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Baseline and Quality Reference Values for Natural Radionuclides in Soils of Rio de Janeiro State, Brazil

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ABSTRACT: A first large-scale systematic survey of natural radioactivity contents of soils of the state of Rio de Janeiro is presented, focused on the establishment of Quality Reference Values (QRVs). Undisturbed soil samples were collected from 243 areas and analyzed by gamma spectrometry. The activity contents varied largely, ranging from 12.2 to 1,029 Bq kg^{-1} for ^{40}K (geometric mean of 111.1 Bq kg^{-1}), from 3.5 to 99.8 Bq kg^{-1} for ^{226}Ra (geometric mean of 29.7 Bq kg^{-1}), and from 5.4 to 314.5 Bq kg^{-1} for ^{228}Ra (geometric mean of 67.1 Bq kg^{-1}). The highest contents of radium isotopes were found in soils developed on igneous rocks (Leptosol), and the lowest in a soil of sedimentary origin (Podzol). Among the different soil types, the radioisotope contents differed substantially. Separate QRVs were calculated for each radionuclide by the 75th and 90th percentile approach, and the QRVs were estimated for each soil type. The results emphasized the restrictiveness of QRVs based on the 75th percentile or of a single overall QRV for all soils. Therefore, rather than estimating a separate QRV for each radionuclide for the State, we suggest the use of an upper threshold value, defined as the 90th percentile, and a specific QRV for each soil type area.

Keywords: radium, potassium-40, quality reference values, soil.

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INTRODUCTION

Natural radionuclides as ^{40}K and those originated in the decay chain of ^{238}U and ^{232}Th are present in soils and contribute with about 80 % to the dose of background radiation received by human beings (Unscear, 2000). Among these natural radionuclides, ^{226}Ra and ^{228}Ra are of particular interest, due to their environmental mobility and consequent capability of entering in the food chain and also because of the high gamma energy of their decay products, and the radon production. Therefore, knowledge about the contents of natural radionuclides in soils is essential for an accurate assessment of possible radiological risks to human health in any region.

Even though ^{40}K and radium isotopes occur naturally in soils, their contens may be increased by the disposal of liquid, air, and solid effluents, or storage of wastes from industries that generate naturally occurring radioactive material (NORM), e.g., oil and gas production, and many conventional mining and milling industries (IAEA, 2014). Moreover, the extensive use of phosphate fertilizers in cultivated soils was mentioned as a potential source of natural radionuclides, affecting soils and crops (Saueia and Mazzilli, 2006; Sheppard et al., 2008; Hamidalddin, 2014; Todorović et al., 2015). Therefore, to assess the effect of soil contamination by natural radionuclides and resulting increase of human exposure to ionizing radiation, a reference database of the natural background in soils is necessary. In this way, quality reference values (QRVs) for radionuclides can be established, using the same methodology as for heavy metal QRVs. The QRVs can be a guide to evaluate soil contamination and to make decisions regarding remediation actions for a more efficient environmental management (Ballesta et al., 2010; Alfaro et al., 2015; Lima et al., 2016).

The National Council of Environment of Brazil (Conama) established a list of QRVs for heavy metals and other substances listed in Resolution 420 (Brasil, 2009), determining soil-quality guidelines of chemical substances. However, this resolution did not include radionuclides, and decisions about remediation of radionuclide-contaminated areas are based on risk analysis (Lauria and Rochedo, 2005; Peres, 2007). For this analysis, local levels of background radionuclides should be available, but in the absence of this information, an approach based on international data is suggested (Marssim, 2000). However, this method is rather uncertain because of the differences among regions. The lack of these data justifies a survey for a baseline evaluation and the development of QRVs of natural radionuclides for specific soils of each region.

Radiological surveys were carried out in many countries to determine the natural content or background contents of radionuclides in soils (Saleh et al., 2007; Laubenstein et al., 2013; Ugur et al., 2013; Garba et al., 2015; Pillai et al., 2016). In Brazil, surveys on the radioactivity in soil were conducted mainly in the areas with high natural background radiation (HBRA), as for example in Poços de Caldas, on the beaches of monazite sand in the Espírito Santo State (Franca, 1963; Roser et al., 1964), and in other specific and restricted areas (Amaral, 1992; Malanca et al., 1993; Amaral and Mazzilli, 1997; Lauria, 1999; Alencar and Freitas, 2005; Santos Júnior et al., 2006; Hiromoto et al., 2007; Umisedo, 2007; Cardoso et al., 2009; Lauria, 2009). However, large-scale systematic surveys on soil radioactivity are not available in Brazil and to date, QRVs for radionuclides were only established in two Brazilian states (Peres, 2007; Peixoto, 2013).

The Rio de Janeiro State (RJ) comprises an area of 43,781.6 km^2 (IBGE, 2016), with different soil types, geology, and climates (Ceperj, 2014). The differences between these variables can give rise to varying levels of natural radionuclides in soils. As a result, the heterogeneity of the environmental variables requires extensive surveys to determine a list of QRVS for these soils. Some major facilities for nuclear energy generation in Brazil are located in Rio de Janeiro: two nuclear power plants and a nuclear-fuel enrichment facility. In the northern region of the State is located a facility for processing monazite sand, which also contains thorium and uranium. Rio de Janeiro has extensive agricultural areas, mainly small-scale vegetable production and sugarcane plantations, with intensive use of fertilizers. Altogether, these potential sources of contamination reinforce the importance of investigating the natural radiation background and establishing reference values for natural radionuclides for the State.

This study surveyed the background contents of natural radionuclides in soils, to investigate the relationships among soil properties and radioactive isotopes and to establish a list of QRVs for natural radionuclides in soils of Rio de Janeiro.

MATERIAL AND METHODS

Study area

The level of industrial development in Rio de Janeiro ranks second nationwide and it is the second most populated State in the country, with around 16 million inhabitants and 92 municipalities (IBGE, 2016). It is divided into eight administrative regions: Northwestern, Northern, Seacoast plains, Metropolitan, Mountain region, Center-South, Medium Valley of the Paraíba do Sul River, and Green Coast (Ceperj, 2014). The Seacoast region comprises a sequence of sedimentary plains of fluvial or marine origin, from the south to the north of the State, with some granite and gneiss mountain massives from the Precambrian. In the center of the State, there is a large chain of granite, migmatite and gneiss mountains, divided into three segments: Serra das Araras, Serra dos Órgãos, and Serra do Desengano, with a maximum altitude of 2,316 m a.s.l. Behind the mountain chain, there is a sedimentary plateau in the direction of the neighbor Minas Gerais State. On the western border with the states of Minas Gerais and São Paulo, another chain of igneous and metamorphic mountains occurs together with a sedimentary plateau, formed by sediments from these hills. In the Northern region of the State, there is a vast plain formed by sediments from the river Paraíba do Sul, and in the Northwestern region, another high plateau with granite, migmatite, and gneiss formations. Alkaline rocks with uranium and thorium associated with minerals are spread in small areas of the State (Silva and Cunha, 2001).

A variety of soils can be found in the State. The main soils types are Red Yellow Ferralsols, Red Yellow Acrisols, Cambisols, Red Acrisols, Fluvisols, Podzols, Gleysols, and Leptosols (Carvalho Filho et al., 2003; WRB, 2014). Its ecosystems are heterogeneous, with lagoons, mangroves, swamps, wetlands, sandbank vegetation, forests, and grassland areas. The climate is also varied, classified according to the Köppen System as Aw, Am, Af, BSh, Cfa, Cfb, Cwb, and Cwa. The rainfall is strongly influenced by the geographical localization and orographic factors. In the mountain region, precipitation is higher than in the Metropolitan and Northern regions and than in the Medium Valley of Paraíba do Sul (Carvalho Filho et al., 2003).

Sample collection and preparation

A total of 243 samples of topsoil (0.00-0.20 m) were collected in a previous survey performed by Lima (2015) to establish the QRVs for heavy metals in soils of Rio de Janeiro (RJ). Undisturbed soils or soils with minimum anthropic interference (natural vegetation or pasture with no fertilization) were sampled in areas of all regions of the State. The sampling points were selected based on a combined analysis of soil, geology, land cover, and land use maps (scale 1:500,000). A road map of the Rio de Janeiro State was used to orient the projection of the sampling areas. The maps were superimposed using the program ArcGIS Desktop 10, produced by the Environmental Systems Research Institute - ESRI (Redlands, CA). To define the locations of sampling points, the cLHS program - *Conditioned Latin Hypercube System* was used. The sampling areas were defined to be at least 200 m away from roads to avoid any contamination. The sampled soils were those with largest area of occurrence in the State: Red Yellow Ferralsols, Red Yellow Acrisols, Cambisols, Red Acrisols, Fluvisols, Podzols, Gleysols and Leptosols (WRB, 2014). According to Brazilian Classification System, the above described soils are respectively *Latossolo Vermelho Amarelo, Argissolo Vermelho Amarelo, Cambissolo, Argissolo Vermelho, Neossolo Flúvico, Espodossolo, Gleissolo*, and *Neossolo Litólico* (Santos et al., 2013). The samples were georeferenced and labeled in the field.

The samples were air-dried and sieved through 2 mm mesh at the Laboratory of Soil Pollution of the *Universidade Federal Rural do Rio de Janeiro*, where the chemical and physical-chemical properties were also determined and the soil types classified according to the Brazilian Classification System (Santos et al., 2013) and the FAO/WRB Classification System (WRB, 2014). The particle- size distribution analysis (sand, silt, and clay), pH(H_2O), cation-exchange capacity (CEC), and organic matter were determined by the methodology described by Donagema et al. (2011).

Analytical methods

The soil samples were filled in 300 mL pots, sealed and stored for at least 30 days to ensure the equilibrium between ^{226}Ra and its decay products. Afterwards, the radionuclides in the samples were determined by gamma spectrometry with hyperpure germanium (HPGe) detector systems (Canberra Inc. Meriden, CT, USA) at the Laboratory of Gamma Spectrometry (LSG) of the Institute of Radiation Protection and Dosimetry - IRD (Rio de Janeiro). The activity content of ^{228}Ra was derived from the 338.3 keV, 911.6 keV, and 969.1 keV peaks of ^{228}Ac (Bé et al., 2010) and gamma-ray peaks at 351.9 keV (^{214}Pb) and 609.3 keV (^{214}Bi) were used to determine the activity of ^{226}Ra (Bé et al., 2006). To determine the ^{40}K content, its photopeak of 1,460.8 keV was used. The counting time of the samples was 60,000 s and the background was measured during 230,000 seconds to decrease uncertainty. The detectors were calibrated efficiently with a standard aqueous solution containing various radionuclides in a nitric acid medium, supplied by the Brazilian Laboratory of Metrology of Ionizing Radiations, certified by the Bureau International des Poids et Measures (BIPM), France. The energy calibration was routinely performed with a ^{152}Eu source. The activity contents and associated uncertainties were determined according to the statistical uncertainty of peak area, using Genie2000 software (Canberra Inc, Meriden, USA).

The Minimum Detectable Activity (MDA) value was around 12 Bq kg^{-1} for ^{40}K, 2 Bq kg^{-1} for ^{226}Ra, and 3 Bq kg^{-1} for ^{228}Ra, for a counting time of 60,000 s (IAEA, 1989). To ensure the analytical quality, a customized certified reference material of soil-089 produced by ERA Inc. (Colorado, USA, certified by the National Institute of Standards and Technology - NIST) was analyzed several times as a blind sample among the others. The Laboratory of Gamma Spectrometry (LSG) had a good performance in intercomparisons with that of the Mixed Analyte Performance Evaluation Program, United States Department of Energy DOE-Radiological and Environmental Science Laboratory. The Brazilian Laboratory of Metrology organizes national intercomparison exercises in which the LSG also obtained a good agreement of results.

Statistical data treatment and map design

The results obtained by sample analysis were statistically evaluated with software Statgraphics Centurion XVII for descriptive statistics, frequency histograms, and testing of distribution fitting. The QRVs for radionuclides were established acccording to the Brazilian legislation (Brasil, 2009). The outliers for each radionuclide were identified and removed from the dataset, the frequency distribution of the activity content was tested, and the QRVs were calculated. Software SPSS version 20 (IBM Inc, USA) was used for the multivariate and correlation analyses. The geographical location of the sampling points is shown on the soil map of the State (Figure 1), adapted from Carvalho Filho et al. (2003). The map was designed with the free download software Qgis v.2.12.2 Lyon (Open Source Geospatial Foundation Project, 2016).

RESULTS AND DISCUSSION

Analysis results of the certified reference material

The certified activity contents of the certified reference material (Soil 089/ERA) and the means of the results of the six detection systems used are listed in table 1. The differences were evaluated statistically (confidence interval 95 %). The Z-score values were calculated according to equation 1, in which X_{ob} is the content obtained in this study, X_{cert} is the certified value, and σ is the standard deviation (IAEA, 2012). According to the protocol, the laboratory performance is considered satisfactory if $|z\ score| \leq 2$ and questionable for $2 < |z\ score| \leq 3$. The Z-score values showed satisfactory results for all detection systems and radionuclides.

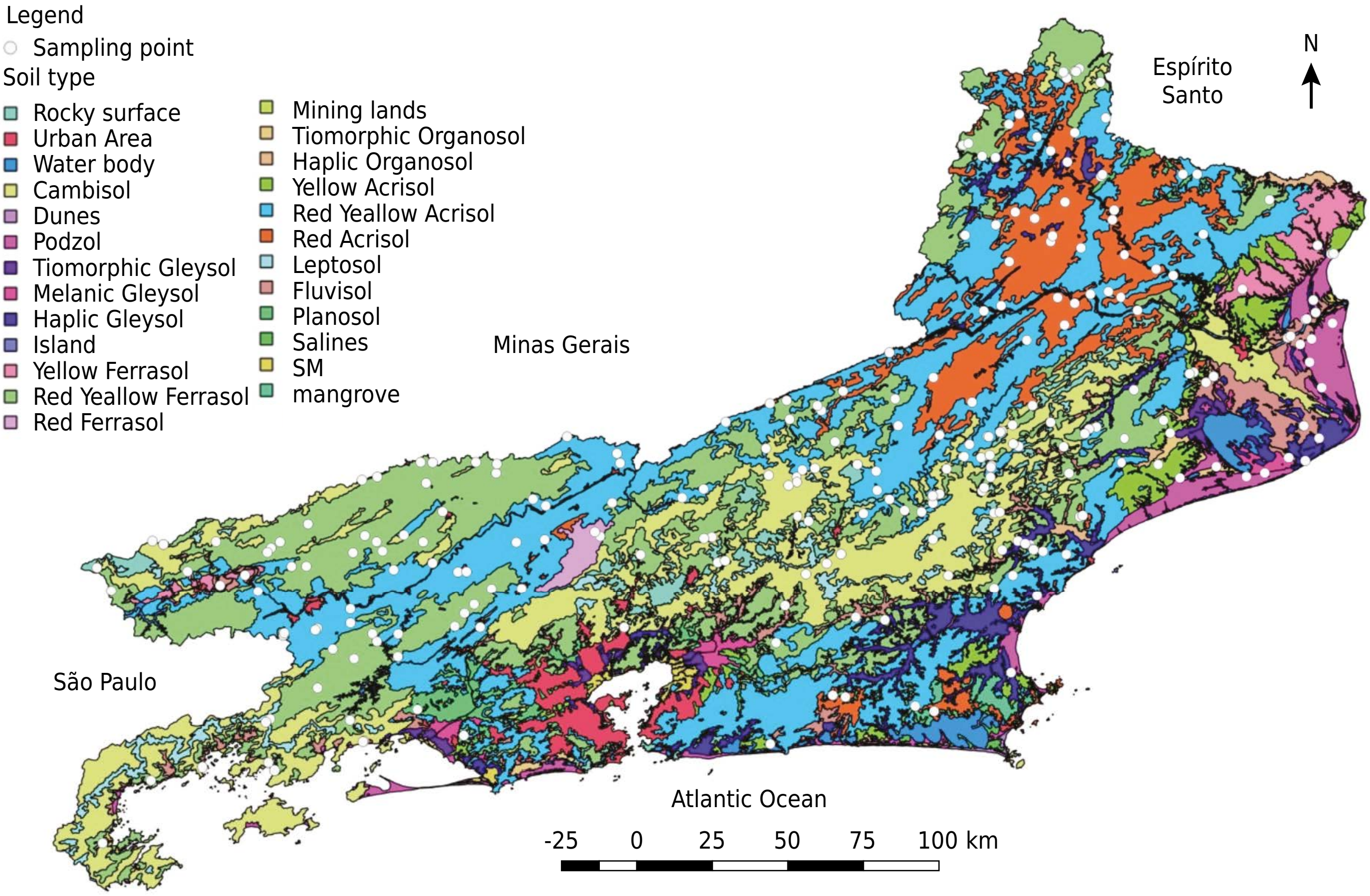

Figure 1. Soil map of the state of Rio de Janeiro (adapted from Carvalho Filho et al., 2003). White points indicate the soil sampling locations.

Table 1. Certified content and results of the analysis of the reference material of soil (089/ERA)

	Reference material	^{40}K	Z score	^{226}Ra	Z score	^{228}Ra	Z score
		Bq kg^{-1}		Bq kg^{-1}		Bq kg^{-1}	
	089/ERA	381.0 ± 66.0		38.5 ± 7.0		46.6 ± 8.1	
Detector number	1	370.8 ± 9.5	-0.2	39.0 ± 0.2	0.2	40.6 ± 0.4	-0.7
	2	383.1 ± 13.8	0.0	38.5 ± 1.5	0.2	38.5 ± 1.5	-1.0
	3	357.5 ± 3.3	-0.4	39.6 ± 2.0	0.3	35.4 ± 0.2	-1.4
	4	391.8 ± 3.4	0.2	42.4 ± 0.6	0.5	44.3 ± 1.4	-0.3
	5	395.4 ± 5.2	0.2	39.9 ± 1.7	0.3	49.7 ± 1.0	0.4
	6	384.6 ± 4.7	0.1	38.5 ± 0.4	0.2	52.6 ± 1.0	0.7

$$Z\ score = \frac{X_{ob} - X_{core}}{\sigma} \qquad \text{Eq. 1}$$

Soil physical and chemical characterization

Table 2 shows the statistical summary of the sample analyses, performed by Lima (2015). Most of the soils are acidic [pH(H_2O) arithmetic mean of 5.4] and have a medium organic matter content (5.3-69.3 g kg^{-1}). The CEC varied from 2.6 to 463 $cmol_c\ dm^{-3}$ (average 76 $cmol_c\ dm^{-3}$) and the average sand content was higher than that of silt and clay.

Descriptive statistics of radionuclide content in all soil samples

Descriptive statistics of the radionuclide activity contents were performed for all soil samples (Table 3). The goodness-of-fit (GOF) test indicated a log-normal distribution of the results and in this case, the geometric mean represents the main tendency. The ^{40}K content ranged from 12.2 to 1,029 Bq kg^{-1}, ^{226}Ra from 3.5 to 99.8 Bq kg^{-1}, and ^{228}Ra from 5.4 to 314.5 Bq kg^{-1}. The geometric means were, respectively, 111.1, 29.7, and 67.1 Bq kg^{-1}. Compared with the worldwide median values for ^{40}K, ^{226}Ra, and ^{228}Ra (400, 35, and 30 Bq kg^{-1}, respectively) (Unscear, 2000), the ^{40}K median value in Rio de Janeiro is nearly four times lower, the ^{226}Ra median value is comparable, and the ^{228}Ra median value is nearly twice as high as the value cited by the UN institution.

Comparison of activity content with other areas in Brazil and worldwide

Table 4 shows comparative data found in the literature for Brazilian soils. Most results were based on arithmetic means, but only the results of authors who reported geometric means

Table 2. Summary of statistical analysis of the physical and chemical properties of soil samples (n = 243)

Property	Arith. mean[(1)]	SD[(2)]	Minimum	Maximum
pH(H_2O)	5.4	0.6	3.3	7.6
H+Al ($cmol_c\ dm^{-3}$)	4.21	2.42	<0.10	16.30
CEC ($cmol_c\ dm^{-3}$)	76.0	66.0	2.6	463.0
OM[(3)] (g dm^{-3})	24.9	9.2	5.3	69.3
Sand (g kg^{-1})	550.14	159.40	41.00	993.00
Silt (g kg^{-1})	170.8	84.7	0.0	563.0
Clay (g kg^{-1})	278.6	118.4	7.0	721.0

(1) Arithmetic mean. (2) Standard deviation. (3) Organic matter: determined by oxidation with $K_2Cr_2O_7$. pH in water (1:2.5, v:v). H+Al: acidity potential extracted with calcium acetate 0.5 mol L^{-1}. Sand, silt clay determined by total dispersion method. CEC: cation exchange capacity at pH 7.0.

Table 3. Summary statistics for the radionuclides analyzed in pooled soil samples (n = 243)

Summary statistics	^{40}K	^{226}Ra	^{228}Ra
Minimum (Bq kg^{-1})	12.2 ± 3.3	3.5 ± 0.3	5.4 ± 0.3
Median (Bq kg^{-1})	113.1	32.1	73.8
Maximum (Bq kg^{-1})	1,029 ± 104	99.8 ± 1.6	314.5 ± 1.9
Arithmetical mean (Bq kg^{-1})	211.9	34.4	78.7
Standard deviation (Bq kg^{-1})	233.4	18. 3	43.6
Coefficient of variation (%)	110	53	55
Geometric mean (Bq kg^{-1})	111.1	29.7	67.1
Geometric standard deviation (Bq kg^{-1})	3.5	1.8	1.8
Standard skewness	10.20	6.50	9.26
Standard kurtosis	6.34	3.60	13.00

Radionuclides ativities concentration were determined by Gamma Spectrometry.

Table 4. Activity content of ^{40}K, ^{226}Ra, and ^{228}Ra reported in other studies for Brazilian soils

Region	^{40}K	^{226}Ra	^{228}Ra	Reference
		Bq kg^{-1}		
State of Rio de Janeiro	12.2-1,029	3.5-99.8	5.4-314	This study
World range	140-850	17-60	11-64	Unscear (2000)
Agricultural soils of Rio de Janeiro	-	28-93	36-117	Lauria et al. (2009)
State of São Paulo	15.3-516	1.0-61.8	3.3-97.6	Hiromoto et al. (2007)
São Francisco de Itabapoana, RJ	-	23-154	71-699	Lauria (1999)
Poços de Caldas, Minas Gerais	-	(135)	(282)	Amaral (1992)
Poços de Caldas, Minas Gerais	-	30-448	181-525	Linsalata and Penna-Franca (1988)
Caetité, Bahia	-	74-196	-	Cardoso et al. (2009)
Phosphate region of Pernambuco	-	14.2-240	-	Amaral and Mazzilli (1997)
Pedra, Pernambuco	-	14-367	-	Santos Júnior et al. (2006)
State of Pernambuco	4.7-2,274	-	-	Santos Júnior (2009)
Sand beaches of Southeast and South of Bahia	25-888	-	-	Veiga et al. (2006)

-: not determined.

will be compared. Thus, the geometric means for ^{226}Ra and ^{228}Ra found in this study are lower than those reported by Amaral (1992) for the areas with highest background radiation of Poços de Caldas (Minas Gerais), and quite similar to those reported by Lauria et al. (2009) for the agricultural area of Paty de Alferes and Teresópolis, also in Rio de Janeiro.

Comparing the range of values, the soils of São Paulo State (Hiromoto et al., 2007) reached lower values than those found in this survey, although our values are lower than those reported by the Brazilian HBRA of Poços de Caldas (Minas Gerais), Caetité (Bahia), the phosphate region of Pernambuco (Amaral and Mazzilli, 1997; Santos Júnior et al., 2006; Cardoso et al., 2009), and in the area rich in monazite sands in São Francisco de Itabapoana, also in Rio de Janeiro (Lauria et al., 1999). For ^{40}K, this study found higher values than those reported by Veiga et al. (2006) for the sand beaches in the southern part of Rio de Janeiro and for São Paulo and Bahia.

In conclusion, most of Rio de Janeiro State was found to be Normal Radiation Background Area, however with a higher radiation level than in São Paulo State. The presence of igneous rocks in a significant part of the State may be responsible for this higher radiation than in São Paulo.

Of the sample data set (n = 243) only seven samples (2.88 %) had higher ^{226}Ra than ^{228}Ra values. This is a typical result for Brazilian soils, known to contain more ^{232}Th than ^{238}U (Pfeiffer et al., 1981; Linsalata et al., 1989). The ^{228}Ra/^{226}Ra ratio varied between 0.79 and 8.77, with an average of 2.52 and geometric mean of 2.28.

The United Nations Scientific Committee of the Effects of Atomic Radiation (Unscear), in Annex B of the publication "*Sources and effects of ionizing radiation*" (Unscear, 2008), reported a range of ^{40}K and ^{226}Ra contents (Table 5) for various countries. The ^{228}Ra is not mentioned, since the available data for this radionuclide are very restricted. Comparisons with ^{238}U and ^{232}Th data were not performed because the radioactive equilibrium of the decay chains is not usually found in open environmental systems (Ivanovich and Harmon, 1992; Berkowitz et al., 2014). It is noteworthy that the ^{40}K contents in this study were lower than those reported for Cuba, China, Republic of Korea, Estonia, Finland, Sweden, Germany, Luxembourg, Ireland, Portugal, Spain, Czech Republic, Slovakia, Slovenia, and Greece. On the other hand, the ^{40}K values were similar to the values of Poland and Switzerland and higher than in Argentina. The ^{226}Ra activity content ranged from 3.5 to 99.8 Bq kg^{-1}, i.e., the highest value is below the range reported for Algeria, USA, Costa

Table 5. Ranges of ^{40}K and ^{226}Ra in soils worldwide [adapted from Unscear (2008)]

Region/country	^{40}K	^{226}Ra	Region/country	^{40}K	^{226}Ra
	Bq kg^{-1}			Bq kg^{-1}	
Rio de Janeiro State, Brazil	12.2-1,029	3.5-99.8	Iceland	40-240	2-15
Algeria	66-1,150	5-180	Lithuania	241-800	10-96
Egypt	29-650	5-64	Sweden	600-1,180	10-1,000
United States	100-700	8-160	Belgium	100-1,000	6-70
Costa Rica	6-380	11-130	Germany	40-1,340	5-200
Cuba	20-2,260	0.5-115	Ireland	11-1,317	6-292
Argentina	559-773	nd	Luxembourg	80-1,800	6-52
China	9-1,800	2-440	Netherlands	120-730	6-63
India	38-760	7-81	Portugal	220-1,230	8-65
Japan	15-990	6-98	Spain	31-2,040	8-310
Indonesia	75-523	7-54	Switzerland	40-1,000	17-140
Malaysia	170-430	38-94	Bulgaria	40-800	12-210
Rep. of Korea	17-1,500	6-140	Czech Republic	262-1,599	18-275
Thailand	7-712	11-78	Hungary	79-570	14-76
Armenia	310-420	32-77	Poland	123-1,020	4.2-124
Azerbaijan	60-180	15-35	Russian Federation	100-1,400	1-76
Iran (Islamic Rep. of)	290-710	20-97	Slovakia	200-1,380	12-120
Iraq	146-518	0.5-35	Slovenia	15-1,410	2-208
Kuwait	4-496	2-28	Croatia	107-748	18-80
Syrian Arab Rep.	87-780	13-32	Cyprus	0-670	0-120
Denmark	240-610	8.5-29	Greece	12-1,570	1-310
Estonia	140-1,120	6-310	Montenegro	78-480	7-166
Finland	300-1,200	13-110	New Zealand	<40-740	<4-56

nd: not determined.

Rica, Cuba, China, Sweden, Germany, Ireland, Spain, Switzerland, Bulgaria, Czech Republic, Poland, Slovakia, Slovenia, Cyprus, and Montenegro, and similar to the values reported for Japan, Malaysia, Iran, and Lithuania. Overall, this comparison showed that the natural radionuclide contents of RJ soils are within the worldwide range.

Evaluation of radionuclide content of each soil type

The frequency distribution and descriptive statistical analyses were performed for each soil type (Table 6). Less than 1.7 % of the total samples were outliers, identified by the Grubb's test and removed from the data set. As commonly observed in environmental data distribution, the results fit a lognormal distribution, and their geometric mean values represent better the main tendencies.

The highest median ^{40}K value was observed in the Gleysol, which may be ascribed to the presence of primary minerals such as mica and K-feldspar, leading to high total K contents and high non-extractable K in lowland soils (Britzke et al., 2012). The highest medians for ^{226}Ra and ^{228}Ra were found in the Leptsol, a shallow and young soil derived from granite and gneisses that are part of those rocks for which above-normal levels of natural-series radionuclides were detected (Leal and Lauria, 2016). The lowest values for the three radionuclides were found in Podzols, which is a generally sandy soil derived from either quartz-rich sands and sandstones or sedimentary debris from magmatic rocks.

Correlation between soil parameters and radionuclides

Correlation analysis was performed to provide an overview of the relationships among radionuclides and soil properties. Table 7 shows the correlations, examined by

Table 6. Statistical summary of activity concentrations (in Bq kg^{-1}) of radionuclides in the different soil types

	Soil	$N^{(1)}$	Geometric mean	Geometric standard deviation	Minimun	Maximum
			Bq kg^{-1}			
^{40}K	Cambisol	36	251.9	2.7	19.3	974.7
	Gleysol	7	300.9	1.7	169.0	694.9
	Leptosol	5	160.6	3.8	18.0	511.1
	Red Acrisol	27	135.1	3.4	12.5	857.9
	Fluvisol	10	107.9	4.9	5.8	732.7
	Red Yellow Acrisol	63	112.6	2.8	10.9	1,029
	Red Yellow Ferralsol	84	63.6	2.7	5.1	397.7
	Podzols	9	29.5	5.0	4.0	205.4
^{226}Ra	Cambisol	36	36.7	1.4	10.2	59.7
	Gleysol	6	33.1	1.2	24.3	40.3
	Leptosol	3	92.2	1.1	86.9	97.0
	Red Acrisol	26	19.8	1.4	6.8	33.5
	Fluvisol	10	22.9	2.8	3.4	68.9
	Red Yellow Acrisol	63	29.1	1.6	11.8	75.5
	Red Yellow Ferralsol	86	33.9	1.7	12.6	99.8
	Podzols	9	10.4	1.7	4.8	26.0
^{228}Ra	Cambisol	36	78.6	1.6	20.5	218.9
	Gleysol	7	71.9	1.0	43.4	176.6
	Leptosol	5	139.5	1.2	107.0	174.0
	Red Acrisol	27	63.8	1.8	21.2	182.0
	Fluvisol	10	48.3	3.1	5.4	194.5
	Red Yellow Acrisol	62	61.9	1.6	20.1	143.7
	Red Yellow Ferralsol	83	74.1	1.5	27.2	314.5
	Podzols	9	15.8	1.7	6.2	55.1

(1) Number of samples without outlier values.

Table 7. Matrix of Spearman's correlation between the soil properties and the studied radionuclides

	$pH(H_2O)$	OM	CEC	Sand	Silt	Clay	^{40}K	^{226}Ra
$pH(H_2O)$								
$OM^{(1)}$	-0.086							
CEC	0.232^{**}	0.296^{**}						
Sand	0.003	-0.420^{**}	-0.275^{**}					
Silt	0.233^{**}	0.376^{**}	0.401^{**}	-0.620^{**}				
Clay	-0.130^{*}	0.309^{**}	0.125	-0.848^{**}	0.181^{**}			
^{40}K	0.232^{**}	-0.003	0.396^{**}	0.059	0.396^{**}	-0.304^{**}		
^{226}Ra	-0.216^{**}	0.104	0.065	-0.090	0.090	0.065	0.160^{*}	
^{228}Ra	-0.067	0.095	0.113	-0.208^{**}	0.165^{*}	0.178^{**}	0.195^{**}	0.604^{**}

(1) Organic matter. ** and *: correlation significant at the 0.01 and 0.05 level (2-tailed), respectively.

Spearman's test. Regarding the natural radionuclides, there was a positive correlation (95 % significance) between ^{40}K and $pH(H_2O)$, cation-exchange capacity (CEC), and silt, and a negative correlation with clay. The ^{226}Ra is negatively correlated with $pH(H_2O)$ and positively with ^{40}K and ^{228}Ra. The test also showed that ^{228}Ra has a negative correlation with sand, but a positive one with clay, ^{40}K, and ^{226}Ra. The high content of ^{226}Ra in acidic soil may be related to the accessory minerals in the acidic bedrock and mechanisms of radium retention in soil. The correlation between the two radium isotopes indicates a common source of the radionuclides.

The statistical treatment by principal component analysis (Varimax rotation method) detected four components, responsible for 75 % of the data variance. The first component combines silt, clay, and OM; the 2nd component OM and acidity (H+Al); and the 3rd component pH(H_2O), OM, silt, CEC, and ^{40}K. The radium isotopes are associated with the 4th component. The low loading values of the radium isotopes within the groups 1, 2, and 3 may indicate a quasi-independent behavior regarding these groups. Therefore, the independence from the other groups of variables and strong correlation between them suggests a probable common natural source (Table 6). Figure 2 shows the principal component in a spatial manner.

Quality Reference Values (QRVs) of radionuclides

The QRVs for the 75th and 90th percentiles of the radionuclides (Table 8) were calculated for each one of the main soils of Rio de Janeiro State, corresponding to more than 80 % of the State territory (Carvalho Filho et al., 2003).

Only for the states of Minas Gerais and São Paulo, the QRVs were established for natural radionuclides in soils, both based on the 75th percentile. Peixoto (2013) studied soils of Minas Gerais and established the QRVs for ^{40}K, ^{226}Ra, and ^{228}Ra (438.9 Bq kg^{-1}, 66.8 Bq kg^{-1}, and 89.9 Bq kg^{-1}, respectively). In a comparison with the values determined in this

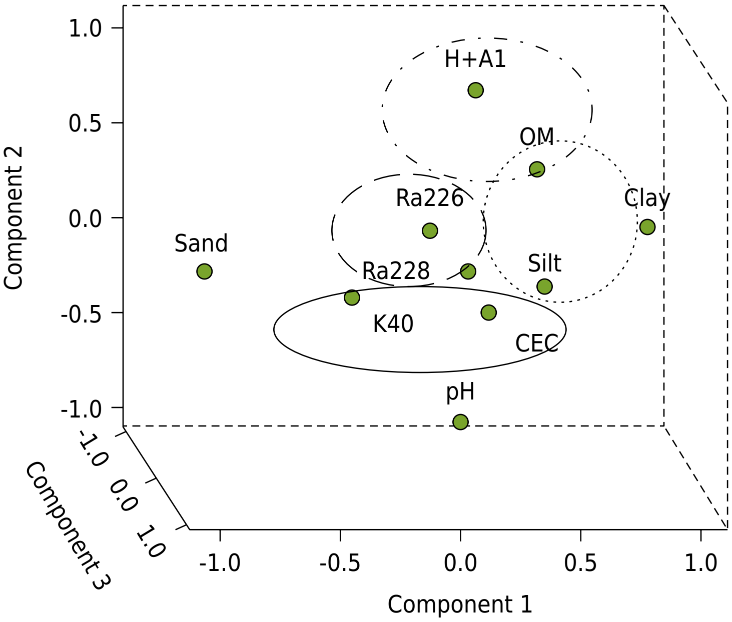

Figure 2. Diagram of principal component analysis (PCA). OM: organic matter; CEC: cation exchange capability.

Table 8. Quality Reference Values of ^{40}K, ^{226}Ra, and ^{228}Ra for each soil class

Soil classification	Percentile					
	P(75)	P(90)	P(75)	P(90)	P(75)	P(90)
	^{40}K		^{226}Ra		^{228}Ra	
	Bq kg^{-1}					
Red Yellow Ferralsol	142.6	252.3	49	65	108	135
Red Yellow Acrisols	241.6	496.2	39	63	89	104
Cambisols	584.8	808.1	43	51	99	130
Red Acrisols	382.8	623.9	25	28	103	110
Fluvisols	521.6	629.8	48	60	102	158
Podzols	158.5	205.4	11	26	25	55
Gleysols	500.9	694.9	36.8	40	74	177
Leptosols	373.9	511.1	97	97	160	174
All soils	291	580	43	63	101	130

study, the QRVs for ^{40}K in Rio de Janeiro soils are lower, except for Cambisols, Gleysols, and Fluvisols. For ^{226}Ra, except for Leptosols, the values estimated here are lower than those for Minas Gerais; and the QRVs for ^{228}Ra for Rio de Janeiro are higher than those for Minas Gerais, except for Podzols, Gleysols, and Red Yellow Acrisols, which are quite similar. For soils of São Paulo State, Peres (2007) reported geometric means of ^{40}K, ^{226}Ra, and ^{228}Ra, respectively, as 86.7, 17.1, and 27.8 Bq kg^{-1}.

The establishment of a single QRV for each radionuclide and State is a common approach in many studies (Peres, 2007; Peixoto, 2013). However, the results of this research showed a large variety of QRVs for the different soil types: e.g., considering the 75th percentile, the QRV for Red Yellow Ferrasol was estimated at 142.6 Bq kg^{-1}, and at 584.8 Bq kg^{-1} for Cambisols (Table 6). Mainly for ^{40}K and ^{226}Ra, a rather large difference was observed between the single overall value and the value for the specific soil types (Table 6). Five of the eight soil types studied had a higher QRV for ^{40}K (75th percentile) than the single overall value for the radionuclide (291 Bq kg^{-1}). This trend was observed for all radionuclides, regardless of the percentile used.

In general, the most weathered soils (Red Yellow Ferralsol, Red Yellow Acrisol, and Red Acrisol) had lower QRV than the single overall QRV. As they represent the majority of soils in the State area (≈ 56 % of the area) (Carvalho Filho et al., 2003), the establishment of a single QRV would lead to the conclusion that most Rio de Janeiro soils are contaminated. The differences among the QRVs for each soil show how challenging the establishment of a single and generic QRV for such diverse environments will be. The results clearly showed the need for determining a soil-type specific QRV, as similarly recommended for heavy metals in soils by Santos and Alleoni (2013).

The Brazilian legislation allows establishing QRVs based on the percentiles 75th or 90th. Some authors suggested QRVs for heavy metals in soils based on the 75th percentile (Cetesb, 2001; Caires, 2009; Santos and Alleoni, 2013; Preston et al., 2014), while few studies suggested QRVs based on the 90th percentile (Paye et al., 2010; Almeida Júnior, 2016). Variations between the 75th and 90th percentile were observed, ranging from 21 to 105 % for ^{40}K, from 9 to 136 % for ^{226}Ra, and from 7 to 139 % for ^{228}Ra (Table 7). The vast difference between the percentiles highlights that the establishment of QRVs based on the 75th percentile can significantly restrict the assessment. Therefore, the use of the 75th percentile may cause misinterpretations regarding contamination by overestimating the environmental pollution. Thus, considering the data variability, we suggest that the QRVs for the studied natural radionuclides should be based on the 90th percentile, which is a less restrictive value.

Figure 3 shows the relative deviation for the 90th percentile of each soil with regard to the use of a single QRV for all soils. The data indicate that the adoption of a single QRV can lead to an overestimation of the radionuclide contents if applied to all soils, e.g., in the case of Podzol, and underestimate the consequences of pollution in other soils.

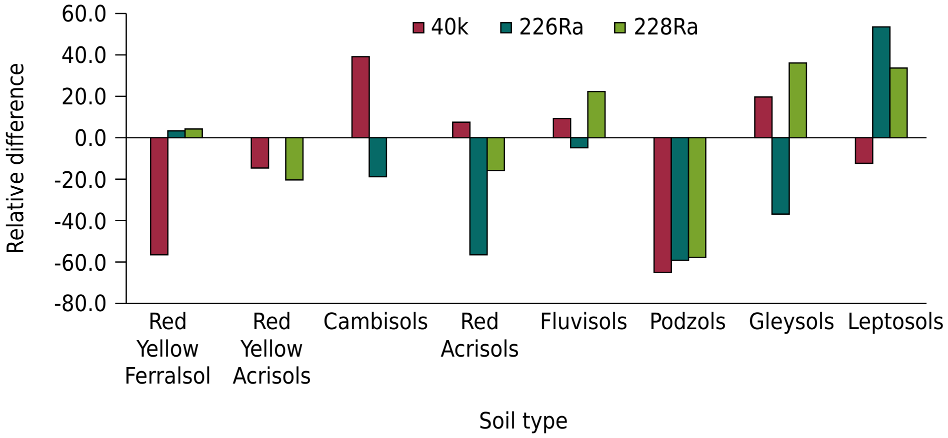

Figure 3. Relative deviation of QRVs for ^{40}K, ^{226}Ra, and ^{228}Ra activity contents for each soil class with respect to the single QRV for all soil types.

CONCLUSIONS

A baseline data set of radionuclides in Rio de Janeiro was established in a systematic and extensive research. The activity contents of ^{40}K, ^{226}Ra, and ^{228}Ra for the main soils of Rio de Janeiro are within the range of normal background radiation areas worldwide. The radium isotopes are strongly correlated with each other, which confirms their common and natural source, while ^{40}K is more related to pH, CEC, and silt. The values of radionuclide contents varied among the soil classes. The radium isotope contents were highest in Leptosol and lowest in Podzol, where the ^{40}K content was also lowest. A list of QRVs for ^{40}K, ^{226}Ra, and ^{228}Ra was established for the eight main soils of the State, based on the 75th and 90th percentiles of their contents. Also, a single overall QRV (for the 75th and 90th percentiles) was estimated for ^{40}K (291 and 580), for ^{226}Ra (43 and 63) and ^{228}Ra (101 and 130). The large differences between the single overall QRV and specific QRVs for each soil type are noteworthy. Furthermore, notable differences were also observed between the 75th and 90th percentile values. Considering the adoption of a single QRV for the State and the establishment of QRV based on the 75th percentile, the adopted QRV would lead to a false positive assessment of contamination. We recommend the establishment of QRVs based on the less restrictive value of the 90th percentile. Moreover, we also suggest the estimation of QRVs for each soil class, instead of a single value for the region, mainly in areas with highly heterogeneous environmental conditions, as found in Rio de Janeiro.

REFERENCES

Alencar AS, Freitas AC. Reference levels of natural radioactivity for the beach sands in a Brazilian southeastern coastal region. Radiat Meas. 2005;40:76-83. https://doi.org/10.1016/j.radmeas.2004.08.003

Alfaro MR, Montero A, Ugarte OM, Nascimento CWA, Accioly AMA, Biondi CM, Silva YJAB. Background concentrations and reference values for heavy metals in soils of Cuba. Environ Monit Assess. 2015;187:4198. https:/doi.org/10.1007/s10661-014-4198-3

Almeida Júnior AB, Nascimento CWA, Biondi CM, Souza AP, Barros FMR. Background and reference values of metals in soils from Paraíba State, Brazil. Rev Bras Cienc Solo. 2016;40:e0150122. http://dx.doi.org/10.1590/18069657rbcs20150122

Amaral ECS. Modificação da exposição à radiação natural devido a atividades agrícolas numa área de radioatividade natural elevada no Brasil [tese]. Rio de Janeiro: Universidade Federal do Rio de Janeiro; 1992.

Amaral RS, Mazzilli BP. Avaliação do equilíbrio entre o ^{238}U e ^{226}Ra e a relação ^{226}Ra/^{228}Ra no capeamento (solo) de jazidas fosfáticas em Pernambuco. In: Anais International Nuclear Atlantic Conference - INAC; 1997. Santos, SP; 1997 [acesso em agosto 2016]. Disponível em: https://www.ipen.br/biblioteca/cd/inac/1997/ENAN/E03_015.PDF

Ballesta RJ, Bueno PC, Rubí JAM, Gimémez RG. Pedo-geochemical baseline content levels and soil quality reference values of trace elements in soils from the Mediterranean (Castilla La Mancha, Spain). Cent Eur J Geosci. 2010;2:441-54. https://doi.org/10.2478/v10085-010-0028-1

Bé M-M, Chisté V, Dulieu C, Browne E, Baglin C, Chechev V, Kuzmenko N, Helmer R, Kondev F, MacMahon D, Lee KB. Monographie BIPM-5 - Table of Radionuclides, Comments on evaluation. Sèvres: Bureau international des poids et mesures; 2006. Vol.3 - A = 3 to 244.

Bé M-M, Chisté V, Dulieu C, Mougeot X, Chechev VP, Kondev FG, Nichols AL, Huang X, Wang B. Monographie BIPM-5 - Table of Radionuclides, Comments on evaluation. Sèvres: Bureau international des poids et mesures; 2010. Vol.7 - A = 14 to 245.

Berkowitz B, Dror I, Yaron B. Contaminant geochemistry: interactions and transport in the subsurface environment. 2nd ed. Berlin: Springer-Verlag; 2014.

Brasil. Conselho Nacional do Meio Ambiente. Resolução nº 420, de 28 de dezembro de 2009. Publicado no DOU nº 249, de 30/12/2009. Dispõe sobre critérios e valores orientadores de qualidade do solo quanto à presença de substâncias químicas e estabelece diretrizes para o gerenciamento ambiental de áreas contaminadas por essas substâncias em decorrência de atividades antrópicas. Brasília, DF: Conselho Nacional do Meio Ambiente; 2009 [acesso em 1 ago de 2012]. Disponível em: http://www.mma.gov.br/port/conama/legiabre.cfm?codlegi=620.

Britzke D, Silva LS, Moterle DF, Rheinheimer DS, Bortoluzzi EC. A study of potassium dynamics and mineralogy in soils from subtropical Brazilian lowlands. J Soils Sediments. 2012;12:185-97. https://doi.org/10.1007/s11368-011-0431-7

Caires SM. Determinação dos teores naturais de metais pesados em solos do Estado de Minas Gerais como subsídio ao estabelecimento de Valores de Referência de Qualidade [tese]. Viçosa, MG: Universidade Federal de Viçosa; 2009.

Cardoso GV, Amaral Sobrinho NMB, Wasserman MAV, Mazur N. Geoquímica de radionuclídeos naturais em solos de áreas circunvizinhas a uma unidade de mineração e atividade de urânio. Rev Bras Cienc Solo. 2009;33:1909-17. http://dx.doi.org/10.1590/S0100-06832009000600040

Carvalho Filho A, Lumbreras JF, Wittern KP, Lemos AL, Santos RD, Calderano Filho SB, Calderano SB, Oliveira RP, Aglio MLD, Souza JS, Chaffin CE. Mapa de reconhecimento de baixa intensidade dos solos do estado do Rio de Janeiro. Escala 1:250.000. Rio de Janeiro: Embrapa Solos; 2003.

Centro Estadual de Estatística, Pesquisa e Formação de Servidores Públicos do Rio de Janeiro - Ceperj. Estado do Rio de Janeiro: Regiões de governo e munícipios 2014 [mapa]. Rio de Janeiro: Ceperj; 2014. Disponível em: http://www.ceperj.rj.gov.br/ceep/info_territorios/Reg%20Gov_2013.pdf

Companhia de Tecnologia de Saneamento Ambiental - Cetesb. Relatório de estabelecimento de valores orientadores para solos e águas subterrâneas no Estado de São Paulo. São Paulo: Cetesb; 2001. (Série Relatórios Ambientais).

Donagema GK, Campos DVB, Calderano SB, Teixeira WG, Viana JHM, organizadores. Manual de métodos de análise do solo. 2. ed. rev. Rio de Janeiro: Embrapa Solos; 2011.

Franca EP. Radioatividade na dieta dos habitantes das regiões brasileiras de elevada radiação natural [tese]. Rio de Janeiro: Universidade Federal do Rio de Janeiro; 1963.

Garba NN, Ramli AT, Saleh MA, Sanusi MS, Gabdo HT. Terrestrial gamma radiation dose rates and radiological mapping of Terengganu state, Malaysia. J Radioanal Nucl Chem. 2015;303:1785-92. https://doi.org/10.1007/s10967-014-3818-2

Hamidalddin SHQ. Determination of agriculture soil primordial radionuclide concentrations in Um Hablayn, north Jeddah west of Saudi Arabia. Int J Curr Microbiol App Sci. 2014;3:623-33.

Hiromoto G, Peres AC, Tadei MH, Soares MR, Alleoni LRF. Radioactive soil characterization of the state of São Paulo, Brazil. In: Proceedings of the annual international conference on soils, sediments, water and energy; 2007. Berkeley: The Berkeley Electronic Press; 2007. p.197-200.

International Atomic Energy Agency - IAEA. Measurement of radionuclides in food and the environment: a guidebook. Vienna: IAEA; 1989. Technical report series No. 295.

International Atomic Energy Agency - IAEA. The environmental behavior of radium: revised edition. Vienna: IAEA; 2014. Technical reports series No. 476.

International Atomic Energy Agency - IAEA. World wide proficiency test: determination of natural and artificial radionuclides in moss-soil and water IAEA-CU-2009-03. Vienna: IAEA; 2012. Analytical quality in nuclear applications series No. 22.

Instituto Brasileiro de Geografia e Estatística - IBGE. Informações sobre a PNAD 2015; 2016 [acesso em 21 jul 2016]. Disponível: http://www.ibge.gov.br/estadosat/perfil.php?sigla=rj.

Ivanovich M, Harmon RS. Uranium-series disequilibrium: applications to earth, marine, and environmental sciences. 2nd ed. Oxford: Clarendon Press; 1992.

Laubenstein M, Plastino W, Povinec PP, Fabbri V, Aprili P, Balata M, Bella F, Cardarelli A, De Deo M, Gallese B, Ioannucci L, Nisi S, Antonecchia D, Del Pinto C, Giarrusso G. Radionuclide mapping of the Molise region (Central Italy) via gamma-ray spectrometry of soil samples: relationship with geological and pedological parameters. J Radioanal Nucl Chem. 2013;298:317-23. https://doi.org/10.1007/s10967-012-2353-2

Lauria DC. Transporte de radionuclídeos naturais e elementos das terras raras leves no sistema lagunar de Buena, RJ [tese]. Rio de Janeiro: Pontifícia Universidade Católica do Rio de Janeiro; 1999.

Lauria DC, Ribeiro FCA, Conti CC, Loureiro FA. Radium and uranium levels in vegetables grown using different farming management systems. J Environ Radioactiv. 2009;100:176-83. https://doi.org/10.1016/j.jenvrad.2008.11.006

Lauria DC, Rochedo ERR. The legacy of monazite processing in Brazil. Radiat Prot Dosim. 2005;114:546-50. https://doi.org/10.1093/rpd/nci303

Leal ALC, Lauria DC. Assessment of doses to members of the public arising from the use of ornamental rocks in residences. J Radiol Prot. 2016;36:680-94. https://doi.org/10.1088/0952-4746/36/3/680

Lima ESA. Valores de referência de qualidade de metais em solos do estado do Rio de Janeiro e Organossolos no Brasil [tese]. Seropédica: Universidade Federal Rural do Rio de Janeiro; 2015.

Lima ESA, Amaral Sobrinho NMB, Paiva FSD, Coutinho IB, Pereira MG, Zonta E. Quality reference values of trace elements in Brazilian organosols. Environ Monit Assess. 2016;188:418. https://doi.org/10.1007/s10661-016-5436-7

Linsalata P, Morse RS, Ford H, Einsenbud M, Franca EP, Castro MB, Lobão N, Sachett I, Carlos M. An assessment of soil-to-plant concentration ratios for some natural analogues of the transuranic elements. Health Phys. 1989;56:33-46.

Linsalata P, Penna Franca E. Final Report. Studies of Transport Pathways of Th, U, Rare Earths, Ra228 and Ra226 from Soil to Plants. Washington, DC, United States Department of Energy, 1988.

Malanca A, Pessina V, Dallara G. Assessment of the natural radioactivity in the Brazilian State of Rio Grande do Norte. Health Phys. 1993;65:298-302.

United States Environmental Protection Agency (USA). Multi-Agency Radiation Survey and Site Investigation Manual - Marssim. NUREG-1575, Rev.1. Washington, DC; 2000.

Open Source Geospatial Foundation Project. Qgis 2.12.2 Lyon. QGIS Development Team; 2016. Available at: http://qgis.osgeo.org.

Paye HS, Mello JWV, Abrahão WAP, Fernandes Filho EI, Dias LCP, Castro MLO, Melo SB, França MM. Valores de referência de qualidade para metais pesados em solos no estado do Espírito Santo. Rev Bras Cienc Solo. 2010;34:2041-51. http://dx.doi.org/10.1590/S0100-06832010000600028

Peixoto CM. Determinação dos valores de referência de qualidade de solo para U e Th no estado de Minas Gerais [dissertação]. Belo Horizonte: Centro de Desenvolvimento da Tecnologia Nuclear; 2013.

Peres AC. Modelo para o estabelecimento de valores orientadores para elementos radioativos no solo [tese]. São Paulo: Instituto de Pesquisas Energéticas e Nucleares; 2007.

Pfeiffer WC, Penna-Franca E, Ribeiro CC, Nogueira AR, Londres H, Oliveira, AE. Measurements of environmental radiation exposure dose rates at selected sites in Brazil. An Acad Bras Cienc. 1981;53:683-91.

Pillai GS, Hameed PS, Khan SMMN. Natural radioactivity levels in the soils and human risk assessment in Tiruchirappalli district (Tamil Nadu, India). J Radioanal Nucl Chem. 2016;307:1265-77. https://doi.org/10.1007/s10967-015-4367-z

Preston W, Nascimento CWA, Biondi CM, Souza Junior VS, Silva WR, Ferreira HA. Valores de referência de qualidade para metais pesados em solos do Rio Grande do Norte. Rev Bras Cienc Solo. 2014;38:1028-37. http://dx.doi.org/10.1590/S0100-06832014000300035

Roser FX, Kegel G, Cullen TL. Radiogeology of some high-background areas of Brazil. In: Adams JAS, Lowder WM, editors. The natural radiation environment. Chicago: University of Chicago Press; 1964. p.855-72

Saleh IH, Hafez AF, Elanany NH, Motaweh HA, Naim MA. Radiological study on soils, foodstuff and fertilizers in the Alexandria region, Egypt. Turkish J Eng Env Sci. 2007;31:9-17.

Santos HG, Jacomine PKT, Anjos LHC, Oliveira VA, Oliveira JB, Coelho MR, Lumbreras JF, Cunha TJF. Sistema brasileiro de classificação de solos. 3. ed. Rio de Janeiro: Embrapa Solos; 2013.

Santos Júnior JA, Cardoso JJRF, Silva CM, Silveira SV, Amaral RS. Determination of radionuclides in the environment using gamma-spectrometry. J Radioanal Nucl Chem. 2006;269:451-5. https://doi.org/10.1007/s10967-006-0417-x

Santos Júnior JA. Avaliação radiométrica do U-238, Ra-226, Th-232 e K-40 em uma área anômala do agreste de Pernambuco [tese]. Recife: Universidade Federal de Pernambuco; 2009.

Santos SN, Alleoni LRF. Reference values for heavy metals in soils of the Brazilian agricultural frontier in Southwestern Amazonia. Environ Monit Assess. 2013;185:5737-48. https://doi.org/10.1007/s10661-012-2980-7

Saueia CHR, Mazzilli BP. Distribution of natural radionuclides in the production and use of phosphate fertilizers in Brazil. J Environ Radioactiv. 2006;89:229-39. https://doi.org/10.1016/j.jenvrad.2006.05.009

Sheppard SC, Sheppard MI, Ilin M, Tait J, Sanipelli B. Primordial radionuclides in Canadian background sites: secular equilibrium and isotopic differences. J Environ Radioactiv. 2008;99:933-46. https://doi.org/10.1016/j.jenvrad.2007.11.018

Silva LC, Cunha HCS. Geologia do estado do Rio de Janeiro: texto explicativo do mapa geológico do estado do Rio de Janeiro. Brasília, DF: Companhia de Pesquisas de Recursos Minerais; 2001.

Todorović N, Bikit I, Vesković M, Mrdja D, Forkapić S, Hansman J, Nikolov J, Bikit K, Krmar M. Radioactivity in fertilizers and radiological impact. J Radioanal Nucl Chem. 2015;303:2505-09. https://doi.org/10.1007/s10967-014-3620-1

Ugur FA, Turhan S, Gören E, Gezer F, Yegingil Z, Sahan H, Sahan M, Tel E, Karahan G. A survey of distribution of terrestrial radionuclides in surface soil samples in and around the Osmaniye province, Turkey. Radiat Prot Dosim. 2013;154:483-9. https://doi.org/10.1093/rpd/ncs259

Umisedo NK. Dose de radiação ionizante decorrente do uso de fertilizantes agrícolas [tese]. São Paulo: Universidade de São Paulo; 2007.

United Nations Scientific Committee on the Effects of Atomic Radiation - Unscear. Sources and effects of ionizing radiation: report to the General Assembly annex B. New York: United Nations Publication; 2000. v.1.

United Nations Scientific Committee on the Effects of Atomic Radiation - Unscear. Sources and effects of ionizing radiation: Report to the General Assembly, annex B. New York: United Nations Publication; 2008. v.1.

Veiga R, Sanches N, Anjos RM, Macario K, Bastos J, Iguatemy M, Aguiar JG, Santos AMA, Mosquera B, Carvalho C, Baptista Filho M, Umisedo NK. Measurement of natural radioactivity in Brazilian beach sands. Radiat Meas. 2006;41:189-9. https://doi.org/10.1016/j.radmeas.2005.05.001

World Reference Base for Soil Resources - WRB: International soil classification system for naming soils and creating legends for soil maps. Food and Agriculture Organization of the United Nations. Rome: IUSS/ISRIC/FAO; 2014. (World Soil Resources Reports, 106).