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Characterization of Heavy Metals in a Uranium Ore Region of the State of Pernambuco, Brazil

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Abstract The concentrations of As, Zn, Co, Cr, and Ba were determined in soil samples from an anomalous uranium ore region in the countryside of the state of Pernambuco, Brazil. The main land use system in this region is dairy farming, and there is a need to evaluate the potential risk of milk contamination. Twenty-three soil samples were activated with neutrons and analyzed using a high-resolution gamma-ray spectrometer system. The results, recorded in mg kg^{-1}, varied from 0.4 to 6.7 for As, from 17.0 to 110.0 for Zn, from 2.8 to 38.4 for Co, from 12.1 to 65.5 for Cr, and from 443.0 to 1,497.0 for Ba. All of the Ba concentrations were higher than the intervention value adopted by the Brazilian National Environmental Board. This finding justifies research in other environmental areas to predict the toxicological risks to the local population.

Keywords Environmental dosimetry · Heavy metals · Neutron activation · Gamma spectrometry · Induced radioactivity

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As a large proportion of rocks that function as soil parent material contain heavy metals, the presence of heavy metals in primary form within the soil derives, among other pathways, from environmental processes (Lu et al. 2012). The natural processes that contribute to the presence of heavy metals in water include rock weathering and leaching from soils. Industrial processes can also introduce heavy metals into the ecosystem, contributing to an increase in their levels.

In recent years, concerns over contamination of soils and surface and subsurface waters have been increasing. These concerns have intensified due to urban and industrial expansion associated with the increase in the production of consumer goods, resulting in the generation of waste that, for many years, was discarded indiscriminately, causing widespread environmental damage (Lu et al. 2012).

Of the 65 existing heavy metals, some are classified as essential. However, depending on their concentrations in the environment, some of these metals can be toxic to living organisms, especially arsenic, zinc, cobalt, chrome, and barium. In high concentrations, these metals can lead to the development of tumors, damage to immune systems, cardiovascular diseases, and even DNA damage (Amin et al. 2013).

Throughout the world, studies of heavy metals have reported high concentrations of these elements in many regions located near urban industrial complexes and mining areas, as well as in areas with high-input agricultural systems. In these ecosystems, abnormal increases in the concentrations of As, Zn, Co, Cr, Ba, and other heavy metals in soils, as a result of processes such as atmospheric deposition, weathering, application of fertilizers and agrochemicals, urbanization, irrigation systems, and disposal of raw industrial wastewater in soils, rivers, and lakes, producing risks that are often unknown.

According to Alloway (1995), heavy metals occur in soils primarily in soluble form, exchangeable form, specifically adsorbed (chemically adsorbed) form, and linked to insoluble and precipitated organic materials, mainly in the form of carbonates, sulfates, phosphates, hydroxides, among others.

Andrade et al. (2012) reported that the mobility of these metals is influenced by a wide range of parameters, including pH, texture, redox potential, ionic potential, the presence of Fe–Mn oxides, the presence of organic materials, and the presence of clays.

To monitor potentially contaminated areas, it is necessary to understand the natural background levels of metals usually present in soils, as well as the variability of these levels in undisturbed soils. Therefore, determining the natural contents of these metals is the first step in defining the guiding parameters in contamination studies. This step is essential in formulating appropriate legislation geared toward the monitoring and legal intervention necessary for a given local situation while avoiding inappropriate interventions that result in financial and social losses (Baize and Sterckeman 2001). In Brazil, the National Council for the Environment (CONAMA 2009), in its resolution 420/2009, proposed a list of values that serve as guidelines for monitoring the presence of heavy metals in ecosystems.

Some authors, such as Campos et al. (2005) and the United States Environmental Protection Agency (US-EPA), have classified thirteen metals as primary pollutants: Al, Sb, As, Ba, Cd, Cr, Cu, Pb, Hg, Ni, Se, Ag, and Zn. The heavy metals with greater mobility in soil are As, Ba, Cd, Cr, Pb, Hg, Se, and Ag. The study of these metals is extremely important in predicting environmental risks.

In the small town of Pedra, in the state of Pernambuco, Brazil, no information can be found concerning studies of heavy metals in areas used for agriculture or cattle raising, although many radioecological monitoring studies have been conducted in which uranium ore anomalies have been registered. Because Pedra is the dairy capital of the state of Pernambuco, in order to estimate the toxicity to the local population, it is crucial to compare the concentrations of these metals in the soil to the levels established as safe by Brazilian legislation.

Materials and Methods

The studied area is located in the town of Pedra, situated at an approximate latitude of 08°29.817′S and a longitude of 36°56.450′W, with an altitude of 593 m above sea level, nestled between the Agreste Mesoregion and the Microrregion of the Valle of Ipanema in the state of Pernambuco, in the Ipanema River basin. This site is in the geoenvironmental region of the Borborema Plateau, which is constituted by the lithotypes of the Cabrobó and Belém do São Francisco complexes, the Peraluminous Leucocratic Intrusive Suite, the Indiscriminate Granite Rock Structures, and the Calc-alkaline Suite.

The municipality of Pedra occupies an area of approximately 848.9 km^2 and is accessed by routes BR-232, BR-424, and PE-217. The total resident population of this municipality was estimated to be 20,944 inhabitants, with 11,998 (57.28 %) in the urban zone and 9,080 (43.35 %) in the rural zone.

Soil sample collection was carried out in an area of approximately 2 km^2, in a systematic manner, considering that both agricultural and cattle raising activities take place in the area. Twenty-three soil samples were collected at an average depth of 45 cm (from the C horizon), with an average mass of approximately 3 kg per sample. These samples were placed in plastic bags and sent to the Environmental Monitoring Laboratory of the Department of Nuclear Energy at the Federal University of Pernambuco (UFPE).

In the Environmental Monitoring Laboratory at UFPE, the soil samples were dried in a greenhouse at 60°C, homogenized, quartered, and reduced to a particle size of less than 63 μm. Sub-samples of the soil with standardized masses of 1.5 g were placed in plastic containers and sent to the Neutron Activation Laboratory of the Energy and Nuclear Research Institute of the National Commission on Nuclear Energy in São Paulo for neutron activation and analysis by gamma-ray spectrometry.

In the Neutron Activation Laboratory, approximately 100 mg of each sample was irradiated for 8 h, together with the standard samples "GS-N (ANRT)" and "BE-N (IWG-GIT)", with an average neutron flow of approximately 4.5×10^{12} n cm^{-2} s^{-1}, in the IEA-R1 model research reactor.

The calculation of the cross section, which is a measure of the occurrence of a specific nuclear reaction, was performed by applying Eq. 1, in which $\dot{A}$ is the activation rate, σ is the cross section in m^2, ϕ is the neutron flow in n m^{-2} s^{-1}, and N is the number of nuclei that were targets of the atom.

$$\dot{A} = \sigma \times \phi \times N \quad (1)$$

The neutron flow transmitted through the material and defined by the exponential law was calculated by applying

Eq. 2, in which $\phi(X)$ is the neutron flow that underwent no interaction after crossing the material of thickness X, ϕ_0 is the incident neutron flow onto the material (n/s cm^2), N is the atomic density of the material (cm^{-3}), and $N \times \sigma_T \times (V)$ is the total cross section.

$$\phi(X) = \phi_0 \times e^{-N \times \sigma_T \times (V) \times X} \quad (2)$$

After the samples underwent irradiation, they were analyzed in a high-resolution gamma-ray spectrometer system consisting of a Canberra® HPGe detector with a resolution of 2.0 keV for an energy of 1,332 keV of ^{60}Co and a nominal efficiency of approximately 20 %, attached to a multichannel analyzer with eight thousand channels. The first reading was carried out 7 days after irradiation, and the second was carried out 15 days later. To correct the dead time, the measurements were carried out at a distance of 12 cm from the detector's surface. A Canberra® Genie® 2000 computational program was used to handle and treat the spectra and analyze the data.

The reference background values used to evaluate the results from the present study site were obtained from the resolution 420/2009 from the Brazilian National Council for the Environment (CONAMA 2009).

Results and Discussion

Figure 1 presents the concentrations of As, Zn, Co, Cr, and Ba in the soil of the agricultural area of the town of Pedra. Among the metals studied, the results only indicate anomalies with respect to Ba, the concentration of which varied from 443.0 to 1,497.0 mg kg^{-1}. Comparisons of these results with those listed in the CONAMA table showed that all the soil samples had Ba levels much higher than the limits allowed for an agricultural area, i.e., 1.5–5.0 mg kg^{-1}. Thus, the study region represents an area with abnormally high levels of barium.

The metal As went practically undetected throughout this study, while the concentrations of Zn, Co, and Cr ranged from 17.0 to 110.0, 2.8–38.4, and 12.1–65.5 mg kg^{-1}, respectively. These values were all lower than the prevention values set forth by CONAMA and, to a certain extent, were not considered indicative of risks to the environment and the local population. It is important to note that the empirically determined detection limits are 0.5 mg kg^{-1} for As and Co, 2.8 mg kg^{-1} for Cr, 4.7 mg kg^{-1} for Zn, and 16.8 mg kg^{-1} for Ba.

Among the studied metals, Ba was the only one detected at concentrations that presented toxicological risks to the population. The Ba levels varied from 443.0 to 1,497.0 mg kg^{-1}; with a mean of 863.3 mg kg^{-1} and a coefficient of variation of 28.2 % (Fig. 2). The concentrations of the metals Zn, Co, and Cr had greater coefficients

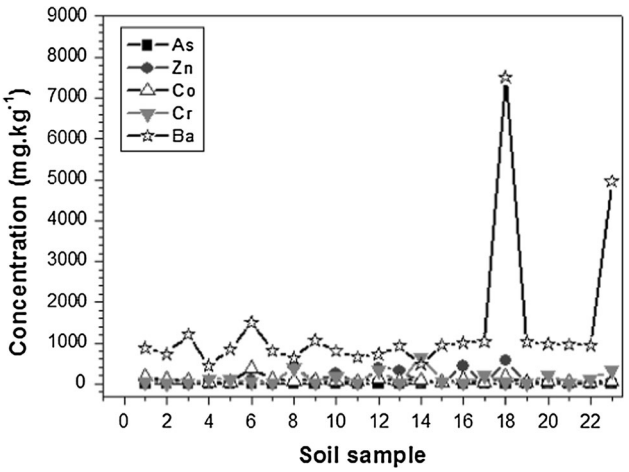

Fig. 1 Levels of heavy metals in the soil of the agricultural area

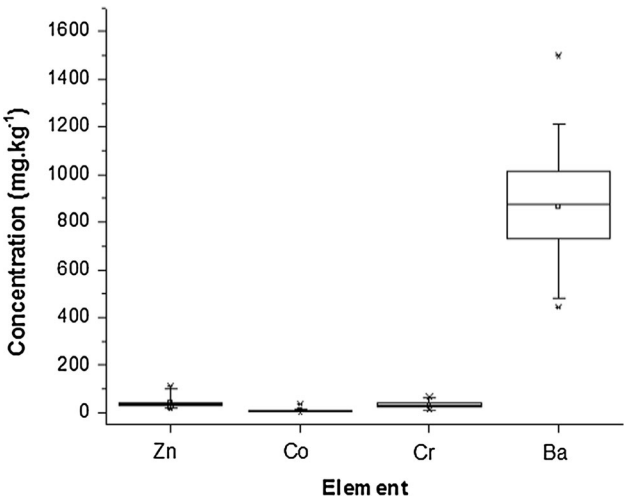

Fig. 2 Diagram box for heavy metals identified in the soil

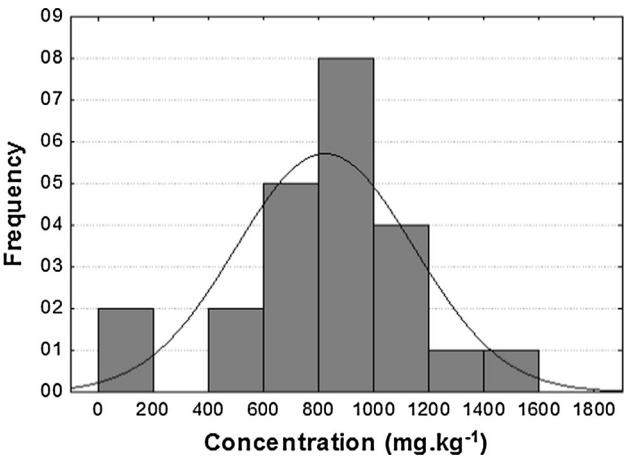

Fig. 3 Frequency diagram for Ba in soil

of variation, with values of 54.1 %, 82.2 %, and 45.5 %, respectively, but these metals were not detected at concentrations that presented toxicological risks.

According to the values shown in the frequency diagram in Fig. 3, the distribution of Ba in the environment produces a coefficient of asymmetry of −0.1, which indicates practically no asymmetry at all but rather a homogeneous distribution for this element within the studied area. A greater frequency was indicated for the class interval, ranging from 800.0 to 1,000.0 mg kg^{-1}, values that are quite atypical for an area without anthropic influence.

Conclusion

Based on the empirically obtained results and considering the reference values established by CONAMA, Ba was concluded to be the only metal considered in this study that was present in the soil samples in concentrations that exceeded the intervention limit. The Ba concentrations observed indicate an environmental risk that justifies research on food matrices, especially those pertaining to milk and dairy products produced in the region.

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