



Model of U and ^{226}Ra uptake by *Spergularia rubra* (L.) J. Presl & C. Presl in an area affected by Cu ore mining

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Abstract

Spergularia rubra (L.) J. Presl & C. Presl has a mycorrhizal resistance that leads to increased uranium uptake. The results show that 35% of the ^{238}U is retained in the carbonate fraction and 59% in the residual or non-reactive fraction. ^{226}Ra shows a different pattern with an average association of 19% in the organic matter fraction, 10% in the carbonate compounds and the remaining 71% in the residual fraction. The relationships between the activity concentrations of ^{238}U and ^{226}Ra in the soil fractions and in *Spergularia* were found to be statistically representative of the carbonate and organic matter fractions, respectively.

Keywords Uptake of radionuclides · Transfer factors · UO_2^{2+} · $^{226}\text{Ra}^{2+}$ · Natural radioactivity · *Spergularia rubra*

Introduction

U and Ra tend to be the most commonly used radionuclides in radionuclide transfer studies in plants as they have isotopes in the three natural radioactive series (uranium, actinium and thorium) [1–3]. The plant selected in our study was *Spergularia rubra* (L.) J. Presl & C. Presl, commonly known as the sand-spurry, which belongs to the

family Caryophyllaceae. *Spergularia* is known for its various medicinal uses such as the treatment of kidney diseases [4], diabetes [5] and as an anti-tartar agent due to its CaCO_3 anti-crusting properties [6]. However, its properties related to its ability to grow in sandy soils with a high salt content [7] and its resistance to mycorrhization [8] make it suitable for radionuclide uptake studies. Mycorrhization resistance guarantees the incorporation of radionuclides into the aerial part of the plant as there is no retention of radionuclides in the fungi vesicles present in the roots of the plants [9]. Moreover, its ability to develop in sandy soils has allowed it to grow on the abandoned Cu mine tailing studied, where concentrations of heavy metals such as Fe, As and Cu, in addition to natural radionuclides are high.

Transfer factors (TF) allow us to evaluate a plant's uptake of radionuclides from the soil [10]. Typical U and Ra TF ranges found in different plants are between 10^{-4} and 1 kg kg^{-1} [11–13]. TFs can either be determined for different plants in a specific area, or they can be determined for the same plant according to different activity concentrations, thus facilitating an uptake model [14]. This model may fit a number of functions: linear, hyperbolic or non-linear [15]. Linear models are satisfied when the radionuclide behaves as a non-essential element and the activity concentrations for a given radionuclide in soil are greater than 10^4 Bq kg^{-1} [16]. However, for commonly found activity concentrations (between 1 and 10^3 Bq kg^{-1}), the TFs would follow the

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models of the essential elements, in other words, fitting non-linear or hyperbolic functions [17, 18]. Although TFs are accepted and widely used by the scientific community, their weakness is that they provide additional information that does not differentiate between the different chemical associations and processes that a given radionuclide undergoes in a given soil [19, 20]. It is therefore necessary to investigate the relationship between TFs and the different physico-chemical characteristics of the soil in order to understand the radionuclide uptake processes in the plants and, therefore, the models they follow.

The mobility of U and Ra in soils is complex and depends on the soil's physico-chemical properties. Plants take up U and Ra when they are released as ions and move to positions close to the plant roots. U sorption processes in soil depend on the presence of [21]: (i) clay minerals; (ii) Al and Fe oxides; (iii) organic matter; and (iv) the presence of microorganisms [22]. Furthermore, pH directly influences U and Ra availability in soils [23]. UO_2^{2+} is the predominant U species in soils with a pH below 5.5, as it is highly mobile in the soil and it is in this way that plants take up U [24]. Soils with a more basic pH have an increased number of negatively charged binding sites, due to the release of protons, causing U fixation [25]. However, pHs between 6 and 10 also have increased carbonate concentration, which forms very stable complexes with U that increase its mobility [26]. On the other hand, in this pH range, UO_2^{2+} reacts with phosphate via precipitation and with Al and Fe oxyhydroxides as the negative charges increase, both processes leading to U immobilisation [27]. In addition, oxidation–reduction reactions due to soil type cause U to be retained as U(IV) at E_h lower than 200 mV, or as UO_2^{2+} at E_h between 200 and 550 mV, in both cases at pH 7 [28]. However, the two Ra sorption processes occur in the presence of clays and, more significantly, organic matter [29]. In addition, Ca^{2+} and Mg^{2+} give rise to competition reactions, with increased immobilisation at a basic pH, leading to decreased uptake by plants [30]. Knowledge of the sorption reactions of U and Ra in soils therefore explains their uptake by plants. This sorption can be explained by associations with different soil fractions that can be determined by sequential extraction methods [31]. These methods make it possible to determine whether U or Ra is retained in the following fractions [32]: (i) exchangeable; (ii) organic matter; (iii) carbonate compounds; (iv) Fe and Mn oxides; or (v) the residual or non-reactive fraction. The extraction method selected was that proposed by Schultz et al. [33], rather than Tessier et al. [34], as it gives the most reproducible results for U and Ra [35, 36].

Based on the above, our working hypothesis is that the uptake of U and Ra in *Spergularia rubra* depends on the association of these radionuclides in the different soil fractions (exchangeable, organic matter, carbonate compounds,

Fe and Mn oxides, and non-reactive). We tested our hypothesis by: (i) studying the correlations between chemical composition (XRF) and natural radionuclides (gamma spectrometry) in the soils where *Spergularia rubra* grows; (ii) quantifying the activity concentrations of U and Ra in the different soil fractions by applying the extraction sequence of Schultz et al and (iii) obtaining the uptake models for ^{238}U and ^{226}Ra in the different soil fractions using the TFs and activity concentration of *Spergularia rubra*.

Materials and methods

Study area

The study area is located in the surroundings and inside the dump of the “Antigua Pilar” mine, in the municipality of Colmenarejo in the Community of Madrid, Spain. This area is characterised by high concentrations of Cu, As and Fe due to the extraction of copper ore. The minerals present in the dump were chalcopirite (CuFeS_2), arsenopyrite (CuFeS_2), malachite ($\text{Cu}_2\text{CO}_3(\text{OH})_2$), azurite ($\text{Cu}_3\text{CO}_3(\text{OH})_2$), siderite (FeCO_3), fluorite (CaF_2), olivenite ($\text{Cu}_2\text{AsO}_4(\text{OH})$) and chalcantite ($\text{Cu}_2(\text{SO}_4)\cdot 5\text{H}_2\text{O}$) [37, 38]. The geology of the study area developed as a result of hydrothermal activity, causing the natural uranium and actinium radioactive series to be much higher than the natural thorium series, as shown in a previous characterisation [39]. The sampling points were determined based on the growth of *Spergularia rubra*, and a total of 15 points were selected (Fig. 1).

Collection and preparation of the plant samples

The characteristics of *Spergularia rubra* are as follows (Fig. 1): it has a stem covered with linear or filiform, slightly fleshy leaves less than 2 cm long, which may have hard tips or spines, accompanied by bright white, lanceolate stipules. Its flowers are small and uniformly pink and are grouped in panicles or cymes [40]. The aerial part of the plant was selected for analysis in this study. The roots were separated at the sampling point to avoid contamination during sampling. The samples were bagged and identified and taken to the laboratory. Subsequently, the samples were washed with deionised water (Milli-Q model ELIX Advantage 3) in an ultrasonic bath (Nahita model 610/10), to remove any possible soil powder adhering to the samples. The plants were left to stand for 1 day on absorbent laboratory paper. They were then heated in an air dryer (Selecta model 2,000,209) at 85 °C until a constant weight was achieved. Finally, the samples were pulverised with an impact mill (IKA model A11 basics).

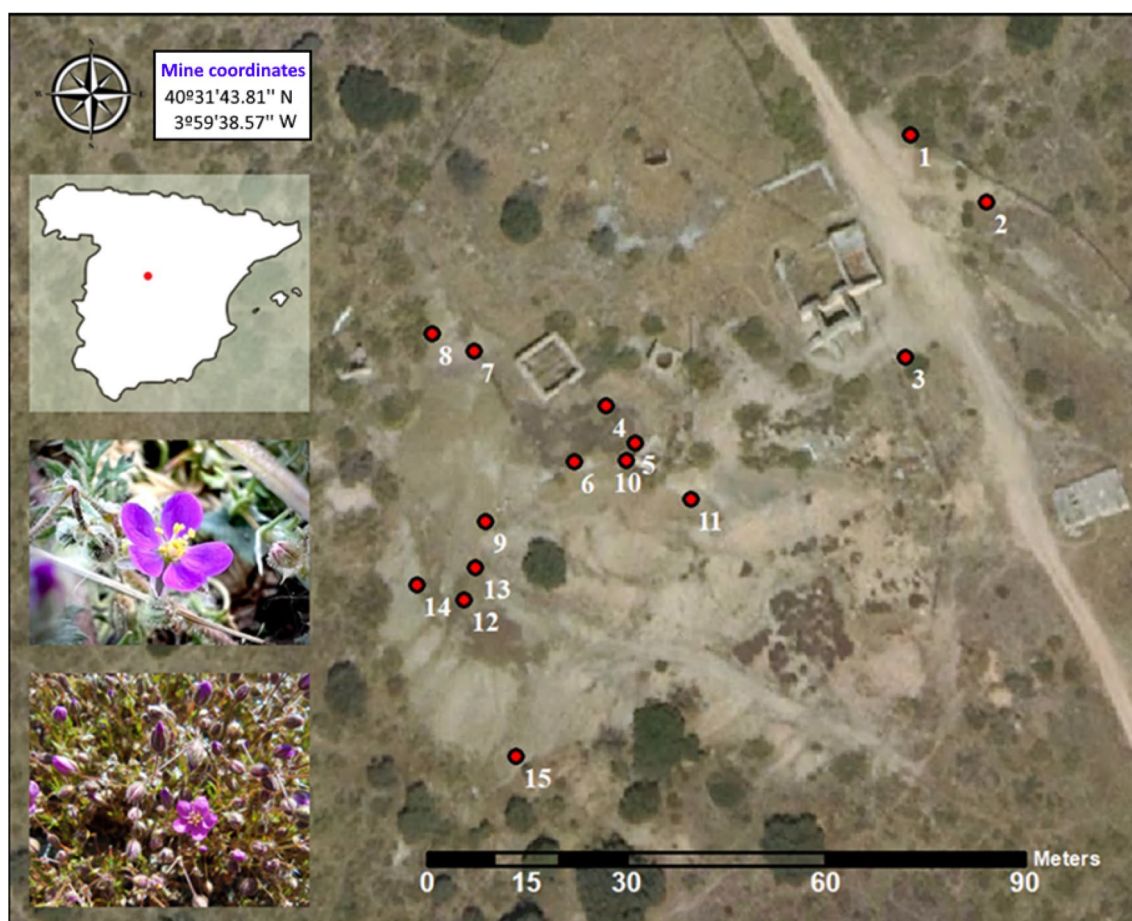


Fig. 1 Location plan of the 15 sampling points in the dump of the “Antigua Pilar” copper mine in the municipality of Colmenarejo in the province of Madrid (Spain). The coordinates where the mine is

located on the Iberian Peninsula are shown in the upper left-hand box. The geographical coordinates of the sampling points are given in Table A1.1. of the supplementary information

Sampling, preparation and physico-chemical characterisation of soil samples

Soil samples were taken as close to the sampled plants as possible, avoiding its rhizosphere zone and removing non-representative stones and roots. Each sample was taken using a $10 \times 10 \text{ cm}^2$ metal grid which was inserted into the soil to a depth of 5 cm. The depth used is representative of the shallow root systems of *Spergularia rubra*. The sample was identified and placed in a plastic bag and transferred to the laboratory. The sample was dried completely in an oven at 105°C to a constant weight and then ground in a planetary ball mill (FRITSCH model pulverisette 5). The sample was sieved to a particle size of $250 \mu\text{m}$ with a 60 mesh sieve. A fraction of 110 mL was placed in a cylindrical container 76 mm in diameter and 30 mm tall, which was closed and sealed to avoid and loss of ^{222}Rn , since ^{222}Rn emanation from a soil is high, although in this case, since it is mixed with part of the mineral, the emanation is lower [41]. The cylindrical geometries were measured using

gamma spectrometry and a different aliquot was used for XRF analysis.

The tests used to physico-chemically characterise the soil samples were: (i) pH measurement; and (ii) determination of the percentage of soil organic matter. The pH of the sample was measured in an emulsion comprising 5 mL of soil in 25 mL of deionised water, in line with the UNE-ISO 10390 standard [42]. The emulsion was introduced into a decanting funnel and shaken for 1 h using a vibroagitator (Heidorf model promax 1020). The pH was measured following a 1-h rest period, after being stirred with a pH meter (Crison model Basic 20+).

The analysis of organic matter was carried out using the loss on ignition method, consisting of a gravimetric determination based on the total calcination of organic matter. A 10 g aliquot of soil was dried at 105°C for 24 h, obtaining the soil dry weight (w_1). Then, the samples were ignited at 650°C for 24 h in a muffle furnace (Hobersal model PR), obtaining the weight (w_2). The percentage of weight lost by ignition (LOI(%)) was determined by the expression [43]:

$$LOI(\%) = \frac{(w_1 - w_2)}{w_1} \cdot 100 \quad (1)$$

The LOI (%) was transformed into organic matter using the following equation [44]:

$$OM(\%) = LOI(\%) \cdot 0.7 - 0.23 \quad (2)$$

Initial characterisation of soil samples using gamma spectrometry and X-ray fluorescence

Gamma spectrometry and X-ray fluorescence were applied to find the relationship between the chemical and radiological composition of the soils. Gamma spectrometry was performed using 3 coaxial HPGe detectors (reverse electrode, extended range and broad energy). All 3 detectors were characterised for efficiency calculation using LabSOCS software [45]. The detectors were connected to a Digital Signal Analyser (Canberra model DSA-LX) containing the high voltage source, the amplifier and the analogue-to-digital converter [46]. The spectra were acquired and analysed with Genie 2000 software [47]. The interference of ^{235}U in the 186 keV photopeak of ^{226}Ra , and ^{228}Ac in the 1460 keV photopeak of ^{40}K , were suppressed using the method described in [48]. The gamma emitters determined were [49]: ^{234}Th (63.30 (2) keV–3.75 (8)%), ^{226}Ra (186.211 (13) keV–3.555 (19)%), ^{214}Pb (351.932 (2) keV–35.60 (7)%), ^{214}Bi (609.312 (7) keV–45.49 (19)%; 1120.287 (10) keV–14.91 (3)%; 1764.494 (14) keV–15.31 (5)%), ^{210}Pb (46.539 (1) keV–4.252 (40)%), ^{212}Pb (238.632 (2) keV–43.6 (5)%), ^{208}Tl (583.187 (2) keV–85.0 (3)%), ^{228}Ac (911.196 (6) keV–26.2 (8)%), ^{235}U (163.356 (3) keV–5.08 (3)%; 205.16 (4) keV–5.02 (3)%; 143.767 (3) keV–10.94 (6)% and ^{40}K (1460.822 (6) keV–10.55 (11)%). The gamma spectrometry technique is accredited by the Spanish National Accreditation Entity (ENAC) in line with the UNE-EN ISO 17025 standard [50].

X-ray fluorescence was performed using a Malvern-PANalytical AXIOS spectrometer. An aliquot of the sample was ground and sieved to a particle size of 74 μm with a 200 mesh sieve. The determination of the elemental composition by WDXRF is done using a semi-quantitative method, developed by Malvern-Panalytical, which uses fundamental parameters for quantification, with at least one standard for each element that ensures a maximum of a 1% precision. The use of this method allows the same sample aliquot to be used for radiochemical analysis and reduces sample handling. The sample is placed in a special sample holder for powder samples and analyzed in the apparatus under He atmosphere. Moreover, the WDXRF technique is very stable and does not need to be calibrated each time it is measured, so the standard deviations of the measurements are very small.

The gamma spectrometry and XRF results were used to perform a principal component analysis (PCA), the results of which were presented in an HJ biplot diagram [51]. Both methods are non-destructive, so sample preparation would not be a factor to take into account in the PCA. Any correlation between variables was removed using the variance inflation factor (VIF). PCA and VIF were applied using the add-in MS Excel Real Statistics Resource Pack, Release 7.6 (www.real-statistics.com, accessed on 1 June, 2023) [52], allowing the correlations between soil chemical composition and natural gamma-emitting radionuclides to be tested.

Determination of activity concentrations of isotopic uranium and ^{226}Ra

The radiochemical methods used to determine isotopic uranium (^{238}U , ^{234}U and ^{235}U) and ^{226}Ra activity concentrations were those developed in previous studies [39, 53]. Both methods started with the mineralisation of 2 g of plant and 0.5 g of soil in an Ethos One microwave oven. The soil was analyzed by radiochemical separation so that the type of methodology was not a factor to be taken into account when statistically analyzing the results of the transfer factors and fractionation of the radionuclides in the soil. The plant samples were mixed with 2 mL H_2O_2 and 8 mL concentrated HNO_3 , and the soil samples with 3 mL HF and 9 mL HNO_3 . The microwave programme consisted of a 60-min cycle at a power of 1000 W and a temperature of 220 $^\circ\text{C}$.

The uranium isotopes were separated by liquid–liquid extraction with tri-*n*-butyl phosphate (TBP) from an 8 M- HNO_3 solution using 0.25 M- EDTANa_2 as a complexing agent [39]. Uranium was re-extracted with 1 M- $(\text{NH}_4)_2\text{CO}_3$ and electrodeposited on a stainless steel planchet using the Hallstadius method [54]. The chemical recovery was determined using a ^{232}U tracer with a certified activity. The samples were measured over 500,000 s in an Alpha Analyst model A450-18AM with 12 vacuum cameras, each with a passivated implanted planar silicon (PIPS) detector. The uranium isotope used in this study was ^{238}U as it has the highest mass percentage (99.284%) and its chemical behaviour is the same as ^{234}U and ^{235}U [55].

^{226}Ra was determined using a method based on selective precipitation [53]. The method started with a precipitation of $[\text{Ba-Ra-Pb}]\text{SO}_4$ in a 1:1 H_2SO_4 medium using 20 mg- Ba^{2+} and 195 mg- Pb^{2+} carriers. $[\text{Ba-Ra-Pb}]\text{SO}_4$ was purified by dissolving the precipitate with EDTANa_2 0.25 M in strongly ammoniacal medium and re-precipitating the BaSO_4 with concentrated acetic acid at pH 4.5. $[\text{Ba-Ra}]\text{SO}_4$ was transformed to $[\text{Ba-Ra}]\text{CO}_3$ with a saturated Na_2CO_3 solution and dissolved with HNO_3 3 M. Then, Ba^{2+} was precipitated as $[\text{Ba-Ra}]\text{Cr}_2\text{O}_7$ and dissolved with concentrated HCl. Thereafter, Ba^{2+} was then precipitated as $[\text{Ba-Ra}]\text{Cl}_2$ with a 6:1 solution of HCl and ethyl ether. Finally, the $[\text{Ba-Ra}]$

Cl₂ precipitate was dissolved in water and [Ba–Ra]SO₄ was precipitated with H₂SO₄ 1 M at 50 °C. The dried precipitate was deposited on a stainless steel planchet and measured for 60,000 s in a ZnS(Ag) solid scintillation detector (Canberra Industries).

The expressions used to calculate the activity concentration, uncertainty and detection limits of ²³⁸U and ²²⁶Ra are given in Appendix 2 of the Supplementary Information. These analyses are not accredited but they involve the same procedure and the same quality controls (internal and participation in intercomparison exercises) as performed for gamma spectrometry.

Transfer factor calculation

The transfer factor (*TF*, kg kg^{−1}) was calculated to estimate the uptake of ²³⁸U and ²²⁶Ra from soil into *Spergularia rubra*. The expression used to compute the *TF* was [56]:

$$TF = \frac{A_r^p}{A_r^s} \quad (3)$$

where A_r^p is the activity concentration of ²³⁸U or ²²⁶Ra in *Spergularia rubra* expressed in Bq kg^{−1} of dry weight and A_r^s is the activity concentration of ²³⁸U or ²²⁶Ra in the soil sampled in Bq kg^{−1} of dry weight. The model used to represent the transfer factor of ²²⁶Ra and ²³⁸U was $TF = \sqrt{a + b \cdot 1/A_r^s}$ which is equivalent to that proposed by Sheppard et al. [14]. The ordinate and abscissa axes were transformed into TF^2 and $1/A_r^s$ respectively to obtain a linear representation of the experimental data.

Sequential extraction method for ²³⁸U and ²²⁶Ra

The Schultz sequential extraction method [33] was used to determine in which fraction of the soil UO₂²⁺ (²³⁸U, ²³⁵U and ²³⁴U) and Ra²⁺ were associated. The activity

concentrations of ²³⁸U and ²²⁶Ra were determined using the radiochemical methods presented in “[Determination of activity concentrations of isotopic uranium and ²²⁶Ra](#)”. The Schultz method considers 5 soil fractions in which, for a solid–liquid ratio of 1:15, the following extractions are performed: (1) water soluble or exchangeable ions (MgCl₂ 0.4 M, pH 5.0, room temperature for 1 h); (2) metals associated with organic matter (NaOCl 5%, pH 5.7, 96 °C in two steps of 0.5 h); (3) carbonate compounds (NaAc 1 M in HAc 25%, pH 4.0, room temperature in two steps of 2 h); (4) Mn and Fe oxides (NH₂OH·HCl 0.04 M, pH 2 with HNO₃, at room temperature for 5 h); and (5) insoluble residue or non-reactive fraction (by digestion in the Ethos One microwave using the protocol described in “[Determination of activity concentrations of isotopic uranium and ²²⁶Ra](#)”). The activity concentrations of ²³⁸U and ²²⁶Ra in each fraction were used to determine the corresponding *TF*s, again using the model $TF = \sqrt{a + b \cdot 1/A_r^s}$ (see “[Transfer factor calculation](#)”). Finally, a backward stepwise multiple regression analysis was performed using Statgraphics Centurion XVII statistical software (version 17.0.16) to obtain the models relating the activity concentrations of each soil fraction to those of *Spergularia rubra*.

Results

Relationship between radionuclide activity concentrations and the chemical composition of the soil samples

The soils of the studied area are rich in Cu, Fe and As along with other heavy metals, as shown in Fig. 2. The measured Cu concentration was 15,913 mg kg^{−1} which is much higher than the world average of 30 mg kg^{−1} [15]. Additionally, the mean As concentration was 2,641 mg kg^{−1} which is much higher than the global range of 3.3 to 184.6 mg kg^{−1} [57].

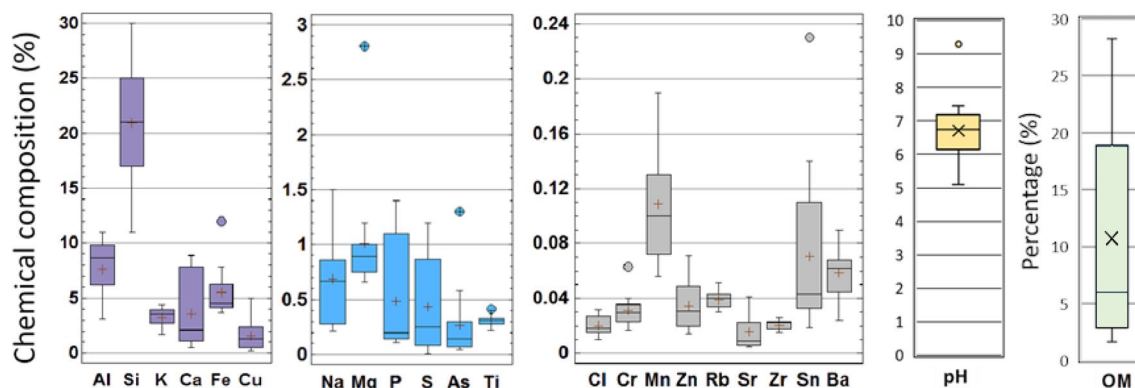


Fig. 2 Chemical composition (%) of the main chemical elements present in the soils from “Antigua Pilar” copper mine tailing obtained through X-ray fluorescence and soil characteristics: pH and organic matter percentage

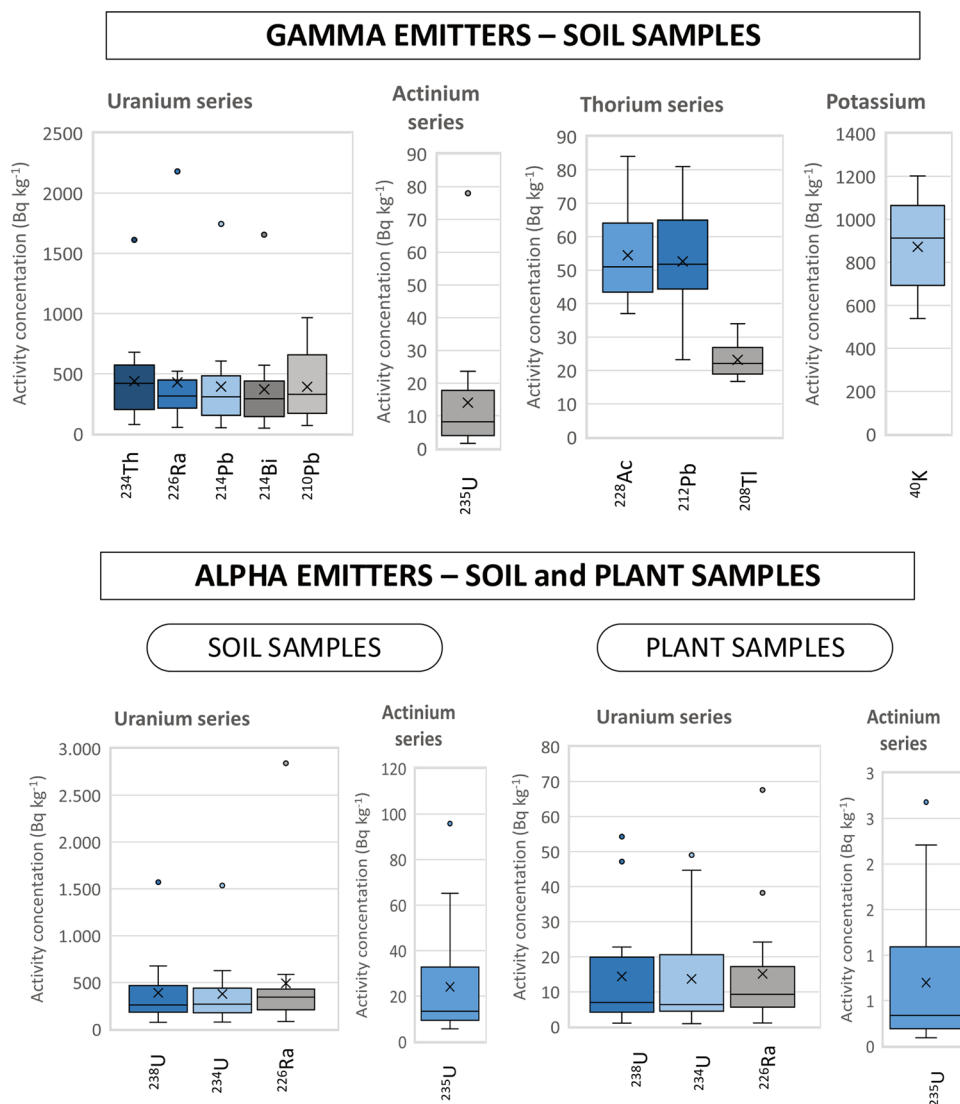
However, the iron concentration was within the usual range, i.e., between 0.2 and 55% [58].

Figure 3 presents box-and-whisker plots of the activity concentrations of the uranium, actinium and thorium series radionuclides together with ^{40}K . The activity concentrations of ^{238}U (through ^{234}Th) and ^{226}Ra , as determined by gamma spectrometry, ranged between $78 \pm 18 \text{ Bq kg}^{-1}$ and $1611 \pm 333 \text{ Bq kg}^{-1}$ for ^{238}U and between $55 \pm 18 \text{ Bq kg}^{-1}$ and $2181 \pm 445 \text{ Bq kg}^{-1}$ for ^{226}Ra . Additionally, ^{214}Pb , ^{214}Bi and ^{210}Pb were in secular equilibrium with ^{238}U and ^{226}Ra . The activity concentrations of the thorium series radionuclides were two orders of magnitude lower than those of the uranium series, ranging from $37.0 \pm 3.8 \text{ Bq kg}^{-1}$ to $84.0 \pm 7.1 \text{ Bq kg}^{-1}$. The U/Th concentration ratio indicates that the geological formation in the studied area had a hydrothermal origin [59].

Figure 4 presents the HJ-Biplots detailing the relationships of soil activity concentration obtained using gamma

spectrometry and the soil chemical composition determined by XRF (Fig. 4a) and the activity concentrations of ^{226}Ra and ^{238}U in *Spergularia rubra* (obtained through radiochemical separation) with soil chemical composition (determined by XRF) (Fig. 4b). The uranium series was represented in the soil samples by the activity concentration of ^{210}Pb as collinearity was found between the remaining gamma emitters (VIF values > 10). Analogously, the radionuclides of the thorium series were represented by ^{212}Pb and the actinium series by ^{235}U . The graph demonstrated how the three natural radioactive series correlated with one another for the soil. Likewise, ^{210}Pb and ^{235}U strongly correlated with the concentrations of S, Cu, Cl and pH (the latter with little statistical weight). The activity concentration of ^{40}K did not correlate with the natural radioactive series as its vector was perpendicular to these. The Ti, Na and Cr concentrations were inversely proportional to the increase of the radioactive content of the samples. The scores obtained in the 15 soils

Fig. 3 Box-and-whisker plots of the activity concentrations of: (1) gamma emitters in the natural radioactive series of uranium (^{234}Th , ^{226}Ra , ^{214}Pb , ^{214}Bi and ^{210}Pb), actinium (^{235}U), and thorium (^{228}Ac , ^{212}Pb and ^{208}Tl); (2) potassium (^{40}K); and (3) alpha emitters of the uranium (^{238}U , ^{234}U and ^{226}Ra) and actinium (^{235}U) series in the 15 soil and plant (*Spergularia rubra*) samples. The data supporting the graphs is given in Annex 3 of the Supplementary Information



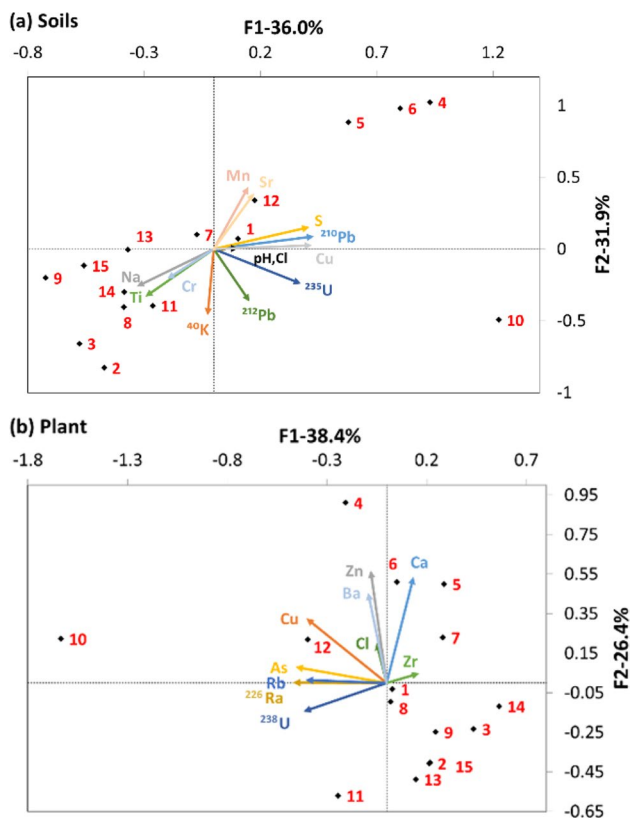


Fig. 4 HJ-Biplots depicting the principal component analysis between the results of the soil chemical composition obtained through X-ray fluorescence (XRF) and the activity concentrations of the soil radionuclides for the uranium, actinium and thorium series together with ^{40}K , obtained using gamma spectrometry (Graph a) and those of the plants obtained through radiochemical separation of ^{238}U and ^{226}Ra (Graph b) for the 15 soil samples analysed at the “Antigua Pilar” copper mine tailing site. The numerical values used to construct the HJ-Biplot graph are given in Annex 3 of the supplementary information

generated 3 different sets. The first set consisted of points 4, 5 and 6, characterised by high contents of the three natural radioactive series and a low ^{40}K activity concentration with a mean value of $567 \pm 90 \text{ Bq kg}^{-1}$. Soil 10 was distinguished from the other samples by its higher concentrations of uranium and actinium series activity. This point had the highest activity concentration as it was located in the main dump where the mineral was deposited. These four samples were from the soils adjacent to the main tailing. The remaining set of soil samples varied according to their proximity to the main tailing due to the disaggregation of minerals caused by the movement of materials. Figure 4b shows how the ^{238}U and ^{226}Ra activity concentrations obtained for *Spergularia rubra* correlated strongly with soil As, Ra and Rb concentrations. However, there was no correlation with essential elements such as Ca, Mg, Zn and Ba. The associations obtained between soil and plant activity concentrations and stable element concentrations were equivalent.

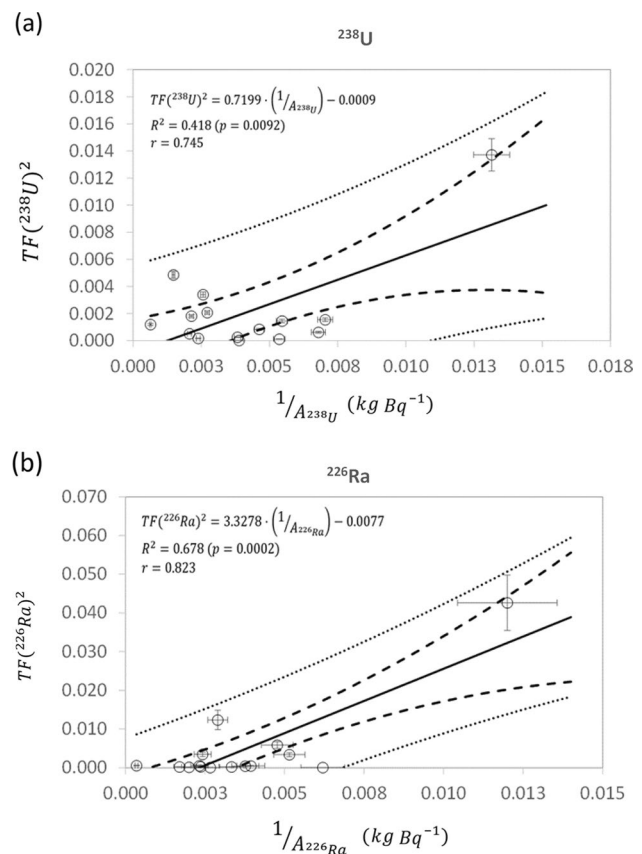


Fig. 5 Transfer factors as a function of the whole-soil activity concentration: **a** ^{238}U and **b** ^{226}Ra . The model used was $y = \sqrt{a + b \cdot 1/x}$ where y is the transfer factor and x is the activity concentration of ^{238}U and ^{226}Ra in the soil. The axes of the graphs have been transformed to obtain a linear representation of the data. The dotted line represents the prediction interval while the dashed lines represent the confidence intervals of the fit for 95% confidence

^{238}U and ^{226}Ra transfer factors from *Spergularia rubra*

The models used to represent the transfer factor as a function of ^{238}U and ^{226}Ra activity concentrations in the soil as a whole showed a statistically significant relationship at the 95% confidence level ($p < 0.05$) (Fig. 5). The models represented 42% of the transfer factor variability in the case of ^{238}U and 68% in the case of ^{226}Ra . The correlation obtained in both cases was greater than 0.7, which can be considered statistically significant [60]. The confidence intervals obtained for the ^{226}Ra absorption model were more accurate than those for the ^{238}U model.

Association of ^{238}U and ^{226}Ra in the different soil fractions

Figures 6 and 7 show the association of ^{238}U and ^{226}Ra in the different fractions of the soils in which *Spergularia*

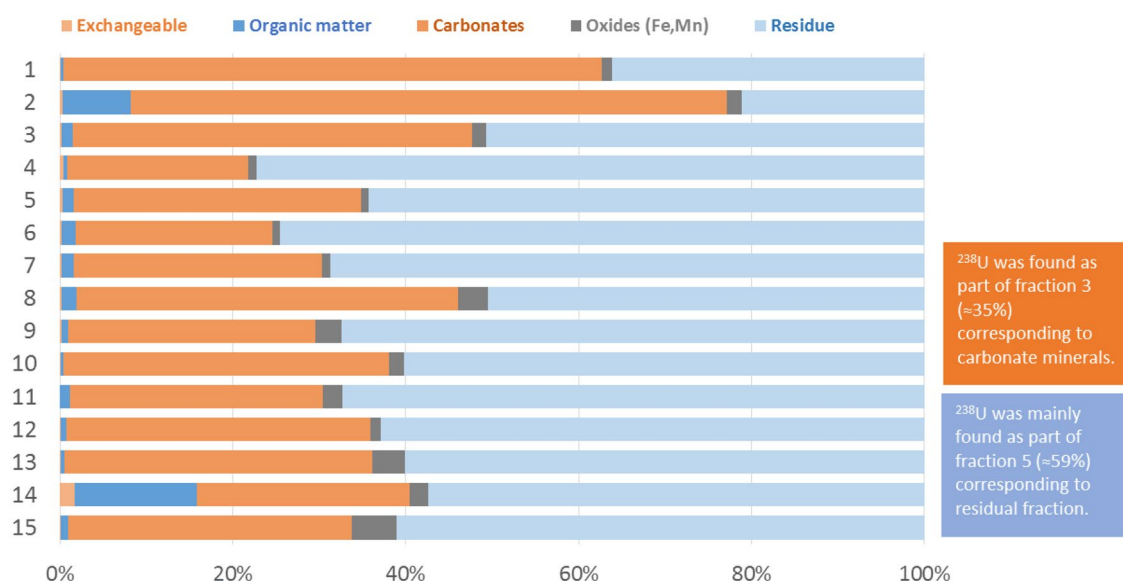
Percentage of ^{238}U in the extracted fractions

Fig. 6 Percentages obtained in the 5 soil fractions for ^{238}U : (1) water soluble/exchangeables; (2) organic matter; (3) carbonates; (4) oxides (Fe/Mn); and (5) residue. The values used in this graph are given in Annex 5 of the Supplementary Information

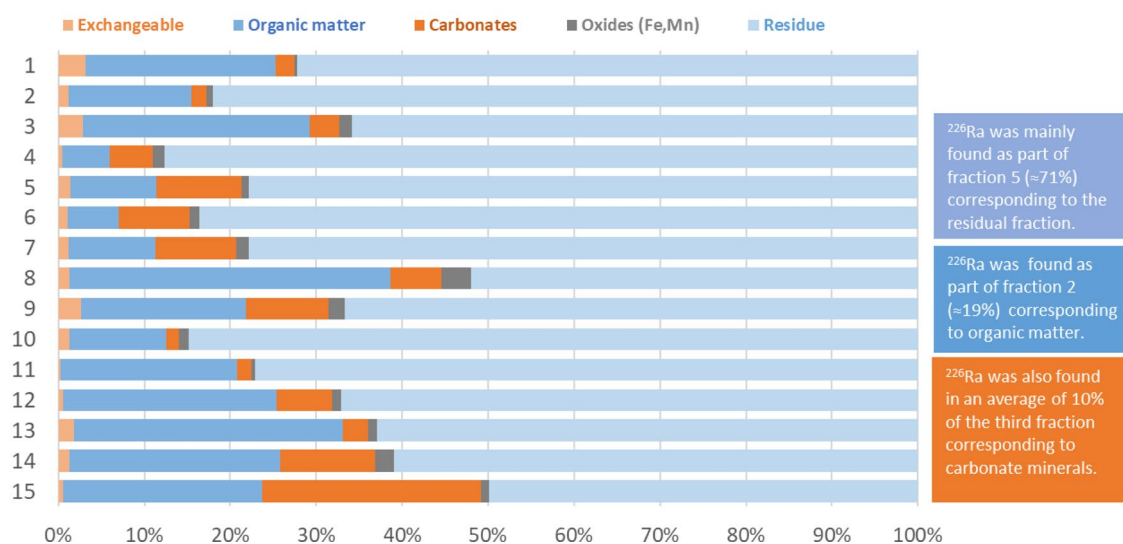
Percentage of ^{226}Ra in the extracted fractions

Fig. 7 Percentages obtained in the 5 soil fractions for ^{226}Ra : (1) water soluble/exchangeables; (2) organic matter; (3) carbonates; (4) oxides (Fe/Mn); and (5) residue. The values used in this graph are given in Annex 5 of the Supplementary Information

rubra was sampled. Both ^{238}U and ^{226}Ra were mostly found in the residual or non-reactive fraction, with the average percentage of ^{226}Ra (71.2%) being higher than that of ^{238}U (58.6%). The remaining ^{238}U constituted 36.7% of the carbonate mineral fraction, while ^{226}Ra was present in 7.0% of the same fraction. However, ^{226}Ra was present in the organic fraction at a level of 19.1% compared to 2.3% for ^{238}U . Finally, the average percentage of ^{226}Ra in

the exchangeable fraction (1.4%) was higher than that of ^{238}U (0.79%).

^{238}U and ^{226}Ra Transfer Factors as a function of different soil fractions

Figures 8 and 9 show the transfer factors (TF) of *Spergularia rubra* for ^{238}U and ^{226}Ra as a function of the activity

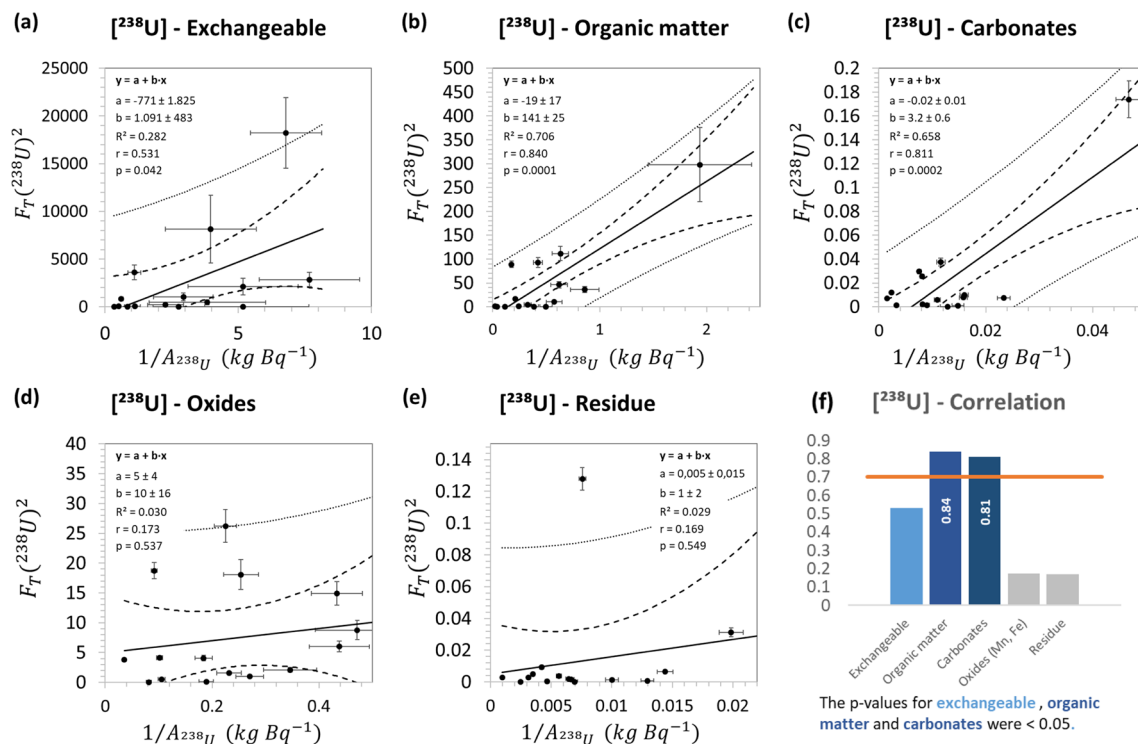


Fig. 8 Transfer factors as a function of activity concentration (Bq kg^{-1}) for ^{238}U in each of the soil fractions ((a) exchangeable, (b) organic matter, (c) carbonates, (d) Fe and Mn oxides, and (e) residue). The fitting function used was the square of y —the inverse of x ($y = \sqrt{a + b/x}$), the coordinate and abscissa axes were transformed to generate a linear function that facilitates the graphic visualisation of how the experimental points fit the obtained model. The graph f

summarises the correlations obtained showing those that exceeded a value of 0.7, which implies a correlation in the data; the bars in blue (light and dark) indicate that the transfer factors and the activity concentration of the corresponding fraction have a statistically significant relationship with a confidence level equal to or greater than 95%. The numerical values used for the different graphical representations are given in Annex 5 of the supplementary information

concentrations in the different soil fractions determined in “Association of ^{238}U and ^{226}Ra in the different soil fractions”. The model applied was the same as that used to represent the TF as a function of the total ^{238}U and ^{226}Ra concentration in the whole soil (Fig. 5). Figure 8f shows a statistically significant relationship ($p < 0.05$) between the TF and the soil activity concentration of ^{238}U in the following fractions: exchangeable, organic matter, and carbonate minerals. Likewise, the organic matter and carbonate mineral fractions gave a correlation of greater than 0.7. These results could indicate that *Spergularia rubra* takes up ^{238}U from these two soil fractions. Similarly (Fig. 9f), ^{226}Ra must be incorporated mainly from the exchangeable and organic fractions, although a statistically significant relationship was also obtained for the insoluble residue or non-reactive fraction.

Discussion

The results confirm our hypothesis that the U and ^{226}Ra uptake can be explained in terms of their associations with the different soil fractions. The radiological characteristics

of the soils reveal that the minerals present in the tailings where *Spergularia rubra* grows originated from hydrothermal processes, as the ratio of the uranium and thorium series is 10 [61]. The correlation between ^{210}Pb (uranium series) and ^{235}U , S, and Cu is greater in soils obtained from the mine tailing. This outcome is in line with the predominance of the mineral chalcopyrite (CuFeS_2) in the mine tailing [38]. Conversely, although the As concentration in the soils is incredibly high and would be expected to be related to the presence of arsenopyrite (FeAsS) extracted from the mine, no correlation was observed, as shown in Fig. 4a. However, this correlation was found when comparing the activity concentrations of ^{238}U and ^{226}Ra with the chemical composition of the soil. Figure 4b reveals a strong correlation between ^{238}U , ^{226}Ra , Cu, and As. The scores obtained in the HJ-Biplot for the samples as a function of the correlations between the soil chemical compositions and the radioactive content of the soils and *Spergularia rubra* were equivalent. Consequently, these results indicate a chemical and radiological concentration dependence relationship with the ^{238}U and ^{226}Ra taken up by *Spergularia rubra*.

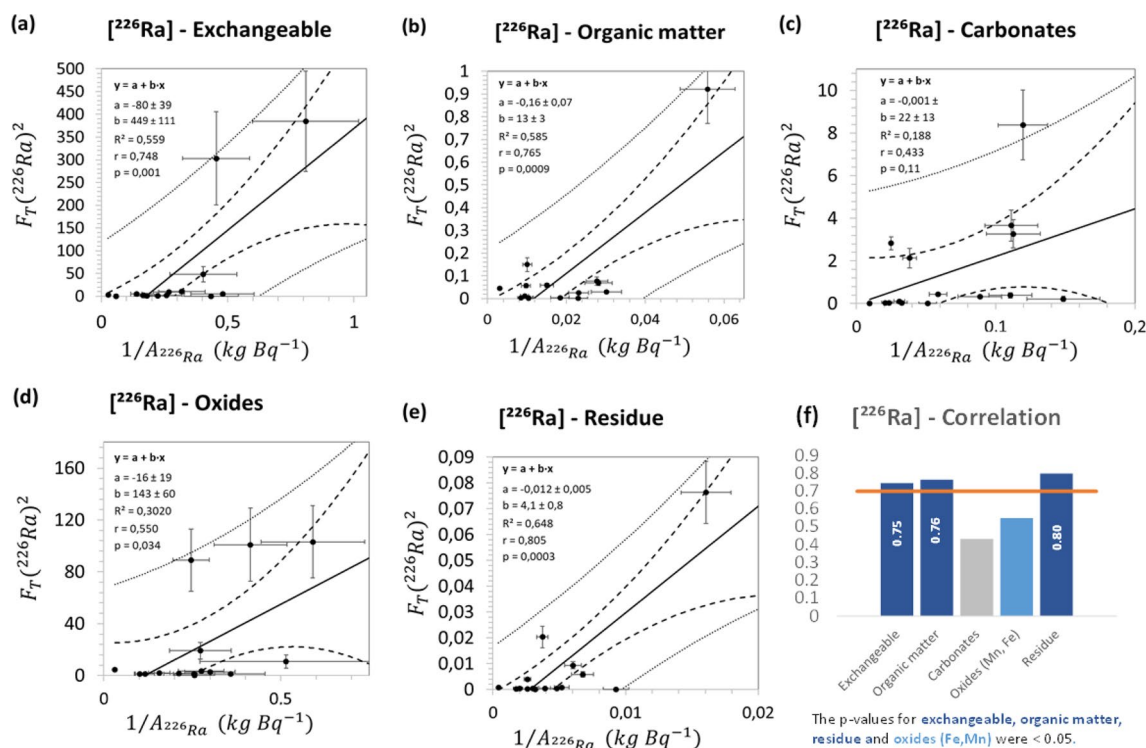


Fig. 9 Transfer factors as a function of activity concentration (Bq kg^{-1}) for ^{226}Ra in each of the soil fractions ((a) exchangeable; (b) organic matter; (c) carbonates; (d) Fe and Mn oxides; and (e) residue. The fitting function used was the square of y —the inverse of x ($y = \sqrt{a + b/x}$), the coordinate and abscissa axes were transformed to generate a linear function that facilitates the graphic visualisation of how the experimental points fit the obtained model. The graph f

summarises the correlations obtained showing those that exceeded a value of 0.7, which implies a correlation in the data, the bars in blue (light and dark) indicate that the transfer factors and the activity concentration of the corresponding fraction have a statistically significant relationship with a confidence level equal to or greater than 95%. The numerical values used for the different graphical representations are given in Annex 5 of the supplementary information

The correlations observed between the radiological and chemical compositions of soils and plants were replicated in the TF values obtained for the entire soil (Fig. 5). The relationship between the activity concentrations of ^{238}U and ^{226}Ra in the soil and the TF was statistically significant ($p < 0.05$), with correlations greater than 0.7 for both radionuclides. However, this explanation is overly simplistic as *Spergularia rubra* has the capacity to take up ^{238}U and ^{226}Ra from fractions containing UO_2^{2+} and Ra^{2+} . It was therefore essential to determine the specific soil fraction containing both UO_2^{2+} and Ra^{2+} .

Our results indicate that ^{238}U is found mostly in the residual or non-reactive fraction (58.6%) and the carbonate mineral fraction (36.7%). The fractions in which UO_2^{2+} is most retained by the soil are: (i) the organic fraction (2.3%) and the Fe and Mn oxide fraction (2.0%), due to the formation of surface complexes [62]; and (ii) the non-reactive or residual fraction [63]. However, the fractions that provide the most availability of UO_2^{2+} for uptake by *Spergularia rubra* are the exchangeable fraction (0.28%) and the carbonate mineral fraction [21]. The type of sandy soil in which *Spergularia rubra* was sampled (E_h between 350

and 550 mV) together with a neutral pH (with a median of 6.7) would cause uranium to be mainly in the form of UO_2CO_3 or $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$, which is consistent with the results obtained for the carbonate fraction and would allow greater U mobility in the soil [23, 25, 64]. The results for the percentage of organic matter determined by calcination at 650 °C were highly dispersed (mean 8.8 and median 15.6) and did not correlate statistically significantly with the results obtained for the activity concentration of ^{238}U in the organic fraction. However, our results are in agreement with those obtained by Roit et al. [65] for soils from the weathering of different rock types.

The results of the ^{226}Ra association in the different soil fractions showed that 78.4% of ^{226}Ra was in the residual fraction and 15.8% was in the organic fraction. The remaining percentages were 1.3% in the exchangeable fraction, 5.2% in the carbonate minerals, and 1.2% in the Fe and Mn oxides. The percentage of immobilised ^{226}Ra in organic matter is consistent with the behaviour of ^{226}Ra in soils [29]. Štok and Smodiš [66] obtained equivalent results in the area surrounding a uranium mine in Slovenia where 40% of the ^{226}Ra was part of the organic fraction.

The TFs obtained from the percentage of ^{238}U in the organic and carbonate fractions showed a statistically significant relationship with the concentration of ^{238}U activity in the soil. These relationships may indicate that *Spergularia rubra* incorporates ^{238}U from both fractions. However, since the activity concentration in the plant is higher than that in the soil organic matter fraction, it is reasonable to assume that *Spergularia rubra* takes up ^{238}U from this fraction. This reasoning would be consistent with the conclusions of Ramaswami et al. [67], who stated that U associated with organic matter is less accessible to plants. Considering that the soil sample was taken outside the influence of the rhizospheres of *Spergularia rubra* and other plants, it does not seem logical that *Spergularia rubra* would remove ^{238}U from the soil organic fraction. On the other hand, Ebbs et al. [68] proved that plants such as *Pisum sativum* mainly incorporate free UO_2^{2+} when soil pH is below 5.5. This behaviour was also observed in a previous study on *Spergularia rubra* from soils with pHs of 5.5 [8]. The TFs of *Spergularia rubra* for U were equivalent to those obtained in this paper (ranging between 0.011 and 0.056 kg kg $^{-1}$). However, the pH of the soils sampled in this study would cause UO_2^{2+} to mobilise from UO_2CO_3 , $\text{UO}_2(\text{CO}_3)^{2-}$ and $\text{UO}_2(\text{CO}_3)^{3-}$ making it accessible to the plant, although to a lesser extent than if it were in the form of free UO_2^{2+} [69]. This statement was contradicted by Shahandeh and Hossner [70] who observed that, for calcareous soils, free carbonate would cause an accumulation of UO_2^{2+} in plant roots and not in shoots [70]. This observation is related to the retention of U in plant roots by fungi [71, 72]. However, one of the characteristics of *Spergularia rubra* is its resistance to mycorrhization, preventing symbiosis with fungi in its roots and, consequently, U retention [73–75]. For this reason, U uptake under the conditions in our study should be related to the carbonate compound fraction. To confirm this, we performed a backward stepwise multiple regression analysis of the activity concentration of ^{238}U in *Spergularia rubra* as a function of the activity concentrations in the 5 soil fractions, checking for the absence of collinearity beforehand. This analysis confirmed the results obtained with the TFs by obtaining the model: $A_{S(238U)} = 1.142 + 0.083 \cdot F_3$, (R^2 representing 78.5% of the dispersion of the TF) in which $A_{S(238U)}$ is the activity concentration of ^{238}U in *Spergularia rubra* and F_3 is the activity concentration of ^{238}U in the carbonate compound fraction in the soil. The other fractions were eliminated in the regression because they gave values of $p > 0.05$ in the analysis of variance (ANOVA). Our results therefore allow us to conclude that *Spergularia rubra* in the analysed soils would take up U from the soluble uranyl carbonate complexes which, due to the pH of the soils, is more accessible for *Spergularia rubra*; this is consistent with the conclusions reached by other authors, including Vandenhove et al. [19, 36].

The TFs obtained for ^{226}Ra from the different soil fractions showed a statistically significant relationship for the exchangeable, organic and residual fractions. The uptake of ^{226}Ra by *Spergularia rubra* could be explained by the competitive action it maintains with Ca^{2+} and Mg^{2+} together with a basic pH value for the soil [76]. Although Vanderhove et al. [29] hypothesised that the Ca^{2+} and Mg^{2+} exchange is low because of the ion radii (Ra^{2+} 0.140 nm, Ca^{2+} 0.099 nm and Mg^{2+} 0.065 nm), Mortvedt [76] stated that the uptake of Ca^{2+} and Ra^{2+} would be considerably reduced by the presence of Mg^{2+} , NH_4^+ and K^+ at a basic soil pH. Soil 14 revealed this condition as the Ca^{2+} and Mg^{2+} concentrations were the highest (2.8 and 8.4% respectively) and the pH was 9.3, giving a TF for the whole soil (Fig. 5b) in the exchangeable and carbonate fraction of 0.0070, 0.49 and 0.026 kg kg $^{-1}$ respectively. The uptake of ^{226}Ra is therefore closely related to the exchangeable fraction, which also depends on the action of microorganisms to release Ca^{2+} , Mg^{2+} and Ra^{2+} from the organic fraction [77] and, possibly, from the non-reactive fraction [78]. However, because the Ca^{2+} and Mg^{2+} concentrations were determined using XRF we do not know the soluble fractions of these cations in the soil; this will be studied in future work. As in the case of ^{238}U , multiple backward stepwise regression was performed between the activity concentrations of ^{226}Ra in *Spergularia rubra* and in the soil, giving $A_{S(226Ra)} = -1.312 + 0.195 \cdot F_2$ (R^2 represents 63.0% of the TF dispersion) with F_2 being the activity concentration of the organic fraction. Although the soil fraction obtained for ^{226}Ra in the multiple regression analysis does not coincide with the individual TF results obtained, this equation is consistent, since the ^{226}Ra activity concentration in *Spergularia rubra* is higher than the exchangeable fraction and of the same order as the organic fraction. Our results therefore indicate an uptake of ^{226}Ra from the organic fraction without ruling out uptake from the exchangeable fraction.

It is clear, then, that the TF of ^{238}U obtained for the whole soil does not really explain its uptake in *Spergularia rubra*, as the fractions in which statistically significant proportions were obtained (carbonate compounds and organic matter) represent 39.0% of the total U activity concentration in the soil. The TF of ^{226}Ra obtained for the exchangeable, organic and non-reactive fractions represents 95.5% of the ^{226}Ra activity concentration and, for this reason, it could be assumed to be equivalent to the whole-soil TF. However, these conclusions can only be reached from the findings of the individual soil fractions. For this reason, it is necessary to know the associations of a given radionuclide in each different study area.

Conclusion

Transfer factors (TF) are a very useful tool for estimating the uptake of radionuclides into plants and from plants into the food chain. However, the general information provided by TFs can mask the sorption processes that radionuclides undergo in the various soil fractions due to their different chemical properties. This study demonstrates that UO_2^{2+} is retained more strongly than Ra^{2+} in organic matter due to its high ionic charge, preventing its uptake into *Spergularia rubra*. On the other hand, knowledge of the associations of U and Ra in the different soil fractions allowed us to check whether the TF obtained for the whole soil correctly represented the uptake into *Spergularia rubra*. The results indicate that the TF of ^{226}Ra for the total sample better represented the uptake than that of ^{238}U , thereby demonstrating the need to know the various associations of these radionuclides in the different soil fractions.

The behaviour of radionuclides in the natural radioactive series once again demonstrates that, despite the fear and danger associated with radioactivity, it is a useful tool that has existed in the earth's crust since its formation, and which must be investigated both from its own perspective and from that of other possible analogies with other stable elements.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10967-024-09626-z>.

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Author contributions V.M. Expósito-Suárez: Conceptualization, Methodology, Validation, Investigation, Writing—Review & Editing, Visualization, Supervision; J.A. Suárez-Navarro: Conceptualization, Methodology, Validation, Formal analysis, Investigation, Data Curation, Writing—Original Draft, Visualization, Supervision, Project administration; A. Caro: Software; M.B. Sanz: Writing—Review & Editing; M.B. Gómez-Mancebo: Conceptualization, Methodology, Validation, Investigation, Supervision; M. Barragán: Resources; M.J. Suárez-Navarro: Validation, Writing—Review & Editing; A. Ferreira: Methodology, Resources; T. Fitzgerald: Resources; P. Sánchez-Sánchez: Resources; E. Gil-Pacheco: Conceptualization. All authors have read and agreed to the published version of the manuscript.

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Data availability Raw data that support the finding of this paper are available from the corresponding author upon request.

Declarations

Conflict of interest The author declare no conflict of interest.

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