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# Radionuclides Quality Reference Values in Basalt derived Soils of Forest Conservation Areas

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**A B S T R A C T**

To explore radiochemical differences and similarities between contaminated, intact, and disturbed soils, specially for decision making and regulating norms, it is important to establish Quality Reference Values (QRV) related to natural radionuclides. This study aims to determine the concentrations of $^{232}$Th, $^{238}$U, and $^{40}$K, as well as their respective QRVs, in natural soils derived from basaltic lithology in an area of 22,851 km² in Paraná, Brazil. Seventy-two soil samples from the A horizon in Environmental Conservation Areas were collected and analyzed by gamma spectrometry. The total QRVs (including all the sampled soils) at the 75th percentile were 57.34 Bq·kg$^{-1}$ (14.1 ppm eTh), 36.63 Bq·kg$^{-1}$ (3.0 ppm eU), and 56.28 Bq·kg$^{-1}$ (0.18% K). The results indicated higher values of $^{232}$Th and $^{238}$U and lower values of $^{40}$K in soils with higher maturation and clay content (Oxisol and Ultisol). This trend was associated with the degree of weathering of the soils and their mineralogical evolution. Principal Component Analysis (PCA) further clarified these patterns. The QRVs were also determined by soil classes, helping distinguish between natural variability and supporting comparative studies of soils with similar properties.

Keywords: geochemistry, environmental monitoring, gamma-ray spectrometry, basaltic lithology.

# Valores de referência de qualidade de radionuclídeos em solos derivados de basalto de áreas de conservação florestal

**R E S U M O**

Para explorar diferenças e semelhanças radioquímicas entre solos contaminados, intactos e perturbados, especialmente para tomada de decisões e normas regulatórias, é importante estabelecer Valores de Referência de Qualidade (VRQ) relacionados a radionuclídeos naturais. Este estudo tem como objetivo determinar as concentrações de $^{232}$Th, $^{238}$U e $^{40}$K, bem como seus respectivos VRQ, em solos naturais derivados de litologia basáltica em uma área de 22.851 km² no Paraná, Brasil. Foram coletadas 72 amostras de solo do horizonte A em Áreas de Conservação Ambiental e analisadas por espectrometria gama. Os VRQ totais (incluindo todos os solos amostrados) no percentil 75 foram de 57,34 Bq·kg$^{-1}$ (14,1 ppm de Th), 36,63 Bq·kg$^{-1}$ (3,0 ppm de U) e 56,28 Bq·kg$^{-1}$ (0,18% de K). Os resultados indicaram valores mais elevados de $^{232}$Th e $^{238}$U e valores mais baixos de $^{40}$K em solos com maior grau de maturação e teor de argila (Latossolos e Nitossolos). Essa tendência foi associada ao grau de intemperismo dos solos e à sua evolução mineralógica. A Análise de Componentes Principais (ACP) esclareceu ainda mais esses padrões. Os VRQ também foram determinados por classes de solo, ajudando a distinguir entre a variabilidade natural e fornecendo subsídios para estudos comparativos de solos com propriedades semelhantes.

Palavras-chave: geoquímica, monitoramento ambiental, espectrometria de raios gama, litologia basáltica.

## Introduction

Most radiation exposure originates from natural sources, including radioactivity released by volcanic activity, natural ores, and cosmic radiation. Isotopes such as $^{40}$K, $^{232}$Th, and $^{238}$U, along with their respective decay series, are the primary contributors to the natural radioactivity of the Earth's crust, constituting the main sources of radiation in air, water, and soil. The human environment has always been radioactive, accounting for up to 85% of the annual human radiation dose. Consequently, all minerals and raw materials contain naturally occurring radionuclides (Lopez-Perez et al., 2021).

Terrestrial radiation levels vary geographically due to differing radionuclide concentrations in the Earth's crust, influenced by geological and environmental factors, (United Nations Scientific Committee on the Effects of Atomic Radiation [UNSCEAR], 2000). Exposure levels of most human activities involving minerals and raw materials remain close to natural background values. However, specific anthropogenic interventions, such as coal combustion, fertilizer production and use, mining, and oil and gas exploration, can increase radionuclide exposure compared to undisturbed conditions, affecting their occurrence and availability (Jeelani et al., 2022; Nowak et al., 2022; Perevoshchikov, Perminova, Menshikova, 2022).

Pedogenesis is influenced by a complex interplay of factors, including parent material, climate, topography, and biotic activity. Each soil class, a product of these combined factors, exhibits distinct behavior regarding radionuclide retention and migration (Filgueiras et al., 2022; Leal et al., 2020; Semioshkina & Voigt, 2021). Therefore, to effectively assess and mitigate environmental and health risks associated with radioactivity, each region needs to establish its own Quality Reference Values (QRVs) for soil radionuclides tailored to local geological characteristics and industrial activities (Chandra et al., 2023).

Few studies have published QRVs for soil radionuclides. In Brazil, the National Environmental Council (CONAMA) issued Resolution 420/2009, which provides Prevention and Investigation Values for various chemical substances and recommends that each state establish its QRVs for soils. However, this resolution does not include Prevention or Investigation Values for radionuclides, specifically for $^{238}$U, $^{232}$Th, and $^{40}$K (Brasil, 2009). Consequently, international values are often used for comparison, disregarding geological, pedological, and climatic differences across regions.

The decay series of elements $^{238}$U, $^{235}$U, $^{232}$Th, and $^{40}$K, have radioisotopes that produce gamma rays of energy and intensity that can be measured by gamma-ray spectrometry. As $^{238}$U and $^{232}$Th do not emit gamma rays, their concentrations are estimated indirectly through the gamma-ray photons emitted by their daughters (International Atomic Energy Agency [IAEA], 2003). Based on the activities obtained for $^{226}$Ra, an estimate of the $^{238}$U and eU contents in the soil samples was made and thus presented and discussed.

In this context, the present study aims to determine the concentrations of natural radionuclides $^{232}$Th, $^{238}$U and $^{40}$K in basaltic soils by gamma spectrometry and to establish their respective QRVs. This research aims to develop specific standards for different classes of soils formed under basaltic lithology, contributing to more accurate environmental analyses and providing subsidies for comparative studies of soils with similar properties.

## Materials and methods

### *Study area*

The study area, Paraná River Basin 3 – (PRB3), is in the western region of Paraná, Brazil, between latitudes 24º 01' S and 25º 35' S and longitudes 53º 26' W and 54º 37' W, with a general inclination to the west-northwest (Figure 1).

The geological formation of the region occurred during the Jurassic and Cretaceous periods and was related to the fragmentation of the Gondwana and the opening of the Atlantic Ocean (Waichel, 2005). The geology predominant in the region consists of basaltic rocks from the Serra Geral Formation, formed by extensive volcanic flows of basic eruptive rocks. Only a narrow strip in the northwest of the region is associated with the sandstone rocks of the Bauru Group Caiua Formation (Santos et al., 2006), (Figure 2).

The soils of the studied area have already been reported in previous studies that mention the predominance of Oxisol (Latosols), Ultisol (Nitosols), and Entisol (Neosols) (Bocardi et al., 2018). Land use in this region is essentially agricultural and associated with relief sectors with low dissection and deeper soils characteristic of the region. The forest remnants in the region are located mainly on the banks of water courses, as

well as in sectors where there are more significant physical and natural limitations, such as high slopes and soils with low natural fertility, which prevent the development of anthropic activities (Rocha et al., 2016).

The study area has a humid subtropical climate with an average temperature in the coldest month below 18°C and an average temperature in the hottest month above 22°C and a tendency towards rainfall concentration in the summer months; however, without a defined dry season. Based on the climatic charts of the state of Paraná, the average annual precipitation in the basin ranges from 1600 to 2000 mm (Caviglione et al., 2000).

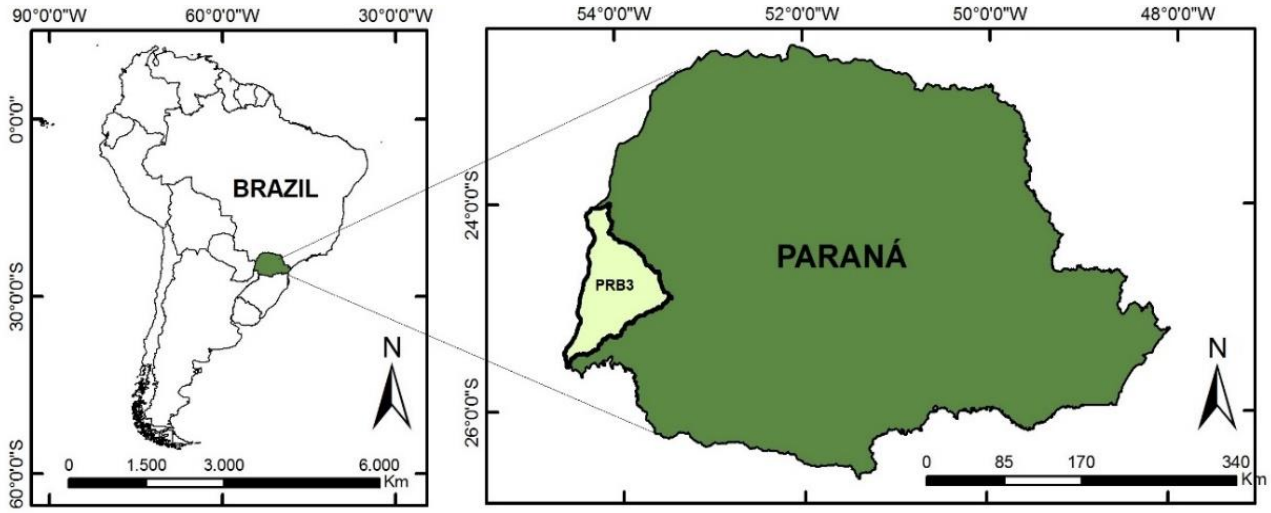


Figure 1. Study area, Paraná River Basin 3 (PRB3), Brazil (Adapted from Rocha et al., 2016).

*Sampling*

The collection sites were selected to characterize areas with no or minimal anthropic influence. Soil samples were collected with the aid of stainless-steel shovels at four points surrounding a central point, with an approximate distance of 2 to 3 m between points, from which five simple samples were taken to obtain a composite sample.

The samples were obtained from a depth of 0–20 cm (Horizon A) from 72 different locations (Figure 2), packed in plastic bags. The densimeter method was used to determine the textural class, Table 1, based on the sedimentation of the particles that make up the soil (Teixeira et al., 2017).

*Determination of Th, U, and K contents*

After being naturally dried, the samples were broken down and disaggregated manually using a porcelain mortar and pestle. The natural gamma spectrometry analysis used around 120 g of soil sample, placed in hermetic plastic containers to prevent $^{222}$Rn to escape, measured after 30 days to guarantee the $^{226}$Ra sub-series secular equilibrium. Measurements were performed using a GammaRad 5 gamma spectrometer from Amptek Inc., with a NaI(Tl) scintillator detector, measuring 76 mm in diameter and 152 mm in height, coupled to a photomultiplier and digital pulse processor (DP5 – Amptek). The peaks used for radioelement concentration estimates are 2614 keV for $^{208}$Tl ($^{232}$Th), 1120 keV for $^{214}$Bi ($^{238}$U series), and 1461 keV for $^{40}$K. The spectrometer/ sample set was shielded with 8 cm of lead and the measurement time for each sample was 86,400 s. The spectra were acquired and analyzed using DppMCA digital acquisition software (Amptek, Inc.).

The quantitative analysis is comparative, the soil sample's radiation is compared with radiation from known standards. The efficiency calibration of the system was carried out using the prescriptions of the IAEA (2003) and the IAEA reference materials for the analysis of natural radioelements in geological matrices, known as RG-Set. The RG-Set is a set of three standard samples, RG-K-1, RG-Th-1, and RG-U-1, with known concentrations of potassium, thorium, and uranium. According to the IAEA certification report, the RG-U-1 and RG-Th-1 samples present the $^{238}$U and $^{232}$Th series in secular equilibrium (IAEA, 2003).

The activity concentrations of the radionuclides $^{238}$U and $^{232}$Th were estimated using gamma-ray photons emitted by their daughter in Bqkg$^{-1}$. Using the following conversion factors of

the International Atomic Energy Agency, activity concentrations were also expressed as uranium equivalent (eU) and thorium equivalent (eTh) in ppm and K in % (IAEA, 2003):

1% K = 313 Bq.kg$^{-1}$ $^{40}$K

1 ppm U = 12.35 Bq.kg$^{-1}$ $^{238}$U, or $^{226}$Ra

1 ppm Th = 4.06 Bq.kg$^{-1}$ $^{232}$Th

The Critical Limit (LC), Detection Limit (LOD), and Quantification Limit (LOQ) were calculated according to Adams and Gasparini (1970) and are shown in Table 2.

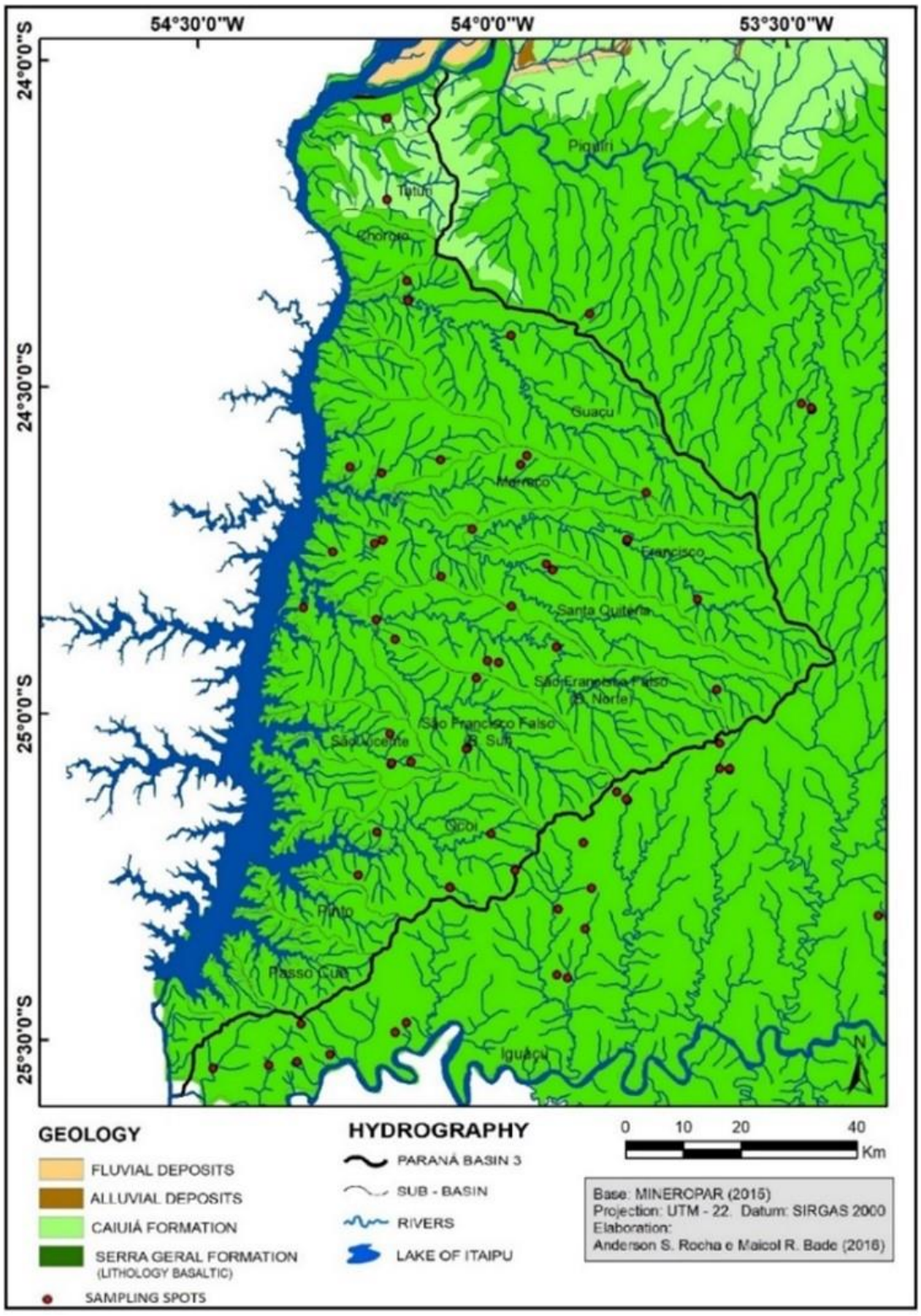


Figure 2. Sampling points (Adapted from Rocha et al., 2016).

**Table 1.** Sampling point location, lithology, taxonomy and textural

| P | Latitude | Longitude | Litology | Soil taxonomy[1] | Soil textural (%) | | |
|---|---|---|---|---|---|---|---|
| | | | | | Sand | Silt | Clay |
| 1 | 24°50'55.38"S | 54°20'35.99"W | Basalt | Oxisol | 9,13 | 28,47 | 62,40 |
| 2 | 24°45'54.74"S | 54°17'27.49" W | Basalt | Entisol | 46,49 | 27,71 | 25,80 |
| 3 | 24°50'57.26"S | 53°40'9.82" W | Basalt | Ultisol | 18,63 | 19,57 | 61,80 |
| 4 | 24°57'47.17"S | 54° 3'3.19" W | Basalt | Entisol | 37,53 | 35,77 | 26,70 |
| 5 | 24°56'27.04"S | 54° 0'41.47" W | Basalt | Entisol | 28,87 | 27,83 | 43,30 |
| 6 | 24°52'10.73"S | 54°13'8.68" W | Basalt | Ultisol | 4,31 | 26,39 | 69,30 |
| 7 | 24°54'4.57"S | 54°11'14.75" W | Basalt | Entisol | 38,17 | 40,03 | 21,80 |
| 8 | 24°47'59.26"S | 53°54'55.98" W | Basalt | Entisol | 38,04 | 29,46 | 32,50 |
| 9 | 24°47'26.15"S | 53°55'36.36" W | Basalt | Entisol | 37,41 | 32,69 | 29,90 |
| 10 | 25° 4'13.95"S | 54° 4'5.46" W | Basalt | Entisol | 18,40 | 33,20 | 48,40 |
| 11 | 25° 4'18.01"S | 54° 4'13.80" W | Basalt | Entisol | 27,42 | 37,78 | 34,80 |
| 12 | 25° 5'22.39"S | 54° 9'56.93" W | Basalt | Entisol | 29,53 | 39,77 | 30,70 |
| 13 | 24°45'29.25"S | 53°47'17.99" W | Basalt | Ultisol | 9,67 | 34,93 | 55,40 |
| 14 | 24°45'21.30"S | 53°47'14.66" W | Basalt | Entisol | 29,01 | 35,49 | 35,50 |
| 15 | 24°41'4.46"S | 53°45'11.70" W | Basalt | Oxisol | 9,04 | 22,96 | 68,00 |
| 16 | 24°38'15.73"S | 53°58'3.87" W | Basalt | Ultisol | 24,82 | 32,98 | 42,20 |
| 17 | 24°37'26.37"S | 53°57'22.12" W | Basalt | Ultisol | 18,30 | 33,00 | 48,70 |
| 18 | 24°26'20.10"S | 53°58'45.11" W | Basalt | Oxisol | 5,91 | 15,99 | 78,10 |
| 19 | 24°24'31.72"S | 53°50'37.19" W | Basalt | Oxisol | 13,51 | 41,19 | 45,30 |
| 20 | 24°45'13.29"S | 54°13'8.35" W | Basalt | Ultisol | 5,13 | 26,87 | 68,00 |
| 21 | 24°44'55.22"S | 54°12'16.62" W | Basalt | Alfisol | 11,67 | 64,33 | 24,00 |
| 22 | 24°38'42.97"S | 54°12'15.39" W | Basalt | Ultisol | 4,57 | 22,23 | 73,20 |
| 23 | 24°38'6.07"S | 54°15'31.00" W | Basalt | Oxisol | 5,47 | 21,43 | 73,10 |
| 24 | 24°44'6.82"S | 54° 3'8.04" W | Basalt | Entisol | 25,67 | 40,33 | 34,00 |
| 25 | 24°37'40.01"S | 54° 6'11.79" W | Basalt | Ultisol | 20,25 | 29,95 | 49,80 |
| 26 | 24°22'56.60"S | 54° 9'11.00" W | Basalt | Entisol | 21,69 | 38,81 | 39,50 |
| 27 | 24°21'6.12"S | 54° 9'15.88" W | Basalt | Ultisol | 17,52 | 35,18 | 47,30 |
| 28 | 24°13'36.63"S | 54°11'3.97" W | Basalt | Oxisol | 14,57 | 18,83 | 66,60 |
| 29 | 25° 6'44.20"S | 53°37'10.17" W | Basalt | Molisol | 30,88 | 29,12 | 40,00 |
| 30 | 24°59’20.33"S | 53°38’23.74” W | Basalt | Oxisol | 4,20 | 17,80 | 78,00 |
| 31 | 24°51’18.31"S | 53°59'14.98" W | Basalt | Ultisol | 7,14 | 24,96 | 67,90 |
| 32 | 24°48'23.22"S | 54° 6'23.79" W | Basalt | Entisol | 22,03 | 37,27 | 40,70 |
| 33 | 24°33'11.08"S | 53°29'6.96" W | Basalt | Oxisol | 8,13 | 23,87 | 68,00 |
| 34 | 24°33'45.51"S | 53°28'5.60" W | Basalt | Ultisol | 10,09 | 15,31 | 74,60 |
| 35 | 24°33'34.25"S | 53°28'7.82" W | Basalt | Ultisol | 17,13 | 25,47 | 57,40 |
| 36 | 25°19'12.12"S | 53°55'9.23" W | Basalt | Ultisol | 12,22 | 32,28 | 55,50 |
| 37 | 25°15'34.91"S | 53°59'27.24" W | Basalt | Entisol | 32,61 | 25,99 | 41,40 |
| 38 | 25°12'9.03"S | 54° 1'53.72" W | Basalt | Ultisol | 15,48 | 42,42 | 42,10 |
| 39 | 25° 5'32.20"S | 54°11'59.87" W | Basalt | Entisol | 29,73 | 15,47 | 54,80 |
| 40 | 25° 5'24.88"S | 54°11'55.40" W | Basalt | Alfisol | 27,60 | 38,40 | 34,00 |
| 41 | 25° 2'43.70"S | 54°12'2.27" W | Basalt | Oxisol | 9,81 | 34,79 | 55,40 |
| 42 | 25°11'42.85"S | 54°13'36.27" W | Basalt | Ultisol | 5,15 | 26,85 | 68,00 |
| 43 | 25°15'40.56"S | 54°15'37.85" W | Basalt | Ultisol | 33,63 | 25,67 | 40,70 |
| 44 | 25° 9'19.80"S | 53°47'45.02" W | Basalt | Entisol | 28,81 | 35,79 | 35,40 |
| 45 | 25° 9'13.25"S | 53°47'52.12" W | Basalt | Entisol | 15,91 | 33,45 | 50,64 |
| 46 | 25° 8'32.17"S | 53°48'51.84" W | Basalt | Oxisol | 17,55 | 17,85 | 64,60 |
| 47 | 25°16'57.50"S | 54° 6'15.37" W | Basalt | Ultisol | 20,39 | 25,61 | 54,00 |
| 48 | 25°16'59.34"S | 54° 6'13.61" W | Basalt | Entisol | 25,94 | 41,96 | 32,10 |
| 49 | 25°13'9.26"S | 53°52'24.58" W | Basalt | Oxisol | 17,31 | 30,19 | 52,50 |
| 50 | 25°17'22.58"S | 53°51'41.15" W | Basalt | Ultisol | 10,09 | 31,41 | 58,50 |
| 51 | 25°21'6.18"S | 53°52'25.14" W | Basalt | Ultisol | 12,00 | 32,90 | 55,10 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| 52 | 25°19'13.60" | 53°55'8.63" W | Basalt | Ultisol | 13,53 | 35,07 | 51,40 |
| 53 | 25°25'34.27"S | 53°54'18.65" W | Basalt | Ultisol | 4,00 | 13,50 | 82,50 |
| 54 | 25°25'15.55"S | 53°55'23.85" W | Basalt | Oxisol | 13,75 | 34,55 | 51,70 |
| 55 | 25°20'24.66"S | 53°22'8.46" W | Basalt | Entisol | 13,86 | 49,54 | 36,60 |
| 56 | 25° 4'16.06"S | 53°38'9.36" W | Basalt | Entisol | 18,97 | 65,13 | 15,90 |
| 57 | 25° 6'34.54"S | 53°38'13.36" W | Basalt | Oxisol | 12,17 | 22,63 | 65,20 |
| 58 | 25° 6'36.25"S | 53°37'10.70" W | Basalt | Molisol | 26,22 | 34,58 | 39,20 |
| 59 | 25° 6'34.14"S | 53°19'12.46" W | Basalt | Oxisol | 17,97 | 42,73 | 39,30 |
| 60 | 24°56'12.80"S | 54° 1'52.82" W | Basalt | Ultisol | 8,57 | 38,13 | 53,30 |
| 61 | 25°29'20.52"S | 54°11'2.47" W | Basalt | Oxisol | 5,55 | 18,65 | 75,80 |
| 62 | 25°30'11.90"S | 54°12'13.68" W | Basalt | Ultisol | 3,81 | 29,59 | 66,60 |
| 63 | 25°32'5.95"S | 54°19'0.64" W | Basalt | Ultisol | 7,44 | 25,96 | 66,60 |
| 64 | 25°38'19.74"S | 54°26'28.41" W | Basalt | Oxisol | 9,94 | 30,86 | 59,20 |
| 65 | 25°38'16.94"S | 54°26'24.25" W | Basalt | Oxisol | 10,96 | 45,74 | 43,30 |
| 66 | 25°37'0.55"S | 54°28'48.94" W | Basalt | Ultisol | 9,04 | 24,36 | 66,60 |
| 67 | 25°33'4.79"S | 54°31'6.69" W | Basalt | Oxisol | 5,05 | 15,75 | 79,20 |
| 68 | 25°29'14.28"S | 54°21'51.94" W | Basalt | Oxisol | 6,27 | 20,53 | 73,20 |
| 69 | 25°32'39.66"S | 54°22'23.24" W | Basalt | Ultisol | 5,71 | 26,99 | 67,30 |
| 70 | 25°32'54.95"S | 54°25'19.78" W | Basalt | Alfisol | 7,38 | 58,62 | 34,00 |
| 71 | 24°55'5.20"S | 53°54'44.24" W | Basalt | Entisol | 18,05 | 28,65 | 53,30 |
| 72 | 25°19'30.80"S | 54° 2'19.76" W | Basalt | Oxisol | 14,82 | 31,18 | 54,00 |

P - Collection points. [1]United States Department of Agriculture (USDA, NRCS, 1999).

**Table 2.** Critical Limit (LC), - Detection Limit (LOD), Quantification Limit (LOQ) of K, U, and Th by Gamma Spectrometry

| Radioelements | LC | LOD | LOQ |
|---|---|---|---|
| K (%) | 0,010 | 0,019 | 0,058 |
| eU ppm | 0,29 | 0,59 | 1,8 |
| eTh ppm | 1,1 | 2,2 | 6,7 |

The QRV of $^{238}U$, $^{232}Th$, and $^{40}K$ overall and by soil class were obtained. The results were evaluated by univariate statistical methods and multivariate techniques using the STATISTICA® 8.0 software. The QRV were determined in the 75th and 90th percentiles of the sample universe, according to CONAMA guidelines (Brasil, 2009), for each radionuclide (Th, U, and K) from the detection and exclusion of outliers. For the detection of outliers, box-plot graphics were used as exploratory and visual analysis of the data; in addition, the upper (OS) and lower (OI) outliers were calculated based on the 75th percentile (P75) and 25th percentile (P25) of the concentrations of each radionuclide, according to Ander et al. (2013); Reimann and Caritat (2017), equations 1 and 2.

$$OS = P75 + 1,5 \times (P75 - P25) \quad (1)$$
$$OI = P25 - 1,5 \times (P75 - P25) \quad (2)$$

## Results and discussion

*Natural concentration of Radioelements in the soil*

The radioelements determined were presented with varying concentrations in all soil formations of PRB3. Table 3 shows the average, minimum, and maximum radionuclides obtained among the 72 collection points.

The geological formation of the study area is predominantly basaltic. In the case of soils derived from basalt (basic rock), it is not expected to find high concentrations of radioelements (Dickson & Scott 1997; Kabata-Pendias, 2013; Łukaszek-Chmielewska et al., 2024; Tositti et al., 2016). The abundance of both elements (Th and U) tends to increase with silica content so that igneous rocks of granitic composition are strongly enriched in Th and U compared to more basic rocks, poor in silica (Bastos & Appoloni, 2009; Kabata-Pendias, 2013; Mingareeva et al., 2022; Taboada et al., 2006). However, Kabata-Pendias (2013) reports average levels commonly found for mafic rocks (basalts and gabbros), based on several sources ranging from 1-4 ppm for Th and 0.3-1 ppm for U, while in soils, the same author points out levels that vary from 3.4 to 13.5 ppm for Th and from 0.79 to 11 ppm for U.

**Table 3.** Descriptive analysis of the elemental concentration of eTh, eU in ppm and for K in %.

| Radioelement | N | $\bar{X}$ | Min. | Max. | CV |
|---|---|---|---|---|---|
| **eTh (ppm)** | 72 | 11,727 | 3,692 | 27,018 | 40,563 |
| **eU (ppm)** | 65 | 2,286 | <0,590 | 5,908 | 55,084 |
| **K (%)** | 51 | 0,189 | <0,019 | 0,888 | 94,342 |

N – number of analyzed samples, < LOD – Less than the method's detection limit, CV (%) CV -Coefficient of Variation, $\bar{X}$ mean, Min. Minimum, Max. Maximum

This evidence can be explained by the strong tendency that Th and U have to complex or adsorb in the mineral and/or organic phases, providing an increase in the total concentration of Th and U dissolved in the soil (Dina et al., 2022; EPA, 1999). In the United States, average concentrations of U and Th in surface soils of 3 ppm and 6 ppm, respectively are reported (ATSDR, 2013; ATSDR, 2014).

Even with the homogeneity compared to the rock that originated the analyzed soils, wide ranges were verified in the contents of eTh, eU, and K, that is, high coefficients of variation, Table 3. This result allowed evidence that the contents of the elements depended greatly on the degree of soil development and the pedological and geographic conditions of each scenario. The different conditions existing in the mobility system of metals (losses, transport, and additions) can contribute to delineating the base concentration of elements in the soil (Belivermis et al., 2010; Guimarães et al., 2022).

It is essential to point out that the concentrations of eTh were higher than those of eU in the studied soils. This evidence can be explained by the distribution of Th in the environment, which is usually more abundant than uranium (Asokan et al., 2020; Galahom, Mohsen, Amrani, 2022; Patel et al., 2023; Xu et al., 1993). The intense weathering process that most soils in the region underwent (predominance of Oxisols and Ultisols), concomitant with the different degrees of solubility between Th and U ions, may also contribute to higher Th levels. Th exists only in the +4 oxidation state in nature, while U exists in different valences, but the +4 and +6 oxidation states predominate. Under oxidizing conditions, Th remains in the tetravalent state, which is insoluble in water, whereas $U^{+6}$ tends to form soluble compounds and frequently leaches (Bourdon et al., 2003; EPA, 1999; Han et al., 2024; Mitchell, Perez-Sanchez, Thorne, 2013). This result corroborates the observations of Kabata-Pendias (2013), Mingareeva et al. (2022); Pérez et al. (1997), and Xu et al. (1993).

In the Table 4, the results are presented in $Bq.Kg^{-1}$ to facilitate comparisons with other studies in the literature.

**Table 4.** Mean concentration of natural activity in $Bq.kg^{-1}$ of $^{232}Th$, $^{238}U$, and $^{40}K$ in soils from PRB3, compared with data compiled from other researhes

| Radionuclide | **PRB3** Present study | PR[a] | EG[b] | IN[c] | IT[d*] | BG[e] | WA[f] |
|---|---|---|---|---|---|---|---|
| **$^{232}$Th or Th*** | 47,6 | 36,4* | 18,0 | 48,0 | 71,9* | 30,0 | 45,0 |
| **$^{238}$U or U*** | 28,2 | 29,4* | 37,0 | 52,0 | 50,1* | 40,0 | 33,0 |
| **$^{40}$K** | 59,0 | 503,9 | 320,0 | 840,0 | 970,3 | 400,0 | 420,0 |

PRB3 Paraná River Basin 3 (present study)
PR[a] Paraná, MINEROPAR (2005).
EG[b] Egypt, UNSCEAR (2000).
IN[c] India, Jananee et al. (2021).
IT[d] Italy, Tositti et al. (2016).
BG[e] Bulgaria, UNSCEAR (2000).
WA[f] World average, UNSCEAR (2000).

The arithmetic mean of $^{238}U$ determined in PRB3 soils was very similar to that reported in PR B horizon soils (MINEROPAR 2005), Table 4. For $^{232}Th$, the average PRB3 content was lower than that found in Italy (Tositti et al., 2016), Table 4. The high grades in Italy were also related to the geology of the study area, characterized by magmatic rocks potentially enriched with U and Th and the presence of a geothermal field widely exploited as a spa by tourism, in which they release surface fluids enriched with radon (Tositti et al., 2016).

The average levels of $^{232}Th$ and $^{238}U$ reported in this research were similar to the world average levels of UNSCEAR (2000), Table 4.

The average of $^{40}K$ obtained in this research is much lower than that reported in other surveys (Table 4). This result is associated with parent material and the degree of soil development. The easily weatherable primary minerals (mica and feldspar) contribute primarily to the total K, mainly for the younger-developed sandstone soils. As the soil evolves, potassium minerals derived from the parent rock become increasingly rare as they are released and removed by leaching (Britzke et al., 2012; Hamdan & Ahmed, 2013; Lu et al., 2022). Furthermore, as the soil samples were obtained from conservation areas, natural levels of metals without anthropic influences are expected. Becegato et al. (2008); Minina, Makhmutov, Sinelnikova (2022); Nguyen, Huynh, Hao (2020) recorded an increase in the levels of radionuclides in arable soils attributed to the use of phosphate fertilizers with different compositions of nitrogen, phosphorus, and potassium in their formulations.

*Statistical analysis of the natural concentration of Radionuclides in soil classes*

To obtain a more detailed view of the results obtained from the 72 soil samples collected in PRB3, they were separated by classes.

The analytical results of the $^{232}Th$, $^{238}U$, and $^{40}K$ radionuclides of the Oxisol, Ultisol, Entisol, Alfisol, and Molisol classes were presented in Box Plot diagrams using the STATISTICA® 8.0 program (Figure 3). These diagrams display information about data location, distribution, asymmetry, concentration tendency, and the presence of candidate data for outliers (Massart et al., 2005).

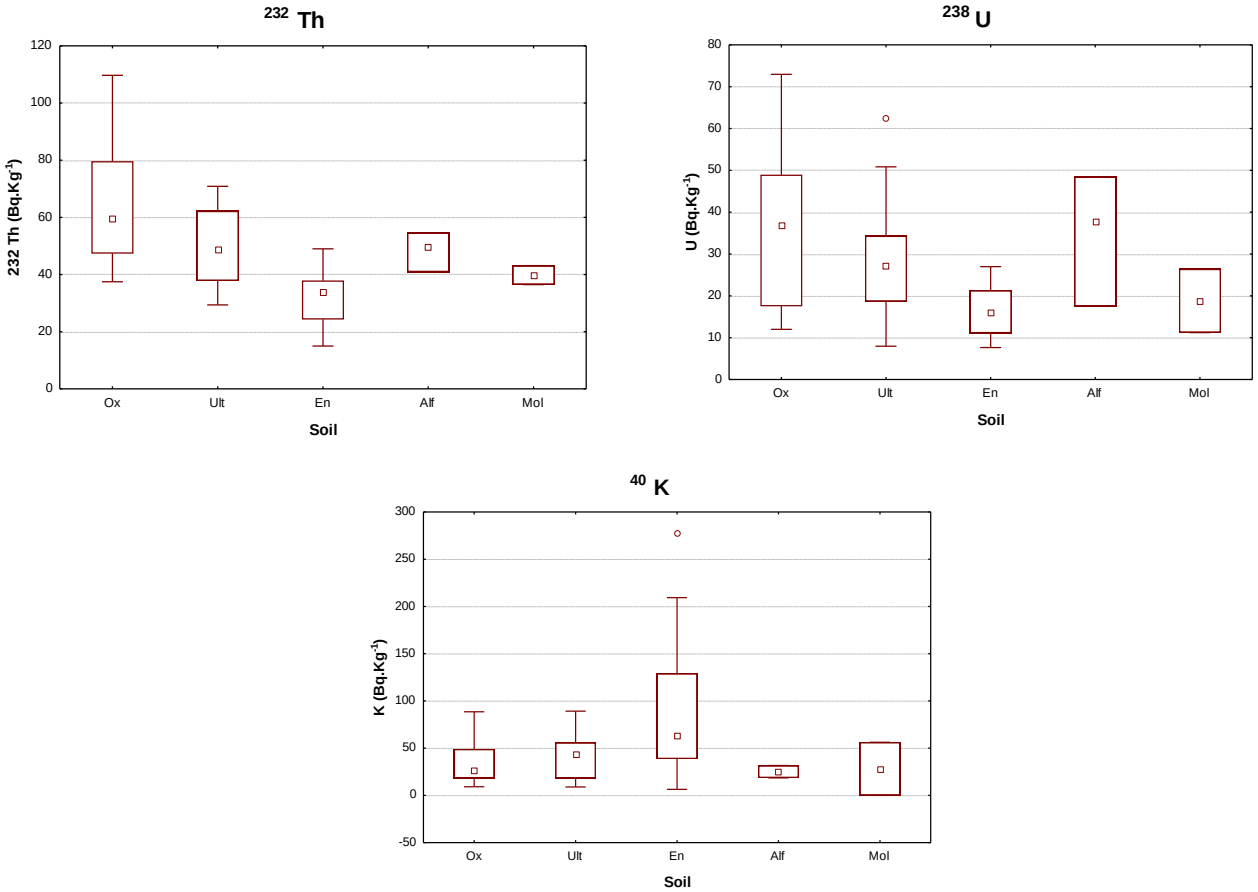


Figure 3. Box plot diagrams of radionuclids $^{232}Th$, $^{238}U$ and $^{40}K$ in Bq.kg$^{-1}$ in different classes of basaltic soils. □ Median; □ 25%–75%; ⌶ Non-Outlier Range; ° Outliers. En – Entisol; Ox – Oxisol; Ult – Ultisol; Al –Alfisol; Mol Mollisol.

The variability of soil classes in the study area can explain an important part of the variation in global acceptance. The contents of $^{232}$Th and $^{238}$U radionuclides behaved similarly when evaluated by soil classes, Figure 3. Oxisols and Ultisols were the classes that stood out in levels of $^{232}$Th and $^{238}$U. The finer texture characteristic of these classes may be a consequence of this result. This evidence agrees with previously published works, in which they verified that the distribution of $^{232}$Th and $^{238}$U in the soil is dependent on the particle size (Frindik & Vollmer, 1999; Landsberger et al., 2013; Lu et al., 2022; Mingareeva, 2023; Patra et al., 2013; Taboada et al., 2006). Several studies have shown that the concentrations of radionuclides $^{232}$Th and $^{238}$U or $^{226}$Ra in clayey soils were higher than in sandier soils, mainly due to the greater adsorption capacity of clay, which has a larger contact surface (Kamalakar et al., 2024). Anisimova et al. (2024), demonstrated that the coefficient of uranium accumulation by plants on soils of lighter texture is higher than on heavy-textured soils. This evidence may justify the bass levels of $^{232}$Th and $^{238}$U in the class of Entisol that presented coarser texture (Figure 3), typical of poorly transmitted soils.

The Alfisols showed average contents of intermediate $^{232}$Th, higher than Entisols and lower than Oxisols. However, he found that the average range of $^{238}$U in Alfisols was higher than in all other classes. The poorly drained environment associated with the reducing environment of these soils may have contributed to this result. The uranium (IV) species dominate in reducing environments and tend to hydrolyze, forming strong hydrolytic complexes that favor the breakdown of the mineral (EPA, 1999).

The activity concentrations of $^{40}$K in the soil classes of BP3, presented in Figure 3, did not follow the same trend observed for $^{232}$Th and $^{238}$U. Among the main classes analyzed, the highest levels of $^{40}$K were found in Entisol, while the lowest were recorded in Oxisol. This behavior can be attributed to the lower degree of development of the Entisol. The presence of rock fragments, primary minerals, and lithic contact at shallow depths favors the retention of potassium near the surface in these soils (Mingareeva, 2023). The relationship between the mineralogical composition of the soils and their potassium retention capacity was also verified in the research conducted by Lu et al. (2022), who demonstrated that 2:1 clay minerals, such as vermiculite, montmorillonite, and mica, due to their interlayer structure that allows more significant interaction with cations, result in a higher potassium retention capacity than 1:1 minerals like kaolinite. Thus, in Oxisols, the higher degree of weathering and the predominance of 1:1 minerals contribute to a lower potassium retention capacity.

The data were submitted to a Principal Component Analysis (PCA), which explained 74.81% of the evaluated data and could qualitatively relate the variables sand, silt, clay, and the activity concentrations of the radionuclides $^{232}$Th, $^{238}$U, and $^{40}$K for 72 samples of soil. The closer the points were positioned on the PCA, the greater their similarities, Figure 4.

Positive correlations were verified in the PCA, Figure 4, between the variables $^{232}$Th, $^{238}$U, and Clay content and, at the same time, $^{40}$K and Sand content. On the other hand, it is also possible to verify that $^{232}$Th, $^{238}$U, and Clay correlated with Sand and $^{40}$K. The silt content did not show correlations with the other variables. These results demonstrate, as already described in the soil classes, the associations between granulometric fractions and radionuclide concentrations. The results verified in the obtained soils are consistent with Mingareeva (2023) e Taboada et al. (2006), in which they reported the lowest concentrations of $^{232}$Th and $^{238}$U in the sandy fractions and the highest in the clayey fractions for both elements. These authors claim that the concentrations of $^{232}$Th and $^{238}$U in soils depend mainly on the content of the primary material (relation to mineralogy) and the intensity of weathering and pedogenesis.

In addition, PCA showed an essential correlation between the radionuclides $^{232}$Th and $^{238}$U, which can be explained in terms of the similarity between these elements. Both belong to the Actinidae group and have a lithophile character, as they are concentrated notably in the lithosphere, particularly in the upper parts of it (MINEROPAR 2005). Th and U can occur in nature in the tetravalent oxidation state, in which they have similar radii; consequently, the two elements can be extensively substituted for each other, which explains their geochemical coherence (Mitchell, Perez-Sanchez, Thorne, 2013; Park et al., 2024). U and Th have a strong affinity for oxygen and have similar reactivity in geochemical processes (Xu et al., 1993).

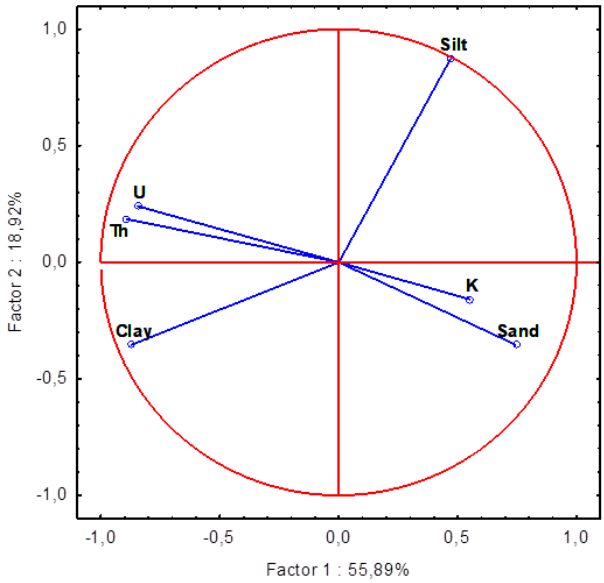


Figure 4. PCA with the correlation between the variables evaluated in the basalt soils

*QRV for radionuclides*

The QRV of the $^{232}$Th, $^{238}$U, and $^{40}$K radionuclides were calculated for all soils and individually for each of the three main soil classes (Oxisols, Ultisols, and Entisols), which correspond to 92% of the classes obtained in this study, Table 5. The other classes had a small number of samples: Molisols 2 samples, and Alfisoils 3 samples, Table 1. With a small number of samples, the QRV per class was not calculated; however, the data from these classes were used to determine the QRV of all soils.

**Table 5.** Quality Reference Values (QRV) of $^{232}$Th, $^{238}$U, and $^{40}$K radionuclides in PRB3 soil classes.

| Soil taxonomy[1] | QRV Percentile | | | | | |
|---|---|---|---|---|---|---|
| | P 75 | P 90 | P 75 | P 90 | P 75 | P 90 |
| | $^{232}$Th | | $^{238}$U | | $^{40}$K | |
| | ----------Bqkg$^{-1}$ ---------- | | | | | |
| Oxisol | 79,69 | 85,93 | 48,97 | 58,06 | 49,01 | 51,46 |
| Ultisol | 62,26 | 66,79 | 32,89 | 41,14 | 55,92 | 79,12 |
| Entisol | 37,92 | 41,28 | 21,31 | 26,96 | 123,59 | 207,08 |
| Total* PRB3 | 57,34 | 66,79 | 36,63 | 48,97 | 56,28 | 89,17 |

Total* refers to the QRVs for all 72 PRB3 samples.
USDA[1] United States Department of Agriculture (USDA, NRCS, 1999).

Statistical diagnosis in the soil QRV is not a worldwide consensus in environmental studies. The use of the percentile (75) shows very restrictive QRVs. Even though in international legislation it is typical for QRVs with percentiles of up to 98%, in Brazil, most studies adopted the 75th percentile as the upper contamination threshold, guaranteeing caution to suspects that could be included in the data (Fabrício Neta et al., 2016; Preston et al., 2014; Santos & Alleoni, 2013). However, when it comes to the QRV of radionuclides in soil, there have been publications so far in only 3 Brazilian states in which different statistical parameters have been used in establishing their QRV, and not all include the three same radionuclides ($^{232}$Th, $^{238}$U, and $^{40}$K) from this survey. In São Paulo, the geometric mean from the activity was chosen to represent the statistical distribution of the data, where values of 33,2 Bqkg-1 for 228Th, 17,1 Bqkg-1 for $^{226}$Ra, and 86.7 Bqkg-1 for 40K were obtained (Hiromoto et al., 2010). In Minas Gerais, the 75th percentile was

used with values for $^{232}$Th, $^{238}$U, and $^{40}$K of 75.7 Bqkg-1, 101.6 Bqkg-1, and 438.9 Bqkg-1 respectively (Peixoto et al., 2013). In Rio de Janeiro, the QRV in the 75th and 90th percentiles were published for the radionuclides $^{40}$K, $^{226}$Ra, $^{228}$Ra; however, the authors defend the less restrictive use of 90, (580 Bqkg-1, 63 Bqkg-1e 130 Bqkg-1 respectively) for all soils and also values individuals by soil class (Ribeiro et al., 2018).

In Germany, reference values were calculated at the 90th percentile and grouped under geological units, and main land uses. The levels reported for U ranged from 0.9 to 6.2 ppm, corresponding to 11.1 to 76.57 Bqkg$^{-1}$ (Utermann & Fuchs, 2008).

The Canadian Environmental Council (CCME) provides a soil quality guide that uses environmental and human health protection criteria according to the environment. The levels presented by the legislation for Total U are 23 ppm (284 Bqkg$^{-1}$) for residential and agricultural areas, 33 ppm (407 Bqkg$^{-1}$), and 333 ppm (4112 Bqkg$^{-1}$) for commercial and industrial respectively. Even though they do not refer to Total U, the data obtained in the present study are much lower than those allowed in residential and agricultural areas by Canadian legislation, which does not present soil quality parameters for other radionuclides (Canadian Council of Ministers of the Environment, 2007).

Oxisols and Ultisols showed approximate QRV for the three radionuclides, probably due to the similarity between these soils, which are deep, with high clay content, and quite weathered. The Entisols showed unequal QRV for the three radionuclides compared to the other classes and with the QRV obtained for all soils of PRB3 (Table 5). In addition, the total QRV was, in some cases, lower than the values obtained for individual soil classes, with a more pronounced effect observed for the QRV of $^{40}$K in the Entisol class (Table 5). These results highlight the importance of considering the specific characteristics of each soil class to ensure a more accurate assessment of radioactivity and to avoid erroneous conclusions that may incorrectly suggest disturbances or contamination in the soils. Results similar to this were reported in the research by Ribeiro et al. (2018) in the soils of Rio de Janeiro, in which they emphasize the importance of obtaining Reference Values by classes, especially in areas with heterogeneous environmental conditions.

## Conclusions

The $^{232}$Th and $^{238}$U contents showed similar trends between soil classes. However, the $^{232}$Th concentration activities were higher than those of $^{238}$U, and the $^{40}$K contents were much lower than the other studies. These results were associated with the level of weathering of soils in the region and the chemical specificity of each element.

The predominantly basaltic geology of the study area allowed evidence that the size of the particles and the degree of soil development were the main factors that outlined the concentration activities and the behavior of the radionuclides $^{232}$Th, $^{238}$U, and $^{40}$K in the soil.

The reference quality values (QRVs) for the radionuclides $^{232}$Th, $^{238}$U, and $^{40}$K determined in this study, from basaltic soils free of anthropogenic contamination, can serve as baseline levels or standards for environmental radioactivity monitoring studies. Obtaining QRVs specific to each soil class highlighted the heterogeneity in the distribution of these radionuclides across different soil types. This approach is essential to avoid erroneous interpretations, provides important support for more detailed investigations into the variability of natural radioactivity, and provides subsidies to the comparative study of soils with similar characteristics.

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