Radiological assessment of the agriculture use of phosphogypsum in SW Spain: results of a three-year field experiment[1]

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Abstract. Phosphogypsum (PG) is a NORM material generated as a by-product of the phosphate fertilizer industries. Some 3000 t of PG are generated annually in SW Spain. Since the 1970s, PG has been used as a Ca amendment for sodic soils in the Guadalquivir River area. Agriculture use of PG has been explicitly allowed in recent Spanish regulations. Nevertheless, attention should be paid in order to ensure radiological safety and acceptable levels of heavy metals (e.g. Cd) in agriculture products. A three-year field experiment has been conducted in a 6 ha farm in the area of Marismas de Lebrija. The farm has been divided into 12 elemental plots of 0.5 ha each (20 m × 250 m).Two treatments (control and 25 t/ha PG repeated every two years) have been applied in triplicate. Tile drains are placed at 1 m below the soil horizon, longitudinally distributed and spaced every 5 m. The following potential effects of PG have been studied: ^{222}Rn exhalation in soils, ^{226}Ra and U-isotopes losses in drainage waters, ^{226}Ra in aerosols following PG application, ^{226}Ra, U-isotopes and ^{210}Po activity profiles in soil, and soil to plant transfer of radionuclides. ^{222}Rn exhalation (measured by the charcoal canister method) showed averaged values of 30 ± 5 Bq h^{-1} m^{-2}, with slightly higher means and dispersions for PG plots. No significant differences between treatments could be found in ^{226}Ra and ^{238}U concentrations in drainage waters, with typical concentrations around 5 and 200 mBq/L for Ra and U, respectively. ^{226}Ra activities found in aerosols resulted in negligible doses for exposed workers. Radionuclide profiles in soils showed a relative enrichment of concentrations in the surface horizon (0–30 cm) for ^{226}Ra, U-isotopes and ^{210}Po in the plots treated with PG. Finally, preliminary studies on soil to plant transfer showed ^{226}Ra and ^{238}U concentrations under MDL in tomatoes produced in the zone.

1. Introduction

FERTIBERIA, a fertilizer factory located in Huelva (SW Spain) owns a non-active PG stack lying in the right bank of the Tinto River. From this PG stack, of about 1 km^2 and 8–10 m deep, PG could be extracted for agriculture uses.

PG has being traditionally used since the late 1970s as a Ca amendment for the reclaimed soils from the salt-marsh area of the Guadalquivir River. Recent Spanish regulations (R.D. 824/2005, from July 2005) explicitly allow the use of PG as soil amendment. European regulations (CE 466/2001) establish upper limits for concentrations of some heavy metals (Hg, Cd and Pb) in food. The USEPA has specific regulation for the agriculture use of PG (64 FR 5574), allowing it if ^{226}Ra concentration is below 370 Bq/kg. Consequently, attention should be paid in order to ensure radiological safety and acceptable levels of heavy metals (e.g. Cd) in agriculture products.

The main goal of this work is the radiological and alimentary assessment of the agriculture use of phosphogypsum (PG), a by-product of the fertilizer industry, as a Ca amendment in reclaimed salt-marsh soils in SW Spain. The work-plan included: PG characterization (concentrations of radionuclide and heavy metals), experimental field studies attending to the effect of PG in agriculture soils and drainage waters, and the soil-to-plant transfer of radionuclides and heavy metals.

2. Materials and methods.

The experimental site is located in Marismas de Lebrija (see Fig. 1) where marsh soils were reclaimed from the estuarine region of the Guadalquivir river, southwest Spain (36°56'N, 6°7'W). A tile drain system was installed in 1977. After reclamation, these marsh soils were classified as Aeric

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Endoaquepts. In the 6 ha experimental farm, six rectangular (250 m x 20 m) plots were established. These plots were crossed lengthwise with ceramic drainage lines 250 m long and spaced 5 m apart. These tiles were placed at a depth of 1 m. The experimental design consists in two treatments: PG (25 t/ha) and control, with three replicates each, randomized distributed. PG was first applied in March 2003 and repeated in September 2004. With actual practices, PG is applied over a previously tilled soil; with additional deep-tillage immediately alter PG application.

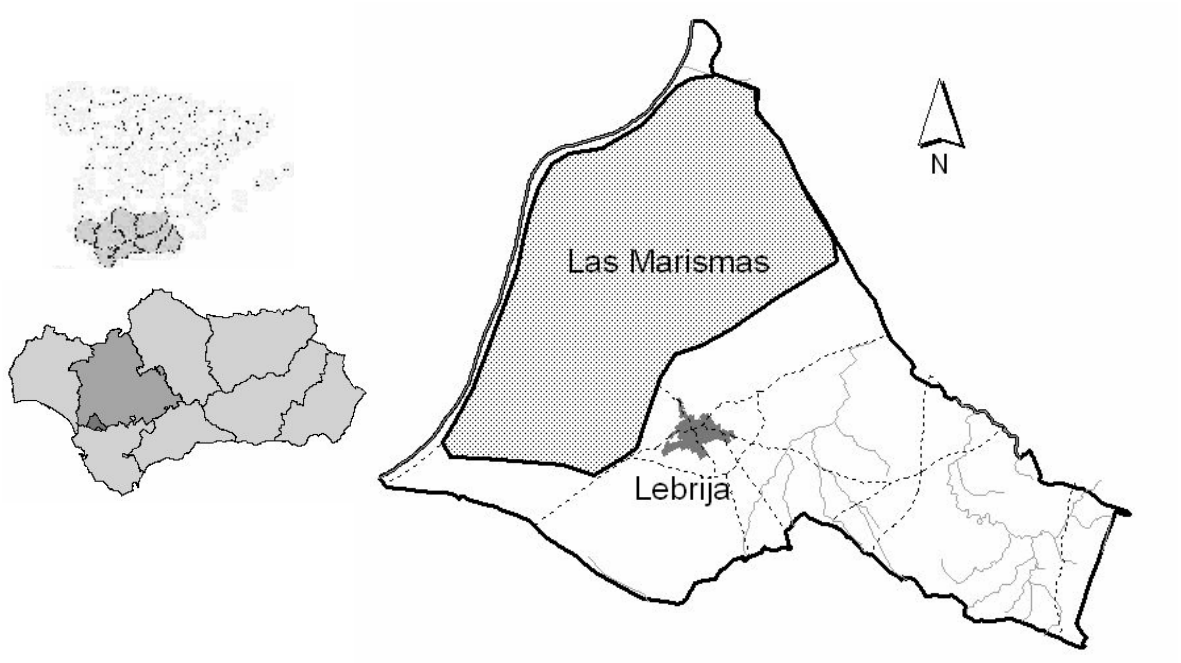

FIG. 1. Location of "Las Marismas de Lebrija" in SW Spain

^{222}Rn exhalation was measured, using a total of 78 charcoal canisters, sampled in four campaigns (September and October 2004, February 2005 and February 2006), with 3 canisters per sampling point (at the centre of each control and PG-amended plots), and some additional quality controls.

Studies on ^{222}Rn exhalation from PG stacks and PG characterization for radionuclides and heavy metals content are presented in a separated work [1]. ^{226}Ra was measured by liquid scintillation, providing activity concentrations of 720 ± 260 Bq/kg. ^{210}Po and ^{238}U activity concentrations (measured by alpha spectrometry) resulted in 660 ± 160 Bq/kg and 170 ± 110 Bq/kg, respectively. Cd concentrations (measured by ICP-MS) were 2.0 μg/g. For the rest of the elements considered in the USEPA 200.8 method, concentrations were not much higher than the corresponding ones for soils (H_g was not measured).

Soil in the experimental site was sampled at three different depths (from 0 to 30, 30 to 60, and 60 to 90 cm) with three sampling points for each plot. Sampling campaigns were carried out in March 2003, September and October 2004 and January 2006.

Soil samples have been characterized for several agronomical parameters: humidity, pH, EC, cations (Na, Ca, Mg, K), P-Olsen, RAS and different forms of N. Radionuclides were measured in soil samples by gamma (^{226}Ra, ^{40}K, ^{228}Ac) and alpha spectrometry (U isotopes and ^{210}Po). Multielemental analyses of soils have been carried out by ICP-MS following EPA method 200.8 and after pseudo-total acid digestion.

Instantaneous fluxes of drainage waters were monitored using a simply designed recording meter based on the ultrasonic measurement of water levels in a slotted U pipe [2]. Samples of drainage water were collected following irrigation episodes in 2003 (furrow-irrigated cotton crop), 2004 (sprinkled irrigated sugar beet crop) and 2005 (furrow-irrigated cotton crop). Na and Ca concentrations were

measured in these drainage waters (by AA). Multi-elemental analyses of dissolved metals have been carried out by ICP-MS following EPA 200.8 method. Composite water samples from 2005 were analyzed for ^{226}Ra content.

Industrial tomatoes and surface soils were sampled from several farms in the area of Marismas de Lebrija for analyses (radionuclides and heavy metals). Additional tomato samples were taken from a market survey attending to different origin of production in Spain.

Soil to plant transfer experiments have been conducted at greenhouse level using soils from the control plots and PG from the FERTIBERIA stack, and growing industrial tomatoes, reported elsewhere [3].

3. Results and discussion.

3.1. ^{222}Rn exhalation

Results are summarized in Table 1. ^{222}Rn exhalation showed high spatial and temporal variability, with averaged values higher for the PG-amended plots (34 Bq h^{-1} m^{-2} versus 24 Bq h^{-1} m^{-2} for the control plots) but differences are not statistically significant due to the high dispersion. In all the cases ^{222}Rn exhalation decreased after deep-tillage (applied at the end of September 2004). The highest exhalation rate, found in September 2004, was 55 ± 19 Bq h^{-1} m^{-2} (PG plots). In all the cases, they are within the range of reference values for typical agriculture soils (40 to 200 Bq h^{-1} m^{-2} [4]).

TABLE 1. Rn-222 EXHALATION FOR CONTROL AND PG AMENDED PLOTS

Measurement campaign	^{222}Rn exhalation (Bq h^{-1} m^{-2}) [a]	
	Control plots	PG- amended plots
September 2004	39 ± 13	55 ± 19
October 2004	23 ± 7	30 ± 7
February 2005	13 ± 7	28 ± 29
February 2006	21 ± 8	26 ± 8

[a] Mean and standard deviation of 9 canisters (3 canister per sampling point at the centre of each plot, with 3 plots per treatment).

3.2. Soil analysis.

3.2.1. Agronomical parameters

Humidity increased with depth from 13–15% in the 0–30 cm horizon up to 20–28% in the 60–90 cm depth interval. The pH was quite uniform, with a mean value of 8.4. The EC increased with depth due to the saline water-table. Na and Mg strongly increased with depth, while K concentrations did not show any significant variation. In PG-amended plots, the Ca concentration increased in the 0–30 cm soil horizon. Differences in P-Olsen and RAS among control and PG-amended plots were not statistically significant

3.2.2. Radionuclide and Cd concentrations

Results are summarized in Table 2 for soils sampled in January 2006. The short-term effect of two consecutive PG applications (04-2003 and 09-2004) cannot be statistically solved (p_1) from the concentrations in surface soils (0–30 cm) for control versus PG plots. Nevertheless, activity concentrations for the elements from the ^{238}U series are quite far away from the situation of secular equilibrium, and the upper soil horizon (0–30 cm) is enriched in these radionuclides with respect to deeper layers. Both results are congruent with the cumulative effect of the historical applications of PG carried out in the area. It has to be taken into account that radionuclides from the ^{238}U series are in secular equilibrium in the phosphate ore rock, but 90% of ^{226}Ra remain in PG, while about 85% of the ^{238}U is separated with the phosphoric acid [5]. Thus, in 2006 ^{226}Ra and ^{210}Po activity concentrations in soils (0–30 cm) were around 38 and Bq/kg, respectively, versus 13 Bq/kg for ^{238}U. The corresponding

activity concentrations at the sub-surface level (30–90 cm) were 26, 23 and 10 Bq/kg for ^{226}Ra, ^{210}Po and ^{238}U, respectively. The whole set of data agrees with autochthonous activity concentrations around 8–10 Bq/kg for ^{238}U and its daughters, over which superposes the cumulative effect of historical PG applications equivalent to 13–15 usual doses of 20 t/ha. The input of radionuclides associated to PG is primarily associated with the 0–30 cm soil horizon, from where they subsequently progress to deeper layers, remaining nowadays in the arable layer (0–30 cm) about 50% of the total historical input.

TABLE 2. ACTIVITY CONENTRATIONS AND Cd CONTENT IN JANUARY 2006 SOIL SAMPLES

Sample	Activity concentration (Bq/kg)					
	^{226}Ra (γ,^{214}Bi)	^{210}Po (α)	^{228}Th (γ, ^{228}Ac)	^{238}U (α)	^{40}K (γ)	Cd content (μg/g)
C1 (0–30 cm)	37.6 ± 1.3	22.9 ± 0.6	30 ± 2	13.1 ± 0.3	590 ± 12	0.19 ± 0.02
C2 (0–30 cm)	34.5 ± 0.6	24.8 ± 0.7	29.9 ± 1.0	11.5 ± 0.3	630 ± 13	0.21 ± 0.02
C2 (30–60 cm)	28.7 ± 0.7	17.7 ± 0.5	35.8 ± 1.1	8.5 ± 0.2	680±15	0.13 ± 0.01
C2 (60–90 cm)	22.8 ± 0.8	32.8 ± 0.8	33.9 ± 1.3	9.1 ± 0.3	622 ± 8	0.09 ± 0.01
C3 (0–30 cm)	36.1 ± 0.9	36.1 ± 0.9	29.9 ± 1.1	11.5 ± 0.3	640 ± 8	0.21± 0.02
PG1 (0–30 cm)	33.9 ± 1.0	36.1 ± 0.9	30.7 ± 0.7	14.8 ± 0.3	607 ± 9	0.20 ± 0.02
PG2 (0–30 cm)	41.7 ± 0.9	32.9 ± 0.9	31.6 ± 1.3	13.2 ± 0.4	648 ± 7	0.14 ± 0.01
PG2 (30–60 cm)	29.1 ± 0.9	22.8 ± 1.4	33.5 ± 1.2	10.9 ± 0.3	670 ± 8	0.09 ± 0.01
PG2 (60–90 cm)	24.0 ± 0.9	16.8 ± 0.4	36.8 ± 1.4	9.9 ± 0.2	663 ± 7	0.07 ± 0.01
PG3 (0–30 cm)	41.7 ± 0.9	24.1 ± 0.6	36.2 ± 1.0	13.2 ± 0.3	681 ± 7	0.22± 0.02

Note: ^{226}Ra measured by γ spectrometry through the 609.4 keV γ-emission from ^{214}Bi, assuming secular equilibrium in sealed samples after one month of storage. (α) denotes measurements by α-spectroscopy. Cd measured by ICP-MS. Measurements carried out by the Central Research Facilities of the University of Seville (CITIUS) and reported with 1σ analytical uncertainties.

Although the cumulative effect of PG can be recognized in these agricultural soils, actual levels of activity concentrations are within the range of environmental reference values for the ^{238}U series (up to 70 Bq/kg with most frequent values ranging from 20 to 40 Bq/kg).

Results for Cd are in good agreement with the above mentioned situation for ^{238}U and its daughters. Thus, the concentration in the arable layer (0–30 cm) was 0.2 μg/g, twice the value for deeper layers. Although Cd is also present in the phosphate fertilizer, total inputs associated with PG amendments are one order of magnitude higher. The rest of elements included in EPA 200.8 method (results not shown here) have concentrations with a practically uniform distribution in depth, except for Sr and Ni with decreasing and increasing concentrations with depth, respectively.

In terms of legal reference levels for some hazardous metals for considering an agricultural soil to be polluted [6], actual measured levels for Pb, Zn, Cu, Cd, Tl and Co are one order of magnitude below such limits. Measured concentrations for As, Cr and Ni were 5 times lower than the respective limit concentrations and only the concentrations for V were a factor 2 below such a limit. Attending to the most restrictive concept of PNEC (predicted non-effect concentration) for Cd in soil (1 ppm), actual levels are still a factor 5 below this limit

3.3. Drainage waters.

Measurements of Na and Ca concentrations in irrigation and drainage waters (by AA) along with the corresponding hidrograma, allowed the estimation of net losses. Thus, net Na losses for a furrow-irrigated cotton crop during the whole irrigation period in 2005 were 400 ± 50 kg/ha and 500 ± 200 kg/ha for the control and PG-amended plots, respectively.

Cd was below the MDL (0.2–0.4 ppb) in most of the cases, with maximum measured concentrations below 2 ppb. For the rest of the elements included in method EPA 200.8 for which concentrations

were over their respective MDL, concentrations were generally within the EPA standards for drinking water. Concentrations generally decreased with increasing drainage flows (note that the total volume of drainage decreased along the irrigation season as a consequence of the progressive closure of big cracks, governing the preferential flow).

The dispersion of data did not enable any statistically significant difference to be distinguished between treatments (PG and control) in drainage waters for years 2003 and 2004. In 2005 (after two PG amendments), concentrations in drainage waters for Fe, Co, Ni, Sr and U (this last shown in Fig. 2) were significantly higher in the PG-amended plots in most of the irrigation episodes. Finally, the measurement of ^{226}Ra concentration in drainage waters (sampling campaign of 2005, shown in Fig. 2) revealed non-significant differences between treatments (PG and control) and averaged values around 4 mBq/L, the same level as in unperturbed natural aquatic ecosystems. Water applied for irrigation was analysed by ICP-MS (5 independent samples). Cd was under MDL in all the cases, while ^{238}U concentration was 1.51 ± 0.09 ppb.

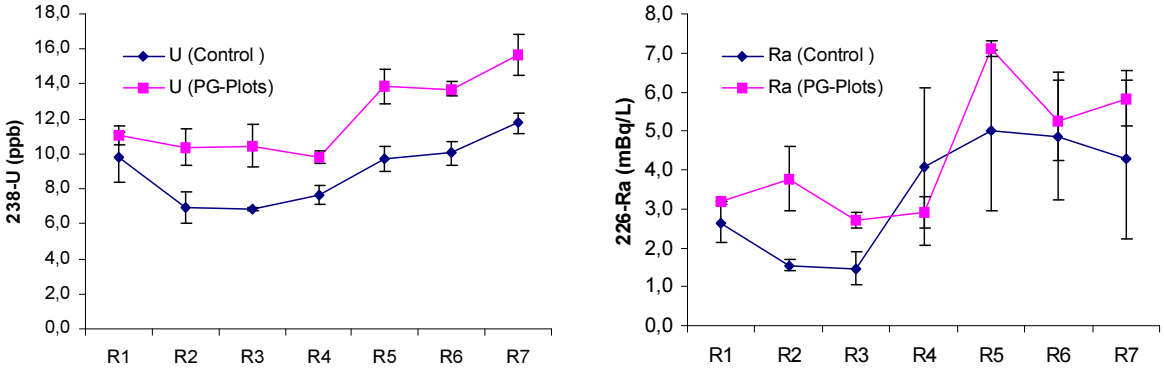

FIG. 2. ^{238}U and ^{226}Ra concentrations in composite samples of drainage waters for the seven irrigation episodes corresponding to the summer of 2005 (furrow-irrigated cotton crop). Results show averaged concentrations for each treatment (3 replicates) with the corresponding standard deviations.

3.4. ^{226}Ra in aerosols following PG application

During the application of PG (in March 2003), aerosol samples were taken at different points in the farm and analysed for ^{226}Ra. Results showed activity concentrations of up to 3.80×10^{-4} Bq/m^3. Doses by inhalation/ingestion of aerosols were estimated for a worker spending 8 h per working day and 100 working days per year under these conditions. The resulting maximum doses were 11×10^{-5} mSv/a, a negligible contribution to the allowed limit of 1 mSv/a.

3.5. Soil to plant transfer.

Industrial tomatoes were sampled from several farms in the area for analyses. ^{238}U concentrations were below the MDL in all the cases. Cd concentrations ranged from 6 to 14 ppb (on a fresh weight basis). These concentrations were similar to those found in the plant-plot experiments [3] and were below the threshold limit of 50 ppb. Cd concentrations in fruit were positively correlated with ^{226}Ra concentrations in soil (and thus, with the accumulated application of PG), as shown in Fig. 3.

Additional tomato samples were taken from a market survey attending to different origin of production in Spain. Cd concentrations in tomatoes from the market were in the range 0.014 to 0.058 ppm (dry weight), one order of magnitude lower than the industrial tomatoes from Lebrija. ^{238}U was below the MDL.

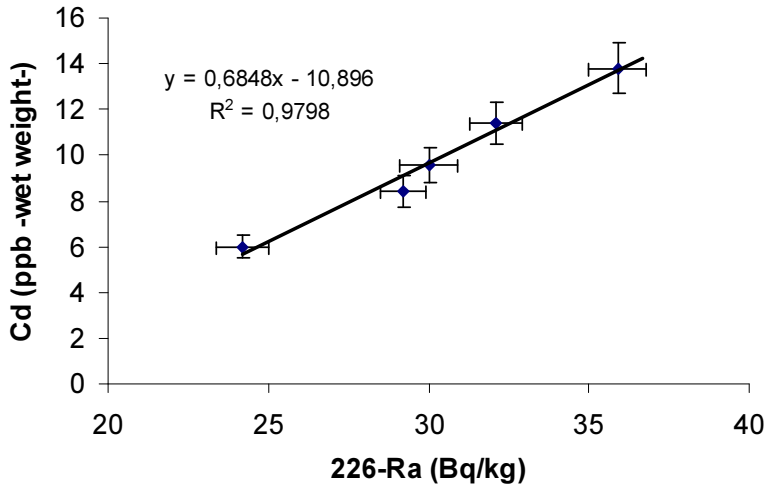

FIG. 3. Cd concentration in tomato simples from several farms in Marismas de Lebrija versus ^{226}Ra activity concentration in surface soils

3.6. Radiological and alimentary assessment.

An estimation was made of the contribution of the radionuclides from the ^{238}U series to the radioactive doses by ingestion of food. The control group was defined as consuming 80.5 kg/a of vegetable and fruit (the averaged value for Spain), but produced exclusively in the area. Activity concentrations found in tomatoes (or the corresponding MDL) were assumed to be representative of mean activity concentrations. The resulting annual doses were 9.6 μSv/a. The consumption of red crabs (potentially living in the drainage canals) was considered as the critical pathway for the contribution to the radioactive doses. Assuming a consumption of 20 kg/a (4 times the averaged consumption of molluscs and crustaceans in SW Spain), the dose received was 0.04 mSv/a (from the contribution of ^{226}Ra and U-isotopes).

To evaluate potential future risks, a scenario was defined in which PG was repeatedly applied at the usual rates of 20 t/ha every two years over a period of 100 years. As a conservative hypothesis, the associated inputs of radionuclides and Cd were be considered to be homogenised in the 0–30 cm soil horizon. Assuming ^{222}Rn exhalation rate to be proportional to ^{226}Ra concentration in this soil layer, the expected exhalation rate was 160 Bq h^{-1} m^{-2}, still within the range of reference environmental values (the contribution to dose was not evaluated since this last is given by ^{222}Rn concentration in air, defined by factors on a geological scale more than by local exhalation rates). The estimated contribution to radioactive dose by ingestion of food from vegetable origin (by using the concentration factors found in this work) increased to 0.15 mSv/a. Finally, the Cd concentration in tomatoes was close to the upper limit of 50 ppb (fresh weight).

4. Conclusions

This work proved that the actual ^{222}Rn exhalation rates in agricultural soils (averaged values of 34 Bq h^{-1} m^{-2} and 24 Bq h^{-1} m^{-2} for PG amended and control plots, respectively) are relatively low compared with reference values for soils.

Actual levels of activity concentrations in soils for radionuclides from the ^{238}U series are in the range of typical environmental values. The same is true for Cd concentrations in soil. ^{238}U activity concentrations in drainage waters are close to the standards for drinking waters, but they are relatively high compared with typical values for natural non-perturbed aquatic ecosystems.

The Cd concentration in tomatoes produced in the area are within the standards of CE rules, but were higher than in market-tomatoes originating from elsewhere.

As a final conclusion, PG produced in Huelva has been used in the area during the last 30 years as a Ca amendment in the agricultural soils of this area. All the experimental evidence indicates that current practice could still continue safely for several decades in compliance with current safety regulations.

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