Journal of Radioanalytical and Nuclear Chemistry (2024) 333:5493–5501
https://doi.org/10.1007/s10967-024-09742-w

Activity concentration of natural radionuclides (^{238}U, ^{226}Ra, ^{232}Th, ^{228}Ra and ^{40}K) in lettuce cultivated in soil amended with niobium tailings

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Received: 5 February 2024 / Accepted: 28 August 2024 / Published online: 12 September 2024

Abstract

This study evaluates the possible agricultural application of calcium carbonate derived from niobium extraction. This carbonate is stored in dams, and it is enriched with radionuclides from ^{232}Th series, which imposes restrictions on its use. Activity concentration evaluation in soil was performed before the tillage of lettuce (*Lactuca sativa L.*) and the soil–plant transfer factor was determined. Results showed the dilution factor applied to the carbonate in the soil causes insignificant increments in soil activity concentration. In cultivated lettuce, high activity concentrations of ^{228}Ra and ^{226}Ra were found independently when using either the control or carbonate amended soil.

Keywords Environmental radionuclide · NORM · Gamma spectrometry · Soil analysis · Activity concentration · Soil and lettuce analysis

Introduction

The exploration of mineral resources, as in mining, must be understood in an integrated way alongside social environmental aspects -given its impacts in terms of waste generation and social vulnerabilities of the neighboring population—and economic ones, such as the generation of work posts and earning improvements [1].

The extraction and processing of ores may be associated with naturally occurring radioactive material (NORM) due to the presence of radioactive elements such as uranium and thorium in the mineral deposits which may be present in different concentrations. If these wastes are not managed and controlled properly, they may present risks to human health and to the environment. International and national standards play a fundamental role in creating clear and consistent guidelines for radiological safety and protection [2–4].

A possible use of mining residues to mitigate socio-environmental problems is the use of waste in activities such as civil construction or soil improvers. For the last application, the residues can be used to provide chemical elements considered as micronutrients for plants [5] while reducing their disposal in the mining sites and also reducing the use of fertilizers [6].

Brazil possesses the largest operating niobium reserve, being the leader in ferroniobium production (90% share). A large part of its production goes to the steel sector for use in metallic alloys, given that its presence increases the resistance and malleability of the alloy [7, 8]. One of the byproducts of this process is mainly composed of calcium carbonate that, due to its content in radionuclides and metals, presents restrictions for its use and therefore it is stored in dams.

Mining in Brazil is under several laws and regulations, both state and federal, which define norms and guidelines from concession to inspection and compliance with Brazilian mineral and environmental legislation.

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According to Brazilian standards, in regard to radiological protection and radioactive waste management, CNEN 3.01 and CNEN 8.01 standards [9, 10], materials with natural radionuclides are not subjected to safety and radiological protection requirements when activity concentrations of Th and U natural series radionuclides are below 1000 Bq kg^{-1}, making possible the utilization of such materials without incurring non-assessed risks to workers, the public and the environment.

The radionuclides activity concentrations in the residue object of this study already determined, vary around 2000 Bq kg^{-1} for ^{232}Th and ^{228}Ra [11], a value that is double the recommended amount in legislation and the activity concentrations of ^{238}U and ^{226}Ra are around 10 times lower [12].

The proposal that these residues can be used as soil conditioners may be a viable alternative as long as their safe use for human health and minimal impact on the environment is demonstrated and supported by studies in different areas, such as the analysis of the involved radionuclides behavior [13–17]. It is well known that the activity concentrations of natural radionuclides in food and water can significantly contribute to an individual's contact with radiation, whether through exposure or ingestion and vary according to several factors, such as local geology, climate and agricultural practices [18].

In agriculture, the use of calcium carbonate has the potential of substituting the liming process (addition of quicklime to the soil) used to increase the performance of crops in acidic soils in tropical and subtropical regions due to the increase in pH, making nutrients like phosphorus more available, in addition to supporting microbial activity and decreasing or extinguishing the phytotoxicity of other elements, such as aluminum and manganese. Liming is advantageous for increasing the water absorption capacity of plants, as well as nutrient absorption [19].

The main objective of this work is to evaluate the availability of natural radionuclides, considered important from the point of view of radiological protection (^{238}U, ^{232}Th, ^{226}Ra, ^{228}Ra and ^{40}K), present in calcium carbonate, generated during niobium production as a possible agricultural input. For this purpose, trials were carried out with lettuce plantations. The analysis carried out seeks to understand the radiochemical behavior of these elements present in carbonate and their behavior in the soil, in the plant and in possible absorption through ingestion.

Experimental

Sampling

The carbonate samples were supplied by a NORM industry, located in Catalão, Goias, Brazil. The soil used in this study, classified as sandy clay loam [20] soil, was collected in Taubaté town, São Paulo State, from the A horizon. For the experiment, 1 m^3 of soil was mixed with carbonate or limestone, according to each proposed treatment, and a portion was left as control, without any mixture.

The planting and care of the lettuce (*Lactuca sativa L.*) (n = 30) samples was conducted at the University of Taubaté on the Agronomy campus. There were two crops of lettuce, each of them having five samples of each treatment for analysis, in a total of 15 samples per crop. The lettuce seedlings were germinated in a greenhouse for two weeks and then transplanted into plastic pots of 20 cm in diameter. Completely randomized design (CRD) model, in a 4 × 5 factorial scheme, was applied: soil and limestone; soil and carbonate; and, control soil, each with five repetitions [21]. In each crop a proportion of 1 kg of soil for 3 g of the amendment was used [19, 22]. Two plantings were made, using the same pots, without soil reposition, following the recommendation that in the first planting the soil is not adequately conditioned for the plant's nutritional development while in the second, the lettuce is able to better absorb the nutrients necessary for its development [23]. At the moment of the lettuce sampling, in each harvesting, a portion of soil was also collected to perform the proposed analysis.

Gamma spectrometry

The activity concentrations of ^{226}Ra, ^{228}Ra and ^{40}K of carbonate and soil samples were measured by gamma spectrometry which was performed using the EG&G Ortec HP-Ge detector, with a nominal efficiency of 60% and a resolution (FWHM) of 0.9 keV for the photopeak of 122 keV of ^{57}Co and 1.8 keV for the photopeak of 1332 keV of ^{60}Co. For detector calibration, reference materials (RM) IAEA RGU-1, IAEA RGTh-1, and IAEA RGK-1 were used and measured in the same geometry as the samples. Background correction as done by a measurement of the empty sample flask for 172,800 s and subtracted from RM and samples counting. Carbonate, soil samples and RM were placed in polyethylene flasks of 5 cm diameter and 1.5 cm height, sealed and set apart for about four weeks, prior to the measurements, to ensure they reached a radioactive equilibrium between ^{226}Ra, and its short-living decay products was reached and counted for 86,400 s. The ^{226}Ra activities were determined by taking the mean activity of three separate photopeaks of its daughter nuclides: ^{214}Pb at 352 keV and ^{214}Bi at 609 keV. The ^{228}Ra content was determined by measuring the intensities of the 338 keV and 911 keV gamma-ray peaks from ^{228}Ac. ^{40}K was determined directly through its photo peak with an energy of 1460 keV.

Mineralogical characterization of niobium mining exclusion

The mineralogical analysis of the destruction carbonate samples (n = 6) was carried out using X-ray Diffraction (XRD). This direct application technique allows for the identification of the minerals present and matches studying their crystallographic characteristics. The analysis technique consists of focusing a beam of X-rays, of a known wavelength, on a thin layer of powder. As a consequence, the beam diffracts on impact and reflects with angles that are characteristic of the crystalline lattice, resulting in the corresponding diffractogram [24].

The diffractograms were obtained using SmartLab SE equipment, from the Rigaku brand, operating with a copper tube (wavelength kα1 = 1.54059 Å), linear detector Dtex Ultra 250. The conditions for measuring the samples, in powder form, were: Scanning (2θ) from 5° to 70°, at a speed of 2°/minute with a step of 0.02°. All samples were rotated at 60 RPM during the diffractogram acquisition.

Instrumental neutron activation analysis

All the samples were analyzed by instrumental neutron activation analysis (INAA) for Th, U and K determination. The carbonate and soil samples were dried for one day at a temperature of 40 °C until constant weight had been reached. Stones, gravel, leaves, and roots were removed from the sample, and then it was weighed. In the sequence, these samples were dried in an oven at 100 °C for 24 h to attain constant dry weight, crushed into a fine powder, and homogenized by passing it through a 125-µm sieve. The dried and crushed samples of about 120 mg were packed in polyethylene bags and irradiated in the IEA-R1 nuclear reactor along with reference materials (Estuarine Sediment, SRM 1646a from the National Institute of Standards and technology (NIST), and Syenite, Table Mountain (STM-2) from the United States Geological Survey (USGS)) used for concentration determination by the comparative INAA method. The measurement of induced gamma activity was performed using the same gamma detector described above. Details of the analytical methodology are described in [25]. The detection limit for INAA was calculated as proposed by Currie [26]. The average of detection limit is 86, 0.09, and 0.5 mg kg^{-1} for ^{40}K, ^{232}Th, and ^{238}U, respectively.

Radiochemical separation for ^{226}Ra and ^{228}Ra in lettuce samples

For analysis, the lettuces were weighed and calcinated at 1000 °C for 1 h, obtaining lettuce ash. Two 0.5 g aliquots of each lettuce sample were dissolved in a microwave oven with concentrated HNO_3, after which the samples were led to 1 L with ultrapure water on a hot plate. Stable Ba carrier, with a concentration of 20 mg mL^{-1}, and 50 mL of H_2SO_4 3 mol L^{-1} were added under heating and stirring for the precipitation of $(BaRa)SO_4$ with the addition of 40% NH_4OH (20–30 mL). After 24 h, the supernatant was discarded and, to the precipitated, 2 g of nitrile tri-acetic acid-NTA (Titriplex I), 7 mL of NaOH (6 mol L^{-1}) and 40 mL of ultrapure water were added. The solution was heated for solubilization, then 5 mL of $(NH_4)_2SO_4$ (25 g L^{-1}) and glacial acetic acid (10 mL) were added for Ra isotopes and Ba precipitation.

In the precipitate containing the radium isotopes, 2 g of ethylene di-amino-tetra-acetic acid – EDTA (Triplex III), 7 mL of 40% NH_4OH and 40 mL of ultrapure water were added; the solution was heated for the precipitate solubilization. After solubilization, $(NH_4)_2SO_4$ (25 g L^{-1}) and glacial acetic acid were added for $Ba(Ra)SO_4$ precipitation and the solution was vacuum filtered; the chemical yield of the procedure was determined gravimetrically [27].

The methodology for analyzing the radiochemical yield of Ra in lettuce samples and soil used in planting was carried out as described in [28].

The dried precipitate was measured by gamma spectrometry using the determination of the photo peak of 186.21 keV for ^{226}Ra and the photo peaks in 911.1 keV and 968.9 keV, corresponding to ^{228}Ac, for ^{228}Ra. The radiochemical procedure removes interferences such as ^{235}U and, for this reason, the peak of 1857 keV is not observable in the samples' spectra.

The detection limit for radiochemistry was calculated as proposed by Curie [29]. The average of detection limit for peak of 186.21 keV for ^{226}Ra is 2.3 Bq g^{-1} and 0.18, 0.26 Bq g^{-1} for peaks in 911.1 and 968.9 keV, respectively, corresponding to ^{228}Ra.

Transfer factor (TF)

The TF of trace elements within the soil–plant chain is a part of the biochemical cycling of chemical elements. It is a complex process of natural and anthropogenic factors [30]. The study of TF can provide a long-term understanding on what could be the behavior of other elements present in the calcium carbonate, if they can pollute groundwater or bio-accumulate in lettuce. The TF was calculated as the ratio of ^{238}U, ^{232}Th, ^{226}Ra and ^{228}Ra concentrations in the plant divided by that in the corresponding soil as shown in Eq. (1) according to [31]

$$TF = \frac{C_{plant}}{C_{soil}} \tag{1}$$

where, C_{plant} and C_{soil} are the radionuclides activity concentration at dry weight sample (mg kg^{-1}) for each different soil crop.

Results and discussion

Activity concentrations in carbonate and soil

The activity concentrations of radionuclides in the carbonate, soil prior the plantation, and soil amended with the carbonate and limestone after the plantation are presented in Table 1. For comparison the radionuclides activity concentrations in other soil amendments and their respective control soils are also presented. Also, the activity concentration of residues from other NORM activities and the global mean for soil [32] are presented in the same table.

The activity concentration of the carbonate presents values higher than 2000 Bq kg^{-1} for the ^{232}Th decay series radionuclides, which prevents its utilization according to the Brazilian regulation. These high activities are directly related to the mother rock forming the niobium deposit [40]. Among the other soil amendments, it is seen that higher activity concentrations occur mainly for ^{226}Ra in fly ash and red mud. ^{238}U In the carbonate is at the same level as that found in phosphogypsum and ^{40}K is the same order of magnitude as that presented by red mud and fly ash.

In order to present a comparison between the activity concentration of the soil amended with carbonate and the control soil used in this study, the ratios of activity concentration for each radionuclide were calculated, which are: 4.81 for ^{40}K, 0.98 for ^{238}U, 0.79 for ^{226}Ra, 1.43 for ^{232}Th, and 1.10 for ^{228}Ra. These values show that adding carbonate to the soil in the same proportion recommended for limestone addition, the activity concentrations remain practicality the same even for the Th series radionuclides. As there is still no regulation for the use of carbonate residues as a soil conditioner, the results obtained were compared with phosphogypsum and other amendment materials (Table 1).

The activity concentrations found in the soil used for lettuce plantation in this study, although higher than the global mean reported by UNSCEAR [32], are comparable with the control soil reported in other studies and it is noticeable that the application of the amendment does not significantly change the soil activity concentrations even with the use of the carbonate.

There is a tendency for Brazilian soils to have higher levels of ^{228}Ra than ^{226}Ra due to the concentrations of thorium being higher than those of uranium [41, 42].

The average concentration of ^{40}K activity in the soil in this work is below the value obtained for the unfertilized soil (448 ± 18 Bq kg^{-1}), and also for the soil fertilized with ammonium phosphate [15].

Table 1 ^{232}Th and ^{238}U activity concentration ± deviation [Bq kg^{-1}] in soil, carbonate, soil condition with carbonate and soil condition with limestone of this work and activity concentrations studied in the literature

Sample used in harvesting	^{40}K	^{238}U	^{226}Ra	^{232}Th	^{228}Ra
Carbonate (this work)	471 ± 91	160 ± 65	264 ± 21	2187 ± 278	2198 ± 316
Control soil	52 ± 2	91 ± 1	74 ± 35	155 ± 7	91 ± 1
Soil + limestone	181 ± 12	66 ± 1	< 1.92	154 ± 5	< 0.18
Soil + carbonate	250 ± 9	89 ± 2	58 ± 4	222 ± 8	100 ± 4
Phosphogypsum [33]	11 ± 4	196 ± 6	630 ± 4	–	8.9 ± 0.5
Control soil	760 ± 50	23.5 ± 0.5	27.7 ± 0.4	–	32.3 ± 1.0
Soil + PG	798 ± 27	23.9 ± 1.0	39.3 ± 2.3	–	32.2 ± 1.0
Phosphogypsum [34]	–	< 0.9	320 ± 10	130 ± 20	210 ± 10
Control clay soil	–	140 ± 20	58 ± 2	100 ± 30	96 ± 3
Clay soil + PG	–	130 ± 20	58 ± 2	53 ± 1	100 ± 5
Control sandy soil	–	39 ± 6	15 ± 1	32 ± 2	29 ± 3
Sandy Soil + PG	–	45 ± 7	15 ± 1	31 ± 1	30 ± 4
Fertilized Punjab field [15] means	554 ± 25.7	42.2 ± 1.1	51.2 ± 1.7	72.9 ± 0.8	–
Unfertilized Punjab field — means	448 ± 18	37.2 ± 0.2	48.3 ± 1.8	57.2 ± 1.1	–
Fly ash [35]	376	–	100	–	141
Soil + fly ash	260	–	31	–	75
Fly ash range for 16 EU countries [36]	157–900	–	75–815	37–140	–
Calcium carbonate derived from phosphogypsum (India) [37]	–	80 ± 20	760 ± 3	–	–
Red mud—range [38]	169 ± 66	–	155 ± 66	332 ± 127	–
Dewatered sewage sludge [39]	–	37.3	14.4	–	13.5
UNSCEAR [32]	412	45	–	30	–

–Not reported in the cited references

Mineralogical characterization of the carbonate residue

These conditions were sufficient for the intensity of the most intense peak (calcite) to reach more than ten thousand counts. In Fig. 1 it is observed that all residue samples presented the same diffraction peaks, indicating homogeneity in relation to the mineral phases. The relatively broad peaks occur due to the fact that the samples are natural and, despite being crystalline, they present deformations in the lattice that provide the broadening of the diffraction peaks.

Another reason that contributes to this enlargement is the overlapping of the peaks of the different phases present (Fig. 1), which were identified, including minerals, calcite—$Ca(CO_3)$, fluorapatite—$Ca_5(PO_4)_3F$, biotite—$KFeMg_2$ $(AlSi_3O_{10})(OH)_2$, dolomite—$CaMg(CO_3)_2$, barite—BaO_4S and Richterite, a silicate mineral from the group of sodium-calcium amphiboles of the type $(Na_2,Ca)2(Mg,Fe,Mn)_5Si_8O_{22}(OH,F)_2$.

In Fig. 1 all standard diffractograms presented were obtained from the ICSD- Inorganic Crystal Structure Database, through the Capes periodic portal. The phases were divided into two parts for easier viewing. Although the samples are of mineral origin, we did not observe the presence of quartz and other important minerals present in the mineralogy of the Brazilian soil. This fact is easily explained when we observe that the samples are the result of the separation of carbonatites [11, 43] from an extraction mine and that, after the first flotation process of these carbonatites, only some of the mineral phases present were physically separated and used for this work. Quartz and other minerals are separated in subsequent flotations until reaching the mineral of interest, pyrochlore, from which niobium is extracted, a metal commercially exploited in this mine.

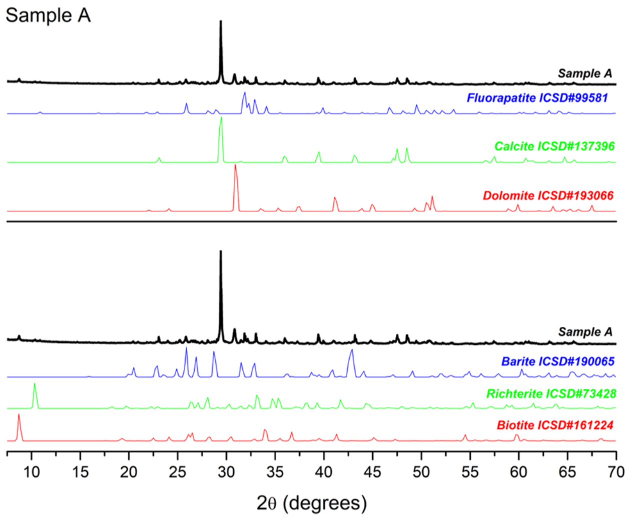

Fig. 1 Identification of the mineral phases present in niobium tailings

Activity concentration in lettuce

In Table 2, the average activity concentrations of radionuclides from the uranium series, ^{238}U and ^{226}Ra, from the thorium series, ^{232}Th and ^{228}Ra and ^{40}K are presented in lettuces obtained from the two harvestings.

It can be observed from Table 2 that the activity concentrations, except ^{40}K, of the analyzed radionuclides in lettuce samples reported in the literature varies from mBq kg^{-1} to tenths of Bq kg^{-1}, even when dry weight is reported. The activity concentration of the U and Th decay series radionuclides in plants depends on their mobility in soils and their transfer pathways, which in turn depends on the type of soil and plant, climate, relief, vegetation season, and the radionuclide content in soil [54]. In this study, ^{232}Th activity concentration in soil is greater than that of U. In clay soils, the radionuclides activity concentrations tend to be higher than in sandy soils [34].

In the samples presented in this study, it is observed that the activity concentration of ^{228}Ra is significantly higher in lettuce than that of ^{226}Ra, in all cases measured, and both are greater than the concentrations of ^{232}Th and ^{238}U, respectively. Except for the samples reported by Carvalho et al. [53] the ^{226}Ra activity concentrations tend to be higher than those of ^{238}U, probably due to its chemical resemblance with calcium, an essential element to plants [55].

Considering the standard deviation of the five replicates of each treatment, no significant variation occurred from the first to the second plantation.

The concentration of U and Th activity was also evaluated in lettuce roots, as shown in Table 3.

It has been reported in numerous publications that U and Th activity concentrations in roots are higher than in leaves and in seeds [54, 56]. In general, roots serve as a natural barrier preventing the transport of many trace metals, including radionuclides to the plant's aerial parts. Moreover, the rate of radionuclide translocations from roots to shoots is probably species-dependent [54].

Transfer factor

The soil–plant transfer factor (TF) is an important parameter that can be used to estimate the levels of different elements in plants and can simplify the estimation of transfer of these elements through the food chain. Table 4 presents the TF values for radionuclides present in lettuce. As the roots also plays a fundamental role in the radionuclide's distribution in the process of soil elements absorption, its concentrations of ^{238}U and ^{232}Th, determined by INAA were also determined and presented in the same table. The small amount of root samples did not allow the determination of Ra isotopes by the radiochemical separation process.

Table 2 Activity concentrations' average ± deviation per radionuclide [Bq kg^{-1}] in lettuce's fresh mass for this work (n = 2) and in literature

	Sample [Bq kg^{-1}]	^{40}K	^{238}U	^{226}Ra	^{232}Th	^{228}Ra
First harvesting	Lettuce control	368 ± 5	0.061 ± 0.008	49 ± 11	0.026 ± 0.002	63 ± 22
	Lettuce in limestone	694 ± 16	0.07 ± 0.02	123 ± 95	0.118 ± 0.003	222 ± 69
	Lettuce in carbonate	423 ± 5	0.010 ± 0.003	53 ± 30	0.076 ± 0.003	87 ± 26
Second harvesting	Lettuce control	748 ± 12	< 0.006	45 ± 13	0.001 ± 0.004	120 ± 91
	Lettuce in limestone	540 ± 5	< 0.006	157 ± 93	0.108 ± 0.003	147 ± 49
	Lettuce in carbonate	675 ± 10	0.035 ± 0.009	52 ± 23	0.121 ± 0.003	128 ± 52
Works of literature	[44]	89.6 ± 0.7	–	0.17 ± 0.03	0.38 ± 0.05	–
	[45]	54 ± 2	–	0.2 ± 0.1	0.160 ± 0.003	–
	[34]	–	< 0.03	3.00 ± 0.03	0.0080 ± 0.0003	0.63 ± 0.06
	[46]	–	0.02 ± 0.07	0.05 ± 0.05	–	0.08 ± 0.06
	[47]	54.3 ± 1.63	0.40 ± 0.01	0.24 ± 0.00	0.8667 ± 0.0267	–
	[48]	–	0.12 ± 0.02	0.599 ± 0.061	0.094 ± 0.009	0.39 ± 0.06
	[49]	–	4.35 ± 1.14	–	2.50 ± 1.55	–
	[50]	–	–	0.025–0.063	–	0.030–0.072
	[44] (dry weight)	317 ± 6	–	22.1 ± 1.4	29.6 ± 1.2	–
	[51]	371	12.07	13.50	16.4	–
	[52] (dry weight)	1235 ± 9.9	–	6.9 ± 0.6	–	4.30 ± 0.4
	[13] (dry weight)	–	–	1.5	–	0.88
	[53]	–	123 ± 4	29.7 ± 3.5	4.3 ± 0.3	–
	[46] (dry weight)	–	0.3–1.37	1.01–2.77	–	1.31–4.94

–Not reported in the cited references

Table 3 ^{232}Th and ^{238}U average activity concentration ± deviation [Bq kg^{-1}] in lettuce's root (*Lactuca sativa*) (n = 2)

Sample [Bq kg^{-1}]		^{232}Th	^{238}U
First harvesting	Lettuce's root in soil	15.56 ± 4.57	20.36 ± 3.84
	Lettuce's root in limestone	23.43 ± 2.26	21.25 ± 0.80
	Lettuce's root in carbonate	< 4.36[a]	18.97 ± 0.83
Second harvesting	Lettuce's root in soil	60.58 ± 3.90	109.05 ± 69.92
	Lettuce's root in limestone	24.44 ± 1.24	19.71 ± 0.95
	Lettuce's root in carbonate	< 4.36[a]	20.26 ± 0.72

[a] Limit of detection

It has been reported in numerous publications that U and Th activity concentrations in roots are higher than in leaves and seeds [54, 56]. In general, roots serve as a natural barrier preventing the transport of many trace metals, including radionuclides to the plant's aerial parts. In this work, on the other hand, the activity concentrations of ^{232}Th in lettuce roots treated with the carbonate was lower than the detection limit. This probably is due to the presence of phosphate compounds in the carbonate, as shown by the XRD diffractograms, indicating the presence of phosphate minerals such as flourapatite. Thorium phosphates are highly insoluble, and it has been already shown that the phosphate addition to the soil significantly reduce Th absorption by the roots [57].

Moreover, the rate of radionuclide translocations from roots to shoots is species-dependent [54] and probably dependent of other factors such as foliar absorption of dust, the intensity of wind uplift, and the concentration of thorium in water used for irrigation [58, 59].

Several factors affect the TF, including how the nuclide is present in the soil, the type of soil and the physico-chemical characteristics of the soil, such as texture, pH, exchangeable K and Ca, the type and amount of clay and organic matter, plant species and crop management practices [30, 47, 61].

There was no evident difference between the TF for lettuces in the two plantations for the radionuclides analyzed. The TF values for ^{226}Ra, ^{228}Ra and ^{232}Th in this study are lower than the values found by [34, 46, 47], in which the TF of lettuce was obtained for different types of soil conditioned with phosphogypsum in the first two cases and the control soil in the last study.

Table 4 TF for radionuclides ^{238}U, ^{226}Ra, ^{232}Th and ^{228}Ra in lettuce and roots from different treatments

	Sample	^{238}U	^{226}Ra	^{232}Th	^{228}Ra
First harvesting	Lettuce control	0.00067 ± 0.00001	0.7 ± 0.2	0.0004 ± 0.0002	0.7 ± 0.2
	Lettuce in limestone	0.00104 ± 0.00002	1.3 ± 1.3	0.0008 ± 0.0003	2.4 ± 0.8
	Lettuce in carbonate	0.000108 ± 0.000002	0.9 ± 0.5	0.0003 ± 0.0002	0.9 ± 0.3
	Lettuce's root in soil	0.0120 ± 0.0002	1.4 ± 0.3	0.005 ± 0.003	1.1 ± 0.1
	Lettuce's root in carbonate	0.0128 ± 0.0003	1.3 ± 0.2	[a]	1.33 ± 0.07
Second harvesting	Lettuce control	[a]	0.6 ± 0.5	$8.2\ 10^{-6} \pm 4\ 10^{-7}$	1.3 ± 1.0
	Lettuce in limestone	[a]	1.3 ± 0.5	0.0007 ± 0.0003	1.6 ± 0.5
	Lettuce in carbonate	0.000391 ± 0.000008	0.9 ± 0.4	0.0005 ± 0.0003	1.3 ± 0.5
	Lettuce's root in soil	0.12 ± 0.04	0.8 ± 0.3	0.07 ± 0.04	2.8 ± 0.5
	Lettuce's root in carbonate	0.029 ± 0.006		[a]	2.77 ± 0.07
	[34]	–	0.02	0.000257	0.021
	[46]	0.0005 ± 0.052	0.001 ± 0.055	–	0.001 ± 0.068
	Water spinach's root [60]	–	0.20	0.38	–
	[47]	0.012 ± 0.001	0.00967 ± 0.00003	0.0070 ± 0.0003	–

–Not reported in the cited references

[a] Not possible to calculate because the activity concentration is lower than the detection limit

Conclusion

The calcium carbonate generated as a niobium mining residue showed high values for the activity concentration of radionuclides ^{238}U, ^{232}Th, ^{228}Th, ^{226}Ra, ^{228}Ra and ^{40}K. When added to the sandy clay soil used in this study it did not cause a significant increase in activity concentrations of the radionuclides. The control soil and the mixture soil + carbonate were similar to the values observed in other studies.

The calculated radiological indices showed that the use of the carbonate does not pose a threat for the public and workers exposed to the amended soil. The ^{228}Ra activity concentration in lettuce was higher than the other analyzed nuclides and was the one that most contributed to the effective dose for ingestion, followed by ^{226}Ra. This pattern was observed both in the control soil and in the amended soil with limestone and carbonate residue. It was verified that in the conditions in which this experiment was realized, the absorption of radium isotopes was favored, shown by their TF. Although in high concentrations in the carbonate, the ^{232}Th and ^{238}U activity concentrations have an insignificant contribution to this dose, with low TF values.

The amount of ^{232}Th and ^{228}Ra classify this residue as not suitable for utilization according to the Brazilian regulations. Nevertheless, the results showed that, in spite of these values, its use as a soil amendment does not pose a threat for consumers from the point of view of radiological implications for ingestion. It is important to note that the environmental impact and the long-term application still need to be assessed.

Acknowledgements The authors would like to acknowledge the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for the scholarship and financial support (n. 140439/2019-6). Authors are grateful to Mr. Ferreira and CMOC International for authorizing the sampling.

Funding CNPq, 140439/2019-6, Rafaella Menezes Ayllon.

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