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Pb-210 in Rock and Soils of the Semi-Arid Agreste Region of Pernambuco, Brazil

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Abstract The aim of this research was to determine ^{210}Pb concentrations in rocks and soils of farms located in the municipalities of Pedra and Venturosa. In these farms, rolled blocks of mafic rock with a high percentage of U_3O_8 were found. The concentrations of ^{210}Pb varied from 3.2 to 201 kBq kg^{-1} in rock samples and from 195 to 86,400 Bq kg^{-1} in soil samples. The high levels of radioactivity found in the samples, indicate the need to conduct more detailed studies to evaluate the risk of radionuclide ingestion due to milk consumption by the population in the state of Pernambuco.

Keywords Radioactivity · Forage · Dairy cows

The diet of the dairy cows in the semi-arid Agreste region of the state of Pernambuco derives predominantly from grazing of the native vegetation. Due to the semi-arid climate, during the dry season, the pastures are generally overgrazed, causing mineral deficiencies in the herds (SEBRAE 2002). According to Fries et al. (1982), grazing of degraded pastures may contribute significantly to accidental ingestion of soil by dairy cows.

The accidental ingestion of soil adhered to the plants that are utilized as fodder is the principal pathway of internal radionuclide contamination in dairy cows (Beresford and Howard 1999). ^{210}Pb is one of the descendants of the ^{238}U radioactive series and may be found in soils due to the natural fallout. The ingestion of soil is an important pathway of contamination by ^{210}Pb in animals, also being responsible for the transference of this radionuclide in fodder to the cow's milk (Amaral et al. 1988). This is very important from the point of view of radiological protection, because cow milk is considered as one of the greater sources of radionuclide ingestion by humans, particularly where milk production is based on the ingestion of fresh fodder by dairy cows (Beresford and Howard 1999).

^{210}Pb, a beta emitter, has an affinity for hard tissue, with potential health hazards to humans. Therefore, the study of the transport of this radionuclide through the human food chain, as well as the determination of the parameters involved in it, is of interest for the long-term environmental impact assessment of regions with high levels of ^{210}Pb. In this context, the aim of the present study, developed by the "Empresa Pernambucana de Pesquisa Agropecuária", was to quantify ^{210}Pb concentrations in rock and soil samples from milk producing farms located over the main uranium anomaly in the semi-arid Agreste region of the state of Pernambuco.

Materials and Methods

During November 2007 (dry period), eleven samples of amphibole bearing calcium-silicate rocks were collected together with their respective soils, in two farms of the municipalities of Pedra and Venturosa. The soil samples were collected from the surface around each rock. The ion-exchange resin method was used (Godoy et al. 1998) to determine the ^{210}Pb concentrations in the rock and soils samples. Initially, 500 g of rocks and soils were ground ($\leq$150 μm) and placed to dry at 60°C. The proposed

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method starts with an overnight leaching of 2 g dry rock and soil sample with 100 ml 0.5 M HBr and 1 g hydroxylamine hydrochloride, for a period of 12 h. The solution was filtered and 1 ml of lead carrier (20 mg Pb^{2+} ml^{-1}), that was previously dissolved with nitric acid, was added. After this, the solution was put to percolate into a column that contained ion-exchange resin type BIO-RAD DOWEX 1-X8 50-100 mesh chloride form. During this stage, the ^{210}Pb was retained in the resin and was subsequently eluted with 50 ml of nitric acid (HNO_3) 1 M. The solution obtained was heated until was totally dry. About 50 ml of deionized water was added and the pH corrected with ammonium acetate 40% to reach levels between 4.5 and 5.0. The solution was heated until boiling and then 2 ml of sodium chromate (Na_2CrO_4) 25% were added. The solution was filtered in quantitative paper, covering the precipitate (lead was precipitated as $PbCrO_4$) and then taken to the detector to determine the beta counting. For this, a Canberra Tennelec S5E detector of low background was used, which presented a mean background of 0.27 cpm on the beta plateau and a mean counting efficiency of ^{210}Bi of 20%. The concentration of ^{210}Pb ($C_{Pb\text{-}210}$) in Bq kg^{-1} was determined using the Eq. 1 (Jia and Torri 2007):

$$C_{\mathrm{Pb-210}} = \frac{A_{\mathrm{L}}}{(1 - \mathrm{e}^{-\lambda_{\mathrm{Bi}} t})\eta y w} \quad (1)$$

where A_L, the liquid counting obtained in the detector (cpm); t, the ^{210}Bi ingrowth time (min); λ_{Bi}, the ^{210}Bi decay constant (min^{-1}); η, the detection efficiency for ^{210}Bi (cpm/Bq); y, the chemical yield; w, the sample dry weight (kg).

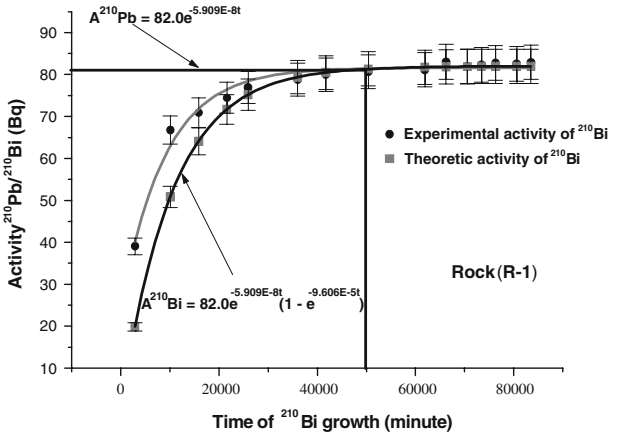

Fig. 1 Time of ^{210}Bi growth in the R-1 after elution

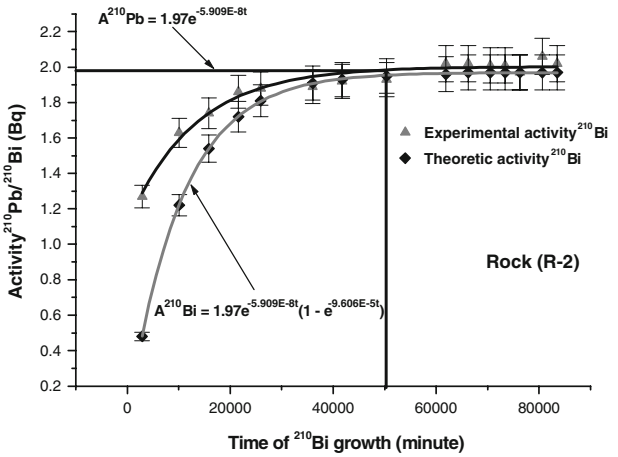

Fig. 2 Time of ^{210}Bi growth in the R-2 after elution

Results and Discussion

The mean chemical yield of the technique used was 92 ± 8%. This result indicates the great adaptability and applicability of the ion exchange resin method in the quantification of the ^{210}Pb in rock and soil samples. However, according to Jia and Torri (2007), the accuracy of the final result is directly affected by the purity of the ^{210}Pb sources. According to these authors, the beta emitter radionuclides of the thorium and uranium natural radioactive series, greatly interfere in the ^{210}Pb quantification in analyses of environmental samples. On the other hand, according to Godoy et al. (1998) and Jia and Torri (2007), the ion-exchange resin method, constitutes a highly efficient procedure for separating the ^{210}Pb from other beta emitters in environmental samples. In the present work, the accuracy of the ion exchange resin method was tested to separate the ^{210}Pb from the samples analyzed. For this, three amphibole bearing calcium-silicate rocks were collected from the anomalous uranium occurrence in the farms studied. After the elution of the samples, the radioactive growth of the ^{210}Bi in the two rock samples was observed. Figures 1 and 2 show the ^{210}Bi growth in the samples after elution.

According to Figs. 1 and 2, it can be observed that the experimental data followed closely the theoretical mathematical model, with the secular equilibrium between the ^{210}Pb and ^{210}Bi being reached in ~35 days (50,000 min after elution of the sample). This equilibrium time was also found by Jia and Torri (2007), when they analyzed the presence of ^{210}Pb in rock and soil samples. Therefore, according to Fig. 1, the interference of the other beta emitters in the quantification of ^{210}Pb for the samples of the present study, can be ignored. Thus, the analysis through ion resin exchange appears to be an excellent method of quantifying ^{210}Pb in rock and soil samples in this case.

Table 1 shows the mean ^{210}Pb concentration values for the rock and soil samples from the farms studied. In order to guarantee anonymity, the farms were classified as F-1 and F-2. These two farms are among the major milk

Table 1 Mean concentration of ^{210}Pb in anomalous uranium rock and soil samples

Farm code	Rock concentration (kBq kg^{-1})	Corresponding soil concentration (Bq kg^{-1})
F-1	201 ± 20 (R-1)[a]	86,400 ± 900
F-1	113 ± 11 (R-2)	30,000 ± 300
F-1	72 ± 7 (R-3)	11,000 ± 1,200
F-1	61 ± 6 (R-4)	1,925 ± 100
F-1	27 ± 3 (R-5)	1,284 ± 125
F-1	24 ± 2 (R-6)	669 ± 70
F-1	10 ± 1 (R-7)	528 ± 54
F-1	7 ± 1 (R-8)	459 ± 43
F-2	4 ± 1 (R-9)	441 ± 45
F-2	3 ± 1 (R-10)	306 ± 33
F-2	3 ± 1 (R-11)	195 ± 21

[a] Code of rock sample

producing farms in the region. In the calculation of the mean concentrations of ^{210}Pb an adopted error of 5% was considered in the radiochemical analysis of triplicate samples (Godoy et al. 1998). The main uranium radioactive anomaly was found in the F-1 farm (Santos et al. 2006b). The R-1 rock sample was collected, specifically, in the center of the uranium anomaly. As can be seen in Table 1, this sample presented the greater ^{210}Pb concentration. The R-2 to R-8 rock samples were colleted, respectively, at distances of 30, 60, 80, 110, 140, 160 and 200 m from the center of the anomalous uranium occurrence. Thus, it can be verified that the ^{210}Pb concentrations in the amphibole bearing calcium-silicate rocks, diminishes as one moves away from the center of the anomaly.

Studies carried out by Santos et al. (Santos et al. 2006b), showed that rocks that were present on the F-2 farm belong to the same outcrop of those existing on the F-1 farm. The R-9, R-10 and R-11 samples were taken, respectively, at distances of 300, 320 and 360 m from the center of the uranium anomaly. In accordance with the LSD (least significant difference) statistic test presented by Vieira (2006), there was no significant difference between the mean concentration values of ^{210}Pb in the amphibole bearing calcium-silicate rocks of the F-2 farm. This suggests that the radionuclide concentrations in the amphibole bearing calcium-silicate rocks of the F-2 farm come from the same source.

Studies on ^{210}Pb concentrations in rock samples are very scarce in literature, specially, for the type of rock analyzed in the present work. As a result of this, it was not possible to carry out detailed comparisons with other studies. However, a study carried by Santos et al. (Santos et al. 2006a) showed that phosphatic rocks used in the production of fertilizers in Brazil present varying concentrations of ^{210}Pb, ranging from 329 to 1,414 Bq kg^{-1}. The value of 1,414 Bq kg^{-1} corresponds to only 50% of the lower value for the rock samples from the current study, as shown in Table 1. In the literature there is a lack of data on levels of ^{210}Pb in soil samples from milk producing farms. Regarding the soil samples, the values presented in Table 1 were very elevated in relation to those found in literature. Amaral et al. (1988) determined ^{210}Pb concentrations varying from 60 to 253 Bq kg^{-1} in soils of milk producing farms in the anomalous region of Poços de Caldas in Minas Gerais, Brazil. In the another study, Pereira and Júnior (2002) found a mean ^{210}Pb concentration of 87 Bq kg^{-1} in soil samples from milk producing farms in the vicinity of the uranium concentration unit in Caetité, Bahia, Brazil. The preliminary results presented in the this study showed the extreme need for a complete study to be carried out to investigate the transference of ^{210}Pb in the rock–soil–plant–milk systems, with the aim of evaluating the risk of radionuclide ingestion due to milk consumption by the human population in the semi-arid Agreste region of the state of Pernambuco.

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