

Phosphogypsum Amendment Effect on Radionuclide Content in Drainage Water and Marsh Soils from Southwestern Spain

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ABSTRACT

Phosphogypsum (PG) is a residue of the phosphate fertilizer industry that has relatively high concentrations of ^{226}Ra and other radionuclides. Thus, it is interesting to study the effect of PG applied as a Ca amendment on the levels and behavior of radionuclides in agricultural soils. A study involving treatments with 13 and 26 Mg ha^{-1} of PG and 30 Mg ha^{-1} of manure was performed, measuring ^{226}Ra and U isotopes in drainage water, soil, and plant samples. The PG used in the treatment had $510 \pm 40 \text{ Bq kg}^{-1}$ of ^{226}Ra . The ^{226}Ra concentrations in drainage waters from PG-amended plots were similar (between 2.6 and 7.2 mBq L^{-1}) to that reported for noncontaminated waters. Although no significant effect due to PG was observed, the U concentrations in drainage waters (200 mBq L^{-1} for ^{238}U) were one order of magnitude higher than those described in noncontaminated waters. This high content in U can be ascribed to desorption processes mainly related to the natural adsorbed pool in soil (25 Bq kg^{-1} of ^{238}U). This is supported by the ^{234}U to ^{238}U isotopic ratio of 1.16 in drainage waters versus secular equilibrium in PG and P fertilizers. The progressive enrichment in ^{226}Ra concentration in soils due to PG treatment cannot be concluded from our present data. This PG treatment does not determine any significant difference in ^{226}Ra concentration in drainage waters or in plant material [cotton (*Gossypium hirsutum* L.) leaves]. No significant levels of radionuclides except ^{40}K were found in the vegetal tissues.

PHOSPHOGYPSUM (PG) is the main waste of phosphoric acid factories, which use phosphate rock as raw material. Concentrations of ^{238}U in phosphate rocks are usually high. Uranium-238 activity concentrations ranging from 700 to 1000 Bq kg^{-1} have been described in these materials (Bolívar et al., 1996a). Radium isotopes, essentially ^{226}Ra , are also present in phosphate rock, with activity concentrations ranging between 1000 and 1300 Bq kg^{-1} (Bolívar et al., 1996a). About 85% of U present in phosphate rock passes to resulting phosphoric acid, while about 90% of the ^{226}Ra remains in the PG wastes (Bolívar et al., 1996a).

The Spanish fertilizer industry produces annually 3 million Mg of PG, that are the result of the processing of 2 million Mg of phosphate rocks. This production is located in Huelva (southwestern Spain). The activity concentrations of natural radionuclides in PG are about

50 times higher than the ones in typical soils. For this reason the radioactive impact of this industry has been extensively studied in the recent years (Periañez and García-León, 1993; Martínez-Aguirre and García-León, 1994b; García-León et al., 1995; Bolívar et al., 1996b). There is a public concern about the safety of these disposals and on the need of restoring the environment where these products are accumulated.

Reclamation of sodic soils for agricultural use involves the use of Ca amendments to diminish Na saturation. Phosphogypsum, which contains a high proportion of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, is an efficient amendment that has been widely used in the saline-sodic marsh soils from southwestern Spain (Domínguez et al., 2001). Phosphogypsum also increases P availability for crops, supplies P, and reduces P sorption in soils (Delgado et al., 2002). Additionally, using PG as an amendment in agriculture soils dilutes the radionuclides until concentrations reach background levels. Thus, this practice could contribute to eliminating these wastes with a remarkable additional value for the farmers.

To prevent environmental and health risks, the commercial use of PG in agriculture is permitted in the USA if the certified average ^{226}Ra concentration does not exceed 370 Bq kg^{-1} (USEPA, 1992). However, Cancio et al. (1993) have reported concentrations of ^{226}Ra in Spanish PG ranging from 400 up to 1000 Bq kg^{-1} . It is relevant to study the amount of these isotopes that can move to water and plants to ensure the radiological safety of the use of PG as a Ca amendment. Adsorption of radionuclides to soil components (clay minerals, carbonates, iron oxides) may produce a low activity in soil solution, limiting drainage losses and absorption by crops. Studies about the environmental effect of PG application have been conducted in acid soils from Florida (Alcordero et al., 1999), but there is a lack of information about the dynamics of radionuclides applied with PG in drained marsh soils from the Mediterranean region with a high sorption capacity, but where the preferential flow to drains may represent an important loss of radionuclides to water. The aim of this work is to study the radionuclide enrichment of soil, drainage water, and crops after PG application at usual rates in the reclaimed marsh soils of southwestern Spain to study the safety of an agricultural practice that can have a positive effect on the fertility of these soils.

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Abbreviations: ICP-MS, inductively coupled plasma-mass spectrometry; PG, phosphogypsum.

MATERIALS AND METHODS

Soils and Soil Analysis

The experimental site was located in the Marismas de Lebrija, in the reclaimed marsh soils of the estuarine region of the Guadalquivir River, southwestern Spain (36°56' N, 6°7' W). Reclamation of soils involved draining (constructing till drains), leaching, and PG amendments. After reclamation, these marsh soils can be classified as Aeric Endoaquepts (Soil Survey Staff, 1998). More detailed information about the area, reclamation practices, and soils can be obtained in Moreno et al. (1981) and Domínguez et al. (2001).

Soil in the experimental site was sampled at four different depths (0–30, 30–60, 60–90, and 90–120 cm). For each depth, a composite sample was made from 32 soil cores randomly taken in the plot. Soil samples were air-dried and ground to pass a 2-mm screen. Particle size analysis was performed by using the pipette method, following treatment with a HOAc–NaOAc buffer (pH 4.75) to remove carbonates (Gee and Bauder, 1986). Organic carbon was determined by dichromate oxidation. The total calcium carbonate equivalent (CCE) was determined from the weight loss on treatment with 6 M HCl. The 1:1 extract obtained using the procedure of Rhoades (1996) was analyzed for electrolytic conductivity, pH, and cationic composition. In the 1:1 extract, Na, K, Ca, and Mg were determined, using flame photometry for K and Na, and atomic absorption spectroscopy for Mg and Ca.

Experimental Design

For the experiment, a randomized block design with two replications was used. Treatments were (i) control (no amendment applied), (ii) 13 Mg ha⁻¹ of PG, (iii) 26 Mg ha⁻¹ of PG, and (iv) 30 Mg ha⁻¹ of manure. The last one was used because manure is a common amendment in the area. Elemental plots were rectangular (250 × 20 m) and flat, longitudinally crossed by three drainage pipelines. The drainage waters were conducted, through a small canal, toward the Guadalquivir River.

Treatments were repeated at two consecutive crop seasons (1998–1999 and 1999–2000) applying the amendments in October. In the first season, sugar beet (*Beta vulgaris* L. cv. *saccharifera* Alef.) was cultivated under sprinkler irrigation (sown in October 1998 and harvested in July 1999; a typical cycle in the Mediterranean region). Irrigation water was applied at 2.5 mm h⁻¹. In this season the total rainfall was 223 mm and irrigation was 780 mm. Fertilizer was applied to all the plots at preplant (52 kg ha⁻¹ of N, 68 kg ha⁻¹ of P, and 43 kg ha⁻¹ of K as a mixture of superphosphate [160 g kg⁻¹ P], urea, and K₂SO₄) and sidedress (100 kg N ha⁻¹ as NH₄NO₃). In the second, cotton was cropped under furrow irrigation (8–10 mm h⁻¹) from March to October 2000, applying the same preplant fertilizer and 268 kg ha⁻¹ of N at sidedress as NH₄NO₃ (also to all the plots). Total rainfall was 160 mm and irrigation was 740 mm during the cotton growing season. Water movement under furrow irrigation was parallel to drains, avoiding water movement from one individual plot to other. The application of P corresponds to 450 kg ha⁻¹ yr⁻¹ of superphosphate.

Rain, irrigation, and drainage events were registered, and regular sampling of drainage water was manually done in each rain or irrigation event during the cropping season (at least four samples per event). Drainage registration allows the construction of the drainage hydrograph for the season. After sampling, drainage water was acidified with HNO₃ (to prevent adsorption onto the container walls) and stored at 4°C before radioisotope determination. We aggregated all the samples from each plot and each irrigation or rain event to get water volumes around 1 L.

The water balance during the campaigns 1998–1999 and 1999–2000 was determined. The total input of water (rain plus irrigation) was about 1000 mm. Surface runoff was negligible and most of the water disappeared by plant transpiration. The total drainage during the season was estimated integrating the drainage hydrographs during the crop season.

Radionuclide Study

The studied radionuclides included ¹³⁷Cs (fallout origin), ²²⁸Ac (natural), and ⁴⁰K (natural). These are not related to the PG inputs and thus they can be used as reference. Also, ²²⁶Ra, Th, and U isotopes (natural occurring), were studied; the concentrations of these can be enhanced by the PG treatment.

Soil was sampled selecting three points along each one of the eight plots (at the center and at 50 m toward the edges in a longitudinal section) in January 2000 to study the content of radionuclides after two amendment applications. At each point, two soil cores were collected at two different depths (0–30 and 30–60 cm; the last one only in control and 26 Mg PG ha⁻¹ plots). Samples were air-dried and ground to pass a 2-mm screen and measured by γ spectrometry. Similar measurements were performed for a nonreclaimed marsh soil (no agricultural use and no PG applied) close to the experimental site and that can be considered a soil with similar properties to the one in the experimental site before reclamation.

The uptake of radionuclides by plants is highly dependent on the isotope, the plant type, and plant organs (International Atomic Energy Agency, 1994). To compare the effects of different amendments on plant uptake, the second crop (cotton) was selected, after two applications of PG when the bioavailability was highest. Radionuclide analysis in plant materials was done by γ spectrometry only in cotton leaves. Leaf samples were taken in September 2000 from the upper part of 25 plants, washed, and dried in a forced-air oven at 65°C, and ground to pass a 1-mm screen. Additional measurements for ²³⁸U concentrations were performed by ICP–MS for two leaf samples to check its possible uptake by plants. Radionuclides were determined by γ spectrometry in PG and manure, as well as in samples of two phosphate fertilizers usually applied in the zone. For fertilizers, additional analysis was performed by ICP–MS to determine ²³⁸U and ²³²Th.

For γ spectrometry, ReGe and HPGe detectors were used to measure samples from Blocks 1 and 2, respectively. The standard geometry for measurements consisted of 50 g of soil prepared in a Petri dish. To measure the ²²⁶Ra through its 186 keV emission it is necessary to solve the interference due to the 185.7 keV emission from the ²³⁵U. In PG and fertilizer samples it was possible to find out the ²³⁵U activity through its 143.8 keV emission, but for soil samples it was under our detection limit. The ²³⁵U concentration in soil was estimated through the measured ²³⁴Th activity (using its 63.3 keV emission) assuming secular equilibrium with its parent (²³⁸U) and the known isotopic ratio ²³⁵U to ²³⁸U (Laissaoui and Abril, 1999). Alternatively the ²²⁶Ra activity can be measured through ²¹⁴Pb, one of its decay products, after achieving secular equilibrium (in encapsulated samples to prevent losses of ²²²Rn), but the first method is faster and appropriate enough for our present purposes.

Radium-226 specific activities in water samples were determined in a volume of drainage water of 0.5 L. For that, the water was neutralized with NH₄OH. Then, 5 mg of BaCl₂ was dissolved in it and about 20 mL of H₂SO₄ was added to the water. Under these conditions, RaSO₄ coprecipitates with BaSO₄ after 20 min of continuous stirring. The sample was then filtered through Millipore (Bedford, MA) filters (0.45- μ m pore size). Activity from the filter was measured using a LB 770 low back-

Table 1. General soil properties.

Depth	Texture				Organic C	CCE†	pH‡	EC‡	Composition of the 1:1 soil extract			
	Sand	Silt	Clay	Type					Na	K	Ca	Mg
cm	g kg ⁻¹				g kg ⁻¹				mmolc L ⁻¹			
0–30	60	258	685	clay	6.4	235	8.65	1.8	2.1	0.5	31	20.6
30–60	182	365	460	clay	3	360	8.2	4.6	2.9	0.7	25.9	14
60–90	122	395	485	clay	3	351	8.2	5.9	4.9	1.1	14.9	18.1
90–120	280	364	410	clay	4	340	8.4	6.9	5.3	1.2	11.6	12.3

† CCE, calcium carbonate equivalent.

‡ Determined in the 1:1 soil extract. EC, electrolytic conductivity.

ground gas flow proportional counter (Berthold Systems, Aliquippa, PA) previously calibrated for total efficiency versus precipitate mass thickness. These procedures have been widely validated and applied (Morón et al., 1986; Periañez and García-León, 1993).

The concentrations of U isotopes in water samples were determined by α spectrometry. A radiochemical method based on a sequential solvent extraction with tributylphosphate (TBP) (Bolívar et al., 1996a) was used to isolate uranium from the water samples. The method is a part of another sequential method that allows the separation of uranium, thorium, and polonium from the same sample (Holm et al., 1984). Uranium-232 was added into the water sample to evaluate the radiochemical yield of treatment. Samples were evaporated to dryness and residues were dissolved with 8 M HNO₃, and after that they were filtered. The solutions were then transferred into a decantation tube containing TBP. Samples were shaken and left for separation of phases. Polonium remains in the aqueous phase, whereas uranium and thorium are extracted by the organic phase. Thorium was recovered from the organic phase using 1.5 M HCl and xylene. Finally, uranium was back-extracted from the organic phase with distilled water. The U solutions were conditioned and electroplated (Talvitie, 1972; García-Tenorio et al., 1986).

RESULTS AND DISCUSSION

Table 1 summarizes the general soil properties. The soil was clayish and calcareous, with a relatively high content in soluble salts, especially below the 30-cm depth. Sodium saturation is also high, with exchangeable Na percentage higher than 15 in all the samples.

Drainage water for the different treatments is summarized in Table 2. It must be noted that drainage water increased strongly in the second year, due mainly to the irrigation system used in the cotton crop (furrow irrigation). The only significant effect of the amendment on drainage water was observed in the first season: drainage was significantly higher ($P < 0.05$) when manure was applied. This fact can be explained by the effect of the organic matter improving soil structure, although the effect is only evident under sprinkler irriga-

Table 2. Drainage water for the different treatments during the two crop seasons.†

Treatment	1998–1999 Season		1999–2000 Season	
	mm			
Control	25 ± 4		320 ± 60	
PG‡, 13 Mg ha ⁻¹	30 ± 14		290 ± 30	
PG, 26 Mg ha ⁻¹	29 ± 11		290 ± 120	
Manure, 30 Mg ha ⁻¹	60 ± 30		300 ± 140	

† Mean and standard deviations for the six tile drains with the same treatment.

‡ Phosphogypsum.

tion (sugar beet), probably because water loss due to preferential flow through big cracks is lower than under furrow irrigation.

Radionuclide Inputs

The PG used in the treatment had 510 ± 40 Bq Kg⁻¹ of ²²⁶Ra (Table 3). This value is in good agreement with the previous measurements reported by Bolívar et al. (1996a) and Cancio et al. (1993). Thorium-234 comes from the radioactive decay of ²³⁸U. It has a half-life of 24.1 d and different solubility than its parent. When the rate of removal by water is not significant (and always after a long storage time of the samples), it is expected to be found in secular equilibrium with its parent. The ICP-MS analysis provided more accurate determinations of ²³⁸U concentrations in fertilizers (Table 4). Other radionuclides (⁴⁰K, ¹³⁷Cs, ²²⁸Ac) were present in PG at lower concentrations than in soil samples (Tables 3 and 5). At 26 Mg PG ha⁻¹, the amendment is incorporating 13.3 MBq ha⁻¹ of ²²⁶Ra and 1.7 MBq ha⁻¹ of ²³⁸U (and half the values for the 13 Mg PG ha⁻¹ treatment).

Manure had ⁴⁰K concentrations comparable with those found in vegetal tissues (see further). Radium-226 was under our detection limits, while the ²³⁵U concentration in this sample could be related to some contamination by fertilizers.

Phosphate fertilizers had high ²³⁸U concentrations (Table 4). Superphosphate had a ²²⁶Ra concentration about two times higher than soils, while ammonium phosphate had a significant ²³²Th concentration (natural occurring radionuclide) but nondetectable ²²⁶Ra concentrations. The application of 450 kg ha⁻¹ yr⁻¹ of superphosphate fertilizer (a usual P fertilizer rate in the zone for intensive agricultural crops; Delgado et al., 2002) represents the incorporation of 0.27 MBq ha⁻¹ of ²³⁸U.

Radionuclides in Soils

Cesium-137 is a man-made radionuclide present in the environment after the atmospheric nuclear weapon tests with a maximum fallout rate in the early 1960s. In accordance with its origin, this isotope did not appear in the deeper layers of the nonreclaimed marsh soil (Table 5). In the surface horizons of experimental plots, ¹³⁷Cs concentrations were lower than in the surface horizon of nonreclaimed marsh soil, probably due to cultural practices (soil removal and leaching losses due to irrigation). Concentration values were similar to those found by Bolívar et al. (1996b) in other agricultural areas of southwestern Spain.

Table 3. Radionuclide concentrations in phosphogypsum (PG), manure, and P fertilizers, determined by γ spectrometry.†

Sample	$^{226}\text{Ra}\ddagger$	^{40}K	^{137}Cs	^{234}Th	^{228}Ac	^{235}U
	Bq kg ⁻¹					
Superphosphate	130 ± 85	31 ± 10	ND§	760 ± 180	16.3 ± 1.7	55 ± 5
Ammonium phosphate	ND	51 ± 10	ND	660 ± 150	ND	34 ± 3
PG	510 ± 40	21 ± 10	ND	65 ± 19	4.7 ± 1.8	15 ± 2
Manure	ND	840 ± 30	ND	ND	9 ± 2	8 ± 3

† Measurement and analytical error (1 standard deviation).

‡ Corrected through ^{235}U activity concentration.

§ Not detected.

Actinium-228 is a naturally occurring radionuclide from the decay series of ^{232}Th . It was present at lower concentrations in PG and phosphate fertilizers than in soils (Tables 3 and 5). Thus, no effect of PG amendment on ^{228}Ac concentration in soil can be expected. Also, the natural occurrence of this radionuclide explains the similar concentrations in surface and subsurface horizons (Table 5).

Potassium-40 concentrations in surface samples, with an average value of 760 Bq kg⁻¹ (30-cm depth), were significantly higher than those described by Bolívar et al. (1996b) in other surface horizons of other soils from southwestern Spain (ranging 150–560 Bq kg⁻¹), but comparable with those observed in subsurface horizons by these authors. Concentrations did not show a clear pattern with depth. Mean concentrations in the experimental plots were significantly higher (about 20%) than in the nonreclaimed marsh soils (Table 5). This can be ascribed to the application of potassium fertilizers and to the irrigation with saline water in drought periods.

Due to its low energy, the net area of the 63.3 keV ^{234}Th photo peak cannot be accurately solved with the HPGe detector, but it is possible with the ReGe. As the soil samples have been measured several months after collection, ^{234}Th is in secular equilibrium with ^{238}U . From Table 5, the soils without PG have a mean ^{234}Th (= ^{238}U) concentration lower than soils with PG (30 cm), but experimental uncertainties are large and the samples measured with the HPGe detector cannot be used for comparison.

Radium-226 raw data in soils (without correction by the ^{235}U interference) were similar for all the treatments, although analyzed subsurface samples and samples taken in the nonreclaimed soil showed significantly lower concentrations. The correction of ^{235}U interference was evaluated only for the ReGe data (samples from Block 1). This correction represented a mean decrease of 20 Bq kg⁻¹ in ^{226}Ra activity concentrations. No significant differences can be established from these corrected data (Table 5). Under the assumption that PG was well homogenized through tilling in the surface horizon of soils (30-cm depth), with a mean bulk density of 1.3 Mg m⁻³ (Delgado et al., 2002), the background ^{226}Ra concentration in soils should be increased about by 3.4 Bq kg⁻¹. This value is less than our present experimental uncertainties (the same is true for the ^{238}U input related to the PG, with a net input of 0.4 Bq kg⁻¹ of soil).

Radionuclides in Drainage Waters

The activity concentrations of U isotopes in drainage waters were similar for all the treatments (Table 6),

and remained constant during the subsequent irrigation events. Thus, from our data one can reject the hypothesis of an enhancement of U isotope concentrations in the drainage waters due to the treatment with PG. However, these concentrations were one order of magnitude higher than those reported from uncontaminated waters, where the typical levels were lower than 25 mBq L⁻¹ (García-León et al., 1995).

The main chemical form of Ra in PG is RaSO₄·2H₂O, which presents a poorly soluble form. On the other hand, PG tends to form large aggregates with a low surface area. That would inhibit the removal of ^{226}Ra by the drainage. Indeed, the activity concentrations of ^{226}Ra found in these waters (Table 7) were similar for all the treatments and comparable with those obtained by García-León et al. (1995), who reported reference levels below 3 mBq L⁻¹ of ^{226}Ra for natural unpolluted environments. Nevertheless, Martínez-Aguirre and García-León (1994a) measured concentrations ranging from 2.4 to 13.7 mBq L⁻¹ in the Guadalquivir River, and they increased up to 31 mBq L⁻¹ in its estuary. Consequently, from the present data one cannot conclude a short-term enhancement of ^{226}Ra concentrations in drainage waters due to the application of PG.

Table 8 summarizes the annual fluxes of U isotopes and ^{226}Ra related to the drainage waters (estimated from the mean radionuclide concentrations, from Tables 6 and 7, and the annual drainage, from Table 2). Radium-226 fluxes were similar for all the treatments, since activity concentrations and cumulative drainage volumes (1999–2000 season) were similar for all of them. The major fluxes of U isotopes were related to manure treatment, since this treatment improved the soil aggregation and enhanced drainage under sprinkler irrigation (1998–1999 season) without significantly increasing U concentrations. On the other hand, the ^{226}Ra output throughout the drainage waters was negligible compared with the annual inputs related to the PG application, but ^{238}U

Table 4. Uranium-238 and ^{232}Th activity concentration in P fertilizers and cotton leaves measured by inductively coupled plasma-mass spectrometry (ICP-MS).†

Sample	^{238}U	^{232}Th
	Bq kg ⁻¹	
Superphosphate	590	846
Ammonium phosphate	496	9.0
Leaves (control)	<0.24	ND‡
Leaves (PG§, 26 Mg ha ⁻¹)	<0.24	ND

† Integration time = 0.3 s channel⁻¹ (0.9 s amu⁻¹). Detection limit = 0.02 ppm. Three measurements were made for each sample, with 2% of relative standard deviation.

‡ Not detected.

§ Phosphogypsum.

Table 5. Radionuclide concentration in soils after two consecutive treatments (two consecutive seasons, 1998 and 1999) and in nonreclaimed marsh soil at different depths determined by gamma spectrometry.†

Treatment	Depth	Radionuclide					
		²²⁶ Ra‡	⁴⁰ K	¹³⁷ Cs	²²⁸ Ac	²³⁴ Th§	²²⁶ Ra§,¶
		Bq kg ⁻¹					
cm							
Control	0–30	76 ± 1	740 ± 20	2.9 ± 1	36 ± 2.5	18	64
Control	30–60	59 ± 4	680 ± 60	1.5 ± 0.2	35 ± 4.5	22	38
Manure	0–30	72 ± 3	740 ± 30	3.4 ± 0.8	34 ± 1	21	59
PG#, 13 Mg ha ⁻¹	0–30	89 ± 2	795 ± 5	2.9 ± 0.5	39 ± 1.5	34	65
PG, 26 Mg ha ⁻¹	0–30	76 ± 4	780 ± 10	3.3 ± 0.4	37 ± 2.5	37	56
PG, 26 Mg ha ⁻¹	30–60	72 ± 0	745 ± 5	2.6 ± 0.1	34 ± 0.5	28	51
Nonreclaimed§	0–30	62	635	11.1	34	17	50
Nonreclaimed§	30–60	42	620	ND††	32	–	–
Analytical error‡‡		<9	<20	<0.4	<2	<10	<11

† Means and standard deviations.

‡ Raw data (without correction by ²³⁸U interference).

§ Measurement and analytical error (1 standard deviation); ²³⁴Th and ²²⁶Ra for Block 1 (ReGe detector).

¶ Corrected by ²³⁵U interference.

Phosphogypsum.

†† Not detected.

‡‡ One standard deviation.

output is about 20% of the annual input related to the phosphate fertilizers. Nevertheless, this input represents less than 0.4% of the estimated ²³⁸U inventory in the top 30 cm of soil (78 MBq ha⁻¹), while the input related to PG is about 2% of this inventory. The higher proportion of applied ²³⁸U that is lost compared with ²²⁶Ra can be explained by the nature of compounds added to (or formed in) soil. Radium-226 is applied as poorly soluble compounds, meanwhile ²³⁸U desorption from sorbent surfaces can be enhanced by carbonates in soil (Bostick et al., 2002). The different behavior of ²²⁶Ra and U isotopes is also apparent from their soil to water concentration ratios, with a mean value of 9300 L kg⁻¹ for ²²⁶Ra and 140 L kg⁻¹ for ²³⁸U.

The isotopic ratio ²³⁴U to ²³⁸U can support a further discussion, since it can be used as a fingerprint. Following Bolívar et al. (1996a), the isotopic ratio in phosphate rock is close to unity (secular equilibrium): 1.04 ± 0.02. The same result was found by these authors in the phosphoric acid and in the phosphogypsum: 1.03 ± 0.03 and 1.04 ± 0.05, respectively. Moreover, García-Tenorio and Bolívar (1994) found an isotopic ratio of 0.98 ± 0.04 in different phosphate fertilizers. In our drainage waters (Table 5) the isotopic ratio is 1.16 ± 0.04 (by excluding

one anomalous result), which is significantly higher than the one associated with both inputs (PG and P fertilizer). This is usually due to the in situ decay of ²³⁸U ($t_{1/2} = 4.6 \times 10^9$ yr) to ²³⁴Th ($t_{1/2} = 24.1$ d) to ²³⁴Pa ($t_{1/2} = 1.18$ m) and then to ²³⁴U ($t_{1/2} = 2.48 \times 10^5$ yr). Following radioactive decay, the recoiled atom can go through many lattice points and enter lattice defects, pores, and fractures and is more readily leached (Chu and Wang, 2000). The preferential leaching of ²³⁴U caused by recoil effects is displayed by a ²³⁴U to ²³⁸U ratio less than 1 in soil particles and greater than 1 in filtered waters (Osmond and Cowart, 1976). Due to the varied half-lives, this process cannot operate in the short term. Consequently, although the superphosphate can contribute in some extent to the U isotopes found in the drainage waters, the major contribution may come from the pool in the soil to explain the enrichment in the isotopic ratio.

Dose Assessment

To estimate the radiological impact of the current agriculture practices, we have to note that from our data no significant levels of radionuclides were found in the vegetal tissues. Potassium-40 is the only radionuclide

Table 6. Uranium isotopes concentrations and isotopic ratios in drainage waters from different treatments and dates, determined by alpha spectrometry.†

Treatment	Date	²³⁸ U	²³⁵ U	²³⁴ U	²³⁴ U/ ²³⁸ U	
		mBq L ⁻¹				
Control	12 Dec. 1998	188 ± 5	7.3 ± 0.6	217 ± 6	1.15 ± 0.04	
	22 Jan. 1999	164 ± 5	5.7 ± 0.6	198 ± 6	1.21 ± 0.05	
	25 Jan. 1999	180 ± 9	7.0 ± 1.1	201 ± 10	1.12 ± 0.08	
	mean‡	177 ± 12	6.7 ± 0.9	205 ± 10	1.16 ± 0.10	
Manure, 30 Mg ha ⁻¹	22 Jan. 1999	200 ± 7	6.9 ± 0.8	229 ± 8	1.15 ± 0.06	
	PG§, 13 Mg ha ⁻¹	12 Dec. 1998	196 ± 10	8.5 ± 1.2	148 ± 11	0.76 ± 0.07
		22 Jan. 1999	174 ± 5	7.0 ± 0.6	198 ± 5	1.14 ± 0.04
PG, 26 Mg ha ⁻¹	23 Jan. 1999	207 ± 8	9.6 ± 1.2	256 ± 10	1.24 ± 0.07	
	mean‡	192 ± 17	8.4 ± 1.3	201 ± 54	1.04 ± 0.30	
	12 Dec. 1998	175 ± 5	7.2 ± 0.5	206 ± 5	1.18 ± 0.04	
	22 Jan. 1999	170 ± 6	7.6 ± 0.7	198 ± 6	1.16 ± 0.05	
	24 Jan. 1999	166 ± 7	5.2 ± 0.7	192 ± 7	1.16 ± 0.06	
	25 Jan. 1999	204 ± 9	7.6 ± 1.0	224 ± 10	1.10 ± 0.07	
	mean‡	179 ± 17	6.9 ± 1.1	205 ± 14	1.15 ± 0.14	

† Measurement and analytical error (1 standard error). Samples are accumulated water volumes from the six tile drains with the same treatment.

‡ Mean and standard deviations for the different dates.

§ Phosphogypsum.

Table 7. Radium-226 activity concentrations measured by alpha counting in samples of drainage waters from different treatment and dates.†

Month (year 2000)	Control	Manure	mBq L ⁻¹	
			PG‡, 13 Mg ha ⁻¹	PG, 26 Mg ha ⁻¹
March	7.0 ± 0.7	6.6 ± 0.7	5.4 ± 0.4	6.2 ± 0.7
April	6.4 ± 0.8	6.2 ± 0.9	6.4 ± 1.0	7.3 ± 1.1
May	6.9 ± 0.6	4.7 ± 0.5	6.0 ± 0.4	7.2 ± 0.6
June	6.1 ± 1.0	6.3 ± 0.7	5.1 ± 0.4	6.2 ± 0.8
July	7.3 ± 0.4	6.1 ± 1.0	5.0 ± 0.7	6.2 ± 0.7
August	7.2 ± 1.0	6.7 ± 0.5	5.6 ± 0.5	4.4 ± 0.3
September	5.8 ± 0.5	6.1 ± 1.0	2.6 ± 0.3	3.8 ± 0.3
Mean§	6.7 ± 0.6	6.1 ± 0.7	5.2 ± 1.2	5.9 ± 1.3

† Measurement and analytical error (1 standard deviation), samples are accumulated water volumes from the six tile drains with the same treatment and for all the drainage episodes during the month.

‡ Phosphogypsum.

§ Mean and standard deviations.

detected by γ spectrometry in the vegetal tissues (Table 9). Uranium-238 and ²³²Th, determined by ICP-MS analysis, were also under the detection limits (Table 4). These results are from cotton, and although they can be representative of other crops, a more extensive study is needed.

The cumulative application of PG may increase the ²²⁶Ra concentration in soils and thus the ²²²Rn exhalation, although this has not been studied within the present work. The red American crab (*Cancer magister*) has prospered in this environment, although more frequently it inhabits rice (*Oryza sativa* L.) fields, where no reclamation practices (including PG amendments) are done. In a very conservative dose assessment, we can consider the consumption of crabs as a critical pathway, with consumption rate, Q , of 20 kg yr⁻¹ (four times the averaged consumption of molluscs and crustaceans in southwestern Spain). The received dose, E (given in Sv yr⁻¹) will be:

$$E = QCD_F$$

where C is the concentration (Bq kg⁻¹) in crabs estimated from the mean concentration in water (Tables 6 and 7) and the recommended concentration factors for molluscs ($F_c = 3.0 \times 10^{-2} \text{ m}^3 \text{ kg}^{-1}$ for ²³⁸U and $F_c = 1.0 \text{ m}^3 \text{ kg}^{-1}$ for ²²⁶Ra; National Radiation Protection Board, 1987). The term D_F is a factor to convert to doses the internal irradiation by ingestion ($D_F = 6.3 \times 10^{-8} \text{ Sv Bq}^{-1}$ for ²³⁸U and $D_F = 3.0 \times 10^{-7} \text{ Sv Bq}^{-1}$ for ²²⁶Ra). Thus, $E = 5.1 \times 10^{-6} \text{ Sv}$ (including the doses from ²³⁴U with the same F_c and D_F values than ²³⁸U), which clearly is under the recommended limit.

Table 8. Estimated annual fluxes of radionuclides related to the drainage waters.†

Radionuclide	Control	Manure	kBq yr ⁻¹ ha ⁻¹	
			PG‡, 13 Mg ha ⁻¹	PG, 26 Mg ha ⁻¹
²³⁸ U	44 ± 8	110 ± 50	60 ± 30	52 ± 20
²³⁵ U	1.7 ± 0.3	3.9 ± 1.8	2.5 ± 1.2	2.0 ± 0.8
²³⁴ U	51 ± 8	130 ± 60	60 ± 30	60 ± 20
²²⁶ Ra†	22 ± 4	18 ± 9	15 ± 4	17 ± 8

† Estimated from mean radionuclide concentrations (see Tables 6 and 7) and drainage (Table 2, 1998–1999 season for U isotopes and 1999–2000 season for ²²⁶Ra).

‡ Phosphogypsum.

Table 9. Potassium-40 concentrations in cotton leaves with different treatments determined by gamma spectrometry.†

Treatment	⁴⁰ K
	Bq kg ⁻¹
Control	422 ± 42
Manure	483 ± 53
PG‡, 13 Mg ha ⁻¹	450 ± 4
PG, 26 Mg ha ⁻¹	431 ± 10
Analytical error§	<20

† Means and standard deviation; two samples per treatment.

‡ Phosphogypsum.

§ One standard deviation.

CONCLUSIONS

The application of PG as soil amendment does not determine any significant increment in radionuclide concentration in soils after two consecutive treatments at the usual rates in the region. For most of the studied isotopes, there is not any significant difference between reclaimed (PG amended during 30 yr) and nonreclaimed (non-PG amended) soils. No significant increment in U isotopes and ²²⁶Ra was detected in drainage waters due to treatments. The U isotope concentrations in the drainage waters are one order of magnitude higher than those found in noncontaminated waters. These concentrations seem to be related to desorption processes mainly related to the natural adsorbed pool present in the soil, as it is suggested by the ²³⁴U to ²³⁸U isotopic ratio (1.16 in drainage waters versus secular equilibrium in PG and P fertilizers). Concentrations of the studied radionuclides in cotton leaves were below the detection limits in all the cases, except for ⁴⁰K. The uptake of this isotope by plants is mainly related to the natural pool of soils, since the amount applied by amendments and fertilizers is negligible.

ACKNOWLEDGMENTS

This work was funded by ENRESA (Spanish Public Corporation of Radiactive Residues) and by the Spain's National R + D Plan (Projects AGF97-1102-CO2-01 and AGL2000-0303-P4-0). Authors wish to thank Cooperativa la Amistad for making available some facilities and the experimental site.

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