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Anthropogenic and naturally occurring radionuclide content in near surface air in Cáceres (Spain)

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ABSTRACT

The anthropogenic (^{137}Cs, ^{90}Sr, $^{239+240}$Pu and ^{241}Am) and naturally occurring radionuclide (^{40}K, ^{234,238}U, ^{228,230,232}Th, ^{226}Ra and ^{210}Pb) content in near surface air present seasonal variations related to natural processes, such as soil erosion, resuspension of fine particles of soil and radon exhalation from soil (^{210}Pb). The objective is to analyze seasonal variations of their concentrations and compare with radiological events (Fukushima fallout and wild fire) in a location without any known source of anthropogenic radionuclides. The ^{210}Pb, ^{40}K, and ^{137}Cs presented annual variations, with maximum activity levels in summer. Solar radiation and rainfall were correlated with ^{210}Pb and ^{40}K. The ^{234,238}U, ^{228,230,232}Th, ^{226}Ra, ^{137}Cs and ^{90}Sr presented positive correlation with monthly mean values of temperature. The ratio ^{90}Sr/^{137}Cs was within the range of those reported for soils in Spain. Finally, the maximal effective dose rate was estimated to be 37 and 88 μSv/y for infants and adults, respectively, well below 1 mSv/y reference level. The main contributor to effective dose was ^{210}Pb, about 92%, followed by:
^{210}Pb ≫ ^{228,230,232}Th > ^{226}Ra, ^{234,238}U > ^{7}Be, $^{239+240}$Pu > ^{40}K, ^{90}Sr > ^{137}Cs > ^{22}Na

1. Introduction

Radionuclide content in aerosol particles can pose a health hazard following an accident involving nuclear material. After an accident, short-lived radionuclides, such as radioiodine, and other long-lived ones, such as radiocaesium can be detected in the vicinities of the accident (Lebel et al., 2016), and even in far off locations (Ferrero et al., 1987; Baeza et al., 2012). However, the occurrence of anthropogenic radionuclides in aerosols is also due to erosion and resuspension processes, as well as the emission and transport of particulate matter due to biomass burning as consequence of wild fires (Paatero et al., 2009; Strode et al., 2012; Evangeliou et al., 2014), and dust transport due to storms (Hernández et al., 2005). Due to these processes, the anthropogenic radionuclide concentration in near surface atmosphere is variable. Naturally occurring radionuclides are also present in airborne particles as they are also present in soil particles able to be eroded, resuspended or transported by the processes previously described, and also due to the radon exhalation from soil, which is especially significant to ^{210}Pb and ^{210}Po. The dust generated in the manipulation of NORM materials can be another pathway to increase naturally occurring radionuclide content in aerosol particles, although in some cases its contribution to the effective dose was assessed to be negligible, such as the use of phosphogypsum as soil amendment (Abril et al., 2009). The knowledge of the seasonal variation of anthropogenic and naturally occurring radonuclide content is of great importance as it lays the background level in order to have an early warning of the radiological impact on members of the public if any major fire or dust event occurs, or to assess occupational exposures.

The main goal of this work is to determine seasonal variations of anthropogenic (^{137}Cs, ^{90}Sr, $^{239+240}$Pu and ^{241}Am) and naturally occurring radionuclide (^{40}K, ^{234,238}U, ^{228,230,232}Th, ^{226}Ra and ^{210}Pb) content in near surface air in order to analyze its influence in the case of a radiological event, as Fukushima fallout, which was first reported in Spain in this location (Baeza et al., 2012) or the effect of ashes from wild fires. Surrounding the selected location, there are no known sources of anthropogenic radionuclides other than global fallout. Regarding the ^{210}Pb, ^{40}K and ^{137}Cs a period from September 2004 until march 2011, previous to Fukushima accident, was analyzed. In the case of α- and/or β-emitters, a period of one year was selected to assess their annual variation and isotope ratio. The

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range of variation due to seasonal variability was compared with the increase due to two events detected in the same location: Fukushima and wild fires. Finally, the effective dose by inhalation for members of the public in normal conditions (no radiological event) was estimated and compared to international reference levels.

2. Material and methods

2.1. Sample collection

Samples were collected using a high-efficiency aerosol sampling station ASS-500C in the LARUEX facilities in Cáceres (Spain), 39° 30′ 20″ N, 6° 20′ 22″ W. It is located west of Spain and about 90 km from the Portuguese border The sampling station was located on an open area (an unused car park) surrounded by a meadow at only one side, and paved areas at the other sides. There is no known source of anthropogenic radionuclides in the surroundings as the nearest nuclear power plant (Almaraz NPP) is located more than 90 km away, and there is no industry involving nuclear material in the surroundings. This sampling point was the first to detect and report aerosol Fukushima particles in Spain (Baeza et al., 2012).

Aerosol samples were collected on 440 × 440 mm Petrianov FPP15–1.5 air filters, able to retain 95.600–99.998% of aerosols with diameter in the range 0.30–1.25 μm. Filters were weekly changed, compressed into a disk and measured by γ-spectrometry. The volume of air was within the range 51,708–151,5022 m^3 per week in the period september 2004 to march 2011. Monthly composite samples were prepared by ashing week filters together at 400 °C in order to remove organic matter previously to radiochemical determinations for U, Th, Ra and ^{90}Sr. These composite samples were considered in order to have enough volume of aerosol for isotope ratios to be calculated from the same sample. Due this considerations, only one year was analyzed. In the case of $^{239+240}Pu$ and ^{241}Am, as their concentration was very low, only three samples were analyzed in order to obtain the order of magnitude.

2.2. Radionuclide determination by γ-spectrometry

One week after collection, samples were compressed into a disk and measured by γ-spectrometry. These analyses were carried out using a germanium N-type detector with a 25% relative efficiency, a 1.87 keV resolution for the 1332 keV ^{60}Co peak, and a peak-to-Compton ratio of 57.5:1. The detector was calibrated using certified multi-gamma cocktail and ^{210}Pb purchased to National Physics Laboratory (NPL, UK), using the same compressed disk geometry. The minimum detectable activities were determined according to Currie methodology. The activity levels for ^{137}Cs, ^{210}Pb, and ^{40}K were systematically analyzed in all samples. The overall quality control of the measurements was guaranteed by the accreditation of the laboratory to carry out radioactivity assays in environmental samples according to UNE-EN ISO/IEC 17,025 (ISO, 2005). Different reference materials were also used to check the quality of the γ-spectrometry measurements: IAEA-385 and Soil 6.

2.3. Radionuclide determination of α- and β-emitters

Prior to the radiochemical separation, aliquots equivalent to 10,000 m^3 (180,000 m^3 for ^{90}Sr) of monthly aerosol samples was acid digested (HNO_3, HCl, HF, 9:3:6 mL) in a microwave digestor at 180 °C for 35 min.

The procedure followed for the strontium extraction in aerosol samples was based in its separation by means of ion exchange columns (Gascó and Álvarez, 1998; HASL, 1976). Strontium was precipitated as $SrCO_3$, and recovery was determined by gravimetry. Once ^{90}Sr–^{90}Y equilibrium was reached, the sample was measured in a low background gas flow proportional counter.

Radiochemical separation of uranium and thorium in aerosol samples was carried out using ionic exchange resins (Dowex 1 × 4 and 1 × 8) and was described in Guillén et al. (2014). The plutonium and americium radiochemical procedure used was based on those proposed by other workers (Holm and Ballestra, 1989; LaRosa et al., 1992; Mietelski et al., 2002) using also ionic exchange resins (Dowex 1 × 4), additional thorium purification of the americium fraction and separation of Am from rare earths elements was done on the Dowex 1 × 8 resin from acid-methanol solutions (Mietelski and Wąs, 1997). Uranium, thorium, plutonium and americium alpha sources were prepared by co-precipitation with NdF_3 (Sill, 1987).

Radium content in the samples was absorbed in MnO_2 precipitate, and the radiochemical procedure described in Baeza et al. (1998) was followed. The recovery was determined by γ-spectrometry of the tracer, ^{133}Ba (302.85 and 356.01 keV), using the germanium N-type detector described in the previous section.

The alpha spectrometric analysis were carried out using silicon detectors with a mean value of efficiency of 23.2% and a resolution of 38.7 keV for a source-detector distance of 6 mm. Reference material, Soil-6 from IAEA, was also used to guarantee the accuracy of the measurements.

3. Results and discussion

3.1. Naturally occurring radionuclides content in near surface air

The ^{210}Pb presented activity levels above detection limit in 93.8% of the 338 weekly air filters analyzed. The mean value was $(0.69 \pm 0.34\ (S.D.)) \cdot 10^{-3}$ Bq/m^3, within the range $(0.12–1.82) \cdot 10^{-3}$ Bq/m^3, which were similar to those reported in the literature for different countries, including sampling points from Portugal and Spain (see Table 1). The occurrence of ^{210}Pb in near surface air can partly be due to soil particle resuspension and radon exhalation from soil. However, the ^{210}Pb content was lower than that of outdoor radon reported in Spain, (0.6–9) Bq/m^3 (Arnold et al., 2009). This may be due to the ^{210}Pb deposition on top soil. Fig. 1a shows the seasonal variation detected for ^{210}Pb during the period september 2004 to march 2011. It presented annual variation, which was confirmed by the corresponding periodogram (see Fig. 1b) with a maximum frequency of 0.019 $week^{-1}$, corresponding to 52 weeks. Mean values for summer and autumn were slightly higher than for spring and winter (see Table 2).

The ^{40}K was detected in 71.0% of the analyzed samples, and its content was lower than that of ^{210}Pb. The mean value was $(3.3 \pm 1.8\ (S.D.)) \cdot 10^{-5}$ Bq/m^3, within the range $(0.02–9.7) \cdot 10^{-5}$ Bq/m^3. The occurrence of ^{40}K can mainly be attributed to resuspension of soil particles. As climate conditions can influence resuspension processes, the range of variation was slightly higher than that reported for Poland, located in a more temperate climate (Grabowska et al., 2003). Fig. 2a shows the seasonal variation of ^{40}K, with an annual period from the corresponding periodogram (see Fig. 2b). Slightly higher mean value was observed in summer and slightly lower in winter, although not statistically significant taking into account the associated uncertainties (see Table 2).

As the ^{210}Pb and ^{40}K aerosol concentrations showed annual variations, metheorological variables can effect it. Fig. 3 shows the seasonal variation of these variables in Cáceres (AEMET, 2014), with a Mediterranean climate (Csa in Köppen climate classification). It can be seen that they also presented an annual variation. Radiation and temperature are expected to be closely related, being the latter a reflection of the former. As air filters were collected weekly, the