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Natural Radionuclides, Rare Earths and Heavy Metals Transferred to the Wild Vegetation Covering a Phosphogypsum Stockpile at Barreiro, Portugal

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Abstract In Portugal, the industrial production of phosphate fertilizers, has been dealing with a specific raw material—north African phosphate rock—with a high content of trace metals and natural radioactive elements mainly from the ^{238}U decay series. A disabled phosphate plant located in the vicinity of the river Tejo estuary has produced phosphoric acid for several decades (1950–1989) and dumped tons of phosphogypsum (PG) on retention lagoons, formerly decanted and deposited into a stockpile. This paper deals with the assessment of radionuclides, rare earth elements (REEs) and heavy metals transfer to plants (fam. Plantaginaceae, *Plantago* sp.) and mosses (fam. Bryaceae, *Bryum* sp.) growing naturally on the PG pile. In *Plantago* sp., the concentration ratio (CR, plant tissue/PG) was 0.187 for ^{226}Ra and 0.293 for ^{210}Pb. The translocation factor (TF, aerial parts/roots) was 0.781 for ^{226}Ra and 0.361 for ^{210}Pb. In contradiction to the high CR, the leachability of ^{226}Ra from PG was low, lower than 2%. The results confirmed the role of mosses as biomonitors. A high quantity of contaminants collected in its biomass confirmed the hypothesis of their significant transport by air and rain water. High concentrations of heavy metals (As, Cd, Zn, W) in samples collected on the stockpile are an evidence of their transport from former industrial zones in the surroundings and present even more important risk for public health and environment than natural radionuclides and REEs from the PG stockpile.

Keywords Heavy metals · Leachability · *Bryum* sp. · Phosphogypsum · *Plantago* sp. · Radium · Rare earth elements

1 Introduction

Highly soluble superphosphates are manufactured by the so-called wet process, where the first step is the reaction of sulphur acid with finely ground phosphate rock to produce phosphoric acid (Luther et al. 1993). The insoluble byproduct of this reaction is a slurry designated as phosphogypsum (PG). Starting in 1950, a Portuguese phosphate plant located in the vicinity of the river Tejo estuary has produced phosphoric acid and dumped tons of PG in sludge ponds (Carvalho 1995). From 1979 until the plant closure, the decanted PG was stockpiled over a selected area of the close shore line, on the northeastern extreme of the Barreiro peninsula, covering ancient salt marshes and salt reservoirs, its thickness reaching approximately 6 m (SIMARSUL 2006).

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This disabled industry was dealing with a specific raw material—North African phosphate rock—with a high content of trace metals and natural radioactive elements mainly from the ^{238}U decay series (Carvalho 1995). By the end of the industrial activity, circa 1.1 × 10^6 m^3 of PG were covering an area of 1.0 × 10^5 m^2 (SIMARSUL 2006).

For being an industrial waste with an enhanced content of natural radionuclides, PG is also classified as a naturally occurring radioactive material (NORM). During the phosphoric acid production, the radioactive equilibrium between the ^{238}U and its daughters (^{226}Ra, ^{210}Pb) is broken and each radionuclide is distributed differently depending of its solubility, being most of the radium transferred to the PG and the major amounts of uranium migrate into phosphoric acid (El Afifi et al. 2009; Renteria-Villalobos et al. 2010).

Apposite description of ^{226}Ra association to mineral phase could be found in Wiramanaden et al. (2015). In accordance with them, ^{226}Ra could belong to one of the three groups of potential associations to minerals: (a) strong = irreversible coprecipitation, (b) intermediate = potentially irreversible surface adsorption, (c) weak = superficial reversible association (e.g., ion exchange). Since the solubility of gypsum is not negligible (pKs = 4.62) ^{226}Ra could be released from this mineral and afterwards associate in another form. Behaviour of ^{226}Ra, its adsorption and mobility, is strongly dependent on concentrations of other bivalent metals, mainly alkaline earth metals. Moreover, Lysandrou and Pashalidis (2008) showed that mobility of ^{226}Ra decreases with the age of PG tailing.

Some phosphate minerals are usually rich in REEs: xenotime, monazite and apatite (Tyler 2004). Apart from organic- and iron mineral-rich soils, topsoil is usually depleted of REEs, mainly of light REEs (LREEs) than heavy REEs (HREEs). It occurs because of weathering of topsoil and solubility of phosphate minerals. REEs are consequently accumulated in lower horizons.

Mobility plays a key role in the availability of elements for plants. The extraction of an available fraction of ^{226}Ra in PG using a single-step dilution with HCl was applied by Sutherland (2002), showing similar results as those obtained with the Community Bureau of Reference (BCR) standard method. Since plants have their own strategy to reach nutrients from soil, extraction of ^{226}Ra with citric acid is an option. Citric acid belongs among the root exudates which are able to complex bivalent elements in soil and so enhance their solubility in soil solution. The effect on the increase of ^{226}Ra concentration in plant biomass by the application of citric acid was described in Mihalik et al. (2011).

Mosses are known as important bioindicators of air and surface water contamination which is related to their capability of absorbing nutrients through the entire surface of their body (Glime 2007). High cation exchange capacity on the surface of moss and low selectivity of the process of nutrients uptake leads to accumulation of heavy metals (Brown 1984; Brown and Bates 1990).

The Barreiro PG stockpile stands as a perfect natural laboratory to study the migration of trace metals and natural radionuclides onto the wild vegetation that in the course of time has covered it. Herbaceous plants and mosses growing spontaneously might reveal the bioavailability of the radionuclides and metals in the PG matrix. The purpose of this work is to quantify the substrate to plant transfer of such elements in these two different taxonomic groups. In a wider environmental context, those accumulated elements in plants and mosses might be spread along herbivorous trophic chains (Borylo et al. 2013), whether the PG stockpile is merely de-classified as non-hazardous and remains in place, or intended to be used as soil nutrient stuff and for the increase of water holding capacity (Abril et al. 2008; Enamorado et al. 2009). Due to the environmental mobility of radium and its capacity to be accumulated by the vegetation (Fesenko et al. 2014), a special attention was devoted to ^{226}Ra in the PG matrix, by performing specific extraction procedures with leaching agents.

2 Material and Methods

2.1 Sampling

Herbaceous plants (family Plantaginaceae, *Plantago* sp.) and mosses (family Bryaceae, *Bryum* sp.) were collected in separate 4-m^2 areas of the PG stockpile (Fig. 1). *Plantago* plants were extracted whole (aerial parts and roots) with the help of a pickaxe and the PG substrate from root insertion layer was collected separately. Mosses covered the sampling area like carpets attached to the surface of PG. Fragments of the moss carpet with attached underlying PG litter were collected with a spatula. Collected materials of each type (plants, substrate and moss carpet fragments) weighed roughly 1.5 kg.

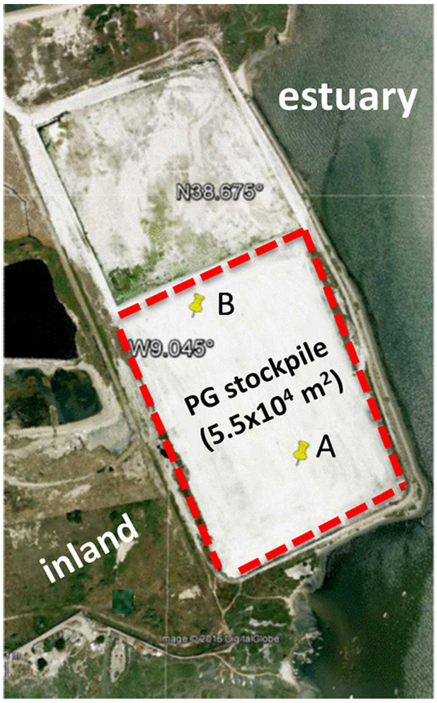

Fig. 1 Google maps view of the Barreiro PG stockpile showing the sampling spots for *Plantago* sp. (*A*) and *Bryum* sp. (*B*)

2.2 Sample Processing

Roots (≈500 g, wet mass) and aerial parts (≈1000 g, wet mass) of five *Plantago* plants were separated and washed in water. The *Bryum* carpet fragments were released of the attached PG litter which was recovered for former treatment. Moss fragments with few litter grains trapped in the vegetative structure, were hand crushed and jet washed inside a nylon mesh (1 mm) envelope for final removal of attached PG. Plants and moss samples were dried at 60 °C and homogenized in a knife mill (Retsch, Grindomix GM 200).

Phosphogypsum from the rhizosphere of *Plantago* sp. plants and detached from the *Bryum* sp. moss carpet was crushed in a porcelain mortar, dried at 60 °C and sieved for the separation and analysis of the grain size fraction <1 mm.

2.3 Analysis of Natural Radionuclides by Gamma Spectrometry

Natural radionuclides were analysed by gamma spectrometry. *Plantago* sp. (64 g roots; 46 g aerial parts) and *Bryum* sp. (45 g) subsamples were packed in polypropylene flasks. PG subsamples (10 g) were kept in Millipore Petri dishes (Ø 47 mm). Containers were closed and sealed with PVC glue to prevent the leakage of ^{222}Rn resulting from ^{226}Ra decay. Measurements were made after 1 month, the time lapse needed for the ingrowth of decay products reaching radioactive equilibrium in the sample matrix.

A 50% relative efficiency broad energy HPGe detector (Canberra BEGe model BE5030), with an active volume of 150 cm^3 and a carbon window was used for the gamma spectrometry measurements. The detector is shielded from the environmental radioactive background by a lead shield with copper and tin lining. Standard nuclear electronics was used and the software Genie 2000 (version 3.0) was employed for the data acquisition and spectral analysis. The detection efficiency was determined using NIST-traceable multi-gamma radioactive standards (Eckert & Ziegler Isotope Products) with an energy range from 46.5 to 1836 keV and customized in a water-equivalent epoxy resin matrix (density of 1.15 g cm^{-3}) to exactly reproduce the geometries of the samples. GESPECOR software (version 4.2) was used to correct for matrix (self-attenuation) and coincidence summing effects, as well as to calculate the efficiency transfer factors from the calibration geometry to the measurement geometry (whenever needed). The acquisition time was set to 24 h and the photopeaks used for the activity determination were: 46.5 keV for ^{210}Pb; 295.2, 351.9and 609.3 keV for ^{226}Ra and 338.3, 911.2and 968.9 keV for ^{228}Ra. The ^{238}U activity was calculated through the ^{234}Th photopeaks (62.3 and 92.5 keV) by assuming secular equilibrium. The stability of the system (activity, FWHM, centroid) was checked at least once a week with a ^{152}Eu certified point source. External QC was assured through the participation in intercomparison exercises organized by international organizations (Merešová et al. 2012). This technique is accredited according to the ISO/IEC 17025:2005 standards.

2.4 Leachability of ^{226}Ra in the PG Matrix

The leachability of ^{226}Ra was examined in two separate extraction procedures using different leaching agents: HCl and citric acid with solid/liquid ratios of 1:5 and 1:10, respectively. The extraction with citric acid was an attempt to mimic the plant ability to dissolve elements in soil by root exudation of low molecular organic acids (Prieto et al. 2013). To examine the pH influence, extractions were done using different concentrations of HCl (Sutherland 2002, El-Reefy et al. 2007).

In one procedure, 10 g PG subsamples were treated with 0.1, 0.5and 1 mol L^{-1} HCl for 3 h. In another procedure, 5 g PG subsamples were treated with 1 and 0.5 mmol L^{-1} solutions of citric acid during 24 h. After the extractions, the PG solutions were centrifuged at 6000 rpm for 15 min. Aliquots of supernatants (10 mL) were mixed with a scintillation cocktail (Opti-Fluor O; PerkinElmer) and stocked for 1 month. The activity of ^{226}Ra was determined by liquid scintillation counting (Tri-Carb 3170TR/SL equipped with alpha/beta discriminator; PerkinElmer).

The pH of PG from sampling points A and B was measured using four 5 g untreated PG subsamples, dried at 104 °C for 24 h and then immersed in a 0.01 mol L^{-1} $CaCl_2$ solution (solid/liquid ratio, 1:10) (Houba et al. 2000). After 3 h of shaking and 1 h of settling, the pH of PG solution was determined with a glass electrode pH meter (pH 211, Hanna instruments) duly calibrated.

2.5 Analysis of Heavy Metals and Rare Earth Elements

The chemical analysis of plants, mosses and PG was performed by instrumental neutron activation analysis (INAA), in order to obtain the total concentration of 21 chemical elements (Sc, Cr, Co, Zn, As, Br, Rb, Zr, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Hf, Ta, W, Th and U). Two reference materials were used, namely soils GSS-4 and GSS-5 from the Institute of Geophysical and Geochemical Prospecting (IGGE). Reference values were taken from data tabulated by Govindaraju (1994). The long irradiations (6 h) of samples and standards were carried out in the core grid of the Portuguese Research Reactor (CTN, RPI) at a thermal flux of 3.96×10^{12} n cm^{-2} s^{-1}, $\varphi_{thi}/\varphi_{epi} = 96.8$ and $\varphi_{th}/\varphi_{fast} = 29.8$, according to Dung et al. (2010) and Fernandes et al. (2010). Two aliquots of each standard were used for internal calibration, and standard checks were performed (QA/QC). A Gamma Analyst Integrated Spectrometer (Canberra), with a broad energy Ge (BEGe) detector (model BE3830) connected to a DSA2000 (Canberra) multichannel analyser, was used. Corrections for the spectral interference from U fission products in the determination of Ba, REE and Zr were made. Details of the analytical method may be found elsewhere in Prudêncio et al. (1986), Gouveia et al. (1992) and Prudêncio (2009). Relative precision and accuracy are in general within 5%, and occasionally within 10%.

2.6 Concentration Ratio (C_r), Translocation Factor (f_{tr}) and Enrichment Factor (EF)

In rooted plants like *Plantago* sp., there is a flux of mineral nutrients and non-essential cations taken from the soil or an artificial substrate as is the case of PG. The ratio between the activity concentrations of natural radionuclides in the dry plant tissue (c_p) and in the substrate (c_s) was used to calculate a concentration ratio ($C_r = \frac{c_p}{c_s}$), which is a widely used parameter in radioecology (Fesenko et al. 2009). On the other hand, the flux from roots to aerial parts may be represented by a translocation factor (f_{tr}), here defined by the quotient of the concentrations of any element in aerial parts (c_{ap}) and roots (c_{rt}), expressed by $f_{tr} = \frac{c_{ap}}{c_{rt}}$.

An enrichment factor (EF) normalized by scandium (Sc) was estimated in order to distinguish sources of contamination of various elements in plants and mosses. Sc was used because it rarely enters the atmospheric aerosol from anthropogenic sources (Klos et al. 2011). The EF values >10 signal that the origin of elements is in remote sources. Values about 1 are typical for elements originated in the local soil. The rationale of EF goes as $\mathrm{EF} = \frac{\left(\frac{c_x}{c_{Sc}}\right)_v}{\left(\frac{c_x}{c_{Sc}}\right)_s}$, where c_x is the concentration of element x and c_{Sc} is the concentration of scandium in the vegetation (v) and the PG substrate (s), respectively.

3 Results and Discussion

3.1 Bioavailable Fraction of ^{226}Ra

The pH of the PG samples taken from the sampling points A and B was 5.3 ± 0.1 and 4.0 ± 0.1 (0.01 mol L^{-1} $CaCl_2$), respectively. This acidity is a consequence of the acidification of phosphates and remains of acidic oxides (e.g., P_2O_5) during PG production. Leaching experiments showed that only 2.2% of ^{226}Ra was released even if 1 mol L^{-1} HCl was applied (Table 1).

Extraction by citric acid showed that approximately 1.6% of ^{226}Ra is available to plants growing on PG site. The citric acid solution represents its extremely high concentration in natural conditions (Jones 1998). The higher concentration of citric acid would release probably more ^{226}Ra as demonstrated in Prieto et al. (2013).

Table 1 Quantities of ^{226}Ra released from PG (Barreiro) by leaching agents HCl and citric acid. The original activity concentration of ^{226}Ra in PG was 600 ± 40 Bq kg^{-1}, dry weight

	Conc. of extraction agent (mol L^{-1})	Activity conc. of ^{226}Ra in eluates (Bq L^{-1})	Activity conc. related to 1 kg of PG (Bq kg^{-1})	Extraction efficiency (%)
HCl	1	2.6 ± 0.4	13 ± 2	2.2
	0.5	0.48 ± 0.21	2.3 ± 1.0	0.38
	0.1	<0.27	<1.4	<0.23
Citric acid	1×10^{-3}	0.80 ± 0.24	7.9 ± 2.4	1.3
	0.5×10^{-3}	0.97 ± 0.26	9.6 ± 2.6	1.6

Therein it was shown that low concentration of citric acid release the highest quantity of radium in the first day after its application. Moreover, solubility of ^{226}Ra is enhanced in acidic conditions.

The addition of 0.1 mol L^{-1} HCl, which simulates human digestion (Selinus et al. 2013), released a very low quantity of ^{226}Ra. A higher concentration of 0.5 mol L^{-1} HCl was supposed to release the bioavailable fraction as demonstrated in Sutherland (2002). The quantity of ^{226}Ra released by 5 mmol L^{-1} citric acid was between those released with 0.5 and 1 mol L^{-1} HCl. It means that the plant strategy to obtain nutrients through their complexation is very effective and could cover all bioavailable fractions.

In comparison with Brazilian PG (Santos et al. 2006) which contained up to 18% of bioavailable ^{226}Ra, the PG from the Barreiro stockpile seems to be safer for application in agriculture or industry.

These results show that a very small amount of ^{226}Ra is leachable even if a strong acid and complexing agent was used. This confirms the assumption that the majority of ^{226}Ra is bounded strongly in a crystalline matrix and only a small amount is adsorbed on the mineral surface or in an ion-exchangeable form. The low bioavailability of ^{226}Ra from PG is also referred by other authors. El-Reefy et al. (2007) reached similar results applying 0.5–1 mol L^{-1} HCl as a leaching agent. Using ethylenediaminetetraacetic acid (EDTA) (Saueia et al. 2013), the quantity of bioavailable ^{226}Ra was also very low (2%).

3.2 Uptake of Radionuclides, REEs and Heavy Metals by *Plantago* sp. and *Bryum* sp.

The results obtained with *Bryum* sp. confirmed the ability of mosses to accumulate metals in their tissues. Radionuclides ^{226}Ra and ^{210}Pb (Table 2), reached several fold higher concentrations in biomass than in the PG substrate. Compared to mosses from natural soils in Canada, Greece and Balkan countries (Fesenko et al. 2014), ^{226}Ra concentrations are significantly enhanced in *Bryum* sp. from the Barreiro PG tailing. As for REEs (Table 3), concentrations also reached several fold higher values in biomass than in the substrate, which is probably due to ability of hyalocysts and pores on the moss leaves to trap small particles containing radionuclides and REEs (Calabrese and D'Alessandro 2015). Such a possibility is reinforced by the observations of Rutherford et al. (1996) showing that the finest fraction of PG (<20 μm) is enriched in ^{226}Ra and ^{210}Pb. The sources of the elements caught in their tissues are mainly air deposit and elements dissolved in surficial water resulting from rainfall on the PG stockpile. Since mosses absorb nutrients through the entire surface of their body, they are important indicators of contaminant mobility in the environment. Low selectivity of nutrient uptake through ion exchange may contribute to the accumulation of heavy metals (Glime 2007).

Table 2 Activity concentrations (Bq kg^{-1}, dry weight) of natural radionuclides in *Plantago* sp., *Bryum* sp. and respective PG substrate. The variation intervals correspond to the expanded uncertainty of measurement ($k = 2$)

Vegetation component	Type of sample	^{235}U	^{226}Ra	^{210}Pb	^{228}Ra	^{40}K
Plantago sp.	PG Substrate	13 ± 10	740 ± 41	870 ± 130	n.d.	93 ± 43
	Roots	n.d.	140 ± 10	260 ± 41	3.6 ± 2.0	280 ± 37
	Aerial parts	n.d.	110 ± 5	92 ± 14	n.d.	351 ± 33
Bryum sp.	PG substrate	18 ± 4	890 ± 37	1000 ± 132	8.9 ± 1.0	38 ± 12
	Moss tissues	66 ± 14	2900 ± 200	4000 ± 660	36 ± 9	n.d.

n.d. not detected

Table 3 Concentrations of elements in *Plantago* sp., *Bryum* sp. and respective PG substrate, detected by INAA (concentration in mg kg^{-1}, dry weight)

	PG (*Plantago* substrate)	Aerial parts	Roots	PG (*Bryum* substrate)	*Bryum* sp.
Sc	0.658	0.0363	0.0954	0.545	2.72
Cr	11.8	5.14	7.79	13.6	88.1
Co	0.154	0.521	0.566	0.202	1.16
Zn	17.7	54.2	359	18	197
As	1.12	2.05	0.674	1.54	6.64
Br	2.35	390	53.1	0.906	24.6
Rb	4.42	11.4	10.7	4.14	9.46
Zr	25.2	18.1	13.6	58.1	284
La	74.5	3.53	8.82	77.5	387
Ce	29.5	1.45	3.77	34.7	187
Nd	50.4	2.6	6.36	51.2	267
Sm	11	0.5	1.29	11.2	54.5
Eu	2.69	0.126	0.315	2.83	14
Tb	1.95	0.0876	0.221	1.91	9.61
Yb	7.68	0.393	0.969	8.37	41.4
Lu	1.18	0.0564	0.141	1.1	5.64
Hf	0.241	0.0186	0.0385	0.46	1.82
Ta	0.063	0.03	0.043	0.0771	0.244
W	0.331	1.07	0.593	0.127	1.46
Th	2.01	0.0974	0.243	1.98	9.32
U	13.7	1.11	1.39	8.93	53.8

In the vascular plant *Plantago* sp. the REEs concentrations are higher in roots than in the aboveground biomass (Table 3). This finding partly agrees with the results from Tyler (2004) but opposite to it the concentrations of individual elements are relatively higher and the difference between their concentrations in roots and aboveground biomass is not very distinctive. Tyler (2004) reported about the order in which the concentration of LREEs in plant biomass decrease. These results showed an inverse order where La reached the highest concentration and Ce the lowest one. Generally, REEs are poorly bioavailable for plants.

Plantago is a ruderal metallophyte genus able to adapt to hostile conditions (Nagorska-Socha et al. 2013). Shtangeeva et al. (2006) showed the ability of *Plantago major* to accumulate uranium and thorium from soil. They showed that uptake of certain elements influences the uptake of others. When uranium and thorium were applied into soil in mobile forms, their concentrations in leaves increased more than 100 times.

The concentrations of ^{226}Ra determined in *Plantago* sp. plants from Barreiro PG tailing are two orders of magnitude higher than those measured in grasses from natural soils (Fesenko et al. 2014), but lay in the range of the higher concentrations determined in pioneer plants in other NORM-contaminated sites (Soudek et al. 2007). The C_r of ^{226}Ra and ^{210}Pb in the aerial parts reached 0.15 and 0.11, respectively. Any comparison of these results with others being published should be taken with caution mainly due to the artificial origin of the substrates. PG substrates may differ due to differences in the original phosphate rock and also to differences in the industrial processes the raw material went through. Considering that the bioavailable fraction of the ^{226}Ra from the Barreiro PG tailing is only 2%, the major portion of ^{226}Ra in *Plantago* sp. plants should be airborne which was not eliminated despite the washing of leaves. Mineral ions descending onto leaves in rain may slowly penetrate stomata and cuticle (Epstein 1972) and in that manner leaf uptake could play also an important role (Prasad 2008). Moreover, this explanation is supported by the high concentration of ^{226}Ra in mosses.

Th f_{tr} in *Plantago* sp. was 0.781 for ^{226}Ra and 0.361 for ^{210}Pb. The ^{226}Ra uptake and translocation is probably related to the participation of calcium ion channels within the plant cells and a certain role is taken by chelating agents (Gunn and Mistry 1970). Moreover, there is still some possibility that ^{226}Ra passed into plants through leaves when they were immersed in surface water staying after rain on PG stock pile (Prasad 2008). A relatively low translocation of ^{210}Pb into the green aerial parts is consistent with an adaptation to toxicity, once lead affects several aspects of plant physiology including photosynthesis (Sharma and Dubey 2005).

In comparison to the results reported by Shtangeeva et al. (2006) (supplement), the *Plantago* plants growing on PG stock pile of Barreiro reached slightly higher C_r values for heavy metals and Ta than those growing on ferric podzol soil. For other REEs excluding Ta the C_r in the roots is markedly higher in the Barreiro PG than in podzol soil tested by Shtangeeva et al. (2006) but other values are quite similar.

Some elements, namely As, Br, Rb and Zr reached higher concentrations in the aerial organs than in the roots. For As, it is typical that the highest concentration is in the root tissue excluding the case of hyperaccumulator species (Zhao et al. 2009). The concentration of Br in the *Plantago* sp. leaves is remarkably

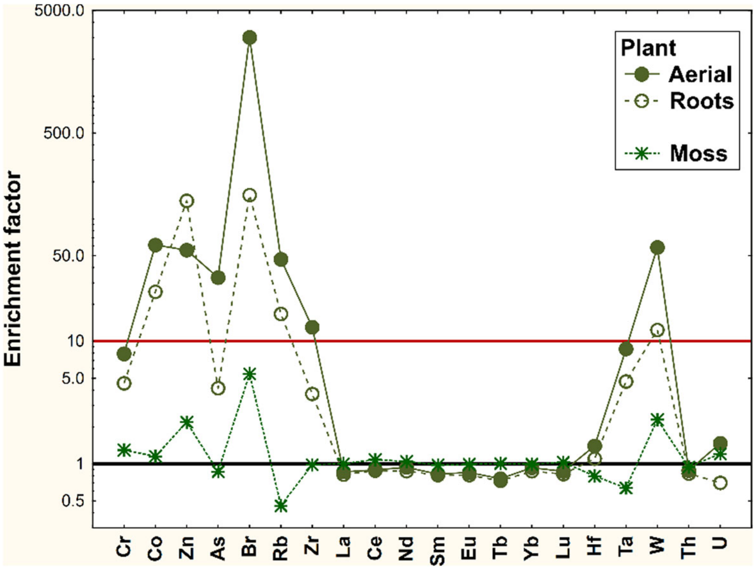

Fig. 2 The enrichment factors of elements determined by INAA in herbaceous plants (*Plantago* sp.) and moss (*Bryum* sp.) biomass

high (390 mg kg^{-1}) and clearly signals the contamination by this element. Kabata-Pendias (2010) reports about the common Br concentration in plants being lower than 50 mg kg^{-1} and only in legume and grass reaching values around 100 mg kg^{-1}. Bromine is easily available from soil with the higher concentration in leaves compared to roots (Kabata-Pendias 2010).

The concentrations of Co, Zn, As, Br, Rb and W do not represent pure transfer from substrate to plants. They rather represent enrichment due to surface contamination.

No element was enriched in the mosses as shown in Fig. 2. Contrary to it, some of the elements were enriched in aerial parts of herbaceous plants. The highest value was reached by Br. In this case it is difficult to determine the source of bromine.

Noteworthy, the heavy metals (Co, Zn, As, Zr and W) were also significantly enriched in aerial parts. They represent elements which could originate from disabled metallurgical industrial plants that have been functioning in the vicinity. According to the historical records of the city of Barreiro during the decades 1950 to 1970, there was a chemical-metallurgical industry processing Cu, Pb, Au, Ag and grey pyrite, and a mechanical-metallurgical industry with iron, bronze and steel factories. The contamination of Barreiro and its surroundings were partially documented in, e.g., Cotte-Krief et al. (2000), Pedro et al. (2008).

The C_r's of U and Th are in the same order of magnitude as those reported by Shtangeeva et al. (2006) (supplement). These elements are not enriched in mosses and plant biomass growing on PG, what corresponds well with the fact that they originate in PG.

It is reasonable to expect that the C_r of radionuclides, REEs and metals would be lower for crops than for *Plantago* sp. The C_r of ^{226}Ra for various crops is generally in the order of 10^{-2} (Enamorado et al. 2009; Tagami and Uchida 2009). For cereals, Tagami and Uchida (2009) reported a C_r for ^{226}Ra in an order of 10^{-3}. Former applications of PG for soil amendment did not have a measurable impact on the increase of C_r of ^{226}Ra and U in crops (Enamorado et al. 2009). Interestingly, Borges et al. (2017) applied PG treatments on saline soils and observed a depletion of the activity concentration of ^{226}Ra in the exchangeable fraction associated with Fe and Mn oxides with a consequent increase in the concentration of the residual fraction of the radionuclide.

4 Conclusions

The source of Th and U in mosses and plant biomass is the local PG substrate whilst the heavy metals originated from disabled metallurgical industries. The heavy metals were likely transported by wind from the surrounding of the monitored stockpiles. The high concentration of ^{226}Ra in mosses confirmed its significant transport on the surface of tailing pile. Both bioindicators, mosses and plants, showed that this area is still significantly harmed by previous industrial activities.

Higher concentration ratios of natural radionuclides from substrate to *Plantago* sp. tissues correspond well with its adaptability to hostile conditions.

The extraction experiments showed the low quantity of the bioavailable fraction of ^{226}Ra which is typical for PG. Despite of it, the concentration ratio for *Plantago* sp. was markedly high.

Use of soil amended with PG for agriculture should not lead to increase of contamination of crops due to low concentrations of toxic elements in substrate and generally lower C_r's of these elements in crops. Nevertheless, preliminary experiments with crops and soil-PG mix would confirm the safe use of PG from the Barreiro tailing.

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