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Assessment of the vertical distribution of natural radionuclides in a mineralized uranium area in south-west Spain

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HIGHLIGHTS

- The Enrichment Factor provides information about the external input of radionuclides.
- Natural radionuclides show a low degree of migration at depth.
- The profiles are similar for the long-lived radionuclides of the ^{238}U series.
- The highest mobility corresponds to U, Th being the least mobile.

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ABSTRACT

Low-level alpha spectrometry techniques using semiconductor detectors (PIPS) and liquid scintillation (LKB Quantulus 1220™) were used to determine the activity concentration of ^{238}U, ^{234}U, ^{230}Th, ^{226}Ra, ^{232}Th, and ^{210}Pb in soil samples. The soils were collected from an old disused uranium mine located in southwest Spain. The soils were sampled from areas with different levels of influence from the installation and hence had different levels of contamination. The vertical profiles of the soils (down to 40 cm depth) were studied in order to evaluate the vertical distribution of the natural radionuclides. To determine the origin of these natural radionuclides the Enrichment Factor was used. Also, study of the activity ratios between radionuclides belonging to the same radioactive series allowed us to assess the different types of behaviors of the radionuclides involved. The vertical profiles for the radionuclide members of the ^{238}U series were different at each sampling point, depending on the level of influence of the installation. However, the profiles of each point were similar for the long-lived radionuclides of the ^{238}U series (^{238}U, ^{234}U, ^{230}Th, and ^{226}Ra). Moreover, a major imbalance was observed between ^{210}Pb and ^{226}Ra in the surface layer, due to ^{222}Rn exhalation and the subsequent surface deposition of ^{210}Pb.

1. Introduction

Certain areas of the world have relatively high-activity concentrations of naturally occurring terrestrial radionuclides (UNSCEAR, 2000), but natural radionuclides are also present in many natural resources where human activities can produce an enhancement either of their activity concentration or of their availability. An example is uranium mining and milling. In this case, human activities increase the presence of natural radionuclides belonging to natural series. Following this, the possible mobilization of these radionuclides may enhance the risk of exposure of humans and livings beings.

Studies addressing the behavior of natural radionuclides in the environment (distribution pathways, mobility, transfers, etc.) are of interest because the information can be used to develop and test models, and to obtain the associated parameter values appropriate for environmental radiological risk assessments (Thiessen et al., 1999). For the radionuclides present in terrestrial ecosystems, information about their migration in soils is crucial, since this process controls their long-term behavior in the environment, their uptake by flora and fauna (including human food chains), and also their potential as groundwater contaminants (Kirchner et al., 2009). On the one hand, the vertical migration of radionuclides from the surface can elicit a reduction in the gamma dose received by the inhabitants directly but, on the other hand, it may lead to groundwater contamination. The vertical migration of radionuclides also affects transfer from the soil to plants, depending on the reticular disposition of the plants, although plants themselves can play an important role in vertical radionuclide re-mobilization (Vera Tomé et al., 2009).

In addition to the interest in the study of natural radionuclides as being responsible for approximately 85% of the annual total radiation dose received by humans (Belivermis et al., 2010), the

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relatively high concentrations found in specific areas of unaltered scenarios would allow the validity of environmental radiological risk assessment models to be checked. In this sense, the scenario of an old uranium mine could offer a suitable laboratory in which the background levels of radionuclides are sufficiently high for analytical purposes. Additionally, some surrounding areas have received an input of radionuclides from the installation due to human activities; this permits study of the environmental migration of the radionuclides in very reduced areas.

In recent years, many authors have studied the behavior of natural radionuclides in surface soils (Tagami and Uchida, 2009; Oyedele et al., 2010; Štrok and Smodiš, 2010; Song et al., 2012). In contrast, studies about the vertical migration of natural radionuclides in soils are quite scarce (Belivermis et al., 2010; Nenadović et al., 2012; Charro et al., 2013).

In this work, the study area was close to an old uranium mine that had been in disuse since 1974. In this area, characterized by a Mediterranean ecosystem, the typical granitic soils present high activity concentrations of the natural radionuclides belonging to the uranium series. Previous studies performed in this area revealed a clear influence of the installation on the surrounding surface soils as well as on other environmental compartments such as surface water or sediments (Lozano et al., 2002; Vera Tomé et al., 2002).

From a surface input coming from the installation, radionuclides can percolate downward from the point itself, but longitudinally, layer by layer, also receiving new supplies and at the same time losing radionuclides. The migration and distribution of radionuclides in the environment are determined by their chemical properties, half-lives, the physicochemical properties of the environment, the peculiarities of the sources and the environmental pathways of the radionuclides (Akyil et al., 2008). In this work we report a study of the vertical distribution in soils of the natural radionuclides ^{232}Th, ^{238}U, ^{234}U, ^{226}Ra, ^{230}Th and ^{210}Pb in an old disused uranium mine.

The concentration of stable elements can help to determine whether the origin of the observed radionuclide activities is due to local alterations of the mother rock or whether external sources would have been involved in radionuclide activities. For this, the Enrichment Factor (*EF*) was used. In assessments of the origin of contaminants in the environment, the *EF* has been used widely (Reinman and De Caritat, 2000; Hee-Lee and Koo-Lee, 2004; Han et al., 2011). To calculate the *EF* for a given element, the measured concentration of that element in the sampling medium investigated is divided by the concentration of the same element in the mother rock. Both concentrations are previously normalized to a "conservative element". "conservative" or "reference" elements are those for which the concentration in the sample medium is influenced almost exclusively by crustal sources. In this work, the *EF* was used only as an index of enrichment, in such a way that only high *EF* values can be considered significant.

Once the possible external input of radionuclides into a given point has been identified with the *EF*, and assuming a pattern of mobility for the radionuclides studied in this area, from a study of the activity ratios of the radionuclides belonging to the same series it is possible to compare the different types of behavior shown by them.

2. Materials and methods

2.1. Sampling area and soil characterization

Soil sampling was carried out at the "Los Ratones" mine, located in the Region of Extremadura in the south-west of Spain (39°15′N, 6°13′W). This installation (see Fig. SM1 in Supplementary Material), with an area of 2.3 km^2, was in production from 1960 to 1974 (Pérez-Estaún et al., 2002), after which it was inactive for several years before restoration work was finally performed (1998–1999). Previous studies carried out in this zone (Vera Tomé et al., 2002) allowed us to characterize the area close to the installation radiologically, and one affected zone was clearly related to the direction of the runoff water from the mine. Further details about the characteristics of this mine as well as other studies of interest performed in this area are given elsewhere (Lozano et al., 2002; Blanco Rodríguez et al., 2008; Blanco et al., 2010).

Four sampling sites were chosen along a thalweg, taking into account the moisture gradient (see Fig. SM1 in Supplementary Material). The topography of the terrain indicates that surface waters and drainage from the slag heaps and rock pile flow towards the Maderos brook along the different courses shown in the figure. Accordingly, the first sampling point (P1) was located on the highest area (close to the main well), and the last one (P4) on the lowest area (next to the Maderos brook). Soil sampling was performed with an EIJKELKAMP split-tube sampler. This sampler reached 40 cm in depth. Once sampled, the 40 cm soil core was frozen and four subsamples of 10 cm each were extracted. At the laboratory, the samples were oven-dried at 80 °C until constant weight. Once the material had been milled and homogenized, representative aliquots were carefully selected from the original bulk soil sample (Riddle, 1993) for radiochemical assays and others for the determination of the concentrations of stable elements and other parameters, such as the LOI (Loss of Ignition), pH, and texture. The results of these analyses are shown in Table SM1 of Supplementary Material.

Major element analyses were carried out with ICP-OES (Yobin-Ivon Mod. Ultima II). Sample digestion prior to the analysis of major elements was performed with a microwave oven (Millestone Mod. ETHOS Plus Microwave Labstation), using the standard USEPA Method 3052, validated for siliceous and organic-based matrices. This uses a combination of HF and HNO_3 (1:3 mL), and temperatures of 180 °C over 20 min.

For textural analyses, the respective homogenized aliquot was classified by mechanical sieving and using Robinsońs pipette method (Pansu and Gautheyron, 2006) in three categories: coarse sand, fine sand, and silt and clay.

2.2. Radiochemical methods and measurement techniques

Sample treatment prior to the radiochemical assays was performed by acid digestion under pressure in a microwave oven (Millestone Mod. Ethos 900). A first attack was performed using HF and HNO_3 (3:6 mL) as reagents (Kingston and Haswell, 1997). After digestion, 2 mL of $HClO_4$ were added to the solution, which was then evaporated to fuming point in order to eliminate the excess fluoride and thus avoid the formation of the highly stable and insoluble thorium fluoride. Two further attacks were then performed using 8 mL of *aqua regia* in order to completely digest undissolved particles (Lozano et al., 2001).

The activity concentrations of the uranium, thorium, and radium isotopes in the different soil fractions were determined by alpha-spectrometry with PIPS semiconductor detectors of 450 mm^2 active area, housed in NIM spectrometers (Canberra, Mod. 7401VR), coupled to low-noise preamplifiers, amplifiers, and a multichannel analyser. For the uranium and thorium isotopes, chemical separation was obtained using tri-n-butyl phosphate (TBP) liquid–liquid extraction, and further thorium purification through an anionic exchange resin (Jiang et al., 1986). Electrodeposition was used to prepare the high-resolution alpha sources (Hallstadius, 1984; Vera Tomé et al., 1994). The method used for the determination of radium was based on chemical purification by the precipitation of $PbSO_4/BaSO_4$, and subsequent source