

# Transfer of Cd, Pb, Ra and U from Phosphogypsum Amended Soils to Tomato Plants

S. Enamorado · J. M. Abril · J. L. Mas · R. Perriñez · O. Polvillo · A. Delgado · J. M. Quintero

**Abstract** About 170 million tons of phosphogypsum (PG) are annually generated worldwide as a by-product of phosphoric acid factories. Agricultural uses of PG could become the main sink for this waste, which usually contains significant radionuclide (from the  $^{238}\text{U}$ -series) and toxic metals concentrations. To study PG effects on pollutant uptake by crops, a completely randomised greenhouse experiment was carried out growing *Lycopersicon esculentum* Mill L. on a reclaimed marsh soil amended with three PG rates (treatments), corresponding to zero (control without PG application), one, three and ten times the

typical PG rates used in SW Spain ( $20 \text{ Mg ha}^{-1}$ ). The concentrations of Cd, Pb, U (by inductively coupled plasma mass spectroscopy) and  $^{226}\text{Ra}$  and  $^{210}\text{Po}$  (by  $\gamma$ -spectrometry and  $\alpha$ -counting, respectively) were determined in soil, vegetal tissue and draining water. Cadmium concentrations in fruit increased with PG rates, reaching  $44 \pm 7 \mu\text{g kg}^{-1}$  formula weight with ten PG rates (being  $50 \mu\text{g kg}^{-1}$  the maximum allowed concentration by EC 1881/2006 regulation). Cd transfer factors in non-edible parts were as high as  $4.8 \pm 0.5$  (dry weight (d.w.)), two orders of magnitude higher than values found for lead, lead, uranium and radium concentrations in fruit remained below the corresponding detection limits— $0.5$  and  $0.25 \text{ mg kg}^{-1}$  and  $0.6 \text{ mBq kg}^{-1}$ , respectively (in a d.w. basis).  $^{238}\text{U}$  (up to  $7 \mu\text{g kg}^{-1}$  d.w.) and  $^{210}\text{Po}$  (up to  $0.74 \text{ Bq kg}^{-1}$  d.w.) could be measured in some fruit samples by  $\alpha$ -spectrometry. Overall, the concentrations of these metals and radionuclides in the draining water accounted for less than 1% of the amount applied with PG.

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S. Enamorado · J. M. Abril · R. Perriñez  
Dpto. Física Aplicada I, EUITA, Universidad de Sevilla,  
Ctra. Utrera s/n,  
41013 Seville, Spain

J. L. Mas (✉)  
Dpto. Física Aplicada I, EUP, Universidad de Sevilla,  
C/ Virgen de Africa 7,  
41012 Sevilla, Spain  
e-mail: ppmasb@us.es

O. Polvillo  
Servicio General de Investigación Agraria, EUITA,  
Universidad de Sevilla,  
Ctra. Utrera s/n,  
41013 Seville, Spain

A. Delgado · J. M. Quintero  
Dpto. Ciencias Agroforestales, EUITA,  
Universidad de Sevilla,  
Ctra. Utrera s/n,  
41013 Seville, Spain

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## 1 Introduction

Phosphogypsum (PG) is the main by-product of the phosphoric acid industrial production, which is amongst the most well-known technologically enhanced—naturally occurring radioactive material ma-

trices. It is composed mainly by  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , but levels of fluoride, certain natural-occurring radionuclides and some heavy metals are relatively high in PG (Rutherford et al. 1994).

Large quantities of PG are produced worldwide (about 170 million tons in 2006), most of it being stockpiled. Agriculture uses of PG are being extensively studied; they could become the main worldwide sink for this waste. Beneficial uses of PG have been demonstrated, amongst others, for improving soil structure and crop yield and reducing soil erosion (May and Mortvedt 1986; Mullins and Mitchell 1990; Zhang et al. 1998).

Several factories devoted to the production of phosphoric acid near Huelva town (SW Spain) have generated more than 80 millions tonnes of phosphogypsum during the last 30 years. This waste has been stored, in a large proportion, in a salt marsh located close to the town, leading to a complicated problem from the environmental point of view (Bolívar et al. 1995; Mas et al. 2006). PG from this origin has a typical fingerprint of  $710 \pm 40 \text{ Bq kg}^{-1}$  of  $^{226}\text{Ra}$ ,  $165 \pm 15 \text{ Bq kg}^{-1}$  of  $^{238}\text{U}$  and  $2.8 \pm 0.4 \text{ mg kg}^{-1}$  of Cd (Abril et al. 2008).

The use of PG as a Ca amendment for sodic soils is of particular interest in the Guadalquivir salt marsh area, comprising some  $1,300 \text{ km}^2$  in SW of Spain (Dominguez et al. 2001). Since the late nineteenth century, different actions have been carried out for reclamation of some of these soils for agriculture use, involving building barriers for tides, drainage of soils and irrigation plans. Besides the initial reclamation, the shallow saline water table in marsh areas requires an accurate salt balance in soil by means of leaching and the periodical use of Ca amendments to avoid an increase in Na saturation in soils (Oster et al. 1999). The latest reclamations were performed in  $140 \text{ km}^2$  of marshland from the Guadalquivir Valley in 1978. Since then, PG from Huelva has been traditionally applied to these soils at recommended rates of  $20\text{--}25 \text{ Mg ha}^{-1}$  repeated every 2–3 years. Main crops in this area are cotton, sugar beet and tomato for industrial uses (*Lycopersicon esculentum* Mill L.). Recently, Abril et al. (2008) reported relatively high cadmium concentrations in tomato fruit produced in this area (in the range  $5\text{--}25 \text{ } \mu\text{g kg}^{-1}$  formula weight (f.w.)) when compared against tomato samples from a market survey ( $2.1 \pm 0.3 \text{ } \mu\text{g kg}^{-1}$  f.w.,  $n=10$ ). However, that experimental setup did not allow a rigorous control of draining waters. Furthermore, it is impor-

tant to note a declining traditional practise in the area, consisting of the use of the tomato plant (after harvested) as forage for cattle. The no reproductive part of the plant was not analysed in that work; hence, an important potential mechanism of toxic elements transference to humans remains unexplored.

The use of PG as soil amendment is regulated in some countries by guides, laws and recommendations. In Spain, although the recent directive 824/2005 allows the use of PG as soil amendment, there is not a recommendation about the pollutant content in the product. The US Environmental Protection Agency (EPA) has a specific regulation for the agriculture use of PG (64 FR 5574), allowing it if  $^{226}\text{Ra}$  concentration is below  $370 \text{ Bq kg}^{-1}$ . However, attention should be paid to study PG effect in radionuclide and metal uptake by crops. Particularly, European regulations establish upper limits for concentrations of some metals (Hg, Cd and Pb) in food (EC 1881/2006 regulation) and animal food (EC 2005/87).

There is a large number of works in the scientific literature referred to the pollutant uptake by crops (International Union of Radioecologists 1994; Tsukada and Nakamura 1998; Köhler et al. 2000; Uchida et al. 2007). However, specific studies on the effect of PG amendments are scarce. Two ways of exposition to metals and radionuclides are possible: the direct transfer to harvested products used for human consumption (e.g. sugar beet or horticultural crops typical in the area) and an indirect transference through the use of crop residues as forage for animal production.

This work is focussed on the study of the PG effect on the uptake of its characteristic elements/isotopes Cd, Pb, U,  $^{226}\text{Ra}$  and  $^{210}\text{Po}$  by *L. esculentum* Mill (used as a representative agricultural product in SW Spain). Special attention has been paid to those potential mechanisms for toxic analytes transference to humans and the environment that have been not studied up to the date (mainly drainage waters and the no reproductive part of the plant). To do that, a pot experimental array has been selected as a suitable alternative to agriculture land field. This approach allows to avoid information overlapping due to the use at field scale of phosphate fertilizers. Leaching of agricultural soils in field conditions could result in increased levels of harmful elements in drainage waters being subsequently transferred to water bodies. Therefore, drainage water after irrigation events in the experiment was also studied for the target analytes. In

this way, characterising the different leaching potentials of the different pollutants is possible.

## 2 Materials and Methods

### 2.1 Experimental Design and Samples

A site located in the “Marisma de Lebrija” (Lebrija Marsh), in the estuarine region of Guadalquivir River, SW Spain (36°56' N, 6°7' W), was selected. Reclamation practises in this area were started in late 1970s by constructing till drains and introducing leaching and phosphogypsum amendment practises. Although a sizeable portion of these soils currently has a low Na saturation, the application of phosphogypsum continues to be a common practise in the region. It is usually added at a rate of 20–25 Mg ha<sup>-1</sup> every 2–3 years. After reclamation, the studied soils can be classified as Aeris Endoaquepts (Soil Survey Staff 1998). A farm was selected in the area (37°1.2' N, 6°7.4' W) for collecting surface soils (in January 2005) for the pot experiment (ca. 0–30 cm soil from ten points randomly collected throughout the plot area). A detailed description of these farm soils can be found in Delgado et al. (2006). Based on the <sup>226</sup>Ra/<sup>238</sup>U activities ratios, Abril et al. (2008) found that soils from this farm had received six typical PG rates roughly distributed in the 0–40 cm soil horizon.

A completely randomised experiment with six replications involving four treatments corresponding to different PG application rates (named C, T1, T2 and T3) has been performed. Treatment corresponded to zero (control, C, without additional PG application), one (T1), three (T2) and ten (T3) typical phosphogypsum amendment doses (20 Mg ha<sup>-1</sup>), respectively. The experiment was carried out growing one plant of tomato in a 15-L pot; each pot corresponding to one replication. Each pot contained 11.6 kg of soil and 0.06 kg of *Osmocote* fertilizer (18% N, 10% P<sub>2</sub>O<sub>5</sub>, 11% K<sub>2</sub>O). The corresponding amounts of PG were 0, 0.06, 0.18 or 0.60 kg for C, T1, T2 and T3 treatments, respectively. Addition of inert material (1/3 v/v ratio of expanded perlite) was necessary in order to favour soil structure for plant growth. PG (from a non-active stack at Huelva disposal site) and soils were air-dried and ground to pass a 2-mm screen. The concentrations of Cd, Pb, <sup>226</sup>Ra, <sup>210</sup>Po and U in the phosphogypsum, soil and

fertilizer used during these experiments were measured to characterise inputs and obtain mass inventories. Phosphate fertilizer was avoided in order to discriminate its effects from that of PG, bearing in mind its relatively high Cd and U contents.

First, the plants were transferred to pots following 1–1.5 months at seedbed. The vegetative (vegetal tissue and leaves) and the reproductive (fruit) parts were collected on June 2005, 111 days after transplanting to the pots and measured for fresh and dry weights. Samples from the vegetative part were dried at 36°C for 48 h after cutting in small pieces, and fruit samples were dried for 5 days after being grinded. The number of fruits and the percentage of ripe fruits were determined for each treatment.

The same irrigation sequence was applied to all the pots, being the total water volume 51 L approximately. Drain water samples were collected for each irrigation episode to account for all the possible terms in the pollutant balance in the pot. The concentrations of <sup>238</sup>U, <sup>226</sup>Ra and stable Pb and Cd were analysed in each drain water sample, as well as in the selected vegetal tissues and fruit samples, which were collected at the end of the experiment.

At the end of the experiment, soil samples were recovered from each plot and carefully separated from roots and inert material. Representative samples were submitted for analysis.

### 2.2 ICP-MS Analysis (Cd, Pb, U)

Collected drain water samples were filtered through 0.25 µm Milipore© filters for analyte determination in the dissolved fraction. A new dilution was required in most of the samples due to the high value of the total dissolved solid content, which were routinely higher than 0.1%. In all the cases, the sample matrix was adapted to 1% HNO<sub>3</sub>.

For vegetal tissue and fruits, a method suitable for elemental concentration by inductively coupled plasma (ICP) spectrometry was applied (Jones and Case 1990). A 0.5-g dry weight (d.w.) aliquot sample was allowed to homogenise with 5 mL of HNO<sub>3</sub> (MERCK, Suprapure grade) for 12 h. After that, the samples were acid-digested on a digestion block at 120°C for 4 h and filtered through 20–25 µm pore size filters. Finally, the sample was diluted to 25 mL with 18 MΩ deionised water (ELGA PURELAB Ultra, Vivendi Corp.).

For soils and PG, the EPA 3051 method for microwave acid digestion was used. In spite of its limitations for certain elements and samples (Florian et al. 1998), this method offers a reasonable estimation of leachable/total contents elements in soil, sediments and sludges (Link et al. 1998). In fact, it allows the analyst the calculation of leached mass instead of the total mass of the starting material to eliminate bias introduced by the variable amount of non-reactive residual material (Gelinas et al. 1998). Briefly, 0.5-g mass amount are transferred to a Teflon beaker on a hot plate and covered with 10 mL HNO<sub>3</sub> 1:1 and a watch glass. Digestion was performed being  $T < 95^{\circ}\text{C}$  for 15 min, subsequently cooled down to room temperature; additional 25 mL HNO<sub>3</sub> are added and the sample is heated under reflux for another 20 min. After cooling down, a few drops of 30% H<sub>2</sub>O<sub>2</sub> are added, the sample is heated for 2 h adding 5-mL aliquots of HNO<sub>3</sub> when necessary and it is finally submitted to filtration through 0.45  $\mu\text{m}$  pore size Millipore filter. Then, the sample is diluted with 18 M $\Omega$  deionised water until reaching a final nitric acid concentration of ca. 1%.

A quadrupole ICP-mass spectrometry (MS) instrument (Thermo X7) was used for ultra-trace analysis with a concentric (Meinhard) Quartz nebuliser. Therefore, different data quality tests were used during any instrumental running, such as replicate, matrix matching and memory effects, as well as digestion, analysis and laboratory reactive blank checking (USEPA 1994).

The suitability of the applied methods (including acid digestions) was tested through the analysis of several certified samples: a high purity standard certified reference material for trace metals in drinking water and mixed fish (IAEA-414) as biological sample. For the last sample, measured U concentration of  $0.091 \pm 0.011$  versus certified 0.084 (0.086–0.094)  $\mu\text{g kg}^{-1}$  indicated total recovery in the digestion method. For a certified sediment sample (IAEA-375) EPA 3051, acid digestion method produced only partial recovery (a yield of 0.64 for U). For soils, it is well established that the EPA 3051 method does not provide a total digestion, but it is a reference method for environmental studies that dissolves almost all the elements in the sample, including those which could be potentially realisable to water and plants.

## 2.3 Radionuclide Measurements

<sup>226</sup>Ra in PG and soil samples (air-dried and ground to pass a 0.5-mm screen) was measured by gamma spectrometry through the 352 keV  $\gamma$ -emission of <sup>214</sup>Pb (after 30 days of storage to ensure secular equilibrium in hermetic-sealed Petri dishes—to avoid <sup>222</sup>Rn losses). Measurements were carried out at the Radioisotopes Service of the University of Seville using a high purity ReGe type germanium detector.

<sup>226</sup>Ra specific activities in water samples were determined following the method described by Periañez and García-León (1993), based on the neutralisation with NH<sub>4</sub>OH, addition of BaCl<sub>2</sub> and addition of H<sub>2</sub>SO<sub>4</sub> to precipitate RaSO<sub>4</sub> and BaSO<sub>4</sub>. The samples were then filtered through Millipore<sup>R</sup> filters, 0.45  $\mu\text{m}$  pore size. Activity from the filter were measured using a LB770 low background gas flow proportional counter previously calibrated for total efficiency versus precipitate mass thickness.

For vegetative and fruit samples, 5 g of dried sample were first acid-digested in Teflon beakers with HNO<sub>3</sub> and HCl to form aqua regia and finally redissolved with 10 to 15 mL of concentrated HNO<sub>3</sub> (Martinez-Aguirre and Periañez 1998). The final solution was taken to 0.5 L with distilled water and then treated as a water sample following the method described in Periañez and García-León (1993).

Selected samples of soils and tomato fruits were submitted for <sup>238</sup>U and <sup>210</sup>Po analysis (by  $\alpha$ -spectrometry) to the Radioisotopes Service of the University of Seville. The obtained concentrations allowed the calculation of the corresponding transfer factors (TF). Transfer factors are defined as the ratio between concentration in vegetative sample and the measured concentration in soil (at the end of the experiment), both given in a dry weight basis. For soils, we defined the remaining available fractions (RAF) for a given analyte as the ratio (given in %) between the measured leachable analyte concentration at the end of the experiment (from EPA-3051 digestion method) and the initial total concentration in substrate (as defined in Section 3.1).

## 2.4 Statistical Analysis

Statistical analysis was performed by using Statgraphics plus 5.1 software.

### 3 Results and Discussion

#### 3.1 Characterisation of Soil and Inputs

All the results for soil (Table 1; 1 mg/kg of natural U is equivalent to 12.4 Bq/kg) are in quite good agreement with previous published data for samples having the same origin (Bolivar et al. 1995; El-Mrabet et al. 2003; Abril et al. 2008). From this data and the known involved masses, it is possible to estimate the whole inventory of each analyte. Table 1 includes the percentage of PG-attributable analyte to the whole inventory for each treatment. Initial available concentrations in the substrate will be defined from the analyte content in soil, PG and fertilizer and their combined mass. Special attention can be posed on the high contribution of PG (with the exception of Pb), because the highest rate amendment (treatment T3) could produce a significant enrichment of analytes in soil and, consequently, an enhanced transfer of the aforementioned pollutants to the plant.

#### 3.2 Biomass Production

Table 2 provides masses (in a fresh and dry weight basis) for the vegetative and reproductive part of tomato plants for each treatment along with the number of fruits and the percentage of ripe fruits. It is easy to see that there are no significant differences amongst treatments, and hence, the efficiency of the PG amendment practise could be reconsidered from the

agronomical point of view. However, it is necessary to remind that the control soil was previously submitted to at least six amendment treatment episodes. The experimental design do not allow distinguishing if the experimental finding is either showing that PG amendment is not efficient at all or a certain number of previous amendments are enough as to get an adequate soil productivity. The agricultural history of the area shows of course that productivity previous to PG amendment was extremely poor (de Haro 2006).

#### 3.3 Analyte Concentrations in Soils and Vegetal Samples

Measured concentrations, TF and RAF of Cd, U and Pb in soils and tomato samples are shown in Table 3.  $^{226}\text{Ra}$  was not measured in soils after the experiment because  $\gamma$ -spectrometry provides the determination of total  $^{226}\text{Ra}$ , and thus, it cannot be expected to discriminate the PG influence in  $^{226}\text{Ra}$  potential environmental availability.

Cd-RAF factor was correlated (at 90% CL,  $p=0.1$ ) with PG concentration in substrate (expressed as kg PG kg<sup>-1</sup> soil) with correlation coefficients of  $-0.912$ . For U-RAF, the correlation factor was  $-0.997$  (at 99% CL). Thus, a PG effect in reducing environmental availability (as previously defined from the EPA 3051 digestion method) can be concluded for U and Cd in soils. On the contrary, RAF factor for Pb did not show any statistically significant dependence on PG concentration.

**Table 1** Cd and Pb average concentrations and U and  $^{226}\text{Ra}$  activity concentrations in soil and phosphogypsum samples

Substrate	Cd (mg/kg)	Pb (mg/kg)	$^{226}\text{Ra}$ (Bq/kg)	U (mg/kg)	$^{210}\text{Po}$ (Bq/kg)
Soil	0.190±0.005	30±4	30±2	1.4±0.2	26±2
Phosphogypsum	2.14±0.07	2.4±0.1	630±4	15.78±0.01	631±22
Irrigation water	N.D.	(1.87±0.09)×10 <sup>-3</sup>	N.D.	(9.7±0.5)×10 <sup>-5</sup>	N.M.
Osmocote Fertilizer	0.25±0.03	0.39±0.03	N.M.	3.0±0.7	N.M.
PG (0.0 g) contribution on C (%) <sup>a</sup>	0	0	0	0	0
PG (0.06 kg) contribution on T1 (%)	5	0.05	11	6	11
PG (0.18 kg) contribution on T2 (%)	15	0.14	27	16	27
PG (0.60 kg) contribution on T3 (%)	37	0.46	55	39	55

Mean and the standard deviations of means over three to six samples

PG phosphogypsum, N.D. non-detected, N.M. non-measured

<sup>a</sup>PG contribution to initial total element inventory (estimated from measured concentrations and added masses). For all the pots, the amount of soil, total irrigation water and fertilizer were 11.6 kg, 51 L and 0.06 kg, respectively

**Table 2** Effect of PG rates on vegetative and reproductive biomass of *L. esculentum* Mill L.

	Treatment			
	C	T1	T2	T3
Vegetal tissue and leaves (g f.w.)	228±13 a	227±21 a	233±44 a	251±25 a
Reproductive part—fruits (g f.w.)	639±23 a	652±42 a	614±43 a	643±25 a
Vegetal tissue and leaves (g d.w.)	49.5±3.2 a	51.3±5.5 a	51.9±7.9 a	58.2±5.6 a
Reproductive part—fruits (g d.w.)	88.1±2.7 a	90.4±3.4 a	87.8±4.0 a	93.6±3.5 a
Number of fruits	27±4 a	29±4 a	32±4 a	39±8 a
Percentage of ripe fruits—in number (%)	66±4 a	62±4 a	62±2 a	58±5 a

Mean and standard deviation of mean ( $n=6$ ). Plants harvested on 15 June 2005, after 111 days growing in the experimental pots. Classes a, b, c,...are applied to means which are significantly different according to the Tukey's honestly significant differences procedure at the 95.0% confidence level

PG phosphogypsum

This finding agrees with the expected behaviour for Cd: Being a divalent cation, it must be mainly adsorbed on negative charged surfaces (essentially clay minerals in these soils; Choi 2006). The amount

of Cd adsorbed to soil particles must be reduced with PG amendment since it supplies Ca. Ca competes with Cd for sorption sites (Voegelin et al. 2001; Thakur et al. 2006) and, as a consequence, the amount

**Table 3** Cd, U and Pb concentrations in soils and tomato (*L. esculentum* Mill L.) samples, with TF and RAF

	Treatment			
	C	T1	T2	T3
Soil				
Cd (mg/kg d.w.)	0.191±0.016 (A)	0.198±0.008 (A)	0.191±0.013 (A)	0.228±0.007 (A)
Pb (mg/kg d.w.)	32.5±0.4 (A)	30.0±0.7 (B)	28.2±0.5 (B)	29.6±1.1 (B)
U (mg/kg d.w.)	1.63±0.06 (A)	1.64±0.03 (A)	1.72±0.11 (A)	1.78±0.06 (A)
Cd-RAF (%)	100±8	97±5	86±6	80±3
Pb-RAF (%)	99±9	92±9	87±8	94±9
U-RAF (%)	109±9	104±8	100±10	81±6
Vegetal tissue and leaves				
Cd (mg/kg d.w.)	0.62±0.04 (C)	0.62±0.03 (C)	0.92±0.07 (A)	0.87±0.05 (B)
Pb (mg/kg d.w.)	1.8±0.3 (A)	1.2±0.4 (A)	2.0±0.2 (A)	1.9±0.3 (A)
U (mg/kg d.w.)	<ICP-MS MDL <sup>b</sup>	<ICP-MS MDL	<ICP-MS MDL	<ICP-MS MDL
Cd-TF (kg/kg)	3.3±0.3	3.2±0.2	4.8±0.5	3.8±0.2
Pb-TF (kg/kg)·10 <sup>2</sup>	5.5±0.9	4.0±1.3	7.1±0.7	6.4±1.0
Reproductive part (fruits)				
Cd (mg/kg d.w.)	0.15±0.03 (C)	0.179±0.013 (C)	0.23±0.04 (B)	0.30±0.05 (A)
Pb (mg/kg d.w.)	<ICP-MS MDL <sup>b</sup>	<ICP-MS MDL	<ICP-MS MDL	<ICP-MS MDL
U (mg/kg d.w.)	<α-counting MDL <sup>b</sup>	<α-counting MDL	<α-counting MDL	0.0073±0.0019
<sup>210</sup> Po (Bq/kg d.w.) <sup>a</sup>	0.46±0.06	0.43±0.05	0.74±0.11	0.68±0.07
Cd-TF (kg/kg)	0.79±0.17	0.92±0.08	1.21±0.23	1.32±0.22
U-TF (kg/kg)·10 <sup>2</sup>	—	—	—	0.41±0.11

Concentrations correspond to mean and standard deviation of mean ( $n=6$  for biological matrices and  $n=4$  for soils). RAF and TF estimated from means, with propagated errors. <sup>226</sup>Ra concentrations in biological matrices were below the detection limit (0.6 Bq/kg) and thus, <sup>226</sup>Ra-TF<0.02. Classes A, B, C,...are applied to means which are significantly different according to the Tukey's honestly significant differences procedure at the 95.0% confidence level

<sup>a</sup><sup>210</sup>Po measured for a single sample. TF for <sup>210</sup>Po are not evaluated due to the radioactive decay chain (daughter of <sup>210</sup>Pb) and its short half-life (138.38 days)

<sup>b</sup>ICP-MS MDL were 0.5 and 0.25 mg/kg for Pb and U, respectively; α-counting MDL for U was 1.0 µg/kg

of leachable Cd decreases as total Ca supply increases. The fate of Cd when low adsorption reduction occurs must be discussed according to both TF and draining water analyses. Regarding U retention in soil, it is expected that it can be adsorbed (mainly as uranyl ion) on Fe oxides for pH around 8.5 (Wazne et al. 2003; Pett-Ridge et al. 2007). Such an association is based on the formation of ternary complexes with carbonates and oxygen in the Fe oxides (Barnett et al. 2000).

The decreasing U retention in soil can thus be explained in two ways. Increasing PG doses can lead to either higher U uptake by the plant or enhance its removal from soil with the leaching waters. The first explanation is related to plant physiology, whilst the second one could in turn be explained by an enhancement of the U soluble species with increasing masses of phosphorus added with the amendment (Vandenhove et al. 2007). Both possibilities are compatible with the fact that the main proportion of U is associated in PG to the refractory fraction (Pérez-López et al. 2007).

Previously established Ra transfer factors are of the order of 0.05 (on a dry weight basis; International Union of Radioecologists 1994). According to  $^{226}\text{Ra}$  soil contents (Table 1), it was expected to find some  $1.5 \text{ Bq kg}^{-1}$  of  $^{226}\text{Ra}$  in vegetal samples, but measured concentrations were in all the cases (non-generative part and fruit samples) below our method detection limit of  $0.6 \text{ Bq kg}^{-1}$ . Thus, only an upper limit of 0.02 can be fixed for the transfer factor of this analyte. Once again, this finding can be related to the high amount of  $\text{Ca}^{2+}$  in the studied soil.

The addition of PG doses can increase by a factor up to 2–3 the overall mass amount of  $\text{Ca}^{2+}$  available in the soil (de Haro 2006). In this way, the enhanced transfer of the nutrient (Ca) can preclude the transfer of the pollutant (Ra), which concentration belongs to the ultra-trace range. That seems in agreement with previous observations on decreasing Ra transfer to plant as Ca (+Mg) available in soil solution increases (Vandenhove et al. 2005), due to absorption antagonism between these elements.

Non-significant differences in Cd concentration between C and T1 were observed in vegetal tissue and leaves (Table 3). As previously explained, these soils accumulate the effects of approximately six amendment episodes; hence, no discrimination amongst six and seven amendment episodes can be

performed using this methodology. On the other hand, treatments T2 and T3 promoted a significant increment in Cd concentration relative to C (around 30%) and then significant higher Cd concentrations in vegetal tissue for treatments T2 and T3 and that must be reflected in the corresponding TF values. It is worthy to note that this fact is good agreement with the previously mentioned decrease in the RAF as the PG dose increases.

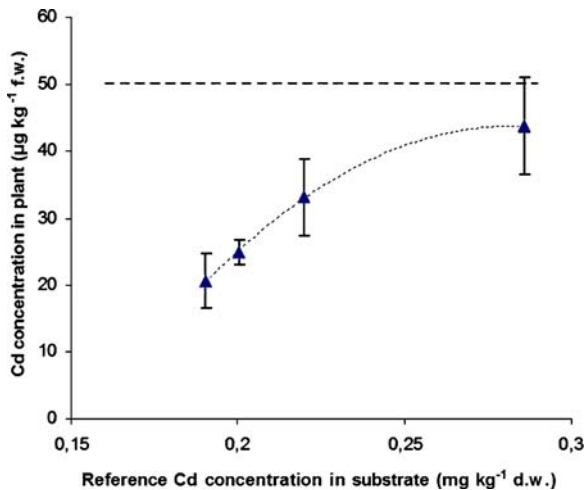
In contrast to the case of Cd, non-significant effects were observed for Pb in plant tissues, reflecting that the application of PG did not enhance Pb uptake by plants. The lack of any remarkable concentration effect is in agreement with the low Pb transfer factor described for non-edible tissues (International Union of Radioecologists 1994): That value is in agreement with the values found in this work, which are within the range 0.04–0.07. The studied soils are slightly alkaline, hence the presence of P can preclude lead absorption by plant due to carbonate and oxides formation, decreasing its availability to plants (Miretzky and Fernández-Cirelli 2008). A similar behaviour has been found for U, as it was not detected in any of the plant samples, even for the highest PG rates. Under these conditions, it is possible to reject one of the hypothesis previously established: U is not significantly concentrated in the plant as PG dose increases and simultaneously the RAF decreases; hence, it is expected that it is to be removed with leaching water. Transfer factors for Cd in vegetal tissue and leaves were two orders of magnitude higher than for Pb (Table 3).

Considering the potential use of crop residues as forage for cattle, the EU established limits for Cd and Pb in green grass ( $1$  and  $30 \text{ mg kg}^{-1}$ , respectively, assuming 12% of water content; Order 2005/87/CE from the European Commission 2005, to be reviewed to reduce Pb limit). Although Pb concentrations were well below the most conservative limit, it is interesting to note that Cd concentration were below but not far from such limit; hence, special attention should be applied if this practise was used in the future.

Only Cd has been detected in the tomato fruits. Pb and U concentrations were below their corresponding detection limits of  $0.25$  and  $0.5 \text{ } \mu\text{g kg}^{-1}$ , respectively. Overall, increasing PG rates resulted in significant increments of Cd concentrations in the sampled fruits (Table 3). The mean concentration for T3 treatment was twice the value for C, whereas Cd concentration

in T1 was not significantly different from C. Those concentrations are within the range previously published by Tsukada and Nakamura (1998). The cadmium concentration in fruit has been represented against the Cd concentration found in the whole substrate (i.e., total leachable Cd mass amount per kg of composed sample soil + PG). A significant relation (95% CL) has been found (Fig. 1) through a second-order polynomial (a linear correlation can be equally established at 95% CL with correlation coefficient 0.971).

In spite of the increase due to the PG application, the Cd concentration in fruits with T3 was still lower than the maximum admissible concentration in the EU legislation ( $50 \mu\text{g kg}^{-1}$  fresh weight; EC 1881/2006). The average values collected here (after correcting the values of Table 3 by the fresh weight/dry weight ratio that can be calculated through the data of Table 2) are 21, 25, 33 and  $42 \mu\text{g kg}^{-1}$  f.w. for treatments C, T1, T2 and T3, respectively. However, special care should be taken because these results reveal that the application of this amendment at usual rates may result in Cd concentrations in fruit above that limit in the long term. These results show a potential risk related to the Cd content in the PG amendment. Further studies focussed on the accumulation of this element in soil and plants are necessary



**Fig. 1** Dependence of Cd content in fruit (in a fresh weight basis) on the total leachable mass amount of Cd per mass unit of the mix soil/PG/fertilizer (estimated from concentrations and masses given in Table 1). Data correspond to the mean and bars to one standard deviation of mean ( $n=6$ ). Horizontal line corresponds to the upper limits established by EC 1881/2006 regulation

for an accurate estimation of the risk related to its supply not only by PG but also by P fertilizers.

Uranium concentration could be measured only in tomato fruit sample for T3 (Table 3), leading to U-TF of  $0.41 \cdot 10^{-2}$ , within the range of those reported by Tsukada and Nakamura (1998) for tomato ( $1.5 \cdot 10^{-3}$ – $2.7$ ).  $^{210}\text{Po}$  concentrations in tomato fruits were in the range  $0.43$ – $0.74 \text{ Bq kg}^{-1}$  (Table 3). Transfer factors for Cd in tomato fruits were also within the range reported in the above reference ( $2.6 \cdot 10^{-2}$ – $2.0$ ).

Finally, it is worth to note the different transfer factors (Table 3) to the vegetative organs of the plant, which can be explained by the different element mobility to the organs. Overall, the Cd concentration in untreated plants was four times higher in vegetative plant tissues than in fruits, which indicates that mobility to fruits was lower than to other organs. This lower mobility to fruits can be explained, as for other nutrients and contaminants, by the lower transpiration rate of fruits when compared with leaves. The Cd transport within the plants should be affected in tomato in a similar way to that already published for other species (Chen et al. 2007). In case the movement is limited within the phloem, the driving force of Cd transference must be related to the movement through the xylem, which is dependent on the transpiration rate. Consequently, those parts having a highest transpiration rate (the leaves) should be the most efficient Cd accumulators. This can explain the smaller TF of fruits relative to other organs.

### 3.4 Drainage Water

The overall released masses of Cd and Pb in drainage water showed a similar behaviour (Table 4). It is necessary to bear in mind that this experimental setup cannot reproduce the environmental conditions of soil structure and draining conditions (drills formation, appearing of preferential leaching ways etc.). The data set that was shown must therefore be understood from the point of view of the corresponding relative contribution to the mass balances. As PG does not significantly increase the total Pb inventory (less than 0.5% for T3 treatment), this effect has to be explained in terms of competition with  $\text{Ca}^{2+}$  (added with PG) for sorption sites and by the increased volumes of drainage water.

As previously shown, Cd-RAF decreases as the PG dose increases. TF in both tissue and fruit and total



**Table 4** Overall drained masses for the studied analytes

	Treatment			
	C	T1	T2	T3
Cd ( $\mu\text{g}$ )	4.3 $\pm$ 0.7 (C)	31.0 $\pm$ 1.2 (A)	20.7 $\pm$ 0.3 (B)	5.3 $\pm$ 0.2 (C)
Pb ( $\mu\text{g}$ )	8.9 $\pm$ 0.2 (C)	87.0 $\pm$ 0.8 (A)	51.0 $\pm$ 0.9 (B)	6.23 $\pm$ 0.12 (D)
Ra (mBq)	280 $\pm$ 12 (C)	310 $\pm$ 12 (B)	330 $\pm$ 14 (A)	219 $\pm$ 14 (D)
U ( $\mu\text{g}$ )	27.3 $\pm$ 0.2 (D)	36.7 $\pm$ 0.3 (B)	42.8 $\pm$ 0.4 (A)	34.3 $\pm$ 0.3 (C)

Uncertainties refer to the average standard deviation of mean ( $n=6$ ). Classes A, B, C,...are applied to means which are significantly different according to the Tukey's honestly significant differences procedure at the 95.0% confidence level

leached mass also increase as PG dose does. That suggests that Cd is partially removed from soil (and PG) and transferred to both the plant and the draining water. Actually, some 20% of Cd present in PG seems to be associated to the oxidisable fraction (Pérez-López et al. 2007). Under these conditions, Cd results readily soluble (Holland and Turekian 2005), so it can be easily transferred to plants after chelation in the presence of humic acids (Wolterbeek et al. 1988) or released with leaching water after dissolution from PG to soil pore water. Regarding lead, no effect associated to PG can be deduced as it is not added with it, but it has been found that increasing PG dose leads (as found for Cd) to a higher leaching rate. A possibility to explain this effect is that the addition of PG increases the available mass amount of P in soil. Then, lead remains fixed to soil, which is mechanically removed during irrigation. The general observed behaviour for all the considered analytes in this work can be summarised as a general leaching increase for small doses and a drastic decrease for the highest dose. This result seems to be in disagreement with that published by Campbell et al. (2005), as analytes leaching rates clearly decreased as a consequence of PG amendment. However, it is necessary to bear in mind the differences amongst the conditions of that experimental setup and that other shown in this work: Soil columns were used instead of free pots, and the amendment was applied in liquid form.

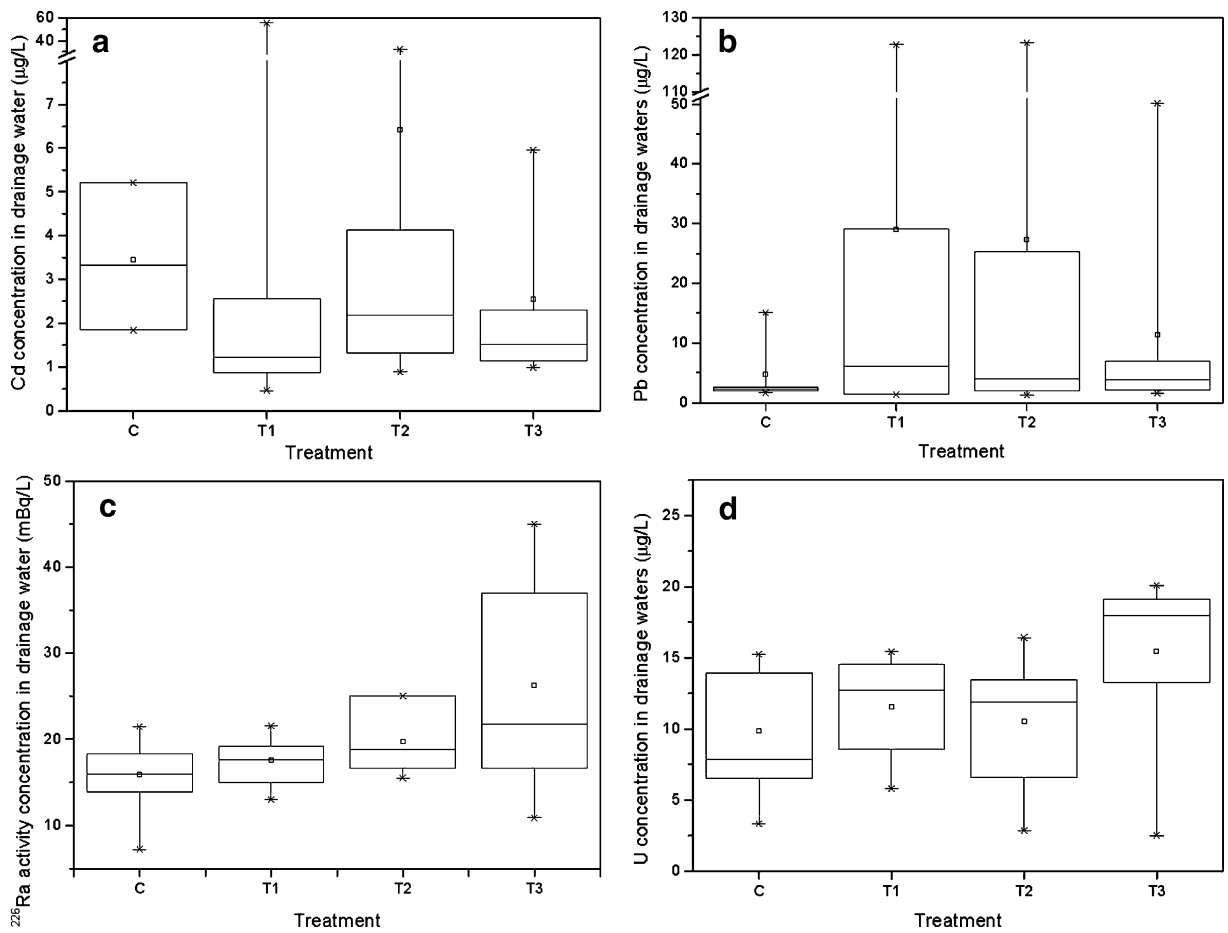
Changes in U concentration in draining water remained within 30% of the initial total available value (concentration in C). Finally, the observed pattern for  $^{226}\text{Ra}$  was quite similar to that of U, although with lower values of draining efficiencies.

The concentrations of these analytes in the dissolved fraction of drainage waters during the considered irrigation events are shown in Fig. 2a–d

as box–whisker plots. It is interesting to note that no systematic differences for average concentrations have been found for Cd and Pb between treatments. However, this is due to the very large statistical dispersion of concentrations during the irrigation events; this way, the average concentration seems to be only a qualitative indicator as its statistical significance is small.

On the other hand, average concentrations in drainage waters are significantly higher for  $^{226}\text{Ra}$  and U when the T3 treatment is applied. This fact is in agreement with the decreased RFA for this treatment, and it seems to indicate that higher involved masses of  $\text{Ca}^{2+}$  preclude both Ra absorption by plant and its retention in soil. The  $^{226}\text{Ra}$  activity concentrations for control treatment are more than twice those found, on an average basis, for drainage waters coming from an experimental farm where PG was also applied for soil amendment (El-Mrabet et al. 2003). Regarding U, it can be drawn that high amounts of PG enhance its solubility with P complexes (Bostick et al. 2002) and, as a consequence, leaching is more efficient once provided the low bioaccumulation. It has been also considered the possibility that due to physical effects on the soil itself, different applications of PG could lead to different efficiencies in particulate matter drifting with the leaching water. As a consequence, even undissolved elements could be leached as suspended matter. However, our results show that the ratio drained mass/drainage water is almost constant for all the applied PG treatments. Hence, such a possibility has been discarded.

A possible concern could thus arise, i.e. if a higher amendment efficiency (from the draining point of view) could lead to a higher release of toxic elements. This could be a problem from a



**Fig. 2** Box-whisker plots for the detected concentrations in drainage waters. **a** Cd. **b** Pb. **c** <sup>226</sup>Ra. **d** U

water management point of view. However, the proportion of mass/activity introduced in the system which is subsequently released with the drain water (as can be seen in Table 4; see Section 3.5 for details) is very small, producing concentrations and activity concentrations several orders of magnitude below the corresponding regulation limits. Indeed, such proportions are commonly smaller than 1%, as should be expected bearing in mind the previously shown results.

### 3.5 Mass Fractions

Table 5 shows the mass fractions (with respect to total initial content) for Cd, Pb, <sup>210</sup>Po and U in drainage water, vegetal tissue and fruit. These results show that essentially all the analytes are retained within the soil substrate, with negligible or little transference to the

plant and fruits. Up to 2.5% of cadmium involved in the experiment is transferred to the plant system (for T2), in agreement with the previously mentioned higher Cd-TF. Furthermore, about 1.4–1.7% of cadmium is transferred to the edible part of the plant. Nevertheless, these percentages applied only for our pot experiment, since under field conditions, the root systems roughly explore only 1/3 of the soil volume (at typical root depths).

Regarding the drained mass fraction, less than 1% of each analyte was released with the draining water. It is interesting to see that a general trend Cd ~ Pb > U is apparent for drained mass. Uranyl ion can be dissolved as carbonate complexes. Opposed to uranium, lead has a high affinity for particulate material (Rios-Arana et al. 2004). Thus, the low drained percentage found in this study agrees with such behaviour.

**Table 5** Mass fractions (with respect to the reference inventory) of Cd, Pb, U and  $^{210}\text{Po}$  for tomato plants and drainage water in the pot system

	Treatment			
	C	T1	T2	T3
<b>Cd</b>				
Reference inventory (mg)	2.22±0.06	2.35±0.06	2.60±0.06	3.50±0.07
Reproductive part—fruits (%)	0.61±0.12	0.67±0.05	0.77±0.14	0.81±0.14
Vegetal tissue and leaves (%)	1.37±0.10	1.55±0.09	1.72±0.16	1.46±0.10
Drainage water (%)	0.19±0.03	1.32±0.06	0.79±0.02	0.15±0.01
Remaining in soil or roots (%)	97.83±0.16	96.46±0.12	96.72±0.21	97.58±0.17
<b>Pb</b>				
Reference inventory (mg)	380±30	380±30	380±30	380±30
Vegetal tissue and leaves (%)·10 <sup>2</sup>	2.3±0.4	1.6±0.6	2.6±0.3	2.9±0.5
Drainage water (%)·10 <sup>2</sup>	0.23±0.02	2.3±0.2	1.34±0.11	0.16±0.01
Remaining in soil or roots (%)	99.975±0.004	99.961±0.006	99.961±0.003	99.969±0.005
<b>U</b>				
Reference inventory (mg)	17.5±1.0	18.4±1.0	20.3±1.0	26.1±1.0
Reproductive part—fruits (%)·10 <sup>2</sup>	N.C.	N.C.	N.C.	0.26±0.07
Drainage water (%)	0.16±0.01	0.20±0.01	0.21±0.01	0.13±0.01
Remaining in soil or roots (%)	≥99.84±0.01	≥99.80±0.01	≥99.79±0.01	≥99.87±0.01
<b><math>^{210}\text{Po}^a</math></b>				
Reference inventory (Bq)	300±23	339±23	415±24	680±27
Reproductive part—fruits (%)·10 <sup>2</sup>	1.4±0.2	1.1±0.2	1.5±0.2	0.95±0.11
Remaining in soil or roots (%)	≥99.986±0.002	≥99.989±0.002	≥99.985±0.002	≥99.991±0.0011

Reference inventories correspond to initial inventory in soil plus controlled inputs (Table 1). Mass balances derived from Tables 2, 3 and 4

N.C. not calculated

<sup>a</sup> Results for  $^{210}\text{Po}$  are only orientative due to the radioactive decay chain (daughter of  $^{210}\text{Pb}$ ) and its short half-live (138.38 days)

## 4 Conclusions

The presented results show that the application of phosphogypsum as a calcium amendment for agriculture purposes could lead to some accumulation of cadmium on both plant tissue and edible parts (fruit). This effect seems to be related with a mainly phloem-driven Cd exchange within the plant. Retention of Cd on soil decreases, possibly as a consequence of competition with Ca for sorption sites. On the contrary, most of uranium, polonium and lead are retained into the soil; thus, a scarce evacuation through leachates released during the irrigation events occurs. In this way, it results clear that the evacuation of irrigation water does not implicate a problem from the point of view of water management. In fact, their released masses are commonly less than 1% of mass available for leaching and absorption by plant. The high proportion of cadmium transferred to the plant

(about 2.5% of the total mass in pot conditions) has resulted to be independent on the intensity of the applied treatment within the range of our experiment setup. This fact suggests that the main mechanism for Cd transference to plant must be the chelation by humic acids in soil. Special care should be taken if vegetable tissue is used as forage crop for cattle as well as with the produced fruit, as the experiment shows that long-term administration of PG could lead to cadmium concentrations near the acceptance limits provided by European regulations.

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