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Exhalation of $^{222}$Rn from phosphogypsum piles located at the Southwest of Spain

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Abstract

Phosphogypsum (PG) is a waste product of the phosphoric acid production process and contains, generally, high activity concentrations of uranium series radionuclides. It is stored in piles formed over the last 40 years close to the town of Huelva (Southwest of Spain). The very broad expanse of the PG piles (about 1200 ha) produces a local, but unambiguous, radioactive impact to their surroundings. In 1992, the regional government of Andalusia restored an area of 400 ha by covering it with a 25-cm thick layer of natural soil and, currently, there is an additional zone of 400 ha in course of restoration (unrestored) and the same area of active PG stacks. Due to the high activity concentration of $^{226}$Ra in active PG stacks (average 647 Bq kg$^{-1}$), a significant exhalation of $^{222}$Rn could be produced from the surface of the piles. Measurements have been made of $^{222}$Rn exhalation from active PG stacks and from restored and unrestored zones. The $^{222}$Rn exhalation from unrestored zones is half of that of the active PG stacks. Following restoration, the $^{222}$Rn exhalation is approximately eight times lower than the active PG stacks. The activity concentrations of natural radionuclides ($^{226}$Ra, $^{40}$K, $^{232}$Th) in the mentioned zones have been determined. This study was also conducted to determine the effect of $^{226}$Ra activity concentration on the $^{222}$Rn

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exhalation, and a good correlation was obtained between the $^{222}$Rn exhalation and $^{226}$Ra activity, porosity and density of soil.

Keywords: $^{222}$Rn; Exhalation; Radioactivity; Phosphogypsum; Piles

1. Introduction

Fertilizers containing phosphate have become essential to the world’s agriculture. They are produced and used worldwide in increasing quantities to replenish natural nutrients depleted from soils because of farming and erosion. The increasing use of phosphate fertilizers in agriculture has resulted in the development of chemical industries devoted to the production of the phosphoric acid from phosphatic rocks. However, the phosphate industry is considered as a potential source of natural radionuclide ($^{238}$U and $^{232}$Th decay series). The mining, processing and use of fertilizer materials in large quantities redistribute natural radioactive materials throughout the environment, principally uranium, radium ($^{226}$Ra) and decay products.

Phosphoric acid is mainly obtained through the so-called “wet chemical treatment” of phosphate rock, which is a procedure well known to have associated with high activities of natural radioactivity. In this chemical process, a by-product, phosphogypsum (PG), is formed, which is mostly calcium sulphate, and is generally stored in extensive piles near the factory or released to the surrounding aquatic systems.

The main environmental concerns associated with PG are movement of fluoride, sulphate, total dissolved solids, certain trace elements and radionuclides from the $^{238}$U decay series below PG stacks into groundwater supplies and also $^{222}$Rn exhalation, which may pose a health risk to workers on the site or people living close to stacks. Extensive studies have been carried out across the world on the environmental impact of such discharges (Othman et al., 1992; Rutherford et al., 1994; Al-Masri et al., 2000, 2002).

The radiological impact of fertilizers depends on the geological origin of phosphate rock used to make the fertilizers. Investigations have reported a wide variation in the concentrations of radionuclides in phosphate rocks (Guimond and Windham, 1975; Pfister et al., 1976; Khater et al., 2001; Ahmed and El-Arabi, 2005; Abbady et al., 2005). Sedimentary phosphate rocks typically contain high $^{238}$U concentrations (about 50–100 times higher than typical soils) and low $^{232}$Th activities, and are sourced from various places in the world (Morocco, Egypt, Florida, Senegal, Togo etc.) and contain about 1000–2000 Bq kg$^{-1}$ of $^{238}$U, with its daughters in near secular equilibrium. Igneous phosphates typically contain normal concentrations of $^{238}$U and appreciable amount of $^{232}$Th and rare earth elements (Habashi, 1980).

A large industrial complex including, among others, one plant dedicated to the extraction of Cu and two factories devoted to phosphoric acid production are located close to the estuary formed by the confluence of the Tinto and Odiel river mouths, nearby Huelva (Southwest Spain; Fig. 1). The city of Huelva has a population of around 140,000 inhabitants, and is situated in the Andalusian region in the Southwest of the Iberian Peninsula near the Atlantic coast. The main activities are chemical industries and fisheries.

From 1968 to September 1997, a percentage (approximately 20%) of the wastes produced by the fertilizer factories were released directly into the Odiel waters, while the remaining 80% (mixed in suspension with seawater) was pumped to designed areas near the banks of the
Rio Tinto, to be stored in PG piles (Bolívar et al., 1995). These factories annually process about $2 \times 10^6$ tonnes of phosphatic rock, which produces $3 \times 10^6$ tonnes of PG. These PG piles form a potential radiological hazard (Bolívar et al., 1998, 2002). Additionally, there are high activities of $^{226}$Ra, which decays to $^{222}$Rn, an alpha emitter and a noble gas that can emanate from the PG into the atmosphere thereby generating an increase in the total dose by inhalation. As radium belongs to the alkaline earth metal group, its chemical behaviour is similar to calcium, and therefore is incorporated into the PG during the chemical processing of the phosphate rock (Silva et al., 2001). Similarly, radium follows the same biological pathway as calcium, leading to incorporation into living organisms.

In 1990, the regional government of Andalusia proposed the restoration of PG piles. The objective was to correct the environmental impact (not only radiological) produced by the deposited wastes and to reduce the increasing contamination of the waters and sediments of

Fig. 1. The location of PG piles around Huelva town.
the Tinto River affected by the wastes. The technological solution adopted for this restoration was to cover the PG piles with a layer of soil having an average thickness of 25 cm (Más et al., 2001). Radiologically, this solution will decrease the gamma radiation emitted in air coming from the PG down to the natural background of this geographical area. About 400 ha of the oldest deposits (20–30 years) have now been restored, and re-vegetation of the soil layer has been accomplished, with the aim of using the area for recreational purposes.

Most studies have concluded that populations living close to PG stacks are not subjected to a significant health risk because air movement readily dilutes $^{222}\text{Rn}$ concentrations. However, it is still not clear whether employees who spend numerous hours on active PG stacks are subjected to a significant health risk. Clearly, further research is required to improve our understanding of the effects of soil caps and vegetation cover on the exhalation of $^{222}\text{Rn}$, because there is not much published literature on the effects of soil caps on the $^{222}\text{Rn}$ exhalation.

The objective of this paper is an evaluation of the effectiveness of remediation on $^{222}\text{Rn}$ management at this PG site, with the view that experience at this very large site will inform remediation at other sites around the world. The paper discusses:

1. the exhalation of $^{222}\text{Rn}$ from different zones (active PG stacks, restored and unrestored zones) to quantify the influence of restoration on $^{222}\text{Rn}$ exhalation;
2. the naturally occurring radionuclides and physical properties of the different zones as they affect $^{222}\text{Rn}$ exhalation; and
3. the correlation between $^{222}\text{Rn}$ exhalation and parameters that affect $^{222}\text{Rn}$ exhalation as well as porosity, density and activity concentration of $^{226}\text{Ra}$ of soil.

2. Material and methods

The method used to carry out $^{222}\text{Rn}$ exhalation measurements involves adsorption of Rn on activated charcoal. The description of this method has been given by Hartley and Freeman (1985). This charcoal is contained in a cartridge manufactured by F&J speciality products, Inc. (USA) as TEDA Impregnated Charcoal. This method has been used extensively since the publication of the paper by Countess (1976). The $^{222}\text{Rn}$ collector is placed on the surface of the soil to be measured and it is allowed to collect Rn for a time period of up to 24 h. The Rn collected on the charcoal is then measured by gamma spectrometry.

The design of the collector minimizes the space between the surface of the soil being measured and the cartridge. The collector consists of the cartridge and a PVC cap. The cartridge is held in place by a rubber retainer ring. The collectors are deployed by firmly twisting the cap into the soil surface to be measured. After 24 h of exposure, the collectors are retrieved. The cartridge is then placed and sealed in plastic containers. The cartridges are weighted before and after the exposure time to determine the moisture content. The Rn collected on the charcoal is allowed to equilibrate for 4 h before counting to allow the ingrowths of $^{222}\text{Rn}$ daughters. The gamma spectrometry system used in this study consisted of an intrinsic REGe detector. Characteristics of the experimental system have been described elsewhere (Dueñas et al., 1999). The 609 keV of $^{214}\text{Bi}$ decay product peak is used to quantify the $^{222}\text{Rn}$ on the charcoal. Also other peaks of $^{214}\text{Pb}$ decay product can be used. A standard of $^{226}\text{Ra}$ adsorbed on charcoal in the same geometry (cartridge) is counted to determine the efficiency. An unexposed cartridge is also counted to determine the background. The $^{222}\text{Rn}$ exhalation is calculated from the net counts, collector area, exposure time, efficiency and a parameter that depends mainly on the moisture adsorbed on the activated charcoal (Quindós et al., 2001). This method of $^{222}\text{Rn}$ exhalation measurement involves two basic assumptions. First, it is assumed that the charcoal is 100% efficient in collecting $^{222}\text{Rn}$. The second assumption is that the $^{222}\text{Rn}$ exhalation being measured is constant over the exposure period. Although it is known that this condition is rare and, if ever met, the errors introduced are relatively small (Hartley and Freeman, 1985).
The samples were taken from three places, namely active PG stacks, the restored and unrestored zones, each of them of approximately 400 ha, from May 2002 through October 2002. The sampling zones are plotted in Fig. 2. The active PG stacks are further subdivided into North pond, South pond and Dividing line, and since the active pile is currently being used and has water ponded in the central areas, only the outer areas and a few interior dikes were readily accessible for $^{222}$Rn exhalation measurement (dividing line). The restored and unrestored zones are parcelled out and have been numbered (see Fig. 2). Each section is represented by a number of samples proportional to the surface it occupies. Every measurement at each location was obtained from the average of three sub-samples (three cartridges) collected from the vertices of an equilateral triangle (side 1 m), yielding a total of $3 \times 186$ measurements.

At every point, samples of about 1–2 kg were collected, and corresponded to the top 15 cm of soil. The samples, after collection, were dried and sifted as a preliminary step in radionuclide determinations. Activity concentrations of $^{226}$Ra, $^{232}$Th and $^{40}$K in samples of soils from different zones were determined by gamma ray spectrometry. The measurements were done using a fixed geometry (cylindrical containers of height 4.75 cm and diameter 5.15 cm) and a special calibration procedure for this geometry was followed. The $^{226}$Ra can be determined by taking the photopeak of its daughter nuclides $^{214}$Pb at 352 keV and/or $^{214}$Bi at 609 keV, while the $^{232}$Th was measured through the 911 keV gamma emissions from its daughter $^{228}$Ac and the $^{40}$K by its emission at 1460 keV. To ensure the existence of secular equilibrium between $^{226}$Ra and its daughters, the samples were sealed and stored at least for 3 weeks before the measurements. Samples were counted for 24–48 h to reach a good statistical accuracy.

![Fig. 2. Sampling locations.](image-url)
The moisture content of soil and atmospheric air were measured using a Protimeter, model MMS (NEURTEK Instruments). The temperatures of soil and atmospheric air were measured with the same equipment.

Particle size analyses were carried out by the sieve method. Porosity and soil density were determined in the laboratory. The procedures to measure these properties of the soil can be seen in Dueñas et al. (1997).

3. Results and discussion

3.1. The measurement and analysis of the radiological and physical properties of the different zones

The characterization of radioactive species should be the first step in trying to evaluate the radiological impact associated with the use of PG. Analyses were carried out on soil samples from active PG stacks, restored and unrestored zones. Table 1 shows the activity concentrations of the radionuclides ($^{226}$Ra, $^{232}$Th, $^{40}$K) present in the samples from different zones. It can be concluded from this table that the activity concentrations of $^{226}$Ra are higher in samples from active PG stacks and unrestored zone than that of restored zone, the means ranged from 740 to 560 Bq kg$^{-1}$ in the active PG stacks and 17 to 210 Bq kg$^{-1}$ in the restored zone. $^{226}$Ra is the major source of radioactivity in active PG stacks (Rutherford et al., 1994).

The activity concentrations of $^{232}$Th are generally low, from 25 Bq kg$^{-1}$ in the restored zone to 8 Bq kg$^{-1}$ in active PG stacks. Activity concentrations of $^{40}$K were very low in the PG piles and the unrestored zone, but are higher in the restored zone due to the addition of soil. It follows from Table 1 that there are strong variations between the data activities of $^{226}$Ra and $^{40}$K in sections 9 and 4 of the restored zone. The parcel 9 shows activities of 180 Bq kg$^{-1}$ for $^{226}$Ra and 170 Bq kg$^{-1}$ for $^{40}$K. These values are intermediate between a typical soil and the PG. These data imply that the soil in parcel 9 is a mixture of typical soil in the upper and PG below. The average activity concentrations in soil reported by UNSCEAR (1988) of $^{226}$Ra, $^{232}$Th and $^{40}$K are 30, 25, and 370 Bq kg$^{-1}$, respectively. The soil from the restored zone shows values of activity concentrations to be 83, 15 and 225 Bq kg$^{-1}$ for $^{226}$Ra, $^{232}$Th

<table>
<thead>
<tr>
<th>Zone</th>
<th>Description</th>
<th>$^{226}$Ra (Bq kg$^{-1}$)</th>
<th>$^{40}$K (Bq kg$^{-1}$)</th>
<th>$^{232}$Th (Bq kg$^{-1}$)</th>
<th>Number of samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG piles</td>
<td>South pond</td>
<td>560 ± 80</td>
<td>30 ± 3</td>
<td>8 ± 2</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>North pond</td>
<td>640 ± 90</td>
<td>20 ± 2</td>
<td>7 ± 2</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Dividing line</td>
<td>740 ± 60</td>
<td>50 ± 6</td>
<td>&lt;8</td>
<td>3</td>
</tr>
<tr>
<td>Unrestored zone</td>
<td>Parcel 6</td>
<td>540 ± 50</td>
<td>&lt;35</td>
<td>&lt;8</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Parcel 7</td>
<td>520 ± 45</td>
<td>70 ± 7</td>
<td>14 ± 5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Parcel 4</td>
<td>660 ± 60</td>
<td>&lt;35</td>
<td>&lt;8</td>
<td>4</td>
</tr>
<tr>
<td>Restored zone</td>
<td>Parcel 10</td>
<td>23 ± 3</td>
<td>360 ± 40</td>
<td>14 ± 5</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Parcel 5</td>
<td>50 ± 10</td>
<td>230 ± 25</td>
<td>13 ± 5</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>Parcel 9</td>
<td>180 ± 60</td>
<td>170 ± 20</td>
<td>&lt;8</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Parcel 4</td>
<td>210 ± 25</td>
<td>&lt;90</td>
<td>10 ± 4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Parcel 2</td>
<td>18 ± 5</td>
<td>200 ± 20</td>
<td>25 ± 6</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Parcel 8</td>
<td>17 ± 5</td>
<td>30 ± 25</td>
<td>20 ± 5</td>
<td>4</td>
</tr>
</tbody>
</table>
and $^{40}$K, respectively. The EPA ruling restricts PG that exceeds 370 Bq kg$^{-1}$ of $^{226}$Ra from being used as an agricultural soil.

According to Papastefanou et al. (2006) and Abbady et al. (2005), the $^{226}$Ra activity concentrations in other countries ranged from 5022 Bq kg$^{-1}$ in phosphate rocks of Tanzania (Arusha) to 10 Bq kg$^{-1}$ for Finland. The $^{40}$K is reported to vary from about 329.4 Bq kg$^{-1}$ in phosphate rock from Egypt (W. El-Mahamid) to 4 Bq kg$^{-1}$ in Taiba-Togo (Guimond and Hardin, 1989). The $^{232}$Th varies between 329.4 Bq kg$^{-1}$ in phoshatic rock from Egypt (W. El-Mahamid) to 2 Bq kg$^{-1}$ in Jordan. A clear conclusion from the observed data is the wide variation in activity concentrations for the $^{226}$Ra. This inhomogeneity cannot be considered surprising and can be attributed to: (1) the source of phosphate rock, (2) the depth of sampling and (3) some $^{226}$Ra migration.

Table 2 reports some of the physical properties of the studied samples such as density, porosity, grain size and soil moisture. Grain size distribution is an important factor determining the $^{222}$Rn exhalation and transport property of a soil (Surbeck and Voelkel, 1988; Chau et al., 2005).

The material bulk density within active PG stacks and the unrestored zone ranged between 880 and 1050 kg m$^{-3}$. Density values in the restored zone are similar to typical soils. Highest porosity values were reported in active PG stacks and in the unrestored zone. Phosphogypsum samples from the unrestored zone had a large proportion of medium- to fine-grained particles (<80 μm), compared to fine particles accounting for 14–58% of the mass in samples from the restored zone. Taking into account the data of Table 2, we can conclude that the soil used for restoration is of sandy nature. These types of soils are associated with low moisture content (6–8%), although zone 4 is an exception (30% moisture), and low $^{40}$K activity. Our results are coherent because the soil used to restore is from Andalusia. It has a concentration in $^{40}$K whose upper limit is more than double than that given by UNSCEAR (QuindoÁœs et al., 1994). By contrast, the PG has slimes and a clay nature with moisture content between 37 and 42%. The water content of PG may vary greatly depending on how long the PG has been allowed to drain after sluicing to the stack as well as on local meteorological conditions.

### 3.2. The estimation of $^{222}$Rn exhalation over different zones

The exhalation rate is the flux density of $^{222}$Rn gas entering the atmosphere from the surface of an $^{226}$Ra-bearing material (Bq m$^{-2}$ s$^{-1}$). $^{222}$Rn exhalation has been identified as one of the

<table>
<thead>
<tr>
<th>Zone</th>
<th>Description</th>
<th>Density (kg m$^{-3}$)</th>
<th>Porosity (%)</th>
<th>Grain size</th>
<th>Moisture (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PG piles</td>
<td>South pond</td>
<td>1050</td>
<td>64</td>
<td>88% &lt; 80 μm (slimes or clays)</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>North pond</td>
<td>900</td>
<td>71</td>
<td>100% &lt; 80 μm (slimes or clays)</td>
<td>42</td>
</tr>
<tr>
<td>Unrestored zone</td>
<td>Parcel 6</td>
<td>920</td>
<td>69</td>
<td>99% &lt; 80 μm (slimes or clays)</td>
<td>65</td>
</tr>
<tr>
<td></td>
<td>Parcel 7</td>
<td>880</td>
<td>69</td>
<td>98% &lt; 80 μm (slimes or clays)</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>Parcel 4</td>
<td>990</td>
<td>63</td>
<td>99% &lt; 80 μm (slimes or clays)</td>
<td>39</td>
</tr>
<tr>
<td>Restored zone</td>
<td>Parcel 10</td>
<td>1530</td>
<td>41</td>
<td>15% &lt; 80 μm (sand)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Parcel 5</td>
<td>1370</td>
<td>49</td>
<td>14% &lt; 80 μm (sand)</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Parcel 9</td>
<td>1320</td>
<td>51</td>
<td>17% &lt; 80 μm (sand)</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Parcel 4</td>
<td>1210</td>
<td>58</td>
<td>58% &lt; 80 μm (sand)</td>
<td>30</td>
</tr>
</tbody>
</table>
main environmental concerns associated with PG piles (Berish, 1990). The factors that determine the \(^{222}\text{Rn}\) exhalation from a source such as PG are the \(^{226}\text{Ra}\) content and its distribution, the emanation coefficient, atmospheric pressure and the diffusion coefficient for \(^{222}\text{Rn}\). The emanation coefficient is a function of physical characteristics of soil, such as porosity, density and radium content and other factors. The diffusion coefficient will vary greatly depending on the temperature and moisture levels. Cracks and crusts on the surface of PG will greatly influence the exhalation.

The present study reported the \(^{222}\text{Rn}\) exhalation from the previously described zones. As \(^{222}\text{Rn}\) exhalation follows a lognormal relationship, Table 3 shows the geometric mean (GM) and the geometric standard deviation (GSD) as well as the ranges that characterize each section in the different zones.

Table 3 and Fig. 3 summarize the results from active PG stacks and for the restored and unrestored zones. Table 3 shows significant variations between the data exhalation of \(^{222}\text{Rn}\) in the different zones. The greatest exhalations were from the active PG stacks and unrestored zones. The GM exhalation for each zone is about 0.523 Bq m\(^{-2}\) s\(^{-1}\) for the active PG stacks and 0.262 Bq m\(^{-2}\) s\(^{-1}\) for the unrestored zone. In contrast, exhalations were lower, with a GM of 0.065 Bq m\(^{-2}\) s\(^{-1}\) for the restored zone. To put these values in perspective, typical exhalations of \(^{222}\text{Rn}\) from soils, the largest source of background \(^{222}\text{Rn}\) in the environment is approximately \((8.3-42) \times 10^{-3}\) Bq m\(^{-2}\) s\(^{-1}\) (Dueñas et al., 1997). The importance given to this radionuclide is illustrated by the maximum regulatory limit of 0.74 Bq m\(^{-2}\) s\(^{-1}\) established by EPA (EPA, 1998). The exhalation of \(^{222}\text{Rn}\) from the active PG stacks (0.523 Bq m\(^{-2}\) s\(^{-1}\)) in this study is lower than the limit established by EPA. The exhalation of \(^{222}\text{Rn}\) from restored zones is approximately eight times lower than the active PG stacks. However, it is difficult to compare these values with the other values from the literature without taking into account the content of radium in phosphate rock and other physical properties of the soil.

Several researchers, such as Windham and Horton (1980), reported the \(^{222}\text{Rn}\) exhalation from two active PG stacks in Polk County (Florida) over several weeks. The mean exhalation was 1 Bq m\(^{-2}\) s\(^{-1}\), although measured rates varied by almost two orders of magnitude. Horton (1986) has also measured the \(^{222}\text{Rn}\) exhalation from two PG stacks in central Florida; the \(^{222}\text{Rn}\)
exhalation was measured to be about 1 Bq m\(^{-2}\) s\(^{-1}\). The exhalation varied by almost two orders of magnitude at various points measured on the pile. This variation can be explained by the non-uniform distribution of radium in the pile material and the moisture content in the pile. Hartley and Freeman (1985) made more detailed measurements of \(^{222}\)Rn exhalation from two PG piles in Florida over a 4-day period. The average \(^{222}\)Rn exhalation was 0.69 Bq m\(^{-2}\) s\(^{-1}\). For the drier areas, the exhalation was 0.42—1.05 Bq m\(^{-2}\) s\(^{-1}\), while for the wet areas it had an average factor of nine or less. Locations on the pile covered with 8—15 cm of soil had an average \(^{222}\)Rn exhalation of about 0.25 Bq m\(^{-2}\) s\(^{-1}\). SENES (1987) found \(^{222}\)Rn exhalation from some stacks in Ontario (clay or topsoil covered stacks) and Alberta (active with bare PG dikes with water-filled ponds) to range between 0.037 and 1.1 Bq m\(^{-2}\) s\(^{-1}\). NESHAPS (1989) summarised by Berish (1990) reported \(^{222}\)Rn exhalation from active and inactive stacks in Florida. The greatest exhalations were from the top on dry non-crusted stacks that were active. This material averaged about 0.7 Bq m\(^{-2}\) s\(^{-1}\). In contrast, exhalations were less than 0.04 Bq m\(^{-2}\) s\(^{-1}\) from cooling ponds and ditches. Exhalation from the top of an inactive stack averaged only 0.15 Bq m\(^{-2}\) s\(^{-1}\) but exhalation from the sides of a different inactive stack was about four times greater.

The U.S. Environmental Protection Agency (1987) has measured \(^{222}\)Rn exhalation at four active PG piles and one inactive PG pile over a year-long period. Measurements were made at weekly intervals and only at 10 sites on each pile. The overall exhalation for all locations on the four active piles was 0.69 Bq m\(^{-2}\) s\(^{-1}\); for the inactive pile for the same period, the exhalation was 0.14 Bq m\(^{-2}\) s\(^{-1}\). Experience in central Florida has shown that when PG piles become inactive, a thick crust forms which acts as a natural barrier to \(^{222}\)Rn exhalations, reducing the exhalation by about a factor of five. However, there is not much published literature on the effects of soil caps and vegetation cover on the exhalation of \(^{222}\)Rn from PG piles.

### 3.3. Factors affecting values of exhalation of \(^{222}\)Rn

A wide range of variation was observed on the exhalations, likely due to several factors, such as inhomogeneous distribution of radium in the material, the structural—mechanical properties of the soil (Dörr and Münnich, 1990), and meteorological conditions. In order to evaluate the effects of the different factors, we performed a regression analysis of the \(^{222}\)Rn exhalation and some factors, including the activity of \(^{226}\)Ra, porosity and density of soil using data from Tables 1—3. In Table 4, the correlation coefficient (\(r\)) and degree of confidence (\(P\)) of regression
The P-values show that there is a statistically significant relationship between the exhalation of \(^{222}\text{Rn}\) and the mentioned factors. After the identification of the variables that affect the exhalation of \(^{222}\text{Rn}\), we need to quantify their influence. On the basis of these assumptions, a multiple regression analysis was carried out between \(^{222}\text{Rn}\) exhalation \((E)\) and the content of \(^{226}\text{Ra}\), porosity and density of soil, in order to determine the extent to which the variations in exhalation might be attributed to the combination of these factors. The software used has been Statgraphics version 5.1. The results are given by the equation:

\[
E = -2.5478 + 0.0010 \text{ density} + 2.3136 \text{ porosity} + 0.0006 \times ^{226}\text{Ra}.
\]

The \(R^2\)-squared statistic indicates that the model explains 80.7\% of the variability of exhalation of \(^{222}\text{Rn}\).

Meteorological parameters such as atmospheric pressure, wind speed, ambient temperature and humidity might potentially influence the \(^{222}\text{Rn}\) exhalation (Dueñas and Fernández, 1983; Dueñas et al., 1997). It is known that a high moisture content may decrease the \(^{222}\text{Rn}\) transport to the atmosphere because the gas has a relatively short half-life, and because diffusion of \(^{222}\text{Rn}\) in water is several orders less than in air (Upchurch et al., 1991). In this case, the measurements were carried out in different conditions both in soil and air. Moisture soil content ranged between 28 and 80\% for restored and unrestored zones while for the active PG stacks it ranged between 80 and 100\%. During the period of measurements, the air temperature oscillated between 20 and 36 °C and the soil temperature in the surface covering ranged between 21 and 35 °C. The number of measurements needed to define an annual average exhalation depends on the homogeneity of the pile and the desired precision of the estimate. A homogeneous pile requires fewer samples than a non-homogeneous pile. In the complex of Huelva, further research is required to improve our understanding of the geochemistry occurring within the different zones and in order to estimate a statistically valid annual average \(^{222}\text{Rn}\) exhalation.

### 4. Conclusions

The exhalation of \(^{222}\text{Rn}\) in the restored and unrestored zones was much smaller than from the active PG stacks. The exhalation from unrestored zones has decreased around 50\% in relation with active PG stacks. The exhalation from restored zones was eight times lower than the active PG stacks. As expected, the exhalation depended on properties of the materials, and a prediction equation was obtained to estimate the \(^{222}\text{Rn}\) exhalation as a function of the activity concentration of \(^{226}\text{Ra}\), porosity and density of the soil.
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References


NESHAPS, 1989. National emission standards for hazardous air pollutants, environmental impact statement for radio-
nuclides. Report No. EPA 520/1-89-005, Office of Radiation Programs (ANR-459), U.S. Environmental Protection
Agency.
Protection Dosimetry 45, 197–201.
Papastefanou, C., Stoulos, S., Ioannidou, A., Manolopoulou, M., 2006. The application of phosphogypsum in agricul-
and Environmental Biophysics 13, 257–264.
Environment 149, 1–38.
SENES Consultants Limited, 1987. An analysis of the major environmental and health concerns of phosphogypsum
Surbeck, H., Voelkel, H., 1988. Radionuclide content vs grain size in soil samples. The Science of the Total Environ-
ment 69, 379–389.
Silva, N.C., Fernandes, E.A.N., Cipriani, M., Taddei, M.H.T., 2001. The natural radioactivity of Brazilian phosphogyp-
water. FIPR Pub. No. 05-022-092.
phosphogypsum stacks-risk assessment. USEPA, Washington, D.C.