



Th-232 Radiological Aspects of Carbonate Niobium Mining Waste Use as Agricultural Amendment

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ABSTRACT

The use of mining residues in agriculture may be possible, as long as there be previous studies in different areas, one of them being the analysis of the involved radionuclides behavior. This study determined the concentrations of 232 Th activity in soil, soil treated with lime, soil with carbonate residue from niobium mining, soil with the mixture of lime and carbonate, in two moments. The transfer factor of 232 Th from the soil to the plant was analyzed, in this case, lettuce (n=20), in the different types of treatment and in two moments. The addition of carbonate to the soils did not significantly alter the levels of radioactivity for 232 Th radionuclide in lettuce. The effective dose resulting from the lettuce ingestion varied from 0.09 to 0.3 µSv y⁻¹.

Keywords: NORM, absorption of Th, niobium.



1. INTRODUCTION

Brazil is the world leader in the ferroniobium production, accounting for more than 90% of world production. This alloy is widely used in superalloys, superconducting magnets and in medical and jewelry applications [1].

The main rocks that contain niobium-enriched mineral deposits are carbonatites, which are defined as igneous rocks with more than 50% carbonate minerals. They are common in complexes of magmatic origin associated with alkaline rocks [2].

To beneficiate the ore, it is necessary to submit the rock to crushing and pre-concentration process by means of magnetic separation, in which the magnetic particles are considered as a product, while the non-magnetic particles are considered as waste. Then, grinding and classification is carried out, followed by unmudding, to remove very fine particles (< 0.010 mm). After this process, the ore pulp is directed to silicate flotation. In this flotation, the pulp has a basic pH around 10. The silica concentrates are obtained from the silicate flotation cleaning step, are the particles from the foam [3].

After obtaining the silicates, carbonate flotation occurs, which also takes place in two stages and this flotation also has a basic pH, of approximately 10. From its foam, the carbonate concentrates are acquired. Then, silica and carbonate concentrates are sent to containment dams, generating process residue deposits [3]. Figure 1 presents the process of niobium beneficiation.



Figure 1: Process of Niobium beneficiation

Due to the geological association of niobium ore with Naturally Occurring Radioactive Material (NORM) and the large amounts of waste produced, by its exploitation, the latter constitute an economic and ecological burden if not properly disposed or re-used. Due to the radioactivity of NORM residues, there is the need of controlling the radiation exposure of workers and general public, in accordance with current national and international standards of safety and protection [4].

According to brazilian standard, in regard to radiological protection and radioactive waste management (CNEN 3.01 and CNEN 8.01 standards), 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, being possible, therefore, that such materials be utilized without incurring in non-assessed risks to workers, public and environment [5,6].

Mining in Brazil is subjected to 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.

The use of mining residues in agriculture may be possible, as long as there are previous studies in different areas, one of them being the analysis of the involved radionuclides behavior. Considering the need of expansion, development and the process of food supply to society, it is necessary to evaluate agricultural production using fertilizers of organic or mineral origin which benefits from ferroniobium production waste, if it does not cause damage to population health, providing the necessary nutrients to the plants.

The objective of this work is to evaluate the ²³²Th activity concentration in niobium mining waste for use as agricultural input in accordance with the newly wasteless concept directed towards the social and technological environment concern. This evaluation has been made with different soil treatments for lettuce culture, observing the transfer factor of ²³²Th from soil to leaves. The analyzed waste is produced in the city of Catalão - GO, Brazil, as tailings in the early stages of the niobium production.

Previous measurements carried out in this waste showed that the ²³²Th activity concentration has mean value of 1,141 Bq kg⁻¹, reaching up to 5,056 Bq kg⁻¹, depending on the lithological domain it comes from [7].

Soil is not only a part of the ecosystem, but also plays a fundamental role in human survival, which is tied to the maintenance of its productivity. Soil has very important and complex functions

as filter, storage, and transformation systems, protecting the global ecosystem against the effects of pollution [8].

Thorium contents in uncontaminated soils worldwide vary within the range of $8 - 11 \text{ mg kg}^{-1}$ and large amounts of Th may be introduced into the biosphere from fossil-fuel power plants and from phosphate fertilizers [8]. This element is widely distributed in the environment and occurs at low levels in water, soil, rocks, plants, and animals. Thorium is a typical lithophilic element and its geochemical behavior is very similar to the rare earth elements (especially cerium), zirconium, hafnium and uranium [9] being a rather immobile element.

Furthermore, Th-232 has sufficient mass to make them chemically toxic and normally accumulate in soils and sediments. The output of this compartment occurs through geological processes such as students, and sometimes by leaching [10].

The study of Th transfer from soil to edible vegetation through root uptake is very important, especially considering accumulation of this radionuclide in food chains. An understanding of the Th mobility in soils and its transfer to different plants requires a detailed knowledge about the interactions of this nuclide with abiotic and biotic soil components. Previous experimental results demonstrated that distribution of Th in soil is highly variable [9]. Despite numerous studies on Th contents in vegetation, there is little information yet related to its uptake rate and storage by different plant species. In general, roots serve as a natural barrier preventing the transport of many trace metals, including radionuclides to upper plant parts. Moreover, the rate of radionuclide translocations from roots to shoots is probably species-dependent. It may be different for different species and even cultivars. Generally, Th concentrations in roots are higher than in leaves and in seeds [11].

Due to the utilization of municipal and industrial wastewater, as well as the uncontrolled use of chemical and livestock fertilizers, leafy vegetables have a high content of heavy metals, like Th [12].

The general public is exposed to Th by means of external gamma radiation, building materials and food consumption. Whether human-made or natural in origin, radioactive material transfers to the human body through the food chain [13].

Vegetables, particularly leafy vegetables, receive more heavy metal through their roots and store them in their tissues than other plants [14].

In regard the intake in the diet, ²³²Th ingestion dose coefficients for all age are up to one order of magnitude higher than ²³⁸U ones [15]. Scarce data are available on ²³⁸U intake with the diet and even less on ²³²Th, and few countries have conducted representative national surveys [16,17].

2. METHODOLOGY

To assess the radiological implications of using the niobium carbonate waste as soil amendment, 40 samples of lettuce (*Lactuca sativa*) from two different harvesting, the first one with 20 samples and 20 from the second one, making use of the same vases of first harvesting to improve nutrients absorption. Lettuce was chosen due to its short time of growing and is a benchmark cases in literature.

The lettuce cultivation was carried out in partnership at the University of Taubaté, UNITAU, in Taubaté campus, in collaboration with the Department of Agricultural Sciences, which was responsible for planting and caring lettuce samples from seeding to seedling growth and transplanting for vases.

The lettuce was cultivated in four different treatments and two harvesting: a) soil, b) soil + lime, c) soil + lime + carbonate and d) soil + carbonate. In the treatments b and d, 3 kg of lime or carbonate was added to 1 m³ of soil. In the condition c, 1.5 kg of lime and 1.5 kg of carbonate was added to 1 m³ of soil. The lettuce samples were arranged respecting the completely randomized design (CRD) [18].

In each treatment, the substrate and lettuce were analyzed by instrumental neutron activation analysis (INAA) for Th determination. In the laboratory, the soil samples were dried for two days at temperature of 40 °C until constant weight has been reached. Stones, gravels, leave and roots were removed from the sample, and then it was weighed. The samples were dried in an oven at 100 °C for 24 h to attain constant dry weight, crushed into 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 used for concentration determination by the comparative INAA method. The statistical treatment of experimental data included a calculation of mean concentrations for two replicates and analysis of variances to estimate statistically significant differences between groups of samples. The measurement of induced gamma activity was performed using a Ge-hyperpure detector.

Estuarine Sediment, SRM 1646a from the National Institute of Standards and technology (NIST), Syenite, Table Mountain and STM-2 from the United States Geological Survey (USGS), both with 120 mg each and synthetic standard solutions (SPEX Certiprep) were used as certified reference materials. Pipetted standards, reference materials and samples were irradiated together

under a flux of the order of 10^{12} n cm⁻² s⁻¹, in the IEA-R1 nuclear research reactor at IPEN-CNEN/SP. Highpure germanium detector was used for the induced gamma radiation measurement in the plant and soil material.

In the comparative method [19,20] the concentration is determined by comparing the peak areas obtained in the gamma spectrum of the irradiated sample with the peak areas of the same elements in the spectra of the reference materials that were irradiated together with the samples, used for the calculation the Eq (1):

$$C_{ai} = \frac{\left(A_{ai} M_p C_{pi}\right) e^{\lambda(t_a - t_p)}}{A_{pi} M_a} \tag{1}$$

Where,

Cai: Concentration of element i in the sample [mg kg⁻¹];

Cpi: Concentration of element i in the reference material [mg kg⁻¹];

Aai: Activity of element i in the sample [cps];

Api: Activity of element i in reference material [cps];

Ma and Mp: Sample and reference material masses, respectively [kg];

 λ : Decay constant of the radioisotope formed [s⁻¹];

ta - tp: Time difference between the sample and reference material counts, respectively [s].

2.1. pH in soil and carbonate

To carry out this analysis, 10 g of carbonate, 10g of soil and 10.3g of the mixture of soil and carbonate (10g, 0.3g, respectively) were placed in a 100 mL beaker, then 25 mL of a 1.0 mol L⁻¹ potassium chloride solution was added, stirred with an individual glass rod and left to rest for an hour. After the time, the sample was shaken again with a glass rod and then the pH was read with a Quimis brand pH meter previously calibrated with pH 4 and pH 7 standard solutions.

2.2. 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 [21]. The TF was calculated as the ratio of Th concentrations in the plant divided by that in the corresponding soil as shown in Eq. (2) according to [22]

$$TF = \frac{C_{plant}}{C_{soil}}$$
(2)

where, C_{plant} and C_{soil} are the ²³²Th activity concentration at dry weight sample [mg kg⁻¹] for each different soil treatment.

3. RESULTS AND DISCUSSION

Physical-chemical parameters of soil

Soil-to-plant transfer of naturally occurring radionuclides is largely affected by the soil physiochemical properties such as pH, cation exchange capacity (CEC), potassium (K), calcium (Ca), phosphor (P) and organic matter [13]. The main soil parameters that govern processes of sorption and desorption of trace elements was presented in **Erro! Fonte de referência não encontrada.** and **Erro! Fonte de referência não encontrada.**.

The measurements of soil pH are presented in Table 1 for soil, carbonate and the mixture of soil plus carbonate. They correspond to the average and standard deviation of two measurements of each sample. It can be observed that the addition of carbonate contributed to pH increase, and that is the reason it is added to correct soil acidity. The soil pH has an influence on the adsorption of Th. In basic soil pH, this element is more easily adsorbed [15].

Sample	$pH \pm deviation$	
Soil	4.97 ±0.02	
Carbonate	8.78 ± 0.01	
Soil and Carbonate	6.18 ± 0.03	

Table 1: Values of pH measurements (mean ± standard deviation) of carbonate, soil, soil and
carbonate samples, n=2

In Table 2, the physico-chemical parameters, CEC, Ca, K, and P concentrations and organic matter are presented.

Sample	CEC	Ca [mmol/dm³]	K [mmol/dm³]	P [mg/dm ³]	Organic matter [g/dm³]
Soil	61.2	25	2.2	7	14
Particle	size and textu	ure g/kg	Clay 264	Silt 141	Sand total 595

Table 2: physical-chemical parameters of soil

The behaviors of heavy metals such as Th radionuclide in soil are significantly related to soil properties. For estimate the toxicity of elements in soil were used the phytoavailability of this heavy metal [23]. The lower the pH value, the higher the bioavailability of Th. In this case, the addition of carbonate waste to soil increased the pH value, reducing the bioavailability of Th to the lettuce.

3.1. Th activity concentrations in soil samples

Thorium activity concentration in the carbonate niobium waste presented mean value of 652 ± 61 Bq kg⁻¹ and in soil with no addition of any amendment (treatment a), the concentration was 37 ± 2 mg kg⁻¹. In the substrates used in treatments b (soil + lime), c (soil + lime + carbonate), and d (soil + carbonate), the concentrations of this nuclide were 30.7 ± 0.3 , 36 ± 7 and 44 ± 2 and respectively. No significant difference is observed in Th concentration for the soil with no amendment and the ones treated with lime, carbonate or both. As a reference, in Table 3 there are values observed in other studies. It has been observed that the soil used in the current study has activity concentration

higher than the global average reported by UNSCEAR but it is in the range of concentrations reported for other locations.

The Th radionuclide is component of the biosphere, and thus occur naturally in all soils and plants, though their concentrations in plants may be rather low [9]. Reported values of Th in soil treated with different types of amendment shows relatively similar results to the ones found in this study. Soil fertilized with ammonium phosphate fertilizer in the region of Maharashtra, India varied its Th mean activity concentration from 57.2 ± 1.1 to 72.9 ± 0.8 Bq kg⁻¹ after treatment [24]. A study conducted in Marismas of Lebrija (Spain) showed that no variation in Th content was observed after phosphogypsum application as soil amendment, with mean values of 32.4 Bk kg⁻¹ for both, control and treated soil [25]. Agricultural lands of Gediz River basin, Western Turkey, showed values of 20.56 and 22.08 Bq kg⁻¹ in fertilized and non-fertilized soil, using phosphate fertilizers[26]. References cited in the same study indicates a range varying from 18.93 to 51,25 Bk kq⁻¹ for treated and non-treated soil using the same type of fertilizers.

The activity concentrations in different types of materials use as soil amendment present a wide range of Th activity concentrations. Reported values for fly ash varies from 40.5 to 101 Bq kg⁻¹ [27]. Biosoil produced using sewage sludge from the Sewage Treatment Station in Jundiaí – SP, Brazil, presented Th activity concentration of 23.5 Bq kg⁻¹ [28] and the sewage sludge collected from an industrial water treatment plant of Japan presented 32 Bq kg⁻¹ of Th [29]. Biochar, charcoal made from biomass in the pyrolysis process, from Poland presented mean value of Th activity concentration of 22.9 Bq kg⁻¹ [30]. Application of bauxite mining residues (red mud) with Th concentrations of about 1350 ± 40 Bq kg⁻¹ was used as soil amendment in Swan Coastal Plain in Western Australia. In this case, the highest rate of red mud application (480 t h⁻¹) led the soil Th concentration to 188 ± 6 Bq kg⁻¹ [31].

Theses results emphasizes the high dilution factor of the elements, including the radioactive ones, when applied as soil amendment, as shown in **Erro! Fonte de referência não encontrada.**.

Sample used in harvesting	Th activity concentration \pm deviation [Bq			
	kg ⁻¹]			
Soil (this work)	<i>37</i> ± <i>2</i>			
Brazil - Cerrado biome [32]	49			
Soil - diferent countries [33]	110.0 ± 0.8			
Clay Soil [34]	100 ± 20			
Sandy Soil [34]	32 ± 2			
UNSCEAR 2000	30			
Treatments				
Soil + lime	30.7 ± 0.3			
Soil + carbonate	44 ± 2			
Soil + lime + carbonate	<i>36</i> ± <i>7</i>			
Carbonate niobium waste	652 ± 61			
Clay soil + phosphogypsum [35]	100 ± 30			
Sandy soil + phosphogypsum [35]	31 ± 1			
Sewage sludge-derived compost [27]	66.4 ± 13.0			

Table 3: 232 Th activity concentration \pm deviation [Bq kg⁻¹]

3.2. Absorption of Th by plants

Studies have shown that thorium in the system soil-plant is preferentially bound to the root of plants and that translocation into the above-ground parts is low [35,36], probably due to its low solubility and high affinity for negatively charged components of the cell wall [37]. Different types of vegetables analyzed for their Th content in southern coastal regions of India, a high background radiation area, indicated that the highest concentrations were found in root, up to 184 mBq kg⁻¹ and green vegetables varied from 26 ± 1 to 62 ± 2 Bq kg⁻¹ [38].

The IAEA determines the reference value for Th ingestion in leafy vegetables as 0.004 mg kg⁻¹ to fresh weight [39]. Leafy vegetables are among the most sensitive foodstuffs from the viewpoint of food safety since they accumulate radionuclides [33].

The concentration of Th obtained in the lettuce samples for the different treatments is shown in Figure 2. It can be observed that the lowest concentration was found in crops in soil without

amendment addition (0.14 \pm 0.03 mg kg⁻¹). In the treatment with lime, carbonate or a mixture of both, no significant difference is observed among them (0.2 \pm 0.2 to 0.45 \pm 0.1 mg kg⁻¹).

In Table 4 the Th activity concentration found in lettuce for different harvesting conditions are shown for fresh and dry weight. Although the soil to plant transfer process depends on soil properties, physicochemical behavior of the radionuclide, plants physiological response to environmental parameters, it can be seen that the Th concentration found in this study is close to the ones reported in literature. The broad range of values can be highlighted by the Th concentration found in fresh weight for the Rio de Janeiro [40] samples and for the dry weight samples from Vietnam [41].

Location	$Th [mg kg^{-1}]$
Malvési - south of France [42]	0.12 - 0.8 (dry)
Buena, Rio de Janeiro, Brazil [40]	0.24 (fresh)
Rio de Janeiro, Brazil [43]	0.00074 – 0.0072 (fresh)
Ho Chi Minh City, Vietnam [41]	0.32 (dry)
Central Poland [44]	0.34 (dry)
Hoai Duc District, Vietnam [45]	2.79 (dry)
Korean cities [46]	0.0005 (fresh)

Table 4: Th activity concentration found in lettuce for different harvesting conditions

In the current study, it was observed that, on average, there was an increase in concentrations of Th in lettuce from the 1st to the 2nd harvesting, as seen in Figure 2. However, due to the standard deviation associated with the measurements, there may be specific cases in which this trend is not observed.



Figure 2: Thorium concentration in lettuce cultivated in (a) soil without treatment, (b) soil + lime, (c) soil + lime + carbonate and (d) soil + carbonate. In blue, first harvesting and in red, second harvesting.

The addition of lime in the mixture in treatments C when compared with the treatment D did not imply a significant difference in the mean values of Th concentrations in cultivated lettuce, since in treatment D there is no lime in soil. When comparing the treatments B (soil+lime) and D (soil+carbonate), the concentration in lettuce presents the same order of magnitude, especially considering the second harvesting. Comparing the results of this study with the ones of [34], the ²³²Th concentration on lettuce cultivated in soils without amendments was of 0.21 ± 0.01 Bq kg⁻¹ in [34], while in this study is of 0.14 ± 0.03 Bq kg⁻¹. Two different treatments were considered in [34]: clay soil with phosphogypsum and sandy soil with phosphogypsum. The results of activity concentration in lettuce for them were of 0.35 ± 0.02 Bq kg⁻¹ and 0.24 ± 0.01 Bq kg⁻¹, respectively. These results are in the same order of magnitude with ones observed in the current study, shown in Figure 2 and also with the ones presented in Table 4.

The elemental transfer from soil to edible plants, in addition to environmental parameters, also depends on the agricultural practices. Generally, in the second planting an increase in the trace elements concentration occurs as a result of increased bioavailability of nutrients after the harvest of the first planting. In this second planting, the plant is able to bio absorb more nutrients. As a consequence, the soil will become poorer, that is, if there is a new planting in this soil without amendments, it would be poor in nutrients. In this study, on the other hand, the Th's bioavailability increased from the first to the second harvesting, nevertheless, because of variability the Th concentration, it is possible the existence of samples in which the bioavailability is greater in the first harvesting than in the second one.

The global average for the activity concentration, reported by the United Nations Scientific Committee on the Effects of Atomic Radiation [16], due to the intake of 232 Th in dry leafy vegetables, is 0.02 Bq kg⁻¹ [34,47], corresponding to 0.005 Bq kg⁻¹ in dry weight. It was also reported that different vegetables consumed in a high background radiation area in Brazil presented mean value of 232 Th concentration 0.002 mg kg⁻¹. In both cases the values are lower than the ones reported here, only for lettuce.

3.3. Effective dose

The effective dose is a measure of the adsorbed dose rate and also the time spent in contact with the radioactive source – occupancy factor, according to the expression 3 [29,32]

$$E\left[mSv\right] = \sum_{j} \sum_{f} C_{fj} \cdot M_{j} \cdot T \cdot h_{j}$$
(3)

Where, E is the committed effective dose (mSv) per group. C_{fj} is the average activity concentration (Bq kg⁻¹) of a radionuclide j in each group of food. M_j is the mass (kg day⁻¹) of a food item f consumed per day. T is the total time (days) considered. h_j is the ingestion dose coefficient (mSv Bq⁻¹) of a radionuclide j.

Considering the mean Brazilian values of ingestion of 2.6 g day⁻¹ of lettuce [5] and the mean values presented in Figure , the effective dose, in this case, varies from 0.12 to 0.4 μ Sv y⁻¹. The reference value reported by UNSCEAR to Th is 0.36 μ Sv y⁻¹, which, from a radiological point of view, the ingestion of lettuce planted in carbonate is unsafe.

Scarce data are available on ²³²Th intake with the diet and few countries have conducted representative national surveys [16,47]. Sathyapriya et al. [38] estimated an effective dose resulting from ²³²Th of 0.038 and 0.050 μ Sv y⁻¹ due to the ingestion of green leafy vegetables for female and male, respectively. The effective dose resulting from ²³²Th ingestion in the daily diet in Poland was reported as 0.2 μ Sv y⁻¹ [44]. The dose due to the ingestion of leafy vegetables from different locations of Cameron Highlands, Pahang, Malaysia was reported as 16.37 μ Sv y⁻¹ [46]. The total diet study made in the HBRA¹ of Poços de Caldas, Brazil, presented effective dose due to ²³²Th ingestion of 3.57 μ Sv y⁻¹ and 1.1 μ Sv y⁻¹ for urban and rural regions, respectively. The wide range of effective dose depends on the ²³²Th activity concentrations and on the daily intake of the analyzed type of food; nevertheless, in all cases the effective dose due to the ingestion of food and water considering all natural radionuclides.

3.4. Transfer factor

The Table 55 shows the average values of TF of Th in lettuce considering the different soil treatments. In the first planting, the ascending order of transfer was Soil < Soil + carbonate < Soil + lime + carbonate < Soil + lime. In the second treatment, the increasing order of TF was Soil < Soil + lime < Soil + lime + carbonate < Soil + carbonate. One of the possible reasons for the change in TF is due to the pH of the soil being acidic and due to the addition of lime, the pH changes to more basic values, increasing the mobility of metals and their absorption by plants.

¹ A HBRA is defined as "an area or a complex of dwellings where the sum of exposures from cosmic radiation and natural radioactivity of soil, indoor and outdoor air, water and food intake result in an annual effective dose to the public above the defined level of the global average of 2.4 mSv y^{-1} (UNSCEAR, 2000).

Soil to plant of Th	Soil	Soil + lime	Soil + lime + carbonate	Soil + carbonate
		First harvesting		
average \pm	3.7 10 ⁻³ ±	$1.48\ 10^{-2}\ \pm$	6.63 10 ⁻³ ±	4.66 10 ⁻³ ±
deviation	8.23 10 -4	4.15 10 ⁻³	4.86 10 ⁻³	1.77 10 ⁻³
		Second harvesting		
average \pm		1.23 10 ⁻² ±	$1.04 \ 10^{-2} \pm$	<i>9.33 10 -3</i> ±
deviation		2.77 10 -3	6.56 10 ⁻³	5.87 10 ⁻³

Table 5: The average values of TF oh Th in lettuce considering the different soil treatments

Several factors affect the TF including the form in which the nuclide is present in soil, its physicochemical properties, the type of soil and the physicochemical characteristics of the soil such as texture, pH, exchangeable K and Ca, the kind and number of clays, and organic matter, the plant species, crop management practices etc. Considering the gross values of the different management, the highest transfer factor for the first and second harvesting were observed for the in the treatment b and the lowest was for the lettuce planted using the treatment d. Considering the standard deviation, while no statistical difference was observed in the second harvesting, for the first one the TF was different probably due to difference in the treatment.

4. CONCLUSIONS

It was analyzed the influence of carbonate waste from niobium mining in the Th soil concentration and in the absorption of this nuclide by lettuce in soil amended with mining residue. The addition of carbonate to soil does not significantly change its ²³²Th activity concentration whose values are in good agreement with treated and non-treated soil reported in literature and is compared with the commonly lime regularly used.

The ²³²Th activity measured in the lettuce leaves varies from 0.14 Bq kg⁻¹, in the soil without treatment, to 0.4 Bq kg⁻¹, in soil treated with the carbonate, of the second harvesting. No difference was observed in ²³²Th activity concentration in the lettuce samples between the ones harvested with lime or the carbonate residue. The effective dose resulting from the lettuce ingestion varied from 0.09 to 0.3 μ Sv y⁻¹, indicating that no radiological harm due to Th ingestion will be posed by the lettuce consumption.

The absorption of ²³²Th by the lettuce cropped using different soil management indicated that the transfer factor may vary, in a short range, according to the type of amendment and to the order of harvesting.

Due to the high activity concentration of ²³²Th in the carbonate niobium residue, further analyses must be carried out in order to determine the behavior, transfer factor and activity concentration in lettuce of ²²⁸Ra, a much more soluble radionuclide present in the Th series.

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REFERENCES

- [1] DA SILVA LIMA, L.; ALVARENGA, R.A.F; SOUZA AMARAL, T.; NOLLI, P. D. T.G.; DEWULF, J. Life cycle assessment of ferroniobium and niobium oxides: Quantifying the reduction of environmental impacts as a result of production process improvements, Journal of Cleaner Production. v. 348, p. 131327, 2022.
- [2] MELFI, A. J.; MISI, A., CAMPOS, D. D. A.; CORDANI, U. G. Recursos Minerais no Brasil: problemas e desafios, 2016.
- [3] RAMOS, G.S. Caracterização mineralógica do processo de beneficamento de Nióbio da Mina Boa Vista, Catalão - GO, Brasil, Universidade de Brasília, 2021.
- [4] MARINGER, F.J.; A. BAUMGARTNER, A.; F. CARDELLINI, F.; CASSETTE, P.; CRESPO, T.; DEAN, J.; WIEDNER, H.; HULKA, J.; HULT, M.; JEROME, S.; F. KABRT, F.; KOVAR, P.; LARIJANI, C.; LUTTER,G.; MAROULI, M.; MAURING, A.; MAZANOVA, M.; B. MICHALIK, B.; MICHIELSEN, N.; PEYRES, V.; PIERRE, S.; PÖLLÄNEN, R.; POMME, S.; REIS, M.; STIETKA, M.; SZÜCS, L.; VODENIK, B. Advancements in NORM metrology – Results and impact of the European joint research project MetroNORM, Applied Radiation and Isotopes, v. 126, p. 273-278, 2017.
- [5] CNEN Comissão Nacional de Energia Nuclear. Diretrizes Básicas de Protecção

Radiológica, Com. Nac. Energ. Nucl. 05 (2011) 1–24.

- [6] CNEN Comissão Nacional de Energia Nuclear. Gerência De Rejeitos Radioativos De Baixo E Médio Níveis De Radiação, 2014, 22p.
- [7] EL HAJJ, T. M., GANDOLLA, M. P. A.; DA SILVA, P. S. C.; TORQUATO, H.; JUNIOR,
 H. D. L. Long-term prediction of non-processed waste radioactivity of a niobium mine in Brazil, J. Journal of Sustainable Mining, v. 18, n. 3, p. 142-149, 2019.
- [8] A. KABATA-PENDIAS. Trace Elements in Soils and Plants, 4th ed., 2011.
- [9] SHTANGEEVA, I. Uptake of uranium and thorium by native and cultivated plants, Journal of environmental radioactivity, v. 101, n. 6, p. 458-463, 2010.
- [10] DOS REIS, R.G. NORM: Guia Prático, 1st ed., Rio de Janeiro, 2016.
- [11] SHTANGEEVA, I.; AYRAULT, S.; JAIN, J, J. Thorium uptake by wheat at different stages of plant growth, **Journal of environmental radioactivity**, v. 81, n. 2-3, p. 283-293, 2005.
- [12] JALALI, M.; MEYARI. Heavy metal contents, soil-to-plant transfer factors, and associated health risks in vegetables grown in western Iran, Journal of Food Composition and Analysis, v. 106, p. 104316, 2022.
- [13] ASADUZZAMAN, K.; KHANDAKER, M. U.; AMIN, Y. M.; BRADLEY, D. A.; MAHAT, R. H.; NOR, R. M. Soil-to-root vegetable transfer factors for 226Ra, 232Th, 40K, and 88Y inMalaysia, Journal of environmental radioactivity, v. 135, p. 120–127, 2014.
- [14] JOLLY, Y. N.; ISLAM, A.; AKBAR, S. Transfer of metals from soil to vegetables and possible health risk assessment, Springerplus. v. 2, n. 1, p. 1–8, 2013.
- [15] VANDENHOVE, H.; OLYSLAEGERS, G.; SANZHAROVA, N.; SHUBINA, O.; REED, E., SHANG, Z.; VELASCO, H. Proposal for new best estimates of the soil-to-plant transfer factor of U, Th, Ra, Pb and Po, Journal of Environmental Radioactivity, v. 100, n. 9, p. 721–732, 2009.
- [16] UNSCEAR. Nations Scientific Committee on the Effects of Atomic Radiation, SOURCES AND EFFECTS OF IONIZING RADIATION United Nations Scientific Committee on the Effects of Atomic Radiation UNSCEAR 2000 Report to the General Assembly, with Scientific Annexes VOLUME I: SOURCES UNITED NATIONS, n.d.
- [17] INTERNATIONAL COMMISSION ON RADIOLOGICAL PROTECTION (ICRP). Publication 72: Age-dependent Doses to the Members of the Public from Intake of Radionuclides Part 5, Compilation of Ingestion and Inhalation Coefficients., 1996.

- [18] COSTA, J. R. Técnicas Experimentais aplicadas às Ciências Agrárias, Embrapa Agrobiologia - Documentos (INFOTECA-E). (2003) 54.
- [19] E. BOSTELMANN, avaliação da concentração de metais em amostras de sedimento do reservatório billings, braço rio grande, são paulo, brasil, 2006. Tese de Doutorado Universidade de São Paulo.
- [20] MOREIRA, E.G. preparo e caracterização de um material de referência de mexilhão Perna perna (Linnaeus, 1758), 2010. Tese de Doutorado Universidade de São Paulo.
- [21] KABATA-PENDIAS, A. Soil-plant transfer of trace elements An environmental issue, Geoderma. v. 122, n. 2-4, p. 143–149, 2004.
- [22] SUSSA, F. V.; FURLAN, M. R.; VICTORINO, M.; & DA SILVA, P. S. C. Soil-to-plant transfer factor for stable elements in lemon balm (*Melissa officinalis L.*) and estimates of the daily intakes, Journal of Radioanalytical and Nuclear Chemistry. v. 331, p. 3107–3115, 2022.
- [23] GUO, P.; DUAN, T.; SONG, X.; XU, J.; CHEN, H. Effects of soil pH and organic matter on distribution of thorium fractions in soil contaminated by rare-earth industries, **Talanta**. v. 77, n. 2, p. 624–627, 2008. https://doi.org/10.1016/j.talanta.2008.06.002.
- [24] PULHANI, V. A. DAFAUTI, S.; HEGDE, A. G.; SHARMA, R. M.; MISHRA, U. C. Uptake and distribution of natural radioactivity in wheat plants from soil, Journal of Environmental radioactivity. v. 79, n. 3, p. 331–346, 2005.
- [25] ABRIL, J. M.; GARCÍA-TENORIO, R.; ENAMORADO, S. M.; HURTADO, M. D.; ANDREU, L.; DELGADO, A., The cumulative effect of three decades of phosphogypsum amendments in reclaimed marsh soils from SW Spain: 226Ra, 238U and Cd contents in soils and tomato fruit, Science of the Total Environment, 403(1-3), p. 80-88, 2008.
- [26] BOLCA, M.; SAÇ, M. M.; COKUYSAL, B.; KARALI, T.; EKDAL, E. Radioactivity in soils and various foodstuffs from the Gediz River Basin of Turkey, Radiation Measurements. v. 42, n.2, p. 263–270, 2007.
- [27] JAMBHULKAR, H. P.; SHAIKH, S. M. S.; KUMAR, M. S. Fly ash toxicity, emerging issues and possible implications for its exploitation in agriculture; Indian scenario: A review, Chemosphere. v. 213, p. 333–344, 2018.
- [28] ARMELIN, M. J. A.; ABREU JUNIOR, C. H.; CATHARINO, M. G. M.; SAIKI, M.; RIBEIRO, A. C. S.; FRANCO, A.; FERNANDES, H. M. G. Determinação de antimônio,

arsênio, cádmio e tório em amostras de caldo de cana cultivada em solo tratado com lodo de esgoto **Journal of the Brazilian Society of Ecotoxicology.** v. 5, p. 81–84, 2010.

- [29] GAO, L.; KANO, N.; SATO, Y.; LI, C.; ZHANG, S.; IMAIZUMI, H. Behavior and distribution of heavy metals including rare earth elements, thorium, and uranium in sludge from industry water treatment plant and recovery method of metals by biosurfactants application, Bioinorganic chemistry and applications, v. 2012, 2012.
- [30] SZEWCZAK, K.; JEDNOROG, S.; WOLOSZCZUK, K.; SZLAZAK, R. ; PODGORSKA, Z. ; RAFALSKA-PRZYSUCHA, A.; GLUBA, L.; ŁUKOWSKI, M. Impact of soil incorporation of biochar on environmental radioactivity, J. Environ. Qual, v. 49, n.2. p. 428–439, 2020.
- [31] COOPER, M.; CLARKE, P.; ROBERTSON, W.; MCPHARLIN, I.; JEFFREY, R. An investigation of radionuclide uptake into food crops grown in soils treated with bauxite mining residues, Journal of Radioanalytical and Nuclear Chemistry, v. 194, n. 2, p. 379-387, 1995.
- [32] MARQUES, J. J.; SCHULZE, D. G.; CURI, N.; MERTZMAN, S. A. Trace element geochemistry in Brazilian Cerrado soils. Geoderma. v. 121, n. 1-2, p. 31-43, 2004.
- [33] El-TAHER, A., ABDELHALIM, M.A.K. Elemental analysis of soils from Toshki by using instrumental neutron activation analysis techniques, Journal of Radioanalytical and Nuclear Chemistry. 300 (1), p. 431–435, 2014.
- [34] MAZZILLI, B. P.; SAUEIA, C. H.; JACOMINO, V. M.; MELLO, J. W. Natural radionuclides and metals intake into soya, corn and lettuce grown on soil amended with phosphogypsum, International Journal of Environmental Analytical Chemistry, v. 92, n. 14, p. 1574–1586, 2012.
- [35] SOUDEK, P.; HRDINOVÁ, A.; VALSECA I.M.R.; LHOTÁKOVÁ, Z.;MIHALJEVIČ, M.; PETROVÁ, S.; KOFROŇOVÁ, M.; MOŤKOVÁ, K.; ALBRECHTOVÁ, J.; VANĚK, T. Thorium as an environment stressor for growth of Nicotiana glutinosa plants. Environmental experimental botany, v. 164 p. 84–100, 2019.
- [36] MORTON, L. S.; EVANS, C. V.; ESTES, G. O. Natural Uranium and Thorium Distributions in Podzolized Soils and Native Blueberry. Journal of environmental quality, v. 31, n. 1, p. 155–162, 2002.
- [37] SOUDEK, P.; KUFNER, D.; PETROVÁ, Š.; MIHALJEVIČ, M.; VANĚK, T. Composition

of hydroponic medium affects thorium uptake by tobacco plants, **Chemosphere**. v. 92, n. 9 p. 1090–1098, 2013.

- [38] SATHYAPRIYA, R., NAIR, S., KAMESH, V., PRABHATH, R., NAIR, M., ACHARYA, R., & RAO, D. Estimation of thorium intake due to consumption of vegetables by inhabitants of high background radiation area by INAA. Journal of radioanalytical and Nuclear Chemistry. v. 294, n. 3, p. 387–390, 2012.
- [39] BOJANOWSKI, R.; RADECKI, Z.; CAMPBELL, M.J.; BURNS, K.I.; TRINKL, A. Report on the Intercomparison Run for the Determination of Radionuclides in Iaea-326 and Iaea-327, Vienna, Austria, 2001. https://inis.iaea.org/collection/NCLCollectionStore/_Public/32/042/32042411.pdf.
- [40] A COSTA LAURIA, D.; ROCHEDO, E. R.; GODOY, M. L. D.; SANTOS, E. E.; HACON,
 S. S. Naturally occurring radionuclides in food and drinking water from a thorium-rich area.
 Radiation and environmental biophysics, v. 51, n. 4, p. 367-374, 2012.
- [41] PHUONG, H. T.; BA, V. N.; THIEN, B. N.; LOAN, T. T. H. Accumulation of lead radionuclides in 18 leaf vegetable types in Viet Nam, Journal of environmental radioactivity, v. 251–252, p. 106960, 2022.
- [42] POURCELOT, L.; MASSON, O.; RENAUD, P.; CAGNAT, X.; BOULET, B.; CARIOU, N.; DE VISMES-OTT, A. Environmental consequences of uranium atmospheric releases from fuel cycle facility: II. The atmospheric deposition of uranium and thorium on plants. Journal of Environmental Radioactivity, v. 141, p. 1-7, 2015.
- [43] SANTOS, E. E.; LAURIA, D. C.; AMARAL, E. C. S.; ROCHEDO, E. R. Daily ingestion of 232Th, 238U, 226Ra, 228Ra and 210Pb in vegetables by inhabitants of Rio de Janeiro City, Journal of Environmental Radioactivity, v.62, p. 75–86, 2002.
- [44] PIETRZAK-FLIS, Z.; ROSIAK, L.; SUPLINSKA, M. M.; CHRZANOWSKI, E.; DEMBINSKA, S. Daily intakes of 238U, 234U, 232Th, 230Th, 228Th and 226Ra in the adult population of central Poland, Science of the total environmement v. 273, n. 1-3, p. 163–169, 2001.
- [45] VAN, H. D.; NGUYEN, T. D.; PEKA, A.; HEGEDUS, M.; CSORDAS, A.; KOVACS, T. Study of soil to plant transfer factors of 226Ra, 232Th, 40K and 137Cs in Vietnamese crops, Journal of environmental radioactivity. v. 223–224, p. 106416, 2020.
- [46] CHOI, M. S.; LIN, X. J.; LEE, S. A.; KIM, W.; KANG, H. D.; DOH, S. H.; KIM, D.S.; LEE,

D. M. Daily intakes of naturally occurring radioisotopes in typical Korean foods, **Journal of Environmental Radioactivity**, v. 99, n. 8, p. 1319–1323, 2008.

[47] NUCCETELLI, C.; RISICA, S. Thorium series radionuclides in the environment: Measurement, dose assessment and regulation, Applied Radiation and Isotopes, v. 66 n. 11 1657–1660, 2008.

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