Extensive radioactive characterization of a phosphogypsum stack in SW Spain: ^{226}Ra, ^{238}U, ^{210}Po concentrations and ^{222}Rn exhalation rate

José-María Abril [a,*], Rafael García-Tenorio [b], Guillermo Manjón [b]

[a] Dpto. Física Aplicada I, Universidad de Sevilla, EUITA, Ctra Utrera Km 1, 41013 Seville, Spain
[b] Dpto. Física Aplicada II, Universidad de Sevilla, ETSA, Avda. Reina Mercedes s/n, 41012 Seville, Spain

A B S T R A C T

Phosphogypsum (PG) is a by-product of the phosphate fertilizer industries that contains relatively high concentrations of uranium series radionuclides. The US-EPA regulates the agriculture use of PG, attending to its ^{226}Ra content and to the ^{222}Rn exhalation rate from inactive stacks. Measurements of ^{222}Rn exhalation rates in PG stacks typically show a large and still poorly understood spatial and temporal variability, and the published data are scarce. This work studies an inactive PG stack in SW Spain of about 0.5 km^2 from where PG can be extracted for agriculture uses, and an agriculture soil 75 km apart, being representative of the farms to be amended with PG. Activity concentrations of ^{226}Ra, ^{238}U and ^{210}Po have been measured in 30 PG samples (0–90 cm horizon) allowing for the construction of maps with spatial distributions in the PG stack and for the characterization of the associated PG inputs to agriculture soils. Averaged ^{226}Ra concentrations for the stack were 730 ± 60 Bq kg^{-1} (d.w.), over the US-EPA limit of 370 Bq kg^{-1}. ^{222}Rn exhalation rate has been measured by the charcoal canister method in 49 sampling points with 3 canisters per sampling point. Values in PG stack were under the US-EPA limit of 2600 Bq m^{-2} h^{-1}, but they were one order of magnitude higher than those found in the agriculture soil. Variability in radon emissions has been studied at different spatial scales. Radon exhalation rates were correlated with ^{226}Ra concentrations and daily potential evapotranspiration (ETo). They increased with ETo in agriculture soils, but showed an opposite behaviour in the PG stack.

Keywords:
Phosphogypsum
^{222}Rn exhalation rate
Phosphogypsum stack
Radionuclides in phosphogypsum
Potential evapotranspiration

1. Introduction

Phosphogypsum (PG) is a NORM material generated as a by-product of some phosphate fertilizer industries that use phosphate rock as raw material. Levels of fluoride, certain natural-occurring radionuclides and some heavy metals are relatively high in PG [1].

Large quantities of PG are produced worldwide. Annual production in 2006 was estimated to be about 170 million tons. Most of the PG produced worldwide is stock piled. Agriculture uses of PG are being extensively studied since they could become the main worldwide sink for this waste. Studies about the environmental impact of PG, including its agriculture use, have been reviewed by Rutherford et al. [1]. Studies on the radiological impact of the agriculture use of PG has been conducted, among others, by Alcordo et al. [2] in soils under bahiagrass pasture in Florida, by El-Mrabet et al. [3] in reclaimed marsh soils in SW Spain, and, more recently, by Papastefanou et al. [4] in Greek soils under rice crop.

The fertilizer industry in Huelva (SW Spain) produces annually three millions tons of PG, processing sedimentary phosphate rocks mostly from Morocco (with ^{238}U concentrations in the range of 1000–1500 Bq kg^{-1}, after Bolívar et al. [5]). About 85% uranium present in phosphate rock passes to resulting phosphoric acid, while about 90% of the ^{226}Ra remains in the PG wastes [5]. PG is disposed in stacks lying in the right bank of the Tinto River, in the vicinity of Huelva city, covering an area of ca. 1200 ha.

From late the XIXth century, a sizeable portion of the Guadalquivir salt-marsh area in SW Spain has been reclaimed for agricultural use (40,000 ha), accounting for one of the largest reclaimed marsh areas in southern Europe. Before reclamation, these soils were highly saline and had a shallow, extremely saline, water table [6]. PG has being traditionally used in this area as a Ca-amendment for soil reclamation [7], but stopped in 2001 due to the public concern about the alimentary safety of this practice. Recent Spanish regulations (R.D. 824/2005, from July 2005) explicitly allowed the use of PG as soil amendment (without mention to its radioactive content). In the USA the EPA has specific regulations for the agriculture use of PG, allowing it if ^{226}Ra concentration

Abbreviations: PG, phosphogypsum; CL, confidence level; ETo, potential evapotranspiration.

* Corresponding author. Tel.: +34 954486473; fax: +34 954486436.
E-mail addresses: jmabril@us.es (J.-M. Abril), gtenorio@us.es (R. García-Tenorio), manjon@us.es (G. Manjón).

is below 370 Bq/kg, and establishing rules for monitoring ^{222}Rn exhalation rate from PG stacks [8].

Exposure to ^{222}Rn gas emanated from PG stack (either active or inactive) is one of the greatest health concerns for workers on the site and for people living in the surroundings. An inactive stack, as defined by US-EPA [8], has not been used for 2 years for further routine addition of PG nor for associate water management. Rutheford et al. [1] reviewed some works on measurements of ^{222}Rn exhalation rates from active and inactive PG stacks in Florida, particularly those reported by NESHAPS [9], based on which the US-EPA adopted an average 0.74 Bq s^{-1} m^{-2} limit on ^{222}Rn emissions from PG stacks. The published data accounting for extensive radiological characterization of PG stacks in other non-USA locations are scarce.

Measured ^{222}Rn exhalation rates in field conditions typically show large spatial and temporal variability (up to two orders of magnitude), being the quantitative analysis of factors affecting such variability still poorly understood. Basic processes governing radon transport from soils to air (as reviewed by Nazaroff [10]) are relatively well understood. Thus, ^{222}Rn is generated by the radioactive decay of ^{226}Ra; and *emanation* (the process that controls the movement of radon atoms from within solid grains into free space of materials) is influenced by moisture, temperature, grain size and the amount and location of ^{226}Ra atoms. Radon transportation through the connected pore space towards the earth's surface involves diffusion (affected by soil moisture, porosity and tortuosity) and advection processes. Advection is governed by intrinsic permeability, moisture and pressure gradients. Other meteorological parameters like temperature difference between soil and surface air, wind velocity and rainfall also affect the advection process [11]. Due to the complexity of the problem, experimental and theoretical studies usually assumes simplifying hypothesis: homogeneous and time-independent soil properties (including moisture content) and local equilibrium for radon partitioning among gaseous, aqueous, and sorbed phases [10], steady-state fluxes with negligible advection [11], or include steady-state advective transport forced under idealized media (isotropic permeability) and boundary conditions [12]. Recently Zhuo et al. [13,14] developed a simplified model for ^{222}Rn flux density from the earth's surface including seasonal changes in soil water content.

Most of the previous assumptions hardly stand under field conditions. Particularly, in PG stacks and bare soils, under sunny conditions, net radiation can lead to significant water evaporation and/or to a transient increase in soil temperature, affecting consequently to radon emissions. Potential evapotranspiration, ETo, is defined for a reference crop and standard soil conditions, and it is a reflection of the energy available to evaporate water, and of the wind available to transport the water vapour from the ground up into the lower atmosphere. Daily ETo, as estimated by the Penman–Monteith FAO56 method [15] is a function of the net radiation, average air temperature, wind speed and water vapour pressure.

In 2002, Dueñas et al. [16] measured ^{222}Rn exhalation rates in the entire disposal site for PG in SW Spain (ca. 1200 ha), covering with some 200 sampling points the active, inactive and restored (covered by some 40 cm layer of natural soil) PG stacks. The major concern was the effectiveness of the accomplished remediation actions (a soil cover). They found a reduction in ^{222}Rn exhalation rates in a factor of 8 in the restored areas. They also found a good correlation among ^{222}Rn exhalation rate and ^{226}Ra activity, porosity and density of soil (measured in 48 selected sampling points distributed in the whole area).

Present work studies an inactive PG stack in the vicinity of Huelva city (SW Spain) of about 0.5 km^2 (roughly 4% of the area studied by Dueñas et al. [16]), and 5–8 m thick. The stack is owned by FERTIBERIA, a fertilizer factory, and devoted to PG extraction for agriculture uses (after the Spanish regulation R.D. 824/2005). This work focuses on the spatial distributions of ^{226}Ra, ^{238}U and ^{210}Po concentrations in PG as a means to characterize this agriculture amendment with view to potential radionuclide uptake by crops. Target radionuclides have been selected by their radiological interest and because their concentrations in PG are roughly one order of magnitude higher than in typical agriculture soils. Sampling density for ^{226}Ra (at least 30 sampling points in the area from where PG will be extracted) has been adapted to the US-EPA guidance [8]. The work also comprises the study of ^{222}Rn exhalation rate, according to the main points in the previous guidance. Agriculture soil from a farm 75 km apart from the stack has been monitored as reference site, because it can be considered as representative of the reclaimed marsh soils in SW Spain that will receive PG amendments. From this framework, the paper tries to identify the major factors affecting the observed variability in ^{222}Rn emissions, and pays special attention to the daily ETo.

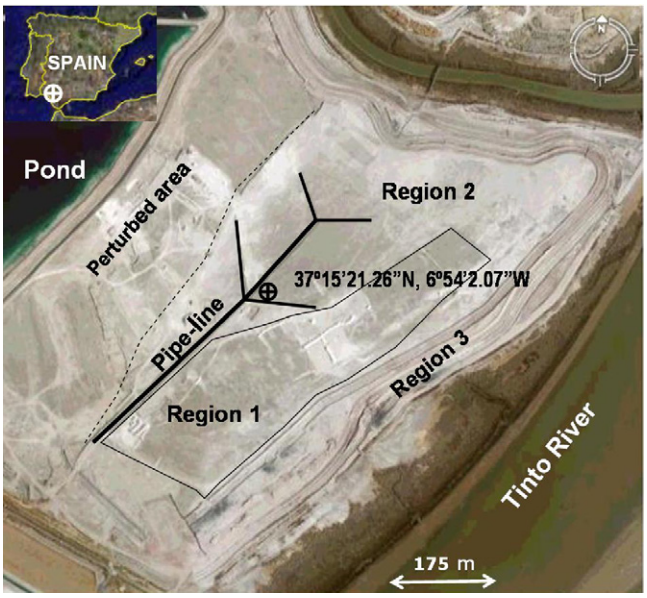

Fig. 1. Aerial view for the studied PG stack, with indication of the three defined regions: Region 1, with flat and tilled surface; Region 2, with flat and untilled surface; Region 3, corresponding to the sides (with a terrace structure).

2. Materials and methods

2.1. Experimental site and sampling

The studied PG stack (37°15.3′N, 6°54′W) lies on the right bank of the Tinto River, besides the city of Huelva (140,000 inhabitants), in South West Spain. It has an approximated rectangular shape with dimensions ca. 0.9 km × 0.6 km and 5–8 m thick. It became an inactive stack at the beginning of the 1990s. It is the remaining part of a larger stack, after the construction of a pond in its western half. The Tinto River flows along its eastern border (see Fig. 1). The old pipeline used in the past for disposing PG in the stack still lies crossing it lengthwise. Most of the western area beyond the pipeline was not considered in this study due to continuous perturbation by the ongoing works for constructing the new pond. PG had been extracted from this stack for agriculture uses, but extracting activities stopped in 2001. As result of extraction practices, approximately 50% of the flat top surface was tilled, showing a different crusting structure and the absence of big cracks. Following US-EPA [8] (method 115 for monitoring ^{222}Rn emissions), three regions

Table 1
^{226}Ra concentration[a] in agriculture soils and ^{222}Rn exhalation rate[b] measured in several sampling campaigns

Sampling point	^{226}Ra (Bq kg^{-1})	^{222}Rn exhalation rate (Bq m^{-2} h^{-1})			
	January 2006	September 2004[c]	October 2004[d]	February 2005[c]	February 2006[e]
A (37°1′18.55″N, 6°7′25.78″W)	36.9 ± 0.7	35 ± 5	21.4 ± 1.0	10.1 ± 1.4	16 ± 3
B (37°1′15.99″N, 6°7′23.09″W)	34.7 ± 0.7	33 ± 4	18.9 ± 1.4	14 ± 5	18 ± 5
C (37°1′14.76″N, 6°7′21.79″W)	34.3 ± 0.9	40 ± 7	30 ± 5	14 ± 6	27.7 ± 2.0
Arithmetic mean	35.3 ± 0.8	36a	23.4b	12.7c	20.6b

There was not significant differences in ^{222}Rn exhalation rate between sampling points within each sampling campaign but differences are significant ($p < 0.0001$) between sampling campaigns (quoted groups a, b, c, by 95% CL LSD method).

[a] Measurement (by gamma spectrometry) with 1σ analytical error. Soil samples from the 0–30 cm horizon.

[b] Mean and standard deviation of mean ($n = 3$, 1 m spaced). Measurements by charcoal canister method.

[c] Un-vegetated and tilled (~20 cm) soil.

[d] Un-vegetated and deep-tilled (~40 cm) soil.

[e] Sugar beet crop at nascence stage.

with different potential ^{222}Rn exhalation rate have been considered in the analysed zone of the PG stack: Region 1, with flat and tilled surface; Region 2, with flat and untilled surface; and Region 3, corresponding to the sides (with a terrace structure).

A rectangular sampling mesh of 50 m × 75 m has been established within Regions 1 (covered with 20 sampling points) and 2 (with 16 sampling points), while for Region 3, 10 sampling points have been regularly distributed along the open perimeter of the stack. Phosphogypsum samples were taken at three depth intervals (0–30, 30–60 and 60–90 cm) at each sampling point from Regions 1 and 2 for radionuclide measurements. A composite sample was made from 3 to 4 cores 4 cm in diameter randomly collected around each sampling point (1 m radius). After drying in the lab, composite samples were prepared integrating the three depth intervals in proportion to their bulk densities. At selected points, samples from the three depth intervals were preserved to study depth distributions for activity concentrations. The so resulting sampling density fulfils the US-EPA [8] requirements.

^{222}Rn exhalation rate has been measured by the activated charcoal canister method, following the procedure described by Dueñas et al. [16]. Each device, provided by Tecnasa—Spain, had some 75 g of activated charcoal in an open faced metal canister of 10 cm diameter. The ^{222}Rn collector is deployed by firmly twisting the cap into the soil surface to be measured, with exposure times of 24 h. Three canisters were systematically placed at each sampling point in the vertices of an equilateral triangle of 1 m side (with one of the vertices northwards orientated). In three selected sampling points, a set of three canisters (hereafter referred as triplet) were disposed in triangle of 0.1 m side instead of a single canister. This will allow for studying variability in ^{222}Rn exhalation rate at small spatial scales. Additional canisters were placed directly over a freshly tilled area to have a proxy to the effect of this factor in ^{222}Rn exhalation rate. Canisters were weighted before and after sampling to determine the moisture adsorbed by charcoal for subsequent corrections in exhalation rate [16].

Due to the short half live of ^{222}Rn (3.82 days) and the technical capacity of our lab, radon measurements were distributed along five sampling campaigns (taking into account that measurements could not be initiated within 24 h of a rainfall): 2–3 February 2005, covering 10 sampling points in Region 1; 10–11 May 2005, covering 10 sampling points in Region 1 and additional measurement in the freshly tilled surface; 6–7 June 2005, covering 10 sampling points in Region 2; 27–28 June 2005, covering 10 sampling points in Region 3, including triplets and 3–4 April 2006, covering 6 sampling points in Region 2, including triplets.

A 6-ha agriculture plot placed some 75 km far from the PG stack (37°1.26′N, 6°7.39′W) has been selected for comparison purposes as reference site. Three sampling points were defined along its central line spaced at ca. 60 m. Soil samples were collected in the 0–30 cm horizon at each sampling point for radionuclide measurements. ^{222}Rn exhalation rate was measured with three charcoal canisters per sampling point and in four sampling campaigns (September 2004, October 2004, February 2005 and February 2006).

Daily ETo for each sampling period was obtained from the closest agro-meteorological station from the Andalusian network (107 stations operating since 2000 with online access) [17]: *Moguer* (37°08′52″N, 06°47′28″W, $h = 87.0$ m) for PG stack and *Lebrija I* (36°58′40″N, 06°07′30″W, $h = 25.0$ m) for the agriculture soil. ETo provided by the Andalusian network is estimated by the Penman–Monteith FAO56 method [15].

2.2. Radon measurements

In total, 165 charcoal canisters were collected. After 24 h exposition canisters were recovered, sealed, weighted (to determine humidity gain) and transferred to lab. ^{222}Rn activity was determined through the 609 keV γ-emission of ^{214}Bi by using three low-level gamma-ray spectrometric systems equipped, respectively, with a 5 in. × 5 in. NaI(Tl) (10% resolution at the 662 keV peak of ^{137}Cs), a HPGe Xtra (37.1% relative efficiency, FWHM of 1.76 keV at 1332 keV of ^{60}Co) and a ReGe (31.4% relative efficiency, FWHM of 1.98 keV at 1332 keV of ^{60}Co) detectors supplied by Canberra (Tecnasa, Madrid, Spain). Typical counting times were 6–18 h per sample. These systems were calibrated with charcoals spiked with a tracer solution of ^{226}Ra (after homogenization), once it was allowed to reach secular equilibrium with ^{222}Rn and daughters. Blank charcoal canisters were also measured for background corrections. More details on the applied method can be found in [16,18].

2.3. Radionuclides measurements

Following collection, soil and PG samples were air-dried and ground to pass through a 0.5-mm sieve prior to analysis.

^{226}Ra in the phosphogypsum samples was determined by liquid scintillation applying the method described in Moreno et al. [19]. This method, briefly, is based on the ashing of the PG at 600 °C during 24 h, dissolution of the ashes in 8 M HNO_3, removal of the actinides by precipitation with Fe^{3+}, and posterior precipitation of the Ra as radium sulphate using Ba^{2+} as a carrier. The isolated Ra-$BaSO_4$ precipitate is finally dissolved with some ml of 0.2 MEDTA in ammonia medium, and the obtained solution transferred into low-potassium glass vials where it is mixed and shacked with a liquid scintillation cocktail (Pharmacia Optiphase Hisafe 3) to obtain an homogeneous solution.

Table 2
Radionuclide depth distributions for selected sampling points in PG stack[a]

Sampling point	Depth (cm)	H_r (% w/w)	^{226}Ra (Bq kg^{-1} (d.w.))	^{210}Po[b] (Bq kg^{-1} (d.w.))	^{238}U[c] (Bq kg^{-1} (d.w.))	^{234}U[d] (Bq kg^{-1} (d.w.))	^{235}U[e] (Bq kg^{-1} (d.w.))
R1-P14	0–30	17.8	828 ± 33	588 ± 13	89.5 ± 2.3	96.0 ± 2.4	5.0 ± 0.4
	30–60	17.4	515 ± 21	513 ± 11	92.5 ± 2.3	94.0 ± 2.3	4.1 ± 0.4
	60–90	20.9	386 ± 15	521 ± 12	117.9 ± 2.7	122.6 ± 2.8	4.3 ± 0.4
R1-P17	0–30	18.6	708 ± 27	585 ± 13	128.2 ± 2.5	131.9 ± 2.5	5.5 ± 0.3
	30–60	18.5	379 ± 16	588 ± 14	182.9 ± 3.6	184.9 ± 3.6	7.2 ± 0.4
	60–90	20.3	317 ± 13	669 ± 15	191.3 ± 3.7	201.7 ± 3.8	8.6 ± 0.4
R1-P18	0–30	18.9	746 ± 29	654 ± 15	147.4 ± 3.6	148.5 ± 3.6	6.7 ± 0.6
	30–60	20.3	739 ± 29	520 ± 12	76.4 ± 2.4	83.6 ± 2.6	3.4 ± 0.4
	60–90	22.3	647 ± 25	588 ± 14	142.5 ± 3.5	144.6 ± 3.6	6.5 ± 0.6
R2-P04	0–30	20.9	818 ± 88	566 ± 13	165.5 ± 3.3	170.6 ± 3.4	6.6 ± 0.4
	30–60	22.0	810 ± 87	671 ± 15	174.9 ± 3.2	178.1 ± 3.2	7.0 ± 0.3
	60–90	22.9	1024 ± 110	590 ± 13	96.7 ± 3.9	101.6 ± 4.0	5.5 ± 0.9
R2-P06	0–30	15.3	404 ± 16	499 ± 12	103.4 ± 2.7	105.3 ± 2.7	4.2 ± 0.4
	30–60	20.5	630 ± 24	601 ± 14	127.5 ± 2.7	133.5 ± 2.8	4.6 ± 0.3
	60–90	20.2	737 ± 28	795 ± 18	448.4 ± 8.0	453.1 ± 8.1	17.2 ± 0.7
R2-P08	0–30	20.9	700 ± 27	617 ± 14	155.8 ± 2.9	157.6 ± 3.0	8.9 ± 0.4
	30–60	21.2	768 ± 29	636 ± 14	160.1 ± 3.0	163.5 ± 3.0	6.4 ± 0.3
	60–90	20.6	672 ± 26	591 ± 13	150.7 ± 2.9	152.1 ± 2.9	6.8 ± 0.3

[a] Measurements and 1σ analytical error.
[b] ^{210}Po/^{226}Ra isotopic ratio 0.97 ± 0.10 (mean and standard deviation of mean).
[c] ^{238}U/^{226}Ra isotopic ratio 0.26 ± 0.04 (mean and standard deviation of mean).
[d] ^{234}U/^{238}U isotopic ratio 1.031 ± 006 (mean and standard deviation of mean).
[e] ^{235}U/^{238}U isotopic ratio 0.044 ± 002 (mean and standard deviation of mean).

The ^{226}Ra activities were measured using an ultra-low background scintillation spectrometer, Wallac Quantulus 1220 equipped with a pulse-shape analyser to discriminate between alpha and beta pulses. The measurements were performed 1 month after radium separation in order to assure secular equilibrium between ^{226}Ra and daughters, as well as the decay of the ^{224}Ra which can be originally present in the sample.

U-isotopes and ^{210}Po activity concentrations were determined by alpha-particle spectrometry (using an alpha spectrometer with 8 independent chambers, equipped each one with a 450-mm^2 PIPS detector) after application of a sequential solvent-extraction radiochemical method to aliquots of the phosphogypsum samples. Briefly, and after tracing the analysed aliquot with known amounts of ^{232}U and ^{209}Po, the radiochemical procedure is based on the dissolution and oxidisation of the sample with HNO_3 and H_2O_2, the precipitation of the U and Po with $Fe(OH)_3$, and the dissolution of the isolated precipitate in 8 M HNO_3. The later dissolution is mixed with TBP, being afterwards sequentially extracted the Po and U fractions following the procedure described in Holm and Fukai [20]. The Po and U isolated fractions were finally conditioned either for the posterior spontaneous deposition into silver planchets (Po), or for the electrodeposition onto stainless steel planchets (U).

2.4. Statistical and other data analysis

Statgraphics Plus 5.1 software was applied to carry out tests for each data set distribution, and analysis of variance (one-way ANOVA) tests for comparison between means. All pair wise contrasts were carried out by Tukey tests at 95% CL, and quoted groups by 95% CL LSD method.

Surfer 5.0 from Golden Software was used for surface mapping.

3. Results and discussion

3.1. Reference values for agriculture soils

Table 1 summarizes ^{226}Ra concentrations and ^{222}Rn exhalation rates from the agriculture soils. ^{226}Ra activity concentrations were 35.3 ± 0.8 Bq kg^{-1} (mean and 1S.D. of mean), in agreement with the average value for soils (35 Bq kg^{-1}) reported by UNSCEAR [21]. Values for ^{222}Rn exhalation rates from the three canisters of each sampling point were normally distributed and Table 1 reports the corresponding mean values. No significant differences (95% CL) were found among means from the sampling points corresponding to the same sampling campaign; but means from sampling campaigns were significantly different ($p < 0.0001$). A regression analysis has been performed involving averaged values of ^{222}Rn exhalation rates per sampling campaign, E_S (Bq m^{-2} h^{-1}) and daily ETo (mm day^{-1}). There was a statistically significant (CL 90%) linear correlation explaining 83% of the observed variability in E_S, as shown in Fig. 2.

3.2. Radionuclide concentration in phosphogypsum stack

Table 2 shows depth distributions of humidity and activity concentrations (^{226}Ra, ^{210}Po and U-isotopes) corresponding to six

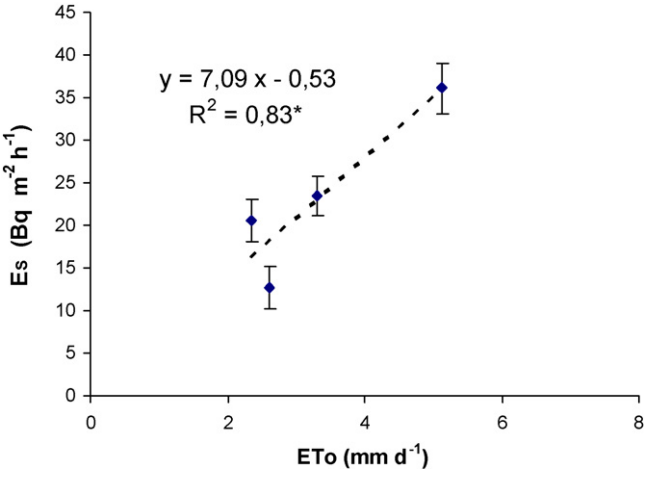

Fig. 2. E_S (mean and 1S.D. of mean of ^{222}Rn exhalation rate for each sampling campaign) from agriculture soil (37°1.26′N, 6°7.39′W) as a function of the daily potential evapotranspiration (ETo).

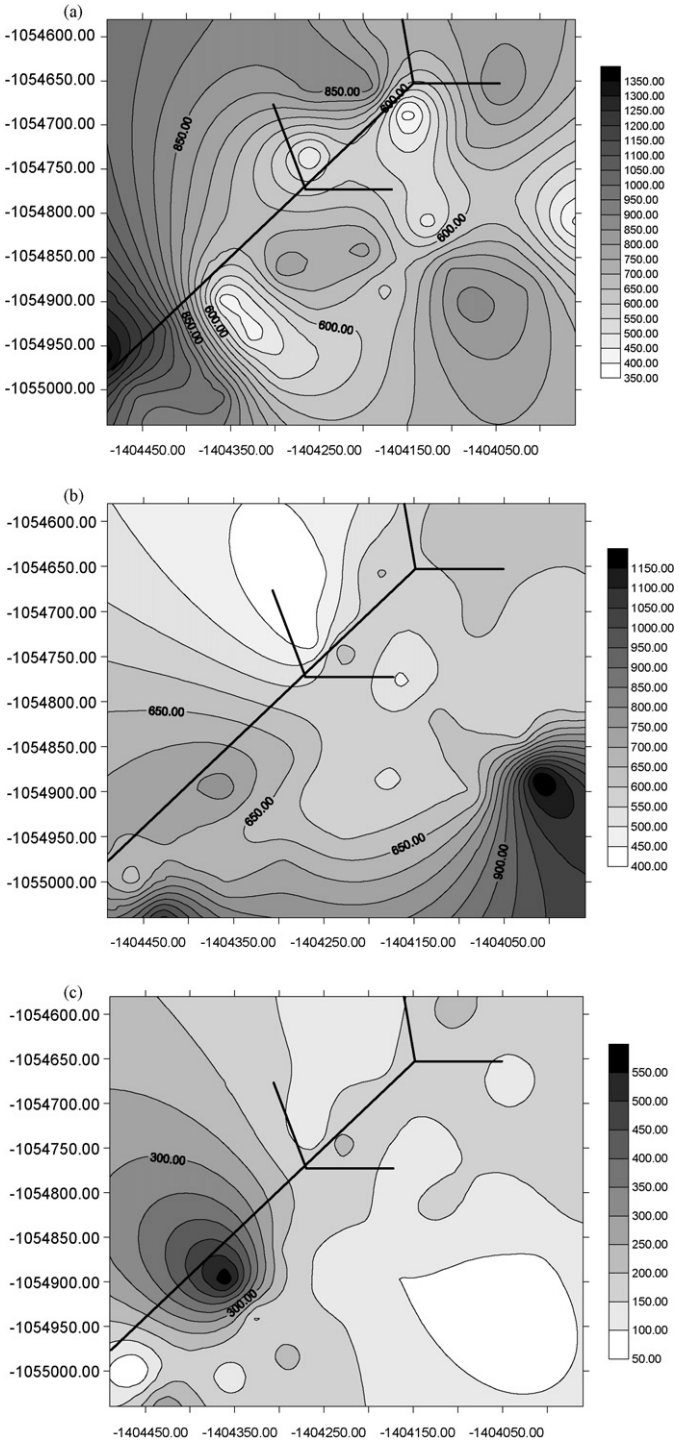

Fig. 3. Spatial distribution maps (coordinates Lambert GISCO, units in m) with the measured activity concentrations (in the 0–90 cm horizon) of ^{226}Ra (a), ^{210}Po (b) and ^{238}U (c), given in Bq kg^{-1} (d.w.). The pipeline has been indicated for the sake of comparison with Fig. 1.

sampling points in PG stack (three in Region 1 and three in Region 2). Humidity slightly increased with depth, but activity concentrations did not follow any clear pattern, as it could be expected from the natural variability in the properties of ore phosphate rock, chemical yield in the P_2O_5 extraction and waste disposal routines during the stack build up.

Fig. 3a–c shows the spatial distribution maps corresponding to radionuclide (^{226}Ra, ^{210}Po and ^{238}U) activity concentrations

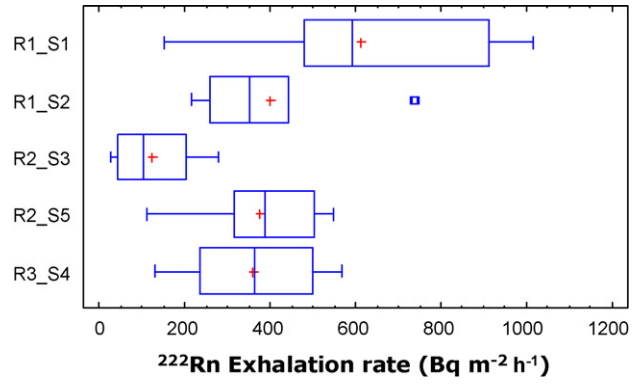

Fig. 4. Box-and-whisker plot for ^{222}Rn exhalation rate in PG stack corresponding to Regions 1–3 as covered with the five sampling campaigns (S1–S5). Data are constructed with average values of the three canisters per sampling point.

in the 0–90 cm horizon. ^{226}Ra activity concentrations followed a normalized distribution with mean value 730 ± 60 Bq kg^{-1} (range 350–1390 Bq kg^{-1}). These values were similar to those found by Dueñas et al. [16] in 2002 for this stack (660 ± 60 Bq kg^{-1}; n = 4) and roughly 20 times higher than those found in reference agriculture soils. ^{226}Ra concentrations in the studied PG stack are, on the other hand, over the threshold level of 370 Bq kg^{-1} established by the US-EPA to allow the agriculture use of PG. ^{238}U activity concentrations in PG samples followed a lognormal distribution with geometric mean 149.7 ± 1.6 Bq kg^{-1} (range 33–600 Bq kg^{-1}), a factor 4 higher than typical concentrations in soils (35 Bq kg^{-1}) [21] and with overall ^{238}U/^{226}Ra ratio of 0.27 ± 0.05. Finally, ^{210}Po followed a distribution compatible with one of Laplace's type with mean of 614 Bq kg^{-1} and scale 0.0109 and overall ^{210}Po/^{226}Ra ratio of 0.97 ± 0.07. There was neither correlation between ^{238}U and ^{226}Ra distributions (at 90% CL) nor between ^{210}Po and ^{226}Ra (at 90% CL).

The application of this PG as Ca-amendment at typical rates used in SW Spain (ca. 20 Mg ha^{-1} d.w.) implies associated inputs of 15, 3.0 and 12 MBq ha^{-1} of ^{226}Ra, ^{238}U and ^{210}Po, respectively.

3.3. ^{222}Rn exhalation rates

Table 3 shows the measurement of ^{222}Rn exhalation rates corresponding to the triplets of canisters placed at three selected sampling points in the PG stack. Significant differences were found in two sampling points among the mean values of the three triplets (spaced ~ 1 m).

^{222}Rn exhalation rates (average value for the three canisters per sampling point) were normally distributed within each sampling campaign. Fig. 4 shows a box-and-whisker plot for the five sampling campaigns. No statistically significant differences (95% CL) were found between the two sampling campaigns needed to cover Region 1, but significant differences appeared between the two samplings in Region 2 (p < 0.05). Values found in sampling 1 were significantly higher than the rest, while values for sampling 3 were significantly lower (values for samplings 2, 4 and 5 were within the same group—95% CL LSD method).

Fig. 5 shows the spatial distribution map for ^{222}Rn exhalation rate (using average values of the three canisters per sampling point). Values ranged from 150 to 1020 Bq m^{-2} h^{-1} in Region 1 (n = 20); from 28 to 547 Bq m^{-2} h^{-1} in Region 2 (n = 16) and from 130 to 570 Bq m^{-2} h^{-1} in Region 3 (n = 10). These values were one order of magnitude higher than those found for reference agriculture soils (Table 1), but they were under the limit of 2600 Bq m^{-2} h^{-1} stated in the US-EPA regulation [8]. Attending to classification by regions, values were statistically different (p < 0.01).

Table 3
^{222}Rn exhalation rate in PG stacks

Sampling point	ANOVA[a]	^{222}Rn exhalation rate (Bq m^{-2} h^{-1})		
		Triplet A	Triplet B	Triplet C
R3-P01 (37°15′09.48″N, 6° 54′02.04″W)	*	180 ± 60	400 ± 30	470 ± 40
R2-P12 (37°15′23.76″N, 6°53′49.86″W)	NS	660 ± 250	410 ± 130	270 ± 90
R2-P14 (37°15′28.02″N, 6°53′44.10″W)	*	110 ± 30	830 ± 210	389 ± 21

Short scale (0.1 m) variability. Mean and standard deviation of mean (n = 3, 0.1 m spaced). Triplets places in triangles of ∼1 m length. Measurements by charcoal canister method.
*Corresponds to 95% CL. NS, not significant.
[a] One-way ANOVA test for significant differences among means.

In order to study potential enhancement in ^{222}Rn exhalation rate by tillage of the PG stack (a traditional practice in this area related to PG extraction for agriculture uses), an area of 2 m × 2 m in Region 1 was dug over (20–30 cm thick). Three charcoal canisters were placed in this area within the routine of the second sampling. ^{222}Rn exhalation rate was 240 ± 80 Bq m^{-2} h^{-1} (mean and standard deviation of mean), which was not significantly different from the mean value for the second sampling (95% CL). Thus, it could be expected that tillage will not significantly contribute to differences in ^{222}Rn exhalation rates between Regions 1 and 2, particularly knowing that last tillage was applied in 2001, and afterwards the surface became sensibly re-crusted.

For a given data set containing n data z_i (i = 1–n) with average value z_m, one can define the normalized variable $z_{r,i} = z_i/z_m$. Normalized variable can be defined within each triplet, generating a set of 27 elements (3 canister × 3 triplet × 3 sampling points). Such a data set resulted normally distributed with standard deviation 0.39, which can be considered as a measurement of the observed ^{222}Rn variability at sub-grid scale 0.1 m (the distance between canisters within each triplet). Such variability can be attributable to variability at this sub-grid scale of factors affecting Rn emissions, particularly un-homogeneities and anisotropy of pore structure and permeability. Variability of ^{226}Ra concentrations at this spatial scale has not been explicitly studied in this work. We note that normalization cancel out the effects of factors affecting the mean values of ^{222}Rn exhalation rates (as climatic conditions and variability in ^{226}Ra concentrations a larger spatial scales).

Normalized variable can be defined with respect to the mean value of each sampling point. This way a set of 138 data is generated (3 canister × 46 sampling points). Similarly, normalized variable can be defined with respect to mean values for each sampling camping (typically, 10 sampling points distributed in a 50 m × 75 m mesh) and the corresponding distributions can be evaluated for the three regions and the whole PG stack. For agriculture soils two spatial scales can be considered: 1 m (distance between canister in each sampling point) and ca. 60 m (distance between sampling points). Similarly, normalized distributions can be defined for ^{226}Ra, ^{210}Po and ^{238}U data. Results are summarized in Table 4. Being ^{226}Ra concentration quite uniform in agriculture soils, variability in normalized ^{222}Rn distribution at sub-grid scale of 1 m has to be attributable to variability at the same scale in soil properties; which results of the same order than the one found in PG for sub-grid 0.1 m. ^{222}Rn variability at sub-grid scale of 1 m was 0.58 in the PG stack, slightly higher than the observed at lower scales.

Variability in normalized radionuclide concentrations in PG (at ∼60 m spatial scale) is of the order of 30%; being attributable to

Table 4
Standard deviation of normalized distributions for Ra exhalation rate and radionuclide concentrations in agriculture soil and PG stack

Analyte	Spatial scale (m)	Agriculture soil	PG stack (global data)	PG stack		
				Region 1	Region 2	Region 3
^{222}Rn	0.1		0.39		0.43	0.31
	1	0.32	0.58	0.60	0.69	0.28
	60	0.26	0.50	0.46	0.62	0.40
^{226}Ra	60	0.04	0.30	0.30	0.30	NM
^{210}Po	60	NM	0.21	0.24	0.15	NM
^{238}U	60	NM	0.44	0.51	0.26	NM

NM: non-measured.

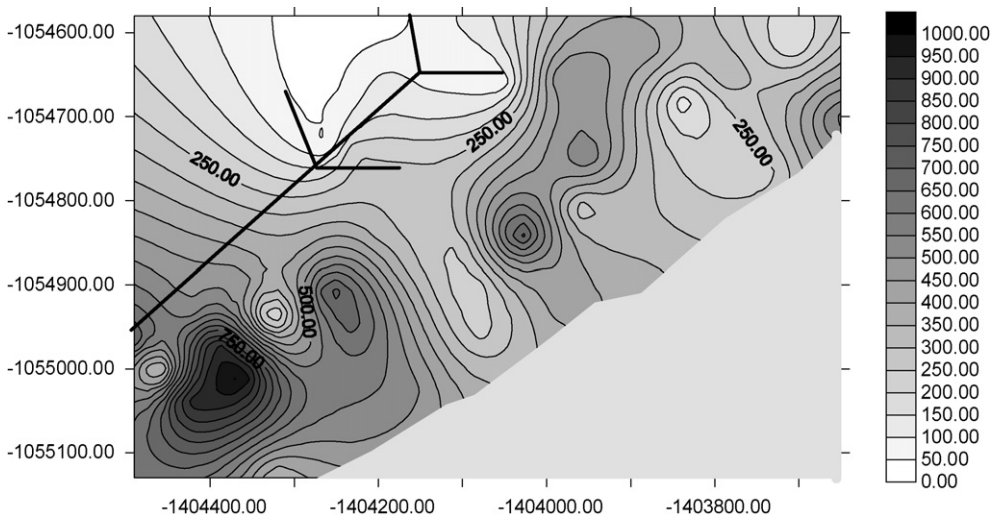

Fig. 5. Spatial distribution map (coordinates Lambert GISCO, units in m) with the measured ^{222}Rn exhalation rates (Bq m^{-2} h^{-1}). Data constructed with average values of the three canisters per sampling point. The pipeline has been indicated for the sake of comparison with Fig. 1.

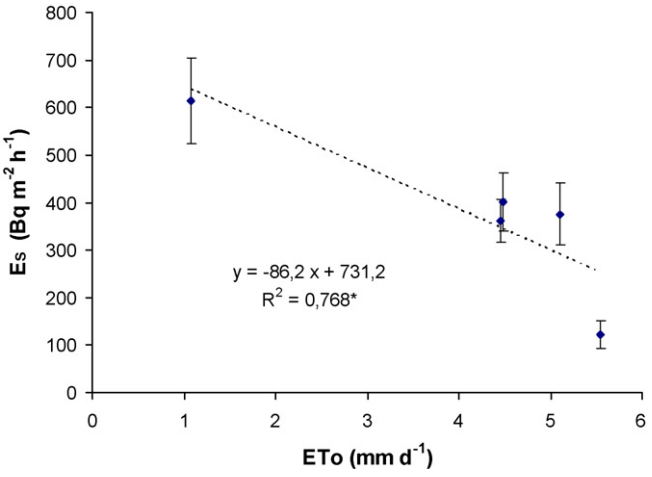

Fig. 6. E_S (mean and 1S.D. of mean of ^{222}Rn exhalation rate for each sampling campaign) for the PG stack as a function of the daily potential evapotranspiration (ETo).

the natural variability in the industrial process and waste disposal routines during the stack build up.

Estimation of ^{222}Rn variability at sub-grid ~60 m involved point-averaged values (three canister per sampling point), what reduced the contribution of variability at sub-grid 1 m, but incorporates the contribution of ^{226}Ra concentration at sub-grid ~60 m (climatic conditions are cancel out since normalization applied for each sampling campaign). Resulting variability was 0.4–0.6.

A multiple-regression test was performed for ^{222}Rn exhalation rate, E (Bq m^{-2} h^{-1}), against factors ^{226}Ra concentration (Bq kg^{-1} d.w.) and daily ETo (mm day^{-1}), involving all the point-averaged values for PG stack and agriculture soil. A statistically significant (CL 99%) correlation was obtained among the variables with the fitted model:

$$E = 281.2 - 69.54\ \mathrm{ETo} + 0.4654\ ^{226}\mathrm{Ra} \quad (1)$$

The model explains 57.4% of the variability in Rn emissions, what is consistent with the previous analysis of sub-grid 1 m scale variability. The contribution of both two variables is statistically significant at CL 99%, withy $p < 0.001$ for ETo and $p < 0.0001$ for ^{226}Ra.

In opposition to agriculture soils, ^{222}Rn exhalation rates in PG stack decreased with ETo. A regression analysis has been performed involving averaged values of E per sampling campaign in the PG stack, E_S, and daily ETo (Fig. 6). There was a statistically significant (CL 95%) linear correlation explaining 76.8% of the observed variability in E_S. We note that Eq. (1) applies for E (point-averaged value) and includes data from agriculture soils (by introducing the averaged value of ^{226}Ra concentrations for the PG stack in Eq. (1), it reduces to a mathematical relationship close but not identical to the one shown in Fig. 6 for E_S and ETo).

In PG stack ^{222}Rn emissions decreased with increasing ETo. This is an unexpected result that will require further study to fully understand the involved processes. Effectively, in bare soils ETo leads to evaporation of available water in soils, and the circulation of water vapour through the porous media forces the convective transport of ^{222}Rn. At time, the effective diffusion coefficient for ^{222}Rn in the porous media increases with temperature. This is consistent with our results for agriculture soils (Fig. 2). Nevertheless for PG stack, present results (Fig. 6) suggest that the induced changes in the porous media structure and permeability due to the available energy for water evaporation are dominant and they reduce ^{222}Rn exhalation rates.

4. Conclusions

- This work proved that actual ^{222}Rn exhalation rates in the studied PG stack were under the US-EPA limit of 2600 Bq m^{-2} h^{-1}, but they were one order of magnitude higher than those found in the reference site (agriculture soil).
- Tillage or digging over of the stack surface did not result in any statistically significant enhancement in ^{222}Rn exhalation rates.
- ^{226}Ra concentrations (in the 0–90 cm horizon) were characterized by a coefficient of variation of 30%. Averaged values for the stack were 730 ± 60 Bq kg^{-1} (d.w.), over the US-EPA limit of 370 Bq kg^{-1}.
- The application of this PG as Ca-amendment at typical rates used in SW Spain (ca. 20 Mg ha^{-1} d.w.) implies associated inputs of 15, 3.0 and 12 MBq ha^{-1} of ^{226}Ra, ^{238}U and ^{210}Po, respectively, in the treated agricultural soils.
- Variability in normalized ^{222}Rn exhalation rates at spatial scales <1 m was 30% in agriculture soils and ranged between 30% and 70% in PG stack. Such variability can be attributable to variability at this sub-grid scale of soil/PG properties, particularly to unhomogeneities and anisotropy of pore structure and permeability (variability of ^{226}Ra concentrations at this spatial scale have not been explicitly studied in this work).
- In agriculture soils, ^{226}Ra concentrations varied less than 4% (at spatial scales of ~60 m) and averaged values of ^{222}Rn exhalation rate per sampling campaign, E_S (Bq m^{-2} h^{-1}), were positively correlated with potential evapotranspiration ETo (mm day^{-1}): $E_S = 7.09\mathrm{ETo} - 0.53$ ($R^2 = 0.83^*$).
- In PG, E_S showed a negative correlation with ETo (Fig. 6): $E_S = 731 - 86.2\mathrm{ETo}$ ($R^2 = 0.77^*$). Understanding the reasons of these unexpected results requires further study.
- The point-averaged values of ^{222}Rn exhalation rate, E (Bq m^{-2} h^{-1}) for all the PG and soil measurements showed a statistically significant (CL 99%) correlation with daily ETo and the ^{226}Ra concentration, explaining 57.4% of the variability in Rn emissions: $E = 281.2 - 69.54\mathrm{ETo} + 0.4654\ ^{226}\mathrm{Ra}$.

Acknowledgements

This work was funded by ENRESA (Spanish Public Corporation of Radioactive Residues), I+D Code 78.5.5.4.3.05; and by the IFAPA-C039 project from the regional Andalusia government. The authors thank the collaboration from FERTIBERIA.

References

[1] P.M. Rutherdord, M.J. Dudas, R.A. Samek, Environmental impacts of phosphogypsum, Sci. Total Environ. 149 (1994) 1–38.
[2] I.S. Alcordo, J.E. Recheigl, C.E. Roessler, R.C. Littell, Radiological impact of phosphogypsum applied to soils under bahiagrass pasture, J. Enviorn. Qual. 28 (1999) 1555R–1567R.
[3] J.M. El-Mrabet, R. Abril, G. Periáñez, R. Manjón, A. García-Tenorio, L. Delgado, Andreu, Phosphogypsum amendment effect on radionuclide content in drainage water and marsh soils from southwestern Spain, J. Environ. Qual. 32 (2003) 262–1268.
[4] C. Papastefanou, S. Stoulos, A. Ioannidou, M. Manolopoulou, The application of phosphogypsum in agriculture and the radiological impact, J Environ. Radioact. 89 (2006) 188–198.
[5] J.P. Bolivar, R. García-Tenorio, M. García-León, On the fractionation of natural radioactivity in the production of phosphoric acid by the wet acid method, J. Radional. Nucl. Chem. Lett. 214 (1996) 77–78.
[6] F. Moreno, J. Martín, J.L. Mudarra, A soil sequence in the natural and reclaimed marshes of the Guadalquivir River, Seville (Spain), Catena 8 (1981) 201–211.
[7] R. Domínguez, M.C. Del Campillo, F. Peña, A. Delgado, Effect of soil properties and reclamation practices on phosphorus dynamics in reclaimed calcareous marsh soils from the Guadalquivir Valley, SW Spain, Arid Land Res. Man. 15 (2001) 203–221.
[8] USEPA, Potential Uses of Phosphogypsum and Associated Risks. Background Information Document for 40 CFR 61 Subpart R. Natl. Emission Standards for

Radon Emissions from PG Stacks, USEPA 402-R92-002, USEPA, Washington, DC, 1992.
[9] National Emission Standards for Hazardous Air Pollutants (NESHAPS), Environmental Impact Statement for Radionuclides, Report EPA 520/1-89-005, Office of Radiation Programs (ANR-459), U.S. Environmental Protection Agency, 1989.
[10] W.W. Nazaroff, Radon transport from soil to air, Rev. Geophys. 30 (1992) 137–160.
[11] K. Sun, Q. Guo, W. Zhuo, Feasibility for mapping radon exhalation rate from soil in China, J. Nucl. Sci. Technol. 41 (2004) 86–90.
[12] J.A. Rabi, A.A. Mohamad, Parametric modelling and numerical simulation of natural-convective transport of radon-222 from a phosphogypsum stack into open air, Appl. Math. Model. 30 (2006) 2546–2560.
[13] W. Zhuo, T. Iida, T. Furukawa, Modeling radon flux density from the Earth's surface, J. Nucl. Sci. Technol. 43 (2006) 479–482.
[14] W. Zhuo, Q. Guo, B. Chen, G. Cheng, Estimating the amount and distribution of radon flux density from the soil surface in China, J. Environ. Radioact. 99 (2008) 1143–1148.
[15] R. Allen, L. Pereira, D. Raes, M. Smith, Crop evapotranspiration, FAO Irrigation and Drainage Paper 56, FAO, Roma, 1998, 300 pp.
[16] C. Dueñas, E. Liger, S. Cañete, M. Pérez, J.P. Bolívar, Exhalation of ^{222}Rn from phosphogypsum piles located at the Southwest of Spain, J. Environ. Radioact. 95 (2007) 63–74.
[17] Andalusian network of agro-meteorological stations, 2008. http://www.juntadeandalucia.es/innovacioncienciayempresa/ifapa/ria/.
[18] L.S. Quindós, P.L. Fernández, M.L. Bordonoba, J. Gómez-Arozamena, C. Sainz-Fernández, J. Arteche, Technical report, 2001.
[19] H.P. Moreno, A. Absi, I. Vioque, G. Manjón, R. García-Tenorio, Application of a liquid scintillation technique to the measurement of ^{226}Ra and ^{224}Ra in samples affected by non-nuclear industrial wastes, J. Radioanal. Nucl. Chem. 245 (2000) 309–315.
[20] E. Holm, R. Fukai, Method for multi-element alpha-spectrometry of actinides and its application to environmental radioactivity samples, Talanta 24 (1977) 659–664.
[21] United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR), Sources and effects of ionizing radiation. Report to the General Assembly, with annexes, New York, United Nations, 2000.