerosol samples collected at the PG sampling point. Values for ^{234}U are not shown since they are similar to those of ^{238}U and reflect the secular equilibrium between them. These results range from 6.6 to 29.2 μBq/m^3 with an average activity of 16.0± 6.1 μBq/m^3. The associated uncertainty is in this case the statistical dispersion of the data set instead of the standard deviation. Uncertainty is calculated as the mean standard deviation. These data are in agreement with previous values reported for the city of Huelva by Querol et al. (2002). Their values are furthermore similar to our data for maximum values, though clearly smaller than those of the reference for minimum values (7 times less) and approximately 50% less for mean values. It is worth to note that the average concentration (μBq/m^3) is up to 16 times higher than the reference data for air concentrations (UNSCEAR, 2000). On the other hand, the ^{238}U contents, in Bq/kg, range from 141 to 653 Bq/kg, with an average activity of 354± 145 Bq/kg. These values are clearly higher than the average ^{238}U content in a typical soil (UNSCEAR, 2000). In the case of the INTA sampling point, ^{238}U activity was below our minimum detectable activity (above 5 Bq/kg). Considering the lower values reported in the city of Huelva for ^{238}U, this fact seems to reflect that there is a contribution to TSP in uranium associated with PG stacks and fertilizer plants, which are located quite close to PG stacks. These uranium contents must have their origin not only in the resuspension of stacked PG, but also either in the evaporation of waters used in its transport or in the gaseous emissions from the four fertilizer plants, as it is well known that the vapour emissions contain significant fractions of residual phosphoric acid which is enriched in U (Bolívar et al., 1996). Phosphoric acid contained in these vapour emissions have concentrations in the range of 1 kBq/kg of ^{238}U, for the stored PG the activity concentration is about 70 Bq/kg, and for waters used in the recirculation system this concentrations is relatively uniform, around 200 Bq/kg (Pérez-Moreno, 2005). Hence, the previously shown high U concentrations could be associated to these sources.

Maximum concentrations of ^{238}U are found in September and February, corresponding to minima TSP contents. Indeed, the uranium contents (μBq/m^3) in TSP are variable throughout the year and are greater in summer when the formation of aerosols is favoured. As previously indicated, the enhancement of U concentration in TSP could be related to sources generated by liquid aerosol particles, a possibility that is reflected in the fact that there is no TSP increase when the U concentration increases. Hence, the most probable hypothesis is the U association to liquid aerosol particles emitted from the water recirculation or the fertilizer plants.

Using a methodology proposed by Berg et al. (1994), enrichment factors (EF) could be used in order to characterize how the aerosol particles are enriched in different analytes. To this end, a reference value for surrounding soil should be defined, and, according to previous references, in Table 1 these reference values have been defined for our geographical area. For ^{238}U, enrichment factors (EF) lie within the range 5–22, with an arithmetic mean of 12. These EF values are very high and therefore indicate a very important contribution to the aerosol particle composition from an additional source different from crustal soil. It is worth mentioning that, according to Querol et al. (2002), crustal soil seems to be responsible for more than 40% of the TSP mass collected at the city of Huelva over the course of a year and a half. About 24% seems to be of anthropogenic origin. Let us remember, however, the differences

Table 1
Reference values for radionuclide contents of the different materials possibly contributing to the TSP mass

Radionuclide	^{226}Ra (Bq/kg)	^{230}Th (Bq/kg)	^{238}U (Bq/kg)
Cover soil	26	20	20
Phosphogypsum	620	280	140
Recirculation water	2	2	200

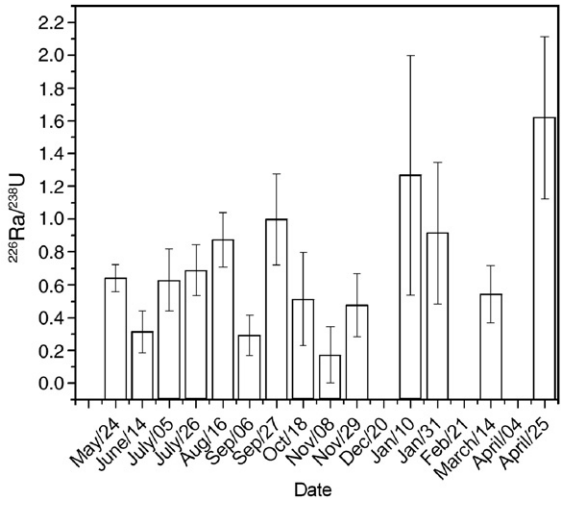

Fig. 4. The $^{226}Ra/^{238}U$ activity ratio at the PG stacks.

between both collection sites. The sampling point at the PG stacks is located quite close to industry; hence, although the frequency of wind precludes a continuous industrial effect, fumigation events from both nearby chimneys and uncovered gypsum stacks are possible. Furthermore, it is necessary to remember that the sampling site is surrounded by a recirculation water system, from where aerosol particles containing relatively high uranium contents could be resuspended and subsequently incorporated into the filters. This possibility will be analysed in detail under the light of results for other radionuclides.

3.3. The ^{226}Ra and ^{230}Th

Fig. 3 shows the ^{226}Ra and ^{230}Th contents, in Bq/kg, in the aerosol samples collected at the PG sampling point. In the case of ^{226}Ra, results range from 64.6 to 600 Bq/kg (2.8 to 18 μBq/m^3) with an average activity of 221±136 Bq/kg (10.3±4.1 μBq/m^3), and in the case of ^{230}Th, from 59.7 to 360 Bq/kg (2.99 to 24.0 μBq/m^3) with an average activity of 162±76 Bq/kg (10.3±4.1 μBq/m^3). As in the case of ^{238}U, the average activity concentration values (μBq/m3) here reported are up to 20 (^{230}Th) and 10 (^{226}Ra) times higher than the reference data (UNSCEAR, 2000). The maximum concentrations are once again associated to the minimum TSP values, as in the case for ^{238}U. These activity concentrations are clearly higher than those corresponding to typical soils. In the case of the INTA sampling point, activities were again below the level of our minimum detectable activity (in the range of 100 Bq/kg for ^{226}Ra and 5 Bq/kg for ^{230}Th depending on the measuring time). These results confirm the previously mentioned origin of the aerosol, i.e., that the enrichment can be associated to the liquid aerosol particles since Ra and Th contents in phosphoric acid are about one order of magnitude less than those of U. However, if the only origin of this contribution were the resuspension of stacked PG, according to published data (in the range of 220 Bq/kg for ^{230}Th and 650 Bq/kg for ^{226}Ra, Mas et al., 2006), the ^{226}Ra and ^{232}Th TSP contents should be considerably higher than those results shown here, i.e., higher than those reflected for ^{238}U.

According to Pérez-Moreno (2005), $^{226}Ra/^{238}U$ isotope ratios are characteristic and well known both for PG (approximately 5) and liquid aerosols coming from the recirculation system and from the gaseous emissions from the fertilizer plants (1/40). Hence, this isotope ratio could be used as a tracer or fingerprint of the sources generating the TSP contained in the filters. A similar reasoning could be applied to the isotope ratio $^{230}Th/^{238}U$. However, the relative magnitude of variation of this isotope ratio is not as high as that of $^{226}Ra/^{238}U$, and therefore it has been not used in this work.

The average value for $^{226}Ra/^{238}U$ isotope ratio is approximately 0. 71 (ranging from 0.17 to 1.61), as can be seen in Fig. 4. This fact confirms that there is a contribution of solid particulate material associated to the PG stacks that should be related with the difference of TSP between the two locations (with an average increment of 16 μg/m^3).

3.4. The ^{210}Pb

The ^{210}Pb data are plotted in Fig. 5. Mean concentration at the PG stacks is about 0.6 mBq/m^3. This value is

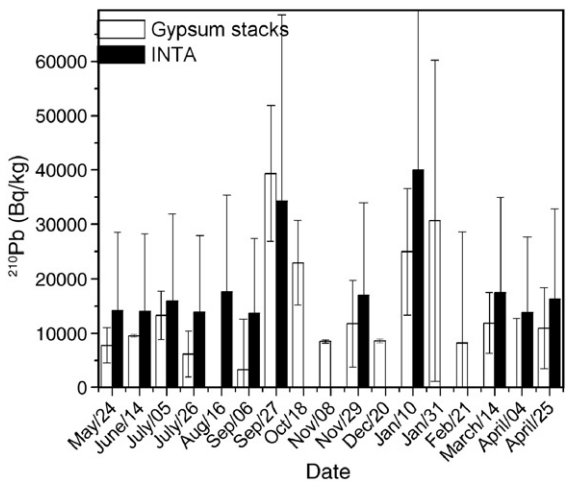

Fig. 5. The ^{210}Pb activity, in Bq/kg, at the PG stacks and at the background location.

comparable with data in the literature for regions having similar latitudes (Carvalho, 1995). As opposed to the case of ^{238}U and ^{226}Ra, the ^{210}Pb concentrations are perfectly detectable at the background location, yielding concentration ranges (0.2–0.9 mBq/m^3) similar to those of the PG stacks. Indeed, the ratio of ^{210}Pb concentration at the PG stacks against that at the background station varies within a very narrow range (0.3–4) with a mean value of 1.10. This result seems to indicate that there is no systematic increase of ^{210}Pb at the PG stacks since the supply of this radioisotope coming from the PG stacks and the surrounding industrial area is negligible in comparison with the elevated concentrations due to ^{222}Rn decay. Bearing in mind the previously mentioned enrichment in the other radionuclides this fact could result slightly surprising. However, it confirms the previous results according to the following reasoning.

It is expected that when soil resuspension is related to the origin of TSP, the TSP mass amount and the ^{210}Pb concentration increase together (Carvalho, 1995). If higher concentrations of ^{210}Pb were associated to lower TSP values, that would indicate that a significant fraction of the measured isotope is associated to the decay of ^{222}Rn present in the air, more than to particle resuspension from the soil. When ^{210}Pb concentrations are expressed in terms of mass activity (Bq/kg), it is found that they are almost systematically higher at the background location (the only exception is quite close to unit, 0.87), with a range of 1.2–4.1 and a mean value of 1.78. This fact first shows that there is no additional source of this radionuclide at the PG stacks and second, it is confirming the higher TSP range at this point. Under these conditions, it should be expected that the PG stacks aerosol particles are characterised by a ^{210}Pb content less than that of the background location. This hypothesis is confirmed by the results: the mean concentration (expressed in Bq/kg) at PG the stacks is 13.6 k Bq/kg, and for the background location is 19.0 k Bq/kg, and the background/PG stacks ratio of activity per mass is 1.40. This value is similar to that of the background/PG stacks ratio of TSP.

3.5. The ^{222}Rn and progeny

Data for ^{222}Rn are shown in Table 2. It is observed, in first place, that average monthly radon values at PG stacks, and also the corresponding statistical dispersion and ranges, were similar throughout the sampling. Moreover, background values (12.7±5.7 Bq/m^3) are typical of coastal areas (UNSCEAR, 2000). This finding may be unexpected bearing in mind that the radon exhalation rates in the PG stacks are 5 to 10 times higher than those for local soils. A greater radon concentration at the PG stacks sampling point would be expected instead of similar results. This homogeneity can be understood in the following way: according to the analysis of the wind data, there are almost no stagnation events near the city of Huelva (Adame, 2005). Indeed, the wind calm relative frequency is less than 10%. This fact is explained by the proximity of the Atlantic Ocean and the usual breeze circulation, which establishes a wind regime that precludes both stagnation and recirculation and induces a high ventilation regime.

Table 2
Rn concentrations (Bq/m^3) and their standard deviations (SD, Bq/m^3) at the PG stacks and at the background location INTA (selected background sampling station)

Sampling location/month	Average (Bq/m^3)	SD (Bq/m^3)	Minimum (Bq/m^3)	Maximum (Bq/m^3)
PG/January	11.7	2.6	3.8	29.4
PG/February	9.8	2.0	18	36.2
PG/March	10.8	2.2	3.5	20.1
PG/April	8	1.8	3.1	34.4
PG/May	15.1	6.0	4.8	37.9
PG/June	18.2	6.9	3.4	67.1
INTA/June	12.7	5.7	6.2	22.7

Therefore, although PG stacks act as a local source of radon, the increment of radon progeny contents in air must be being diluted as consequence of the dispersion produced by the dominant winds, hence no additional effect is registered at the PG sampling point. That could also be the reason why the maximum values at PG stacks are up to three times higher than those measured at background location, i.e., the effect of a higher exhalation is felt with high maximum values although the wind driven dilution effect prevents a drastic radon concentration at that location. In this sense, the radon data set shows a certain negative correlation ($r=-0.8$) with wind speed independent of the dominant address, according to wind data (Adame, 2005).

Secondly, it is interesting to see that that average values corresponding to night (~17.7 Bq/m^3) are approximately twice those collected during the day (~9.0 Bq/m^3). Furthermore, the average wind speed during the night breeze episodes is less than that of day breeze in the same way, as their corresponding dispersion ability. This fact was expected since it is known that the nocturnal coast breeze usually induces thermal inversion episodes (Adame, 2005). The thermal inversion restricts the vertical mixing of the lower layers of air and, in this way, it prevents the dilution of radon concentration.

Table 3
Estimation of the dose increment due to the presence of an extra input of radioactivity in aerosol particles collected at the PG stacks

Radionuclide	Mean activity increment (Bq/m^3)	Dose conversion factor (Sv/Bq)	Volumetric dose increment (Sv/m^3)
^{238}U	1.3×10^{-5}	2.9×10^{-6}	3.9×10^{-11}
^{234m}Pa		3.8×10^{-10}	5.1×10^{-15}
^{234}Th		6.6×10^{-9}	8.8×10^{-16}
^{234}U		3.5×10^{-6}	4.7×10^{-11}
^{230}Th	7.4×10^{-6}	4.3×10^{-5}	3.2×10^{-10}
^{226}Ra	1.1×10^{-5}	3.5×10^{-6}	3.8×10^{-11}
	Dose increment		0.44 nSv/m^3
	Breathed volume		8030 m^3/a
	Occupation factor		0.2
	Dose increment		0.71 μSv/a

Absorption rate type "S" has been assumed for Th and type "M" for the other radionuclides. Radioactive equilibrium is assumed among ^{234m}Pa, ^{234}Th and the parent ^{238}U.

As previously concluded, despite there is a clear increment of radioactivity (^{238}U, ^{230}Th, ^{226}Ra) in aerosol particles of the zone under study due to the presence of PG stacks, there is no in ^{210}Pb volume activity concentrations. As previously explained, however, there is still a certain lack of data on necessary physical and biochemical parameters for an accurate estimation of the doses received by inhalation. A raw estimation of the corresponding dosimetric contribution is given in Table 3, together with the dose rate factors used, in spite of the limitations of this methodology. For this calculation: (i) radioactive equilibrium is assumed among ^{234m}Pa, ^{234}Th and the parent ^{238}U; (ii) the average activity increases are calculated by subtracting the minimum detectable activity obtained at INTA sampling point from the mean activity measured at the PG sampling point; (iii) the net activity increments are converted to dose using the corresponding inhalation factors provided by the Spanish regulations (which follows the EURATOM'96 directive on protection against ionizing radiation, R.D. 173, 2001); and (iv) a breathed yearly air volume of 8030 m^3 is assumed per adult of the population (UNSCEAR, 2000) and a relatively conservative occupation factor of 0.2 (over 40 h per week during 48 weeks). Due to the similarities of the radon concentrations at all the sampling points, no increment is concluded for it. Furthermore, as previously explained, "S" absorption type has been assumed for Th, while type "M" has been assumed for the other radionuclides. This assumption must be kept in mind, as the relative contribution of each radionuclide to the dose received by inhalation would be higher than predicted in this work by a factor in the range of 2–4 if the absorption type were different than assumed (i.e., "M" for Th instead of "S" and the reverse for the remaining radionuclides).

Under the previously mentioned conditions, the effective dose rate increment (i.e., at the phosphogypsum stacks in comparison with the background location) is in the range of 0.71 μSv per year. This value is low compared to the limits for dose rate increments established by both Spanish regulations and the European Directive (1 mSv/year for the general population is the most restrictive limit). Such a fact is a consequence of the very low radionuclide concentrations, in addition to the previously mentioned enrichment in the aerosol particles collected at the analysed site. Indeed, this contribution appears negligible against the calculated background total effective dose rate (including contributions such as radon and progeny, external dose rate due to radionuclides in soil and cosmic rays) in this area, which is approximately 2.4 mSv/year (Mas et al., 2000). However, a more detailed analysis could be performed once additional details are known, and this work is to be undertaken by this group in the near future.

4. Summary and conclusions

According to our results, aerosol particles collected at the Phosphogypsum stacks show an extra content in radioisotopes present in wastes associated to phosphoric acid production. The dosimetric contribution seems to be negligible when compared to both the regulation limits for the population and the background levels. However, this conclusion is not yet definitive as further work, including the determination of particle grain size and radionuclide solubility, must be carried out. The results here shown suggest the need for accurate estimations of the doses received by workers within the factories devoted to the production of phosphoric acid.

No previous information has been published on the dose rate increments due to radioactivity contained in air before beginning restoration work. It is impossible therefore to carry out a comparative study; however, additional information could be supplied when the restoration work is finished. It is worth mentioning however that waters utilized for the transportation of the PG to the stacks use to be dumped into the Huelva estuary, and the uncovered area used to be greater than now.

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