Environmental Pollution 236 (2018) 1–11

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Concentration of uranium in the soils of the west of Spain☆

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ARTICLE INFO

Article history:
Received 7 October 2017
Received in revised form
3 December 2017
Accepted 15 January 2018

Keywords:
Uranium pollution
Background level
Geochemical baseline
Pollution rates
Spatial distribution

ABSTRACT

While determining the uranium concentration in the rock (background level) and soils on the Iberian Massif of western Spain, several geochemical anomalies were observed. The uranium concentration was much higher than the geochemical levels at these locations, and several uranium minerals were detected. The proposed uranium background levels for natural soils in the west of Salamanca Province (Spain) are 29.8 mg kg^{-1} in granitic rock and 71.2 mg kg^{-1} in slate. However, the soil near the tailings of abandoned mines exhibited much higher concentrations, between 207.2 and 542.4 mg kg^{-1}.

The calculation of different pollution indexes (Pollution Factor and Geo-accumulation Index), which reveal the conditions in the superficial horizons of the natural soils, indicated that a good percentage of the studied samples (16.7–56.5%) are moderately contaminated. The spatial distribution of the uranium content in natural soils was analysed by applying the inverse distance weighted method.

The distribution of uranium through the horizons of the soils shows a tendency to accumulate in the horizons with the highest clay content. The leaching of uranium from the upper horizons and accumulation in the lower horizons of the soil could be considered a process for natural attenuation of the surface impacts of this radiogenic element in the environment. Environmental restoration is proposed in the areas close to the abandoned mining facilities of this region, given the high concentration of uranium. First, all the tailings and other mining waste would be covered with a layer of impermeable material to prevent leaching by runoff. Then, a layer of topsoil with organic amendments would be added, followed by revegetation with herbaceous plants to prevent surface erosion.

1. Introduction

Uranium and its disintegration products are radionuclides that pose a potential risk to human health due to the emission of ionizing radiation, as well as to its toxicity as a heavy metal. Almost all the uranium found in nature is the ^{238}U isotope. It undergoes radioactive decay through a long series of 13 different radionuclides before finally reaching its ultimately stable form: ^{206}Pb. The intermediate radionuclides emit alpha or beta radiation and some also emit gamma radiation, although of very different energies (Todorov and Ilieva, 2006; Sánchez-González et al., 2014).

Radionuclide contamination is associated with human activities such as atomic testing, uranium and phosphate mining, phosphate fertilizer application, and all aspects of the nuclear fuel cycle (Mortvedt, 1994; Elles and Lee, 2002; Smedley et al., 2006). Most natural radionuclides exist in rocks and soils in concentrations that should not be of concern for human health or the environment (Elles and Lee, 2002). However, there are areas with relatively high concentrations of uranium due to geological conditions that might pose some risk to human health and ecosystems (Barnett et al., 2000). At contaminated sites, uranium can enter the food chain

☆ This paper has been recommended for acceptance by Prof. W. Wen-Xiong.
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https://doi.org/10.1016/j.envpol.2018.01.038
0269-7491/

through soil-animal-plant interactions, surface water, and groundwater (Neiva et al., 2016). Most of the radionuclides released into the environment eventually accumulate in the upper horizons of the soils. Consequently, these could pose a risk to ecosystems, agricultural systems, and human health (Gravilescu et al., 2009).

Soil risk assessment, using trace elements and radionuclides, is a key process in environmental assessment and subsequent management, and thus entails prediction of site-specific background levels (Reimann and Garrett, 2005). To assess whether a soil has a high concentration or is truly contaminated with a certain toxic element, it is essential to know its natural condition. This makes it necessary to sample the soil in areas where there is natural vegetation, and where there is evidence that the area has not been affected by human activity. In this way, it is possible to establish the distribution of toxic elements and to determine those places where we know with certainty there is no contamination. Sampling such places allows us to determine in a reliable way, the natural background level for an element. It is important to sample all the soil units that have developed on the different types of rock in the target territory. For this reason, the choice of sampling points for soil profiles must be based on lithological criteria. This is because 'uncontaminated' natural soils containing radionuclides are derived directly from the parent rock.

The fundamental qualities of soils derive from the mineralogical composition of the parent rock and the weathering processes by which the soils were formed. Consequently, the trace elements present in soils and their concentrations are extremely variable. This makes it inappropriate to adopt the normative values presented in environmental legislation of other countries or regions. This means that soil-related legislation must be based upon valid local or regional data (Santos Francés et al., 2017a).

The quantification of radionuclide background levels is necessary to assess potential environmental risk, to determine the boundaries of a contaminated area, and to determine the level of remediation required (Elles and Lee, 2002). The content and distribution of radionuclides in rock, soil, and surface waters, as well as their effect on the environment, have received increased attention in recent years, but the data available on natural soils is still scarce (Morton et al., 2001; Jerden et al., 2003; Aubert et al., 2004).

The average concentration of uranium in the earth's crust is 2.7 or 1.7 mg kg^{-1}, according to the work of Taylor (1996) and Wedepohl (1995), respectively. The average uranium concentration in ultrabasic rock is 0.001 mg kg^{-1}, in basic rock is 1 mg kg^{-1} and in granitic rock is 3 mg kg^{-1}. In sedimentary rock, the concentrations depend on the redox conditions prevailing during their formation, with the highest content (6–1000 mg kg^{-1}) being in rock with organic facies sedimented in anoxic media, according to the geochemical database for Europe (Forum of European Geological Surveys: FOREGS), and in phosphate sediments (50–300 mg kg^{-1}). Clay minerals have a mean content of 3.7 mg kg^{-1}, sandstone 0.45 mg kg^{-1}, and carbonate rock 2.2 mg kg^{-1} (Turekian and Wedepohl, 1961).

The mean U-content in soils is 0.79–11 mg kg^{-1} (Kabata-Pendias and Pendias, 2001) and in river sediments and streams is ~3 mg kg^{-1}. The average content of U in river sediments and soils in Europe are 2.2 and 2.03 mg kg^{-1}, respectively, according to the geochemical database for Europe. The concentrations of uranium in the granitic rocks of NW Spain vary between 5.3 and 27.7 mg kg^{-1}, and the concentrations in the soils developed from the same rocks are similar (4.8–29.2 mg kg^{-1}) (Taboada et al., 2006). High concentrations of uranium are also found in the Viseu and Guarda Departments in Portugal (Carvalho et al., 2007).

The granitic rocks and slates of western Salamanca Province belong to the Iberian Massif. This constitutes an extensive outcropping of the European Hercynian Chain, which occupies the entire western Iberian Peninsula. These rocks have the highest natural concentrations of uranium in all of Spain, which makes this region ideal for the study of their concentration and distribution in soils. In the west of Spain (mainly in the provinces of Cáceres and Salamanca), abandoned uranium mining sites are common. These were exploited from the 1960s to the 1990s. Therefore, the present study can be considered the documentation of a baseline from which to establish criteria needed to evaluate the degree of uranium contamination in the soils of western Spain.

The calculation of the background uranium level and a geochemical baseline is necessary to assess adequately the degree of contamination of soils that might have been affected by previous or existing mining activities in western Salamanca Province. There are no studies on the spatial distribution of uranium in the soils of this region, leaving this totally unknown. For all these reasons, the soil profiles developed for granitic rock and slate in the region, were analysed with the following objectives: 1) to establish background levels and a geochemical baseline for uranium in the soils developed from the granitic rock and slate of this region of western Spain; 2) to compare the values obtained here, with those in the crust and soils worldwide; 3) to calculate the presence of possible diffuse uranium contamination in the surface horizons of natural soils located in areas far from mining deposits using pollution indices; 4) to analyse the correlation between the total content of U and various soil properties (e.g. pH, clay percentage, and cation exchange capacity); 5) to determine the spatial distribution of uranium in the natural soils of this region; and 6) to estimate the vertical distribution of uranium along the different horizons of the soils (from the surface down to the parent rock).

2. Materials and methods

2.1. Study area

The study area is located in the regions of Ciudad Rodrigo and Vitigudino, which constitute a territory of large extent in western Salamanca Province, in the central-west of peninsular Spain (Fig. 1).

These regions are located 700–800 m above sea level, and have annual precipitation of 500–600 mm, an average temperature of ~12 °C and annual evapotranspiration of 700–800 mm. The climate is sub-humid, temperate, and dry in the summer. The moisture and temperature regime of the soils is xeric and mesic, respectively. The climatophilic vegetation of this area corresponds to supra-Mediterranean silicic oak, as defined by the association *Genisto hystricis–Quercetum rotundifoliae*, which rarely appears in the form of dense forest, but normally occurs in the form of meadows.

2.2. Geological context

The area studied belongs geologically to the Iberian Central-Iberian zone, according to the zoning proposed by several authors (Julivert et al., 1973), considering the different stratigraphic and structural characteristics of the said Massif. The Central-Iberian zone is characterised by the predominance of granitic materials and the considerable extension of the Pre-Ordovician Series. Also present in this area, are Paleogene and Neogene sediments belonging to one of the most important Cenozoic basins of the Iberian Peninsula, the Duero Basin, which includes the Ciudad Rodrigo Trench (Fig. 1).

The geological materials that appear more extensively and that, in addition, are intimately related to the soils studied in this work, are as follows.

The Precambrian-Cambrian is represented by the Greywacke Schist Complex. This lithological unit is constituted of meta-sediments of superior Precambrian age, although the superior