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Occupational dosimetric assessment (inhalation pathway) from the application of phosphogypsum in agriculture in South West Spain

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ABSTRACT

Phosphogypsum (PG) has been traditionally applied as Ca-amendment in saline marsh soils in SW Spain, where available PG has 710 ± 40 Bq kg^{-1} of ^{226}Ra. This work assesses the potential radiological risk for farmers through ^{222}Rn exhalation from PG-amended soils and by inhalation of PG-dust during its application. A three-year field experiment was conducted in a commercial farm involving two treatments: control and 25 t PG ha^{-1} with three replicates (each 0.5 ha plots). The ^{222}Rn exhalation rate was positively correlated with potential evapotranspiration, which explained 67% of the variability. Statistically significant differences between the control and PG treatments were not found for ^{222}Rn exhalation rates, and mean values were within the lowest quartile of the typical range for ^{222}Rn exhalation from soils. Airborne dust samples were collected during the application of PG and sugar-beet sludge amendments. The highest PG-attributable ^{226}Ra concentration in the dust samples was 3.3×10^2 μBq m^{-3}, implying negligible dose increment for exposed workers.

1. Introduction

Phosphogypsum (PG) is the main waste of phosphoric rock processing plants, which use phosphate rock as raw material. In general, levels of fluoride, certain naturally occurring radionuclides and some heavy metals are elevated in PG. Concentrations of these hazardous elements depend on the origin of the rock phosphate sources, the type, and the efficiency of the wet process used (Rutherford et al., 1994).

The worldwide annual production of PG in 2006 was estimated to be about 170×10^6 tonnes, and most of it is stock-piled. Agriculture uses of PG are being extensively studied since they could become the main worldwide use for this waste. Thus, studies have been conducted, among others, on the effect of PG in the improvement of soil structure and crop yield (May and Mortvedt, 1986; Mullins and Mitchell, 1990), reducing soil erosion (Zhang et al., 1998), and increasing levels of available S and P (Delgado et al., 2002).

In SW Spain, PG has being traditionally used as a Ca-amendment for soil reclamation (Domínguez et al., 2001). Initial recommended rates were 20–25 t ha^{-1} with repetition of every two years. Under current practices, PG is applied (after being sun-dried) over a previously tilled soil; with additional deep-tillage immediately after PG application, which provokes dilution in a soil horizon up to 40 cm. No attention is paid to PG grain size and, in practice, it is possible to distinguish from sub-mm up to several cm grain sizes immediately after application. The source of the applied PG in SW Spain is the phosphoric rock processing plant located in Huelva (SW Spain), which has produced a total PG amount of about 8×10^7 tonnes (Borrego et al., 2007). Most of them have been disposed in stacks lying on the right bank of the Tinto River, in the vicinity of Huelva city, covering an area of about 1200 ha. Nowadays, PG production is about 3×10^6 tonnes per year, mainly obtained after processing phosphate rocks from Morocco (with ^{238}U concentrations around 1000 Bq kg^{-1}, after Bolívar et al., 1996). About 85% of the uranium present in phosphate rock goes to the resulting phosphoric acid, while about 90% of the ^{226}Ra remains in the PG wastes (Bolívar et al., 1996).

Recent Spanish regulations (R.D. 824/2005, from July 2005) explicitly allowed the use of PG as soil amendment with no mention to its radioactive content, while the US EPA has specific regulation for the agriculture use of PG (64 FR 5574, USEPA, 1992), allowing it if ^{226}Ra concentration is below 370 Bq kg^{-1}.

Major environmental concerns related to the agriculture use of PG are the radionuclide (and other PG-related pollutants such as Cd) uptake by plants and their build-up in soil (Rutherford et al.,

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1994). The radiological impact related to the agriculture use of PG has been studied, among others, by Alcordo et al. (1999) in Florida, by El-Mrabet et al. (2003) in reclaimed marsh soils in SW Spain, and, more recently, by Papastefanou et al. (2006) in Greek soils. Concerning the inhalation pathway, airborne particulate matter originating from PG during its application as soil amendment is a potential source of radioactivity. With current practices in SW Spain, large clouds of dust are formed when PG is spread over the soil. Increasing ^{222}Rn exhalation from ^{226}Ra-enriched soils is another point of concern. Thus, Alcordo et al. (1999) reported significant increments in ^{222}Rn exhalation rates following PG application in soils under bahiagrass pasture in Florida.

A significant fraction of the total radioactive dose received by the world population is associated with radioactivity inhalation via aerosol particles (UNSCEAR, 2000). In addition, ^{222}Rn and its short-lived decay products are responsible for an important fraction of the total internal dose received by the population.

The present work is aimed to study ^{226}Ra concentrations in particulate matter during the application of PG under current practices in a commercial farm in SW Spain and to monitor ^{222}Rn exhalation rates in PG-amended plots. Measurements of ^{222}Rn exhalation rates typically show large spatial and temporal variability, although the factors affecting such variability are still poorly understood. Thus, attention will be paid to establish the potential effect of agricultural and environmental factors on ^{222}Rn exhalation. All this information will be useful to support a radioactive dose assessment through the inhalation pathway related to the agriculture use of PG in SW Spain.

2. Materials and methods

2.1. Experimental site and experimental design

An experiment was conducted on a 6 ha (250 × 240 m) plot of a commercial farm in the "Marismas of Lebrija", in the marsh area of the Guadalquivir River, SW Spain (37°1.2′N, 6°7.4′W). The plot was flat (0.1% slope) and lengthwise crossed by drainage lines 250 m long and spaced 5 m which were placed at a depth of about 1 m. After reclamation, these marsh soils can be classified as Aeric Endoaquepts (Soil Survey Staff, 1998). More detailed information about this experimental site can be obtained elsewhere (Delgado et al., 2006). The farm soils, as the rest of the area, have received some previous PG amendments before 2001, being not well-documented. Nevertheless, they could correspond to some 6 typical doses of 25 t ha^{-1} each (Abril et al., 2008a).

Two treatments (control – with no additional PG, and 25 t ha^{-1} PG on a sun-dried weight basis, applied in April 2003 and repeated in September 2004) were applied in triplicate and randomly distributed in 0.5 ha (250 × 20 m) plots (see Fig. 1). In April 2003, sugar-beet sludge was applied to three other elemental plots at a rate of 30 t ha^{-1}. Airborne dust samples were collected during the application of these amendments. The ^{222}Rn exhalation was monitored only in control and PG-amended plots. In the first and third seasons (2003 and 2005), cotton (*Gossypium hirsutum* L.) was grown under furrow irrigation (sown in April and harvested in November); in the second, sugar-beet (*Beta vulgaris* L.) was grown under sprinkler irrigation at 2.5 mm h^{-1} (from January to July 2004). For both crops, fertiliser was applied to all the plots at pre-plant stage [52 kg N ha^{-1}, 68 kg P ha^{-1} and 43 kg K ha^{-1} as a mixture of $(NH_4)_2HPO_4$, urea and KNO_3]. A detailed study on ^{226}Ra and ^{238}U in these soils, including depth profiles and a comparison against non-reclaimed soils has been presented in a separate work (Abril et al., 2008a).

2.2. Sampling air filters, soils and charcoal canisters for ^{222}Rn measurements

The PG application lasts only a few hours, but large clouds of dust are formed. Thus, to collect total suspended particles (TSPs) the following suitable solution was adopted: A vacuum-pump aspired air through a Nucleopore polycarbonate filter, 0.45-μm pore size and 47-mm diameter, and a gas-volume meter. The pump was powered by a commercial portable electric generator. Mean flow rate was 3.2 m^3 h^{-1} and typical sampling time was 35 min per filter. Fig. 1 shows the experimental plot-design and the situation of the collected air filters. For a number of measurements, the filter support system was placed at 1.6 m above ground level in the border of the elemental plot while the tractor was applying the amendment. This kind of measurement may roughly represent the situation of a farmer during the PG application. Other samples were collected by placing the filter support in the cabin of the tractor (in the outside mirror) in order to have a proxy to the situation of the driver in the worst and fairly improbable situation of working without (or with open) windows. Filters were weighed (by using a 0.1 mg precision electronic weighing machine) before and after collection to measure TSP (values ranged from 2 to 6 mg for most of the filters).

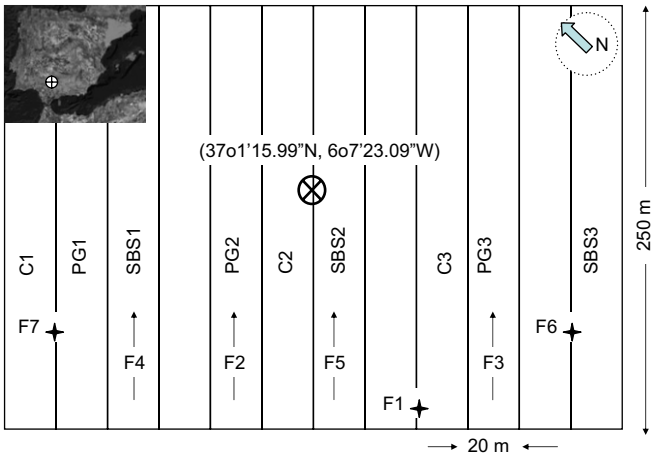

Fig. 1. Situation of the experimental site with a schematic representation of the experimental design and the locations of the dust sampling filters. Filters are numbered following the temporal sequence of sampling; those associated with arrows indicate sampling in the cabin of the tractor during the application of the amendment (PG, phosphogypsum 25 t ha^{-1}; SBS, sugar-beet sludge 30 t ha^{-1}; C, control), and those associated with crosses indicate sampling at a fixed point (filter placed at 1.6 m above ground level).

Soils were sampled (0–30 cm horizon) at the central point of each control and PG-plot in January 2006 to study the ^{226}Ra and ^{238}U contents after the two treatments. Samples were air-dried and ground to pass a 0.5 mm screen prior to analysis.

The ^{222}Rn exhalation was measured by the activated charcoal canister method, following the procedure described by Dueñas et al. (2007). 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 (starting early in the morning). Selected exposure time allows integration of diurnal variations in ^{222}Rn emissions without significant charcoal-saturation effects (after Hartley et al., 1983) and thus, it meets the USEPA method 115 for monitoring ^{222}Rn emissions (USEPA, 1992). Sampling points were defined at the centre of each elemental control and PG-amended plots. 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 orientated northwards). Canisters were weighed before and after sampling to determine the adsorbed moisture by charcoal for subsequent corrections in exhalation determination (Dueñas et al., 2007). The ^{222}Rn exhalation was measured for four sampling campaigns (September 2004, October 2004, February 2005 and February 2006).

In natural soils, under sunny conditions, net radiation can lead to significant water evaporation and/or to an increase in soil temperature, affecting consequently the 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 (Allen et al., 1998), is a function of the net radiation, average air temperature, wind speed and water vapour pressure. For any particular crop and crop conditions, it is possible to estimate actual evapotranspiration from ETo, corrected by an appropriate crop-coefficient. Daily ETo has been selected to study its potential effect on ^{222}Rn emissions. For each sampling period, ETo was obtained from the closest agro-meteorological station from the Andalusian network (107 stations operating since 2000 with online access): *Lebrija I* (36° 58′ 40″ N, 06° 07′ 30″ W, $h = 25.0$ m). ETo provided by the Andalusian network is estimated by the referred Penman–Monteith FAO56 method.

2.3. Radon measurements

In total, 72 charcoal canisters were collected. The ^{222}Rn activity was determined through the 609 keV γ-emission of ^{214}Bi by using 3 low-level gamma-ray spectrometric systems equipped, respectively, with 5″ × 5″ NaI(Tl), HPGe Xtra (37.1% relative efficiency, FWHM of 1.76 keV at 1332 keV of ^{60}Co) and ReGe (31.4% relative efficiency, FWHM of 1.98 keV at 1332 keV of ^{60}Co) detectors. Typical counting times were 6–18 h per sample with typical counting uncertainties below 10%. These systems were calibrated with charcoal spiked with a tracer solution of ^{226}Ra (after homogenization), once it was allowed to reach secular equilibrium with ^{222}Rn and its decay products. Blank charcoal canisters were also measured for background corrections. More details on the applied method can be found in Dueñas et al. (2007) and Quindós et al. (2001).

2.4. ^{226}Ra and ^{238}U measurements in soils

Homogenised soil samples were introduced in Petri dishes, sealed to preclude radon emanation and stored during one month to allow secular equilibrium of ^{226}Ra with its decay products ^{214}Bi and ^{214}Pb. Gamma measurements were carried out on the ReGe and Xtra low-background high purity Ge detectors previously described. Typical counting times were 48 h per sample. The target radionuclides were ^{226}Ra (determined through the 352 keV emission of ^{214}Pb) and ^{238}U (through the 63 keV emission of ^{234}Th, following El-Daoushy and Hernández, 2002), both naturally occurring and whose concentrations may be enhanced by the PG treatment. Efficiency calibration (in Petri dish geometry) was performed using farm soils from the studied site (to ensure the same matrix conditions that the target samples) spiked with known amounts of a multi-γ-emitters tracer solution. Measured efficiencies were cross-calibrated against Monte-Carlo simulations.

2.5. ^{226}Ra measurements in air filters

Filters were dissolved with HCl and HNO_3, to form aqua regia, and the resulting solution was taken to 0.5 L with distilled water. Five milligrams of Ba carrier was added to the sample and precipitation of Ba–$RaSO_4$ was then carried out. The precipitate was collected by filtration through a 0.45-μm pore size Millipore filter. After 20 days (to allow secular equilibrium of ^{226}Ra with its decay products) the alpha activity of the sample was measured in a Berthold LB 770 low-background gas-flow proportional counter previously calibrated for total efficiency versus precipitate mass thickness. The measured background was 0.050 ± 0.003 cpm (mean and one standard deviation, $n = 12$). The procedure is standard and may be seen in more detail, for instance, in Periáñez and García-León (1993).

2.6. Agriculture inputs

Phosphogypsum is usually obtained from a non-active PG stack (37°15′21.26″N, 6°54′2.07″W) in Huelva (SW Spain). The PG stack has been extensively sampled ($n = 42$) to determine its content in ^{226}Ra (by liquid scintillation, using a Wallac Quantulus 1220) and ^{238}U and ^{210}Po (by α spectrometry, using an alpha spectrometer with 8 independent chambers, equipped each one with a 450 mm^2 PIPS detector), resulting (on a dry weight basis) in 720 ± 260 Bq kg^{-1} of ^{226}Ra, 170 ± 110 Bq kg^{-1} of ^{238}U and 660 ± 160 Bq kg^{-1} of ^{210}Po (mean and one standard deviation, Abril et al., 2008b). The PG used in our field experiment came from this stack. A representative sample was submitted for analysis, providing 630 ± 4 and 196 ± 6 Bq kg^{-1} of ^{226}Ra and ^{238}U, respectively, on a dry matter basis. Borrego et al. (2007) provided a reference value of 280 Bq kg^{-1} for ^{230}Th in PG stacks in Huelva. Pérez-Moreno (2005) found 1680 ± 150 Bq kg^{-1} of ^{238}U and non-detectable amounts of ^{226}Ra in diammonium-phosphate produced in SW Spain.

Under field conditions, after being sun-dried, the remaining moisture content in PG was 19%. Thus, at 25 t PG ha^{-1} rate (sun-dried weight), the amendment was incorporating 12.8 MBq ha^{-1} of ^{226}Ra and 4.0 MBq ha^{-1} of ^{238}U. The application of 68 kg P ha^{-1} as diammonium-phosphate incorporates 0.49 MBq ha^{-1} of ^{238}U, and negligible amounts of ^{226}Ra.

2.7. Statistical analysis

Statgraphics Plus 5.1 software was applied to carry out tests for each data-set distribution. An analysis of variance (1-way ANOVA) test was applied 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.

3. Results and discussion

3.1. The effect of PG amendment in radionuclide build-up in soils and ^{222}Rn exhalation

Table 1 summarizes ^{226}Ra and ^{238}U concentrations in soils and ^{222}Rn exhalation rate from control and PG-amended plots for the different sampling campaigns. The ^{226}Ra activity concentrations were 35.3 ± 0.8 and 39.3 ± 2.3 Bq kg^{-1} (mean and one standard deviation of mean), for control and PG-amended plots, respectively. There were no statistically significant differences (95% CL) between the two treatments. Mean ^{226}Ra activity concentrations were close to the average value for soils (35 Bq kg^{-1}) reported by UNSCEAR (2000). Concerning ^{228}U concentrations, measured values were 25.3 ± 0.4 and 23.9 ± 1.5 Bq kg^{-1} for control and PG-amended plots, respectively, without statistically significant differences.

The ^{222}Rn exhalation values from the three canisters of each sampling point were normally distributed. No significant differences (95% CL) were found between means of points corresponding to the same sampling campaign and treatment. There were significant differences ($p < 0.0001$) between mean values from subsequent sampling campaigns (for both control and PG-amended plots). Differences between treatments were not statistically significant (95% CL) except for the sampling of September 2004. Mean exhalation rates were within the range 13–55 Bq h^{-1} m^{-2} corresponding to the lowest quartile of typical ^{222}Rn exhalation rates from soils (30–150 Bq h^{-1} m^{-2}, as reported by Dueñas et al., 1997).

It is important to note that the general absence of statistically significant differences between treatments under our particular experimental setup does not necessarily imply that PG has not any effect on radionuclide enrichment in soils or in increasing ^{222}Rn exhalation. Furthermore, the mean $^{226}Ra/^{238}U$ activity ratio was 1.5 ± 0.1, far from the secular equilibrium, which indicates a PG-attributable ^{226}Ra enrichment (PG from SW Spain has a $^{226}Ra/^{238}U$ fingerprint of 4.3 ± 0.5) due to the cumulative effect of all the previous PG applications, as shown in Abril et al. (2008a).

The ^{222}Rn exhalation rates were positively correlated with the daily potential evapotranspiration ETo ($R^2 = 0.689$ at a CL 95%), as shown in Fig. 2. The ETo explains 67% of the variability in radon emissions.

Table 1
^{226}Ra and ^{238}U concentrations[a] in agriculture soils and ^{222}Rn exhalation[b] measured in several sampling campaigns.

Sampling point	^{226}Ra (Bq kg^{-1})	^{238}U (Bq kg^{-1})	^{222}Rn Exhalation (Bq h^{-1} m^{-2})			
	January 2006	January 2006	September 2004[c]	October 2004[d]	February 2005[c]	February 2006[e]
Control plots						
C_1	36.9 ± 0.7	25 ± 6	35 ± 5	21.4 ± 1.0	10.1 ± 1.4	16 ± 3
C_2	34.7 ± 0.7	24.8 ± 1.3	33 ± 4	18.9 ± 1.4	14 ± 5	18 ± 5
C_3	34.3 ± 0.9	26 ± 4	40 ± 7	30 ± 5	14 ± 6	27.7 ± 2.0
Arithmetic mean control	35.3 ± 0.8	25.3 ± 0.4	36a	23.4b	12.7c	20.6b
PG-amended plots						
PG_1	34.7 ± 1.1	26 ± 3	52 ± 13	27.7 ± 2.6	15 ± 5	24.4 ± 1.0
PG_2	41.0 ± 0.9	21 ± 4	48 ± 9	25.4 ± 2.2	40 ± 30	28 ± 7
PG_3	42.1 ± 1.1	24.7 ± 2.8	66 ± 14	36 ± 4	28 ± 3	18.9 ± 2.0
Arithmetic mean PG	39.3 ± 2.3	23.9 ± 1.5	55a	30b	28b	23.7b
ANOVA	NS	NS	*	NS	NS	NS

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

[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.

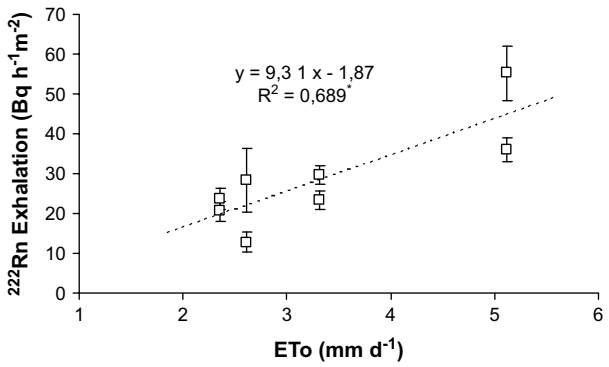

Fig. 2. ^{222}Rn exhalation rates (mean with error-bars corresponding to one standard deviation of mean) as a function of the daily potential evapotranspiration.

Basic processes governing radon transport from soils to air (as reviewed by Nazaroff, 1992) are relatively well understood. They provide a basis for understanding the effect of evapotranspiration in the enhancing of radon emissions. A reduction of soil moisture enhances ^{222}Rn emanation and the transfer of ^{222}Rn from liquid to gaseous phases. Radon transportation through the connected pore space towards the earth's surface involves diffusion (enhanced by temperature, and the increase of connected empty-pore spaces) and advection processes. Advection is governed by intrinsic permeability (affected by moisture) and pressure gradients. Other meteorological parameters like temperature difference between soil and surface air and wind velocity also affect the advection processes.

Three canisters were placed for each sampling point. A normalized variable can be defined as the ratio of the exhalation rate of each canister and the mean value of each sampling point. This way a set of 36 data is generated (3 canisters $\times$ 3 sampling points $\times$ 4 sampling campaigns) for control and PG-amended plots. Data were normally distributed with standard deviations of 0.32 and 0.40 for control and PG-amended plots, respectively. Despite the factors affecting the mean values of ^{222}Rn exhalation rates, there persisted an intrinsic variability of roughly 30% (control) to 40% (PG-plots), which can be attributed to the variability in the $\sim$1 m scale of the micro and meso-pore structure and to irregularities in the PG-grains (sizes and distribution) within PG-amended soils.

3.2. ^{226}Ra in airborne dust samples

Table 2 summarizes results for the measurements of ^{226}Ra activities in air filters (the numbering corresponds to the temporal sequence of sampling). TSP and ^{226}Ra activity were below the corresponding decision threshold (L_C) in laboratory and field blanks (the latter having been sampled before the treatment started). The lowest measured ^{226}Ra activity value was found in filter F2, sampled in the tractor cabin during the first run of the PG application, not being exposed to the dust cloud formed behind the tractor and with still negligible resuspension resulting after the PG spreading. From reference ^{226}Ra concentrations in soils (Table 1) and PG from Huelva (Abril et al., 2008b), and the measured TSP and ^{226}Ra activity, it is possible to estimate the corresponding PG-attributable percentages, as shown in Table 2. Thus, the PG contribution in filter F2 cannot be calculated, but it explains 77% of the measured ^{226}Ra activity in filter F3 (tractor cabin, second run of PG application) with 13% of TSP. The PG-attributable contribution to TSP decreases during the application of the sugar-beet sludge (Filters F4 and F5). The origin of PG in these filters was the resuspension from plots PG2 and PG3 (see Fig. 1) due to the moderate wind blowing laterally. The ^{226}Ra was not detectable in filter F6; sampled in a fixed point without any PG-amended plot upwind (Fig. 1). The highest ^{226}Ra activity value corresponds to filter F7, measured 1.6 m above ground during the third run of PG application. In this case the PG-attributable contribution to TSP was 22%, explaining 86% of the measured ^{226}Ra activity.

There are not many reports on ^{226}Ra concentrations in air. The reference level defined by UNSCEAR (2000) is 1 μBq m^{-3} for a typical dust concentration in air of 30 μg m^{-3} at ground level. Measurements reported in current literature are of the order of such reference level. For instance, in a semi-rural environment in Germany, the mean ^{226}Ra concentration detected during years 1983–1985 was 1.2 μBq m^{-3}, with a mean particle concentration of 59 μg m^{-3} (Hotzl and Winker, 1987). A lower value, 0.6 μBq m^{-3}, has been reported for the USA (UNSCEAR, 2000). Slightly higher concentrations, from 2.9 to 9.31 μBq m^{-3}, were measured during 10-year observations in a rural area of Japan (Yunoki et al., 1995). In Poland, ^{226}Ra in air at ground level was 3.28 μBq m^{-3} (Kownacka et al., 1999) and, in Poland as well, Bem et al. (2004) have found an average concentration of 1.56 μBq m^{-3} for a mean dust concentration of 53.1 μg m^{-3}. Similar values have also been found by Braziewicz et al. (2004). In Greece, Papastefanou et al. (1999) have estimated a ^{226}Ra concentration of 0.87 μBq m^{-3} in ground level air assuming a dust loading of 50 μg m^{-3}.

It may be seen that the results in Table 2 are two orders of magnitude higher than values reported above. This is not surprising since dust concentrations are two orders of magnitude higher too, and ^{226}Ra levels in air are correlated with the dust concentration (Hotzl and Winker, 1987). Obviously, the increase in dust concentration is caused by the application of the PG amendment with the tractor.

Table 2
Analysis of air filters sampled during the application of PG and sugar-beet sludge (SBS) as soil amendments[a].

Sample		Volume (m^3)	Time (min)	TSP (mg m^{-3})	^{226}Ra		Maximum PG-attributable	
					(Bq m^{-3})	Error (%)	% (w/w)	% Activity
F1	Farm blank	1.237	22	ND	ND			
F2	PG amendment. Tractor cabin.	2.207	43	2.4	6.5E-05	70	ND	
F3	PG amendment. Tractor cabin.	1.282	25	1.6	1.9E-04	40	13	77
F4	SBS amendment. Tractor cabin.	2.083	41	2.5	1.9E-04	25	7	62
F5	SBS amendment. Tractor cabin.	2.269	42	2.6	2.5E-04	16	10	71
F6	SBS amendment. Farm	1.596	29	2.5	ND			
F7	PG amendment. Farm	1.931	39	2.1	3.8E-04	13	22	86
F8	Laboratory blank	3.301	60	ND	ND			

Sampling on April 8th 2003 (F1–F7).

[a] TSP was measured by gravimetric method (ND not determined). ^{226}Ra concentration measurements by alpha counting. Decision threshold $L_C = 1.1 \times 10^{-4}$ cps (95% CL, from 12 independent background measurements of 600 min. each) or 6.2×10^{-5} Bq m^{-3} (for a volume of 2.0 m^3 and average yield and efficiency).

Table 3
Estimation of the PG-attributable dose increment due to inhalation of dust during the PG application as soil amendment (current practices in SW Spain).

Radionuclide	Concentration in PG (Bq kg^{-1})	Mean activity increment[b] (μBq m^{-3})	Dose conversion factor[a] (Sv Bq^{-1})	Volumetric dose increment (Sv m^{-3})
^{238}U	165	7.7×10^{1}	1.6×10^{-6}	1.2×10^{-10}
^{234m}Pa			5.5×10^{-10}	4.2×10^{-14}
^{234}Th			5.3×10^{-9}	4.1×10^{-13}
^{234}U			2.1×10^{-6}	1.6×10^{-10}
^{230}Th	280	1.3×10^{2}	2.8×10^{-5}	3.6×10^{-9}
^{226}Ra	710	3.3×10^{2}	2.2×10^{-6}	5.8×10^{-10}
^{210}Pb			1.1×10^{-6}	2.6×10^{-10}
^{210}Bi			6.0×10^{-8}	1.7×10^{-11}
^{210}Po	640	3.0×10^{2}	2.2×10^{-6}	5.9×10^{-10}
		Total volumetric dose increment		5.4×10^{-9} Sv m^{-3}
		Dose increment for exposed workers[c]		12 μSv y^{-1}

[a] Factors for exposed workers with AMAD 5 μm (from Spanish regulation RD 783/2001). Absorption rate type "M" has been assumed for all the radionuclides, expect for ^{210}Pb, with type F.
[b] Radioactive equilibrium is assumed between ^{238}U, ^{234m}Pa, ^{234}Th and ^{234}U and between ^{210}Pb, ^{210}Bi and ^{210}Po. Activity increments for PG-attributable ^{226}Ra correspond to sample F7 as the worst case (Table 2). For the other radionuclides values are derived assuming the same activity ratio than in PG from SW Spain.
[c] Assuming a breathed volume at working rate of 1.2 m^3 h^{-1} during 40 h per week, 48 weeks per year.

3.3. Dose assessment

Table 3 summarizes an estimation of the dosimetric contribution of PG-attributable dust, generated under current practices in SW Spain during its application as soil amendment. Estimations follow the methodology presented by Borrego et al. (2007), based on the Spanish Regulation RD 783/2001 (in agreement with EURATOM'96 directive). Dose assessment due to inhalation was carried out for radionuclides belonging to the ^{238}U decay chain, excluding the ^{222}Rn decay products. Volumetric activity increments for PG-attributable ^{226}Ra corresponding to sample F7 were selected as the worst case (Table 2). For the other radionuclides, volumetric activity increments were derived assuming the same activity ratio as in PG from SW Spain (see Section 2). Radioactive equilibrium between ^{238}U, ^{234m}Pa, ^{234}Th and ^{234}U, and between ^{210}Pb, ^{210}Bi and ^{210}Po was assumed. These activity increments are converted into doses by using the corresponding inhalation factors provided by the Spanish regulations for exposed workers and an AMAD (activity median aerodynamic diameter) of 5 μm. The AMAD value associated to an aerosol indicates that 50% of the activity in the aerosol is associated with particles of aerodynamic diameter greater than the AMAD. Conversion factors corresponding to class M (moderate residence time in lung) were selected for all the involved radionuclides except for ^{210}Pb, for which default class was F (short residence time in lung). The breathed volume was estimated at a light worker rate of 1.2 m^3 h^{-1} (ICRP-66, 1994) with a working occupancy of 40 h per week during 48 weeks per year (after Borrego et al., 2007). The cumulative dose increment estimated in this manner for exposed workers (in the worst and fairly improbable scenario of a farmer assisting PG application outside the tractor or a driver without a protected cabin) resulted in a dose of 12 μSv y^{-1}. This value is far below the limits for dose rate increment established by the European Directive (1 mSv y^{-1} for the general population is the most restrictive limit). We note that dust could be eventually ingested, but dose conversion factors for this pathway are smaller than those for inhalation; thus, the previous estimate can still be considered as an upper limit.

Dose assessment due to ^{222}Rn will not be accomplished within the present work because PG-attributable increments in ^{222}Rn exhalation could not be concluded from our present data. Additionally, in field conditions, the ^{222}Rn concentration in air (which effectively contributes to the radioactive dose by inhalation) depends not only on local sources, but on the general circulation of atmospheric air masses at much larger spatial scales as well. The contribution to doses due to the ^{222}Rn decay products in PG-dust is negligible. Thus, assuming secular equilibrium with ^{226}Ra in PG-dust, the resulting volumetric activity concentration of about 0.3 mBq m^{-3} (see Table 3) is five orders of magnitude lower than typical indoor ^{222}Rn concentrations (40 and 30 Bq m^{-3} for the arithmetic and geometric means of the distribution of worldwide indoor ^{222}Rn concentrations, with a geometric standard deviation of 2.3, after UNSCEAR, 2000).

4. Conclusions

Under our experimental conditions (two PG amendments applied to an agriculture soil with some previous 5–6 PG applications, and mixed in the 0–40 cm soil horizon), no statistically significant differences were found between control and PG-amended plots for ^{222}Rn exhalation rates (except for the first campaign). Measured values were within the lowest quartile of the typical range for ^{222}Rn exhalation from soils (Dueñas et al., 1997).

The ^{222}Rn exhalation was positively correlated with daily potential evapotranspiration, which explained 67% of the variability. Normalized distributions revealed an intrinsic variability in the ~1 m spatial scale from 30% (control) to 40% (PG-plots), which can be attributed to the variability, at this scale, of the soil structure and PG-grains (sizes and distribution in the PG-amended soils).

The ^{226}Ra/^{238}U activity ratios in soils revealed a PG-attributable ^{226}Ra enrichment due to the accumulation effect of recent (within the experiment) plus previous PG applications. The highest PG-attributable ^{226}Ra concentration in the airborne dust samples was 3.3×10^{2} μBq m^{-3}, implying negligible radioactive dose increment (12 μSv y^{-1}) for exposed workers (the total average worldwide exposure to natural radiation sources is 2.4 mSv y^{-1}, being the contribution from inhalation exposure 1.26 mSv y^{-1}, of which 1.15 mSv y^{-1} is due to ^{222}Rn, after UNSCEAR, 2000).

Under current practices (spreading PG and mixing it within the 0–40 cm soil horizon), application of PG as soil amendment in SW Spain does not lead to a significant increment in radioactive doses for farmers through the inhalation pathway and, after three decades of practices, current ^{222}Rn exhalation rates from soils remain well within the normal range.

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