The cumulative effect of three decades of phosphogypsum amendments in reclaimed marsh soils from SW Spain: ^{226}Ra, ^{238}U and Cd contents in soils and tomato fruit

José-María Abril[a],[*], Rafael García-Tenorio[b], Santiago M. Enamorado[a], M. Dolores Hurtado[c], Luis Andreu[c], Antonio Delgado[c]

[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
[c]Dpto. Ciencias Agroforestales, Universidad de Sevilla, EUITA, Ctra Utrera Km 1, 41013, Seville, Spain

ABSTRACT

Phosphogypsum (PG), a by-product of the phosphate fertiliser industries, has been applied as soil amendment to reduce Na saturation in soils, as in the reclaimed marsh area from SW Spain, where available PG has a typical fingerprint of 710 ± 40 Bq kg^{-1} of ^{226}Ra, 165 ± 15 Bq kg^{-1} of ^{238}U and 2.8 ± 0.4 mg kg^{-1} of Cd. This work was focussed on the cumulative effects of PG amendments on the enrichment of these pollutants in cultivated soils and plants (*Lycopersicum esculentum* Mill L.) from the area studied, where PG has been applied since 1978 at recommended rates of 20–25 Mg ha^{-1} every 2–3 years. A field experiment was conducted over three years to compare activity concentrations of ^{226}Ra (^{214}Pb) and ^{238}U (^{234}Th) in non-reclaimed soils, reclaimed soils with no additional PG application, and reclaimed soils with two additional PG applications. A non-significant effect of two PG amendments (in three years) was observed when compared with non-amended reclaimed plots. Nevertheless, a significant ($p < 0.05$) enrichment of ^{226}Ra was observed in the surface horizon (0–30 cm) of reclaimed plots relative to deeper horizons and also when compared with the surface horizon of non-reclaimed soil ($p < 0.05$), thereby revealing the cumulative effect of three decades of PG applications. Furthermore, the effect of a continuous application of PG was studied by analysing soils and tomato fruits from six commercial farms with different cumulative rates of PG applied. Cadmium concentrations in tomatoes, which were one order of magnitude higher than those found in tomatoes from other areas in South Spain, were positively correlated ($r = 0.917^*$) with ^{226}Ra-concentration in soils, which can be considered an accurate index of the cumulative PG rate of each farm.

1. Introduction

Phosphogypsum (PG) is the main waste as a by-product of phosphoric acid factories, which use phosphate rock as raw material. It is composed mainly of gypsum, but levels of fluoride, certain natural-occurring radionuclides, and some heavy metals are relatively high 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 (Rutherdord et al., 1994).

The fertiliser industry in Huelva (SW Spain) annually produces 3 million tons of PG, processing phosphate rocks from Morocco and Senegal (with ^{238}U-concentrations reaching up to 1000 Bq kg^{-1}, Bolívar et al., 1996). PG is disposed of in stacks lying on the right bank of the Tinto River, in the vicinity of Huelva city. Approximately 85% of uranium present in the phosphate rock passes to resulting phosphoric acid, while about 90% of ^{226}Ra remains in the PG wastes (Bolívar et al., 1996). Cd was found in concentrations reaching up to 2 and 7 mg kg^{-1} in PG from phosphate rock, from Morocco and Senegal, respectively (Pérez-Moreno, 2005).

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. Agricultural uses of PG are being extensively studied, since they could become the main worldwide sink 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).

The Guadalquivir salt-marsh area comprises some 1360 km^2 in SW Spain. From the late XIXth century, a sizeable portion of this surface has been reclaimed for agricultural use (40,000 ha), which accounts for one of the largest reclaimed marsh areas in southern Europe and features an important irrigated agricultural production (Moreno et al., 2001). Before reclamation, these soils were highly saline and had a shallow, extremely saline, water table (Moreno et al., 1981). Reclamation practices involved artificial draining (tile-drains), leaching, and soil amendment to reduce Na saturation. In 1978, as one of the latest actions, some 140 km^2 of marsh soils were reclaimed in the area of the city of Lebrija (see Fig. 1). Since 1978, Phosphogypsum has been traditionally used in this area as a Ca-amendment for soil reclamation (Domínguez et al., 2001). Recommended rates were 20–25 Mg ha^{-1} with repetition every two years; although in practice the level of accumulated PG amendment can significantly vary from one farm to another. 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 grain size and, in practice, immediately after application it is possible to distinguish PG grains from submillimetre sizes up to several cm.

The use of PG was interrupted in 2001 due to public concern about the alimentary safety in the agricultural use of this waste. Recent Spanish regulations (R.D. 824/2005, from July 2005) explicitly allowed the use of PG as soil amendment (without mention of its radioactive content). European regulations (EC 1881/2006) establish upper limits for concentrations of some heavy metals (Hg, Cd and Pb) in food. The US EPA has specific regulations for the agricultural use of PG (64 FR 5574), and permits its use if ^{226}Ra-concentration is below 370 Bq kg^{-1}. Consequently, attention should be paid in order to ensure
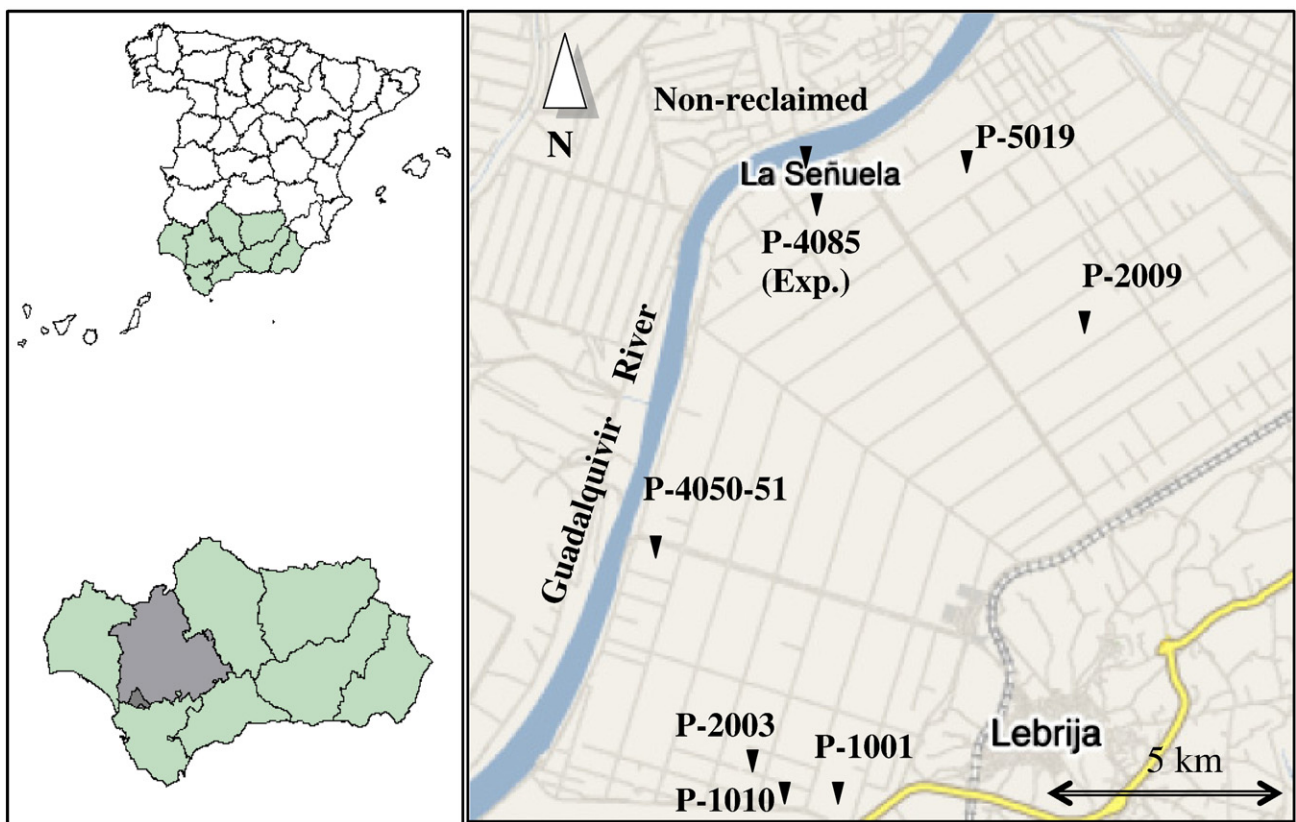

Fig. 1 – Map of the area "Marismas of Lebrija" (SW Spain). Triangles indicate the farm plots included in the sampling campaign (reference numbers correspond to the local identification code). P-4085 was the experimental farm used for the three-year field experiment.

radiological safety and acceptable levels of heavy metals (e.g. Cd) in agricultural products.

Studies on the environmental impact of PG have been reviewed by Rutherdord et al. (1994). Studies on the radiological impact of the agricultural use of PG have been conducted, among others, by Alcordo et al. (1999), in soils under bahiagrass pasture in Florida, and, more recently, by Papastefanou et al. (2006) in Greek soils under rice crop. In the area of Lebrija (SW Spain), El-Mrabet et al. (2003) carried out a two-year field experiment involving PG amendments.

The main objective of this work is to study the cumulative effect of PG in view of several pollutants in reclaimed soils and crops in the area of Lebrija (SW Spain). ^{226}Ra, ^{238}U and Cd are the target elements (with concentrations in PG roughly one order of magnitude higher than those for agriculture soils), although other radioisotopes will be used for control and reference purposes. Other heavy metals have not been included in the present study since their concentrations in PG are comparable to those from soils and PG is diluted some 0.5% in soil under current practices. The radioactive fingerprint of PG can be used to evaluate the cumulative effect (since 1978) of its application as a Ca-amendment. This will provide a unique means of what can be considered a long-term field experiment on the agricultural use of PG.

2. Materials and methods

2.1. The study of the short-term cumulative PG effect (a three-year field experiment)

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 crossed lengthwise by drainage lines 250 m long and spaced 5 m apart that were placed at a depth of 1 m. Tile drains ended in a small channel that carried drainage waters towards the river. After reclamation, these marsh soils can be classified as Aeric Endoaquepts (Soil Survey Staff, 1998). More detailed information about this experimental site is described elsewhere (Delgado et al., 2006). The farm soils, as the rest in the area, had received several (not well-documented) PG amendments before 2001.

Two treatments (control and 25 Mg ha^{-1} PG applied in April 2003 and repeated in September 2004) were applied in triplicate and randomly distributed in 0.5 ha (250×20 m) plots following a randomized block design. In the first and third growing seasons (2003 and 2005), cotton (Gossypium hirsutum L.) was grown under furrow irrigation at a rate of 8–10 mm h^{-1} (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). The total annual rainfall was 694 mm, 407 mm and 241 mm for the years 2003 to 2005, with corresponding mean potential evapotranspiration of 1423, 1444 and 1544 mm, respectively. Applied irrigation water was 1017, 399 and 970 mm for the three consecutive growing seasons. The surface runoff was negligible and the total drainage during the season was estimated by integrating the drainage hydrographs during the crop season, resulting in 70, 4 and 120 mm for the three consecutive crop seasons.

For sugar beet, a 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$_4$)$_2$HPO$_4$, urea and KNO$_3$] and sidedress stage (100 kg N ha^{-1} as HN$_4$NO$_3$). For cotton, the same pre-plant fertiliser was applied and 268 kg N ha^{-1} at sidedress as HN$_4$NO$_3$.

Soils samples were collected at depths of 0–30 cm before the first PG application (2003) for chemical and physical characterization. A composite sample was made from 32 soil cores of 4 cm in diameter randomly collected in the experimental plot. Following collection, samples were air dried and ground in order to pass through a 2 mm sieve prior to analysis.

Soil cores were sampled in January 2006 to study the content of different radionuclides after the two treatments. At the central point of each plot, three soil cores (4 cm diameter) were collected at three different depths (0–30 cm, 30–60 cm and 60–90 cm). A composite sample was prepared for each plot and depth. Samples were air dried and ground to pass a 0.5 mm screen prior to analysis. Additional soil samples were taken below the baseline of the drainage channel (soil horizon c.a. 2.0 m depth).

Non-reclaimed marsh soil (not in agricultural use and not PG applied) was sampled in an area close to the experimental farm (Fig. 1). It can be considered a soil with similar properties to the one in the experimental site before reclamation. Three cores were collected there at four different depths (0–30 cm, 30–60 cm, 60–90 cm and 90–120 cm).

2.2. Long-term PG accumulation: sampling in tomato farms (Lycopersicum esculentum Mill L.)

Depth distributions of radionuclides in the experimental farms and their comparison against those of non-reclaimed soils enable the long-term effect to be studied of PG application in the enrichment of these radiotracers in soils. To study PG effects in crops, in July 2005 a sampling campaign was carried out on six selected farms in the "Marismas of Lebrija" area (Fig. 1) to collect samples of tomato fruits for industrial use (L. esculentum Mill L.) and of surface soils (0–30 cm horizon). Farms (with several PG amendments before 2001) were selected with the support of the agricultural cooperative "Las Marismas" from among those whose different levels of available Phosphorus (^{31}P, ranging from 11 up to 68 ppm) had been determined. This parameter was expected to be a good indicator of the level of cumulative PG amendment (Domínguez et al., 2001). On each farm, composite samples of tomato and soil where made from 10 subsamples randomly collected throughout the plot area (6.5 ha).

Soil samples were treated as described above prior to the radionuclide analysis. Tomato fruit samples were pre-treated by drying at 36 °C for 5 days after having been cut into small pieces. After drying, an aliquot of 0.5 g tomato sample was allowed to homogenise with 5 mL of HNO$_3$ (MERCK, Suprapure grade) for 12 h. In the following step the samples were submitted to acid digestion on a digestion block at 120 °C for 4 h and filtered through 20–25 μm pore size. Finally, the sample was diluted to 25 mL with 18 MΩ deionized water (ELGA PURELAB Ultra, Vivendi Corp.).

2.3. Agriculture inputs

Phosphogypsum used originated from a non-active PG stack in Huelva (SW Spain) owned by Fertiberia. Prior to application, a composite sample was delivered to laboratory for radionuclide and Cd analysis. The PG stack has been extensively sampled (n = 42) to determine its content in ^{226}Ra (by liquid scintillation counting), ^{238}U (by α-spectrometry) and Cd (by ICP-MS analysis), resulting in (on a dry weight basis) 710±40 Bq kg^{-1} (n = 42), 165±15 (n = 42) Bq kg^{-1} and 2.8±0.4 (n = 19) mg kg^{-1}, respectively (Abril et al., in press).

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. Recently, Nziguheba and Smolders (2008) found a mean value of 82.7 mg Cd kg^{-1} Phosphorus (^{31}P) in mineral fertilisers sampled in Europe.

2.4. Soil characterization

Particle-size analysis was carried out by using the pipette method after treatment with Na hexametaphosphate (Gee and Bauder, 1986). Organic carbon was determined by dichromate oxidation (Walkley and Black, 1934). The total CaCO$_3$ equivalent (CCE) was calculated from the weight loss after treatment with 6 M HCl. The Cation Exchange Capacity (CEC) was determined with 1 M NH$_4$OAc buffered at pH 7 (Sumner and Miller 1996), and exchangeable cations by using flame photometry for K and Na, and atomic absorption spectroscopy for Ca and Mg, following extraction with 1 M NH$_4$Oac (three consecutive runs). pH and conductivity were determined in the 1:5 extract. Phosphorus availability was measured by extraction with sodium bicarbonate in accordance with Olsen et al. (1954).

2.5. Radionuclides and Cd study

Homogenised soil samples were placed into Petri dishes and shielded to preclude radon emanation and then stored for a period of a month to allow secular equilibrium among ^{226}Ra and its decay products ^{214}Bi and ^{214}Pb. Gamma-ray measurements were carried out on two low-background high purity Ge detectors supplied by Camberra: a ReGe detector type (31.4% relative efficiency, FWHM of 1.98 keV at 1332 keV of ^{60}Co) and Xtra detector type (37.1% relative efficiency, FWHM of 1.76 keV at 1332 keV of ^{60}Co). 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 can be enhanced by the PG treatment. Other radionuclides studied were: ^{137}Cs (fallout origin), ^{212}Pb (natural, from the ^{232}Th series) and ^{40}K (natural, single occurring), which are not related to the PG inputs and thus can be used as reference. Typical counting uncertainties for ^{226}Ra, ^{212}Pb and 40K were below 5% and lower than 16% for ^{238}U. Due to its low concentration in the analysed soil samples, uncertainties for ^{137}Cs, when detected, ranged from 6% up to 55%.

A Quadrupole ICP-MS instrument (Thermo X7, Thermo, Madrid, Spain) with a concentric (Meinhard) Quartz nebuliser was used for Cd determination. The samples were analysed using the recommendations provided by US EPA 200.8 methodology. Various data quality tests were used during every instrumental running, such as replicate, matrix matching, memory effects, and both digestion analysis and laboratory reactive blanks checking. The suitability of the methods applied was tested through the analysis of certified samples, including biological matrices (IAEA-414).

2.6. Statistical analysis

Analysis of variance (ANOVA) and the Tukey test for comparison between means were carried out by using Analysed-it 1.73 Software. Two tests were carried out for each target variable. The first one (T$_1$) was a two-way ANOVA test with the factors of *treatment* (non-reclaimed, control and PG-amended plots) and *depth* (three depth intervals, from 0–30 to 60–90 cm). The second test (T$_2$) was a one-way ANOVA test for surface soil samples (0–30 cm) and the factor *practice* (use of soil or level of PG amendment), included non-reclaimed (NR), control (C) and PG-amended (PG) plots, the group of commercial plots (CP) and the soil samples from the canal (SC). For both tests, all pairwise contrasts were carried out by Tukey tests at 95% CL.

3. Results and discussion

All the soils in this study were clayish and calcareous, with a relatively high content of soluble salts, particularly the non-reclaimed soil (Table 1). Major differences between soils from commercial plots (reclaimed) are concerned with the Phosphorus content, which was the criterion for the selection of these plots.

3.1. Radionuclide and Cd inputs

The PG used in the study had 630±4 and 196±6 Bq kg^{-1} of ^{226}Ra and ^{238}U, respectively, on a dry matter basis (Table 2). Potassium-40 and ^{212}Pb were present in PG at lower concentrations than in soil samples, ^{137}Cs was not detectable and Cd was found in PG at concentrations of 2.14±0.06 mg kg^{-1}. Under field conditions, after being sun dried, the remaining humidity in PG was 19%. Thus at 25 Mg PG ha^{-1} rate (sun-dried weight), the amendment is incorporating 12.8 MBq ha^{-1} of ^{226}Ra, 4.0 MBq ha^{-1} of ^{238}U, 43.3 g ha^{-1} of Cd, and negligible amounts of ^{40}K, ^{212}Pb and ^{137}Cs. Assuming homogenisation in the soil horizon 0–40 cm (as a result of deep tillage following PG application) and a typical bulk density of 1.3 kg L^{-1} (Delgado et al., 2002), these inputs resulted in increments of the initial concentrations of 2.5 Bq kg^{-1}, 0.76 Bq kg^{-1} and 0.008 mg kg^{-1} for ^{226}Ra, ^{238}U and Cd, respectively.

The application of 68 kg P ha^{-1} as diammonium-phosphate incorporates 6.1 g Cd ha^{-1}, 0.49 MBq ha^{-1} of ^{238}U, and negligible amounts of ^{226}Ra.

3.2. 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 sixties (the accident

Table 1 – Characterization of soils (0–30 cm)

Soil [farm code]	Particle-size distribution			Organic matter	CaCO₃	CEC[b]	Exchangeable cations[c]				Olsen P	EC[c]	pH[c]
	<2 μm	2–50 μm	>50 μm				K^+	Na^+	Ca^+	Mg^+			
	g kg⁻¹				%	cmol$_c$ kg⁻¹	cmol kg⁻¹				mg kg⁻¹	dS m⁻¹	
Experimental	680	260	60	13.9	N.M.[a]	32	2.3	4.9	19.2	5.6	14.8	0.56	8.5
Non-reclaimed	420	410	171	21.5	N.M.	25.8	3.9	3.1	10.7	8.1	N.M	2.6	8.4
P-1001	700	200	100	21.5	6.14	34.2	2.5	1.7	22.3	8	30.3	0.27	8.9
P-1010	700	250	50	15.0	6.08	31.6	2.3	1.4	20.6	7.3	13.9	0.27	8.9
P-2003	650	250	100	14.6	4.68	42.2	2.9	1.6	27.0	10.7	67.7	0.33	8.7
P-2009	750	250	0	17.2	7.19	31.6	2	4.5	15.4	9.7	34.7	0.53	8.1
P-4050-51	550	250	200	12.5	6.38	21.2	1.3	1.2	14.6	4.1	19.0	0.43	8.2
P-5019	750	200	50	14.9	4.59	22.6	1.7	1	14.5	5.4	10.7	0.36	8.5

Soil analysis for the commercial farms provided by the Agriculture Cooperative "Las Marismas" from Lebrija (Spain).
[a] N.M.: not measured. For the experimental farm, the measured calcium carbonate equivalent (CCE) was 235 g kg⁻¹.
[b] CEC, Cation Exchange Capacity.
[c] Exchangeable cations extracted with 1-M ammonium acetate and determined by ICP-OES; EC, Electrolytic conductivity and pH determined in the 1:5 soil extract.

of Chernobyl had a negligible effect in SW Spain, as shown by Carcía-León et al., 1993). Due to its origin, this isotope did not appear in the deeper layers of the non-reclaimed marsh soil (Table 2). In the farm soils, ^{137}Cs-concentrations in surface horizon were similar to those found by Bolívar et al. (1995) in other agricultural areas of SW Spain. The detection of this isotope in soils from the drainage canal indicates a transfer of radionuclides from surface soils, since atmospheric fallout must have been negligible after the opening of the canal in the late 1970s.

As discussed earlier, no effect of PG amendment on [212]Pb concentration in soil can be expected. Lead-212 levels in all the studied soils (Tables 2 and 3) were comparable to the reference concentrations for [232]Th in the earth crust (34 Bq kg⁻¹, Righi et al., 2000). From test T_1, no significant differences were found with factors *depth* and *treatment×depth*, but differences in *treatment* and

practice (T_2) were significant. Thus, Tukey tests revealed that [212]Pb concentrations in the canal and in the 0–30 cm horizon of non-reclaimed soils (both unvegetated areas) were significantly lower than those from control, PG-amended and commercial plots, although no significant differences were found within this last group. Lead-212 has a short half-life ($T_{1/2}$ = 10.64 h); thus, [212]Pb in soil is the consequence of the radioactive decay chain: [232]Th ($T_{1/2}$ = 1.4·10¹⁰ y) → [228]Ra ($T_{1/2}$ = 5.75 y) → [228]Th ($T_{1/2}$ = 1.91 y) → [224]Ra ($T_{1/2}$ = 3.62 d) → [220]Rn ($T_{1/2}$ = 55.6 s) → [216]Po ($T_{1/2}$ = 0.15 s) → [212]Pb. Due to the short half-life of the two Ra isotopes involved, short-term changes in ambient conditions (solid-to-liquid partitioning in saturated porous media) could result in varying [228]Ra/[226]Ra activity ratios with both time (Inoue et al., 2005) and location (Michel and Moore, 1980) which can affect [212]Pb activity. With an expected [232]Th uniform distribution in the soils studied, the absence of a root system in non-reclaimed soils and in the

Table 2 – Radionuclide concentrations in PG, agricultural soils from the experimental farm after two PG treatments (April 2003 and September 2004) and non-reclaimed marsh soils (sampling campaign carried out in January 2006)[a]

Treatment	n	Depth	[226]Ra[c]	[238]U[d]	[212]Pb	[40]K	[137]Cs	AR ([226]Ra/[238]U)
		cm	Bq kg⁻¹					
PG amendment[b]			630±4	196±6	8.9±0.5	11±4	N.D.	3.21±0.10
Control	3	0–30	35.3±0.8	25.3±0.4	33.1±0.7	767±20	2.8±0.6	1.40±0.04
Control	3	30–60	27.7±0.4	23.5±0.5	32.3±1.0	760±50	0.9±0.5	1.18±0.03
Control	3	60–90	24.2±0.7	19.4±1.0	31.9±0.7	750±20	N.D.	1.25±0.06
PG 25 Mg ha⁻¹	3	0–30	39.3±2.3	23.9±1.0	32.2±1.0	798±27	2.3±1.0	1.64±0.13
PG 25 Mg ha⁻¹	3	30–60	29.6±1.8	25.0±2.1	32.8±0.4	814±11	1.0±0.1[e]	1.18±0.12
PG 25 Mg ha⁻¹	3	60–90	24.0±0.9	21.7±2.6	32.1±1.0	780±50	N.D.	1.19±0.14
Non-reclaimed	3	0–30	21.6±0.4	18.9±0.1	26.9±1.0	580±40	2.7±0.7	1.14±0.02
Non-reclaimed	3	30–60	23.5±0.9	19.2±1.1	29.3±0.7	624±22	N.D.	1.22±0.08
Non-reclaimed	3	60–90	22.2±1.4	20.0±1.3	28.7±0.9	647±16	N.D.	1.10±0.10
Non-reclaimed	2	90–120	22.4±1.2	20.5±0.7	29.5±0.2	653±4	N.D.	1.09±0.07
Deep soil (canal)	2	>2.0	18.6±1.4	20.1±1.0	26.5±0.1	794±17	1.7±0.2	0.91±0.08
Analytical error[a]			<1	<4	<1	<20	<0.5	

N.D.: Not detected.
[a] Means and standard deviations of means (on a dry matter basis); PG = phosphogypsum. Radionuclides measured by γ-spectrometry.
[b] For PG, Cd measured by ICP-MS was 2.14±0.06 mg kg⁻¹.
[c] Measured through the 352 keV emission of [214]Pb (sealed sample to prevent [222]Rn losses and stored for secular equilibrium).
[d] Measured through the 63 keV emission of [234]Th.
[e] n = 1; measurement with 1σ-analytical error. For the other two samples [137]Cs<MDL.

Farm code	^{226}Ra [b]	^{238}U [c]	^{212}Pb	^{40}K	^{137}Cs	Cd
			Bq kg^{-1}			mg kg^{-1} d.w.
P-1001	30.2±0.9	19±3	29.1±0.8	690±14	2.4±0.2	0.235±0.012
P-1010	36.1±1.0	23±3	31.2±0.6	737±14	4.5±0.5	0.377±0.019
P-2003	29.5±0.8	22.9±1.8	31.8±0.8	751±14	1.0±0.3	0.140±0.007
P-2009	30.2±0.9	23.4±2.2	33.2±0.9	793±20	1.7±0.2	0.162±0.008
P-4050-51	24.5±0.7	19.0±2.5	30.3±0.6	735±14	2.8±0.3	0.100±0.005
P-5019	33.0±1.0	21±4	31.8±0.6	793±15	1.9±0.3	0.191±0.010

[a] Means and standard deviations of means. Radionuclides measured by γ-spectrometry, and Cd by ICP-MS. ^{238}U in tomato fruit was under ICP-MS MDL (0.03 mg kg^{-1} d.w.).
[b] Measured through the 352 keV emission of ^{214}Pb (sealed sample to prevent ^{222}Rn losses and stored for secular equilibrium).
[c] Measures through the 63 keV emission of ^{234}Th.

drainage canal, together with their special water regimen (being saturated most of the time) could explain the observed relative depletion in ^{212}Pb concentrations, although the mechanisms involved cannot be formally concluded from our present study.

With an abundance of 0.0117%, ^{40}K can be considered as an indicator of the total K. One can expect to find K levels in agricultural soils varying throughout the year depending, among other factors, on the potassium fertiliser supply, phyto-extraction and irrigation levels. Potassium-40 concentrations in the surface horizon of non-reclaimed soils were significantly lower than those from the rest of the soils (and without significant differences within this last group). Thus, enrichment due to fertiliser application can be supposed. Potassium-40 levels in soils from the canal can be attributable to transfers from the agricultural soil, as in the case of ^{137}Cs.

Since the soil samples were measured several months after collection, ^{234}Th was in secular equilibrium with ^{238}U. Concentrations found in all the soil samples (Tables 2 and 3) were comparable to the reference concentrations of ^{238}U in the earth crust (33 Bq kg^{-1}; Righi et al., 2000). Partly due to the large analytical errors associated to ^{238}U-determination by γ-spectrometry, significant differences in ^{238}U-concentrations in soil could be found only for *treatment* (T$_1$, $p<0.02$), with concentrations in PG-amended plots significantly higher than those from non-reclaimed soils and the group of other commercial plots (from T$_2$, $p<0.01$). Moreover, ^{238}U-concentration was significantly higher in the group of commercial farms than in samples from the canal (Tables 2 and 3). In control plots, ^{238}U-concentration in the 60–90 cm horizon was significantly lower than in the 0–30 and 30–60 cm layers ($p<0.01$), thus indicating an enrichment in surface horizons due to an accumulation effect of PG amendment (applied before 2001).

Radium-226 concentrations in natural soils are expected to be close to those from ^{238}U, as corresponds in the case of secular equilibrium. Thus, Greeman et al. (1999) found, in soils from 12 sites in eastern USA, that profile-averaged $^{226}Ra/^{238}U$ activity ratios (AR) were within 10% of unity, but with ^{226}Ra exceeding ^{238}U in most surface soils (AR up to 1.8, av. 1.22). Following the results from these authors, a major factor in ^{226}Ra behaviour can be ascribed to the uptake of this radionuclide by vegetation, which moves Ra from deeper soil to surface soil.

Radium-226 concentrations (Tables 2 and 3) were significantly affected by both factors considered in T$_1$ ($p<0.001$), since these concentrations were significantly higher in control

and PG-amended plots than in non-reclaimed soil, but no significant differences could be found between control and PG-amended plots. Concerning depth distributions, no significant differences were found for the non-reclaimed soil, but concentrations in the first layer of control and PG plots were significantly higher than in the rest of the soil profile. From test T$_2$, differences by *practice* were significant ($p<0.0001$), with ^{226}Ra-concentrations in non-reclaimed soils and canal samples lower than in the rest.
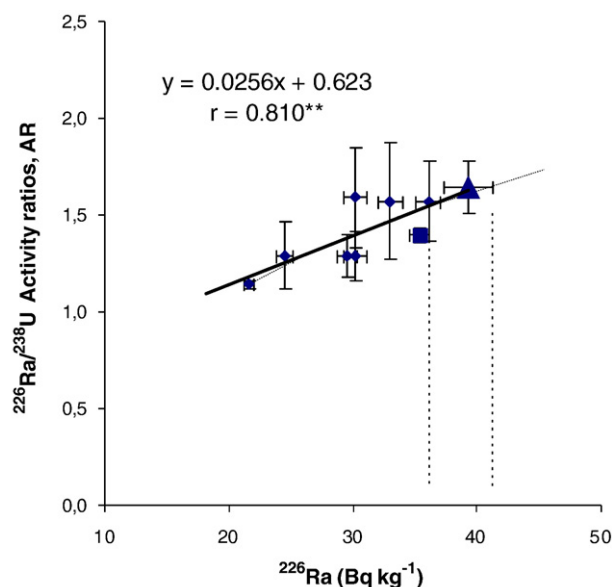

Fig. 2 – $^{226}Ra/^{238}U$ activity ratios (AR) versus ^{226}Ra-activity concentration in the 0–30 cm soil horizon from commercial plots (Table 3), non-reclaimed soil, control (square dot) and PG-amended (triangular dot) plots on the experimental farm (from Table 2, mean values). Error bars correspond to 1σ-propagated uncertainties. Dotted line shows the estimated AR due to repeated PG amendments (20.2 Mg d.w. ha^{-1} assuming mixing in the 0–40 cm interval, and current radionuclide concentrations in surface non-reclaimed soils as initial conditions). Vertical dashed lines are marks for the 6th and 8th PG recommended rates. Continuous line shows the linear fit.

The expected increase of up to 5.0 Bq kg^{-1} in ^{226}Ra-concentration in the 0–30 cm horizon (after two PG doses) could not be solved from our present experimental setup (two PG applications over the cumulative effect of previous historical applications). Nevertheless, the cumulative effect of three decades of PG applications resulted in a significant enrichment in ^{226}Ra-concentrations in the soil surface (0–30 cm) relative to deeper horizon (60–90 cm) and with respect to non-reclaimed soils.

The ^{226}Ra/^{238}U activity ratio (AR) in the entire soil profile of non-reclaimed soils was 1.14±0.03 (determined from data in Table 2), implying little fractionation of ^{238}U and ^{226}Ra. From these unperturbed soils, a local ^{226}Ra-baseline of 22.4±0.6 Bq kg^{-1} (depth-averaged value) can be inferred. On the other hand, ^{226}Ra/^{238}U AR in PG used as amendment was 3.21±0.10 (4.3±0.10 in PG from the stack, $n = 42$).

The ^{226}Ra/^{238}U activity ratio (AR) was significantly related to ^{226}Ra-activity concentration in surface horizons (0–30 cm) from all the agriculture plots (Fig. 2). It is possible to estimate the increase in ^{226}Ra- and ^{238}U-concentrations in soils, and thus, the expected AR ratio, after any arbitrary level of PG amendment (the number of typical PG recommended rates of 20.2 Mg d.w. ha^{-1}). This estimation assumes a soil mixing in the 0–40 cm interval, bulk densities of 1300 kg m^{-3}, radionuclide concentrations in PG from Table 2, the use of the current radionuclide concentrations in surface non-reclaimed soils as initial conditions, and to neglect other sources or sinks. The estimated theoretical relationship between ^{226}Ra/^{238}U AR and ^{226}Ra due to repeated PG amendments up to the 10th application matches the experimental relationship (Fig. 2).

3.3. Inventories and mass balance

From the data of Table 2, it is possible to estimate ^{226}Ra-inventories in the 0–90 cm soil column for control and PG-amended plots and for non-reclaimed soils, resulting in 340±5, 362±12 and 263±7 MBq ha^{-1}. Thus, the ^{226}Ra enrichment in surface layers of agricultural soils cannot be attributable to ^{226}Ra uptake by plants (producing redistribution in depth, but without change in the depth-integrated inventory) since the total inventory in control and PG-amended plots was significantly higher. The excess inventory in PG plots (relative to control) was 22±13 MBq ha^{-1}, which is consistent with the expected excess of 25.6 MBq ha^{-1} (calculated from the amount of PG applied during the experiment). In previous studies in this area (El-Mrabet et al., 2003), typical ^{226}Ra-concentrations of 5 mBq L^{-1} were found in drainage waters, with associated ^{226}Ra-losses of 0.005 MBq ha^{-1} y^{-1}. Thus, ^{226}Ra-losses associated to drainage are expected to be negligible. Radium-226 inputs associated to irrigation water or fertilisers can be considered equally negligible. Extraction by crop can be estimated using concentration factors from the literature (averaged valued of 0.035 for all the parts of the tomato plant, following Köhler et al., 2000) and typical crop yields for the area (8.5 Mg d.w. ha^{-1}), leading to values <0.01 MBq ha^{-1} y^{-1}. The excess inventory of control plots with respect to non-reclaimed soils was 77.5±0.8 MBq ha^{-1}, which roughly corresponds to six applications of typical PG recommended rates in the period 1978 to 2001.

Similarly, ^{238}U-inventories in the 0–90 cm soil column for control and PG-amended plots and for non-reclaimed soils resulted in 265±4, 275±14 and 227±7 MBq ha^{-1}, respectively. El-Mrabet et al. (2003) found typical ^{238}U-concentrations of 180 mBq

Table 4 – Cd in tomato fruits from a market survey (July 2005)[a]			
Sample	Location	d.w. (%)	Cd (mg kg^{-1} d.w.)
Los Palacios — 1	37° 9′ N, 5° 55′ W	6.0	0.032±0.003
Los Palacios — 2	37° 9′ N, 5° 55′ W	5.7	0.014±0.005
Los Palacios — 3	37° 9′ N, 5° 55′ W	6.0	0.035±0.004
Los Palacios — 4	37° 9′ N, 5° 55′ W	6.0	0.059±0.005
San Juan — 1	38° 24′ N, 0° 26 W	5.6	0.014±0.005
San Juan — 2	38° 24′ N, 0° 26 W	5.7	0.036±0.007
El Ejido — 1	36° 46′ N, 2° 49′ W	5.8	0.019±0.008
El Ejido — 2	36° 46′ N, 2° 49′ W	5.9	0.014±0.006
Mazarron — 1	37° 36′ N, 1° 19′ W	6	0.042±0.007
Mazarrom — 2	37° 36′ N, 1° 19′ W	6.1	0.044±0.008
Mean and standard deviation of mean		5.9	0.035±0.005

[a] Measurement and 1σ-analytical errors. ^{238}U in tomato fruit was under ICP-MS MDL (0.03 mg kg^{-1} d.w.).

L^{-1} in drainage waters, which corresponded to ^{238}U-losses of 0.13 MBq ha^{-1} y^{-1}. ^{238}U-inputs associated to fertilisers can be estimated to be 0.49 MBq ha^{-1} y^{-1}. Extraction by crop can be estimated by using concentration factors of 0.032 (from Köhler et al., 2000) and typical crop yields for the area, resulting in 0.007 MBq ha^{-1} y^{-1}.

Excess inventory in PG plots (with respect to control) was not statistically significant. Taking into account the previous components for the mass balance, after two PG applications and three fertiliser applied rates, the expected excess inventory was 9.0 MBq ha^{-1}. After 25 annual applied rates of superphosphate and 6 PG rates, the expected excess inventory for control plots with respect to non-reclaimed soils was 32.8 MBq ha^{-1} versus 38±8 MBq ha^{-1} estimated from the data of Table 2.

Since PG is the dominant component in the mass balance, therefore the estimation of the number of cumulated PG-applied rates from inventories in soil results in good agreement with the one derived from the ^{226}Ra/^{238}U AR analysis (Fig. 2).

3.4. Cadmium concentration in tomato fruits

Table 3 shows results of Cd concentration in *L. esculentum* Mill sampled on six farms from the area studied, given in a d.w. base (mean value 6.1% d.w./f.w.). Table 4 summarises the corresponding results from a set of ten independent samples of tomato fruits (*L. esculentum* L.) from a market survey carried out in July 2005, which covered different origins within Spain. In all the cases, the concentrations of Cd, expressed on a fresh weight basis (Fig. 3), are within the acceptance levels (50 ppb) given by EC 1881/2006 regulation.[1] Nevertheless, Cd levels in tomato fruits from the PG-amended soils were one order of magnitude higher than those for tomato from the market survey. Furthermore, there is a positive correlation ($r = 0.917$*) between Cd concentration in tomato fruits collected from the area studied and the ^{226}Ra-concentration in soil. This last concentration can be understood as an indicator of the

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[1] Commission Regulation of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. Commission of the European Communities. Journal of the European Union. 20.12.2006.
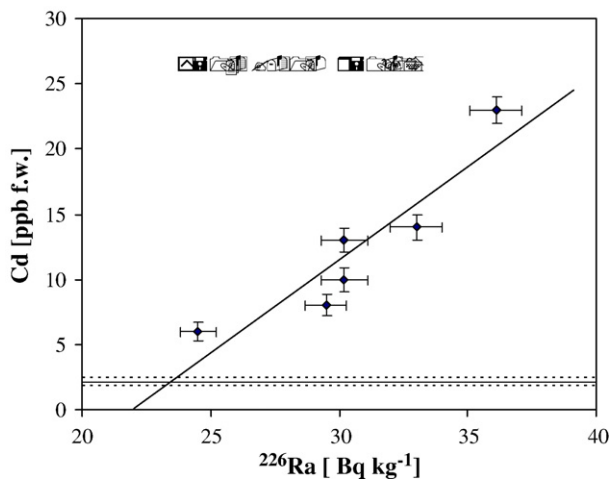
Fig. 3 – Cd concentration (in µg kg^{-1} f.w.) in tomato fruits (*Lycopersicum esculentum* Mill L.) from six farms with different levels of PG amendments versus ^{226}Ra-concentration in surface soils (0–30 cm). Horizontal lines correspond to the mean ± 1 standard deviation for a group of tomato fruits from a market survey covering different origins within Spain (see Table 4).

cumulative PG amendment applied. Thus, it is possible to conclude a direct effect of PG amendment in increasing levels of Cd in tomato fruits.

A rough approximation to the admissible threshold level of PG amendment can be achieved by extrapolation of the tendency given in Fig. 3. Thus, Cd concentration in tomato fruits could reach the 50 ppb f.w. limit with ^{226}Ra-concentrations in soils around 60 Bq kg^{-1}, roughly twice the current levels. Such a limit could be achievable with some 10 additional PG applications, a fairly improbable case because in many soils of the area, low Na saturation levels have been reached, which renders PG amendments unnecessary at the traditional rate.

4. Conclusions

The three-decade application of PG as soil amendment in the area of Lebrija (SW Spain), began in 1978 and produced a significant increment in ^{226}Ra-concentration in soils. A natural ^{226}Ra-baseline of 22.4 ± 0.6 Bq kg^{-1} with ^{226}Ra/^{238}U AR of 1.14 ± 0.03 could be inferred from soil cores sampled in a non-reclaimed marsh area close to the experimental farm. Current levels of ^{226}Ra in surface (0–30 cm) soils from the experimental farm were 35.3 ± 0.8 Bq kg^{-1} (control plots), with ^{226}Ra/^{238}U AR = 1.40 ± 0.04, which provides evidence of the cumulative effect of PG (with AR fingerprint of 4.3 ± 0.4 for PG in stack). From the ^{226}Ra-mass balance, the cumulate PG applied to control plots could be estimated to be 6 typical doses of 25 Mg ha^{-1} (sun-dried weight). The effect of two additional PG applications did not result in any statistically significant differences under our present experimental setup.

Cadmium concentrations in tomato fruits (*L. esculentum* Mill L.) were within the European-Union acceptance levels, but they were one order of magnitude higher than those found in tomatoes from a market survey. These Cd concentrations were positively correlated ($r = 0.917^*$) with ^{226}Ra-concentration in soils (related to the accumulated PG rate applied on each farm).

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