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The use of statistical methods for censored data to evaluate the activity concentration of Pb-210 in beans (*Phaseolus vulgaris* L.)

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ABSTRACT

A survey of ^{210}Pb activity concentration, one of the major internal natural radiation sources to man, has been carried in the most common species of beans (*Phaseolus vulgaris* L.) grown and consumed in Brazil. The representative bean types chosen, Carioca beans and black type sown in the Brazilian Midwestern and Southern regions, have been collected in this study and ^{210}Pb determined by liquid scintillation spectrometry after separation with chromatographic extraction using Sr-resin. Available values in data set of radioactivity in Brazil (GEORAD) on the ^{210}Pb activity concentration in black beans grown in Southeastern region have been added to the results of this study with the purpose of to amplify the population considered. Concerning the multiple detection limits and due to the high level of censored observations, a robust semi-parametric statistical method called regression on order statistics (ROS) has been employed to provide a reference value of the ^{210}Pb in Brazilian beans, which amounted to 41 mBq kg^{-1} fresh wt. The results suggest that the ^{210}Pb activity concentration in carioca beans is lower than in black beans. Also evaluated was the ^{210}Pb activity concentration in vegetable component of a typical diet, which displays lower values than those shown in the literature for food consumed in Europe.

1. Introduction

The study of radionuclide behavior in the environment usually requires analytical determinations in various matrices as foods, soil and water. The tropical regions provide food for large percentage of the world population. The Brazilian Midwest is the second largest producer of food of animal and vegetable origin, commercialized in the global market. Beans are cultivated all the year long, all over Brazil. The highest productivity is obtained in the states of Goiás and Distrito Federal, representing 17% of the total national production of beans (Posse et al., 2010). Among the many bean types cultivated in Brazil, carioca beans are the most produced, sharing 70% of the market. While black beans, the second most produced, are cultivated and consumed mostly in the South of Brazil (states of Rio Grande do Sul, Paraná, Santa Catarina), and Rio de Janeiro, but are also cultivated in other states in smaller amounts. Carioca and black beans stand out among the basic food for the Brazilian population. Previous study have shown the influence of the bean type in the activity concentration of ^{40}K in Brazilian common beans, which was significantly higher in black beans than the carioca beans (Mingote et al., 2013).

The main objective of this study was to carry out a survey of the activity concentration of ^{210}Pb, a naturally occurring radionuclide of radiological interest in common beans (*Phaseolus vulgaris* L.) sown in normal background environments in Brazil and to appraise influence of the bean type in the ^{210}Pb levels. Initially, the activity concentration of ^{210}Pb in samples of beans were obtained from GEORAD (GEORAD, 2013), a database of radioactivity in Brazil. According to the data source, the beans were grown and consumed in the state of Rio de Janeiro where black beans are the most popular type. Insomuch as these data are not representative of the Brazilian production of common beans, both carioca and the black beans samples were collected in farms in the states of Goiás, Paraná and Santa Catarina for ^{210}Pb activity concentration determination.

Activity concentrations of natural radionuclides from the uranium and thorium series in foods are frequently found whose values are lower than the laboratory detection limits and consequently represent a serious problem for the interpretation by the

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data analysts. Statisticans use the term "censored data" for data sets where specific values for some observations are not quantified, but are known to exceed (right-censored data) or to be less than (left-censored data) a threshold value (Helsel, 2012). Methods specifically designed for handling censored data are standard procedures in medical and industrial studies, but they are not usually applied to environmental data analysis. Twenty-eight years ago, Helsel and Cohn (1988) showed that when correctly utilized, less than (left-censored) values frequently contain almost as much information for estimating population moments and quantiles as the same observations within the detection limits. However, the substitution of these values by some fraction of the detection limit persists as the most common procedure employed to deal with censored data in environmental and radiochemistry. Helsel (Helsel, 2006, 2012) emphasizes that substituting values for censored data should rarely be used and generally considered unacceptable in scientific researches. Means, medians, and other statistics should not be substituted by any proxies even though as much as 20% of the data is censored at different reporting limits. The ^{210}Pb activity values in beans obtained in this work showed a high percentage of censored data. Hence, a censored data analysis method was applied in order to evaluate the typical ^{210}Pb activity concentration in Brazilian common beans.

^{210}Pb occurs naturally in the ^{238}U series and was chosen for this study because it is responsible, together its daughter ^{210}Po, for one of the major internal natural radiation doses to man. ^{210}Pb ($T_{1/2} = 22.3$ y) decays by β−emission to ^{210}Bi ($T_{1/2} = 5.0$ d), which again undergoes decay by β−emission to ^{210}Po ($T_{1/2} = 138.4$ d). ^{210}Po decays by α-emission to form the stable lead isotope ^{206}Pb. Variations of the method by using chromatographic extraction with the EiChrom Sr-resin to simultaneously separate lead and polonium have been used to determine ^{210}Pb and ^{210}Po in different environmental and biological materials. The lead has been recovered as PbC_2O_4 or $PbSO_4$ and the ^{210}Pb activity concentration is determined by detection of ^{210}Pb via liquid scintillation spectrometry (Vajda et al., 1997; Taddei and Taddei, 2005; Shakhashiro et al., 2012) or indirectly by the beta activity of its daughter ^{210}Bi measured on a beta proportional counter (Vreček et al., 2004; Bartusková and Bečková, 2006). The present work describes a complete analytical system comprising sample preparation, dissolution and separation of the lead by using chromatographic extraction with the EiChrom Sr-resin, and detection of ^{210}Pb activity in foodstuff by liquid scintillation spectrometry (LSC).

2. Material and methods

2.1. Material

All used reagents were of analytical grade and the working solutions were prepared in deionized water obtained from a Simplicity system from Millipore (Millipore, São Paulo, SP, Brazil). Nitric acid (65%) and hydrochloric acid (37%) were supplied by Quimex (São Paulo, Brazil). Lead carrier (20 mg mL^{-1} Pb) was prepared from $Pb(NO_3)_2$ (Cinética Química, São Paulo, Brazil) in nitric media (0.2% v/v). The yield of the lead radiochemical separation was determined by weight, the lead carrier concentration being previously determined by gravimetric analysis as sulphate (Erdey, 1965). A standard solution of ^{210}Pb supplied by IRD/CNEN (Radioprotection and Dosimetry Institute of National Commission for Nuclear Energy, Rio de Janeiro, Brasil) was used to prepare a working solution with activity concentration of (9.78 ± 0.12) Bq mL^{-1} to determine the calibration settings of liquid scintillation spectrometry measurement in a low-level Quantulus 1220 spectrometer (PerkinElmer, Waltham, MA, USA).

A CEM MARS closed vessel acid digestion system with the MARSXpress option (CEM, Matthews, NC, USA) was used for the decomposition of the samples. Chromatographic columns with 1 cm diameter, filled with 3.0 g of Eichrom Sr-Resin 100–150 μm (Eichrom, Lisle, IL, USA) were used. The columns were prepared, regenerated and repeatedly used, up to 5 times as prescribed by Vajda et al. (1997).

The vegetable species (3–10 kg) of grains (beans, corn, rice), leaves (lettuce, cabbage), roots (manioc, sweet potato), and fruits (tomato) were acquired in local trade at Goiânia, capital of the state of Goiás in the Brazilian Midwestern region. Then carioca and the black bean samples (2 kg) were collected at farm plots cultivated by Embrapa Arroz e Feijão (Embrapa Rice and Beans), a research center of the Brazilian Agricultural Research Corporation near Goiânia. Since this was a pilot study, it was necessary to work with a minimal sample size. Eighteen samples of beans were collected during the years 2010–2011. Most of them were sown in the Midwestern region of Brazil in the state of Goiás (n = 12; 67%), the others were collected from farms in the Southern region, which supplied four samples from the state of Paraná (n = 4; 22%) and two samples of beans from Rio Grande do Sul State (n = 2; 11%). The percent index corresponds to the quantity (n) per total sample collected ($\sum n_i$). The proportion per bean type was similar to the national production of carioca beans (n = 13; 72%) and black beans (n = 5; 28%). The production of beans in the state of Goiás represents 16.9% of national production (Posse et al., 2010).

Regarding the environmental influence on the radionuclide concentration in the grain, the collected samples are as follows: rainfall season (n = 9; 50%), dry season (n = 1; 6%) and winter season (n = 8; 44%). Due to the difficulty in obtaining samples from the dry season, only one black beans sample was collected during this season. Besides, during winter only carioca beans cultivated in the state of Goiás were collected. Several cultivars of carioca beans were considered: BRS Ametista, BRS Estilo, BRS Pontal, Pérola and Requinte. The cultivars of the black beans were BRS Campeiro and BRS Esplendor.

The activity concentration of ^{210}Pb in 17 samples of beans were obtained from GEORAD (GEORAD, 2013), a radioactivity database in Brazil. Only beans grown in areas of "normal" natural background were considered. According to the data source (years 2002–2004), the beans were grown and consumed in the Southeastern region of Brazil, in the state of Rio de Janeiro, where black beans are the most popular type. It is known that the ^{210}Pb activity concentration was indirectly determined through its daughter product ^{210}Bi about two weeks after the separation as lead chromate or lead sulphate by using proportional counters. The method of ^{210}Pb measurement was different those use in this study, therefore multiple detection limits has been obtained to the statistical analysis.

2.2. Food sample preparation for radiochemical analysis

After identifying the samples in the laboratory, they were washed in tap and distilled water, dried at room temperature and then weighed for fresh weight determination. The samples were washed and peeled, when necessary. Subsequently, they were dried in an oven at 80 °C for approximately 24 h. The ashing step is recommended to concentrate the element of interest to determine low concentration values. Therefore, after the determination of the dry mass, the samples were ashed at 450 °C for 48 h (IAEA-TRS-295, 1989), the temperature was gradually increased at the rate 50 °C per hour. The samples were again weighed for the determination of ash weight.

The dissolution and/or digestion of samples is an important step in the radiochemical analysis. The total decomposition of samples is recommended for the natural radionuclides determination since trace concentrations may remain in crystal structure of non-