



## Concentration of uranium in the soils of the west of Spain<sup>☆</sup>

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### 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<sup>-1</sup> in granitic rock and 71.2 mg kg<sup>-1</sup> in slate. However, the soil near the tailings of abandoned mines exhibited much higher concentrations, between 207.2 and 542.4 mg kg<sup>-1</sup>.

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.

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### 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 <sup>238</sup>U isotope. It undergoes radioactive decay through a long series of 13 different radionuclides

before finally reaching its ultimately stable form: <sup>206</sup>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

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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<sup>-1</sup>, according to the work of Taylor (1996) and Wedepohl (1995), respectively. The average uranium concentration in ultrabasic rock is 0.001 mg kg<sup>-1</sup>, in basic rock is 1 mg kg<sup>-1</sup> and in granitic rock is 3 mg kg<sup>-1</sup>. In sedimentary rock, the concentrations depend on the redox conditions prevailing during their formation, with the highest content (6–1000 mg kg<sup>-1</sup>) 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<sup>-1</sup>). Clay minerals have a mean content of 3.7 mg kg<sup>-1</sup>, sandstone 0.45 mg kg<sup>-1</sup>, and carbonate rock 2.2 mg kg<sup>-1</sup> (Turekian and Wedepohl, 1961).

The mean U-content in soils is 0.79–11 mg kg<sup>-1</sup> (Kabata-Pendias and Pendias, 2001) and in river sediments and streams is ~3 mg kg<sup>-1</sup>. The average content of U in river sediments and soils in Europe are 2.2 and 2.03 mg kg<sup>-1</sup>, 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<sup>-1</sup>, and the concentrations in the soils developed from the same rocks are similar (4.8–29.2 mg kg<sup>-1</sup>) (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).

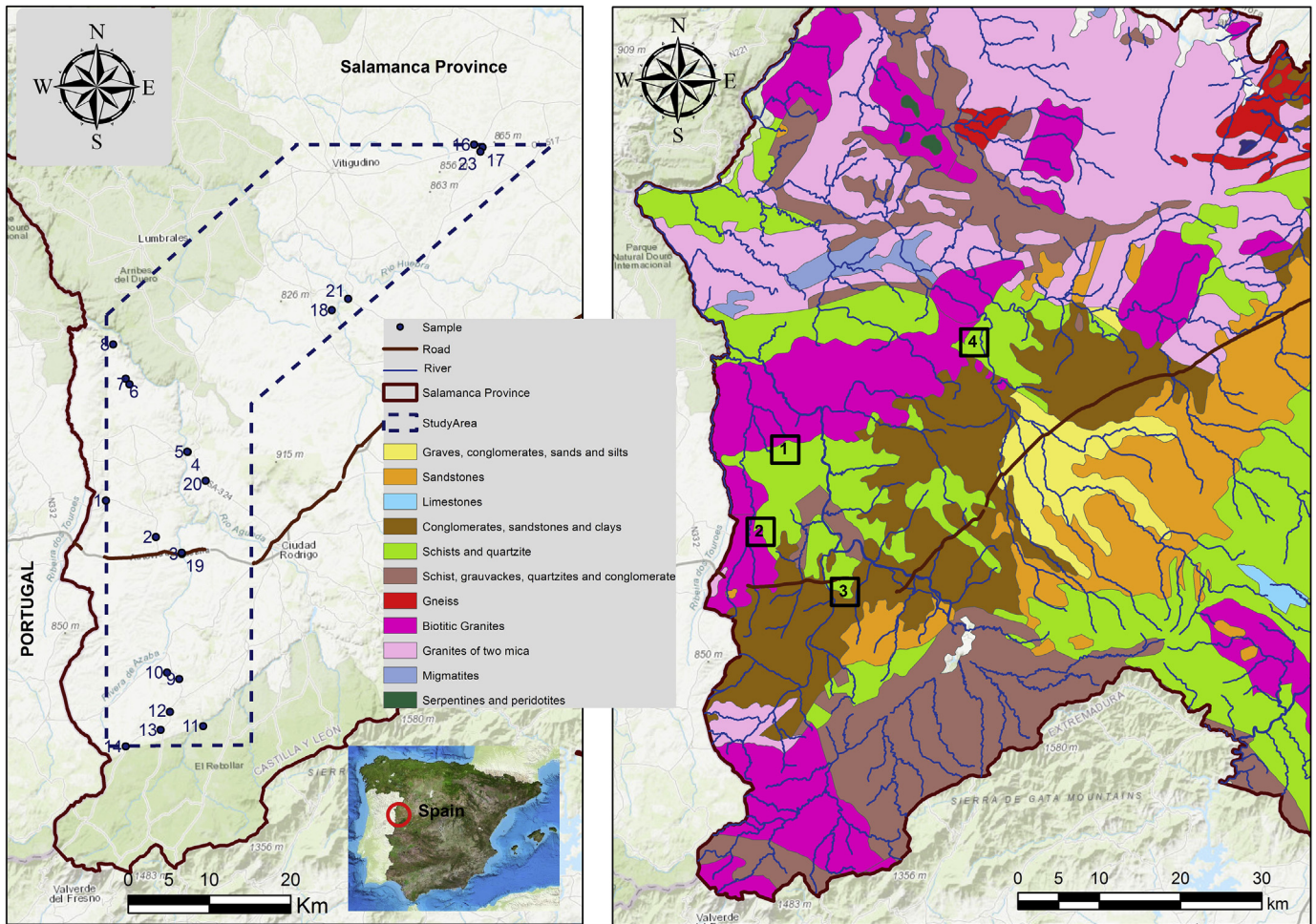
These regions are located 700–800 m above sea level, and have annual precipitation of 500–600 mm, an average temperature of ~12 °C and annual evapotranspiration of 700–800 mm. The climate is sub-humid, temperate, and dry in the summer. The moisture and temperature regime of the soils is xeric and mesic, 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



**Fig. 1.** Geographical and geological situation of the studied area. Geology of the studied area and sampling sites of soil profiles to calculate the background level and geochemical baseline (left) and deposit studied (right): 1-Villar de la Yegua, 2- Alameda de Gardón, 3- Villavieja de Yeltes and 4-Villar de Peralonso.

terms could belong to the lower Cambrian. The fundamental lithologies are slates, grauwacas, and sandstones, between which are interlaced lithologies of smaller cartographic extension, such as quartzites, conglomerates, and carbonaceous black slates. Two large units have been identified in the Greywacke Schist Complex (CEG), which [Rodríguez Alonso \(1985\)](#) and [Díez Balda \(1986\)](#) called the Monterrubio and Aldeatejada Formations. The Inferior Unit, which is ~2000 m thick, is characterised in this sector by having a predominance of slates with intercalations of sandy and conglomerate levels of variable thickness. The Superior Unit, which is ~3000 m thick, is characterised by the presence of levels of black carbonaceous slates associated with lighter and sandy levels.

Igneous rocks can be distinguished in three zones with clear differentiation in Salamanca Province ([López Plaza et al., 2005](#)):

1. Monzonitic grains with cordiorite and granodiorites, from the Central System and foothills (southern area of Salamanca) correspond to the granitic area of the Sierra de Gata and Las Batuecas-Sierra de Francia sector, with the Sequeros-La Alberca batholith. They are the most modern, have a recent emplacement age (280 Mya) and are synchronous to Phase 3 of the Varisca Deformation.
2. Biotytic granites with Muscovite are distributed in western Salamanca Province, constitute extensions of the batholith of Guarda (Portugal) and give rise to the granites of Peñaparda,

Villar de Ciervo, and Fuentes de Oñoro. Their location is posterior to Phase 3 (305 Mya).

3. Leucogranites with intermediate rocks of dioritic composition constitute the igneous sectors of Lumbrales, the Dome of the Tormes, Barruecopardo-Mieza, and Arribes del Duero. They are located between the end of Phase 2 of the Varisca Deformation and Phase 3 (synkamatic F3). These constitute the earliest granites (315–320 Mya).

### 2.3. Soil sampling and analysis

In the present work, soils near the mineralised tailings at five former mines located on granite rock and slates belonging to the Iberian Massif, were studied. In addition, to calculate the background level and geochemical baseline, we collected samples to establish 23 natural soil profiles developed from the aforementioned lithologies in a wide region west of Salamanca Province. In this case, soil sampling sites with no (or minimal) anthropogenic influence (i.e. adjacent areas outside the influence of the mineral deposits) were selected ([Fig. 1](#)). Field observations were generally made at natural cuts or slopes of roads. Four replicate sub-samples of soils were randomly collected at each sampling point within a 1.5 × 1.5 m grid, and mixed to obtain a composite sample of ~750 g. Samples were air-dried and passed through a 2 mm sieve. The

determination of the physical and chemical properties were carried out according to standardised methods for soil analysis (USDA, 2004): organic matter by oxidation with potassium dichromate, particle size analysis using the Robinson pipette method, pH (water 1:1) and cation exchange capacity (CEC) by the ammonium acetate method. The sampling strategy focused specifically on the surface horizons (A and B) and either deep or bedrock (C or R). The assumption was that the latter were unlikely to be contaminated by atmospheric deposition.

Soil classification was performed considering the morphological and analytical data of the samples, using the WRB taxonomy (IUSS, 2015).

The soil sampling strategy within the areas of influence of the mining sites (i.e. near the tailings and mineralised tailings of the mines) was focused specifically on the surface horizon. In the same manner as with natural soils, four sub-samples (replicates) were collected at random from each sampling point within a  $1.5 \times 1.5$  m grid; then mixed to obtain a composite sample of ~600 g.

The total uranium content in the soils was analysed according to the procedure recommended by the European Union Standard (European Soil Bureau, 2000). Extraction was performed with a mixture of nitric and hydrochloric acids in a microwave oven, and determined by ICP-MS (Elan 6000, Perkin-Elmer). The analysis was carried out by the Chemical Analysis Service at the University of Salamanca. For the calibration of the equipment, standard solutions (Panreac) of 1000 mg/l of each of the metals analysed were used, with calibration from 10 to 100 ppb. Duplicate blanks were analysed for quality control. The relative standard deviation (RSD) of the data for all elements analysed were all < 3%.

## 2.4. Statistical analysis samples

SPSS v.23.0 software was used for statistical analyses. The results included aspects such as the arithmetic mean, geometric mean, median, range, standard deviation, kurtosis, and correlation analysis between heavy metals and soil properties. Several pollution indices (Pollution Factor and Geo-accumulation Index) were calculated to determine the levels of contamination of heavy metals in the soils. The degree of spatial variability of uranium was calculated using the inverse distance weighted (IDW) spatial interpolation method. The flow diagram, with the interpolation procedure using ArcGIS, is shown in Fig. 2.

## 3. Results and discussion

### 3.1. Soil study

#### 3.1.1. Soils on granitic rock

In the study area, granites appear mainly in the pediment of the

Vitigudino region and in small areas of the sub-regions of Abadengo, Campo de Argañán, and Azaba pertaining to the region of Ciudad Rodrigo. The landscape is usually wavy or strongly undulating and rocky outcrops (granite boulders) are frequent.

On this type of rock, shallow soil layers, often in lithic phase and light brown, have been formed. They are characterised by a very sandy texture (average sand content 72.5%), low exchange capacity ( $7.7 \text{ cmol kg}^{-1}$ ), low organic carbon content (0.9%), acid pH (5.1) and base saturation of 39.8%. Dystrophic Leptosols, dystrophic Regosols, dystrophic Cambisols, and Leptic Umbrisols predominate (Fig. 3).

#### 3.1.2. Soils on slates

The slates belong to the 'Schist-Greywacke Complex', Precambrian-Cambrian lower age. They originate in an undulating landscape in which there are hardly any rocky outcrops. They extend widely within the region of Ciudad Rodrigo.

The soil layers are thin, but are almost never in the lytic phase. They are characterised by silty textures (45.1% silt), low organic carbon content (0.8%), pH between acid and slightly acid (5.6), moderate changeability ( $11.2 \text{ cmol kg}^{-1}$ ) and some degree of saturation (50.2%). Ecological and physical Regosols, Eutric Leptosols, and Ecistric, Dystroic, and Chromatic Cambisols are predominant.

Within this physiographic unit are small remains of old erosion surfaces, which form flat-topped hills, accompanied by gravel deposits. On these hills, thick soils have formed (Luvisols and chromic Alisols) which have red argillic horizons (Fig. 4).

In the study area, the soils were developed by in situ weathering of granites and slates, and were usually homogeneous as far as the main mineralogy is concerned. However, some profiles show lithological discontinuity as well as the addition of new materials and minerals, generally, to the height of the superficial horizon (rejuvenation by erosive processes). The results from analysis describing the main properties of the soils are presented in Table 1.

### 3.2. Calculation of background level and geochemical baseline of uranium in soils

Comprehensive sampling of all the natural soil units developed over granites and slates located in the west of Salamanca Province was carried out. Soil sampling sites were selected that appeared to have no (or minimal) anthropogenic influence. Twenty-three soil profiles were collected (Table 1), along with 60 samples (surface horizons and underlying rock).

The geochemical background level of a chemical element represents its concentration in uncontaminated soil. The calculation of the level of the natural geological background, without the influence of the soil formation and anthropogenic processes, is made only and exclusively from the subsoil samples, that is, from the soil-parent rock (Santos Francés et al., 2017b).

The calculation of the background level is often a complicated task because soils without contamination are almost impossible to find. This is because of the existence of long-distance atmospheric transport and deposition of trace contaminants, and of human activity (e.g. mining) (Chen et al., 1999).

Generally, the background level is usually replaced by the baseline, which is the average of surface geochemical variations at the time of sampling. The geochemical baseline is influenced by subsoil lithology, soil formation processes and the presence of diffuse anthropogenic pollution (Tarvainen and Kallio, 2002). When one starts from populations obtained over large areas that include a great diversity of geological contexts, it does not make sense to apply the results to a population with a uniquely heterogeneous parameter. Salminen and Gregorauskiene (2000) stated the need to subdivide a heterogeneous population into geological domains

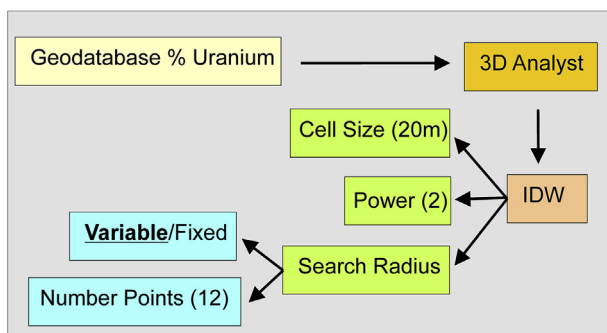


Fig. 2. Flow diagram with the interpolation procedure using ArcGIS.

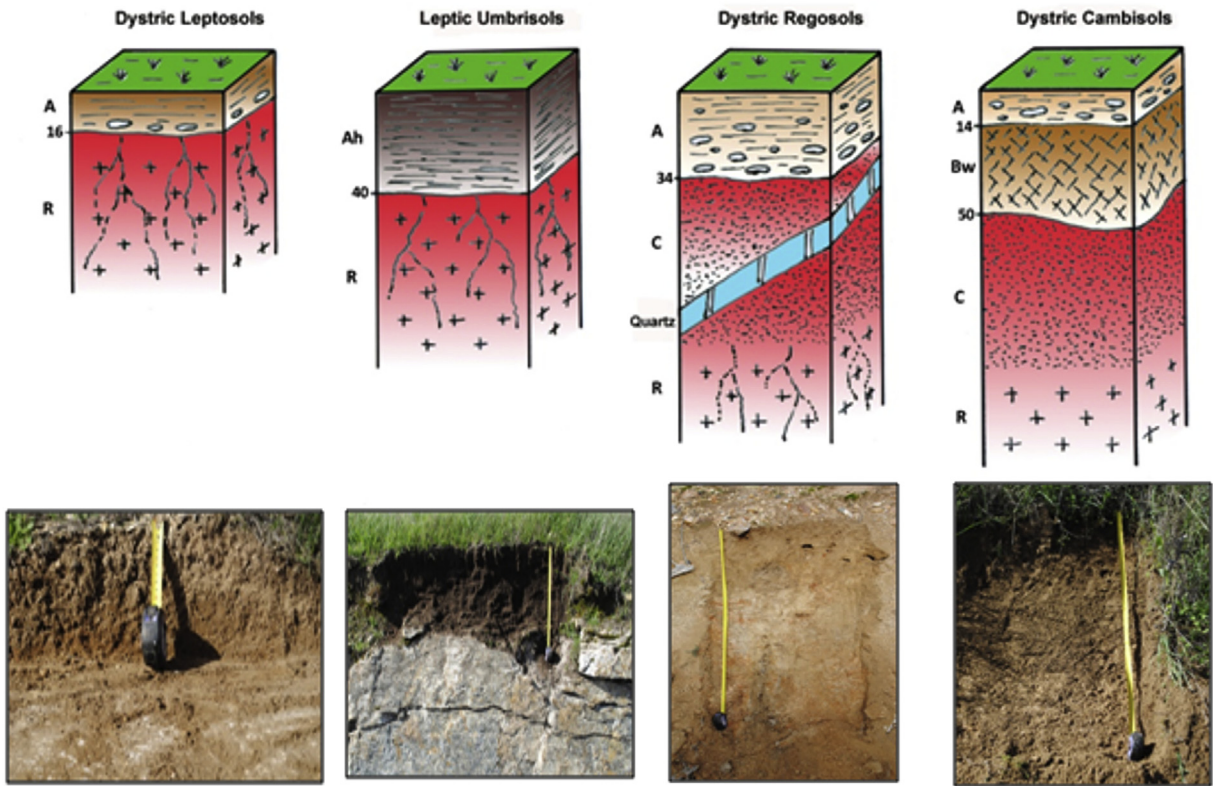


Fig. 3. Morphology of the most representative soils on granitic rocks.

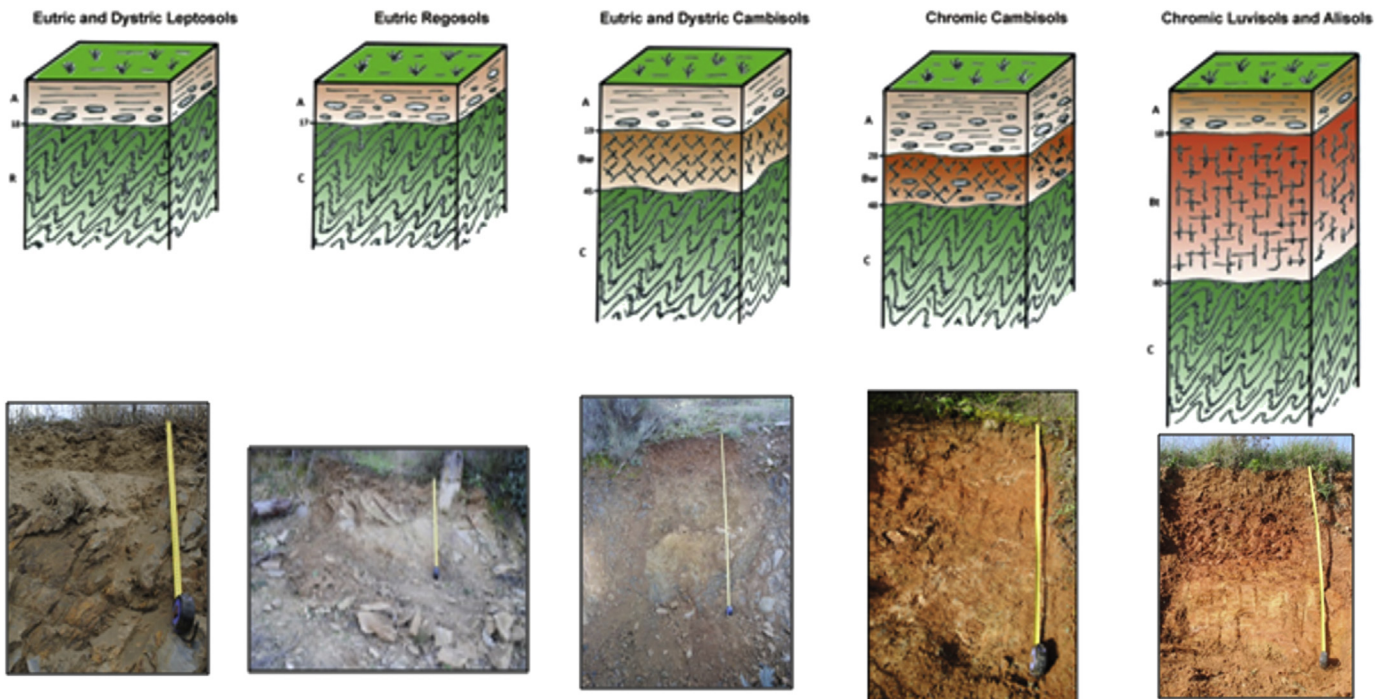


Fig. 4. Morphology of the most representative soils on slates.

with different features, and to establish background levels for each of them. The partition of the population into geochemically more homogeneous subpopulations can be approached from two points of view, by subdivision based upon geological criteria or upon

geochemical features of the (sample) population.

For this reason, the background level and geochemical baseline of uranium were calculated for a region located to the west of Salamanca Province, in which the soils developed on granite rock

**Table 1**  
Analytical data of the main properties and uranium content of the natural soils studied.

Samples	Organic Carbon %	pH-H <sub>2</sub> O 1:1	Granulometric analysis			Removable bases of change				Cation exchange capacity Cm <sub>ol</sub> k <sup>-1</sup>	Degree of saturation in bases %	Uranium mg kg <sup>-1</sup>
			Sand %	Silt %	Clay %	Ca Cm <sub>ol</sub> k <sup>-1</sup>	Mg Cm <sub>ol</sub> k <sup>-1</sup>	K Cm <sub>ol</sub> k <sup>-1</sup>	Na Cm <sub>ol</sub> k <sup>-1</sup>			
1A	0.66	5.2	66.3	26.5	7.2	3.82	0.86	0.22	0.19	7.8	65.2	78.7
1Bw	0.34	5.2	64.8	27.3	7.8	2.56	0.79	0.23	0.14	7.5	50.0	85.1
2A	1.25	7.2	31.3	61.9	6.8	15.21	1.19	0.32	0.31	12.4	100.0	79.6
3A	1.01	5.5	48.1	45.1	6.8	2.71	0.70	0.32	traces	8.9	41.8	102.0
4A	1.17	5.9	60.4	31.8	7.9	6.71	1.68	0.21	0.14	10.2	85.7	41.3
4Bt	0.09	6.2	51.6	21.0	27.4	8.03	3.68	0.09	traces	19.3	61.2	76.3
4BC	0.15	6.8	52.1	31.4	16.6	8.44	4.37	0.05	traces	15.1	85.3	87.3
5A	1.08	5.8	26.4	66.5	7.1	6.88	2.19	0.10	0.08	12.7	72.8	32.6
5Bw	0.29	6.2	16.0	70.8	13.2	11.71	4.50	0.04	0.04	9.3	100.0	31.8
6A	0.61	4.9	73.6	20.1	6.4	0.36	0.18	0.23	0.10	7.3	12.0	34.1
7A	2.35	4.8	76.0	13.8	10.2	3.01	0.68	0.20	0.33	9.2	46.0	76.5
7C	0.60	5.5	90.6	5.9	3.5	1.46	0.39	0.07	0.04	4.7	42.0	72.0
7Ab	0.49	5.7	86.6	7.6	5.8	2.10	0.55	0.10	0.22	4.7	62.9	70.1
8A	1.26	4.9	71.9	19.8	8.3	4.16	1.47	0.19	0.04	9.8	59.8	37.5
8Bw	0.90	4.9	69.8	23.3	6.9	2.79	0.97	0.12	0.14	8.5	47.2	28.8
8C	0.24	5.5	81.4	11.7	6.9	2.44	0.85	0.18	0.02	5.0	70.2	25.0
9A	1.63	5.4	19.4	72.6	8.1	6.82	1.57	0.34	0.44	13.1	69.8	20.7
10A	0.05	6.7	75.2	17.6	7.3	2.91	2.76	0.15	0.18	7.1	84.6	13.5
11A	1.44	5.4	32.7	52.6	14.8	0.36	0.43	0.08	0.08	8.2	11.5	35.2
11Bw	0.18	5.2	13.5	61.8	24.7	0.44	0.95	0.05	0.03	20.0	7.4	31.6
11C	0.09	5.3	16.6	70.9	12.4	0.19	0.91	0.05	traces	16.6	6.9	35.6
12A	1.14	6.7	45.9	39.9	14.2	6.24	1.12	0.54	0.28	11.0	74.2	76.7
12Bt	0.16	6.2	22.0	51.8	26.2	3.49	2.96	0.07	0.26	14.6	46.6	76.1
12C	0.02	5.1	27.6	67.5	4.9	0.34	0.65	0.04	0.05	6.4	16.8	53.3
13A	0.56	5.2	68.3	22.2	9.4	1.48	0.76	0.24	0.10	7.0	36.9	79.2
13Bw	0.27	5.4	62.0	27.6	10.5	3.06	0.95	0.17	0.04	8.6	48.9	84.9
14A	2.81	5.0	67.7	22.8	9.6	0.29	0.20	0.14	traces	14.9	4.2	100.2
15A	1.69	4.6	71.9	18.74	9.3	1.69	0.69	0.04	0.54	9.4	31.5	72.2
15C1	0.35	5.9	86.0	10.25	3.7	0.75	0.54	0.01	0.46	4.1	42.3	72.4
15C2	0.31	6.0	72.8	22.01	5.1	1.52	1.01	0.02	0.58	5.0	63.0	98.8
16A	1.03	4.9	82.1	15.15	2.7	0.41	0.26	0.28	0.08	6.1	16.9	85.9
17A	0.34	4.4	67.4	21.66	10.9	0.61	0.84	0.09	0.14	7.2	23.2	42.5
17C	0.17	4.9	70.9	17.92	11.2	2.24	1.58	0.11	0.11	8.5	47.3	49.4
18A	2.58	5.2	32.8	60.00	7.2	3.00	1.18	0.32	0.06	12.9	35.4	24.1
18Bw	0.28	4.9	13.7	78.78	7.5	0.51	0.59	0.08	0.25	9.6	14.9	38.3
18C	0.21	5.5	11.6	83.63	4.7	3.61	1.08	0.05	0.24	9.2	5.4	33.0
19A	2.55	3.8	54.8	32.43	12.8	3.11	1.79	0.05	0.42	10.6	50.7	26.7
19C	0.42	4.2	67.3	23.71	9.0	0.21	0.52	0.04	0.22	8.5	11.7	21.8
19Cg	0.41	4.2	66.0	25.01	9.0	0.21	0.52	0.06	0.17	7.8	12.2	22.8
20A	1.34	5.8	45.8	44.84	9.4	5.70	1.14	0.92	0.46	11.5	71.5	11.2
21A	0.63	5.0	31.7	60.96	7.3	1.54	0.42	0.23	0.15	9.0	26.1	17.5
21Bw	0.51	5.0	35.1	49.55	15.4	3.48	1.08	0.12	0.18	13.3	36.5	17.8
22A	1.48	6.3	30.3	38.86	30.8	19.6	5.53	0.91	0.23	31.2	84.6	40.9
22Bt	0.69	6.0	29.3	32.36	38.3	29.1	9.78	0.41	0.36	43.7	90.8	70.6
23A	1.76	4.8	57.6	28.43	14.0	1.11	0.23	0.28	0.22	8.6	21.3	39.7
23Bw	0.97	5.2	61.6	25.44	13.0	1.77	0.47	0.23	0.21	7.7	34.7	96.5
23C	0.47	5.6	72.4	18.14	9.5	2.01	0.67	0.16	0.34	5.0	63.8	20.0

and on slates were clearly differentiated. To calculate the geochemical baseline of uranium in these soils, the uranium concentrations at the soil surface horizons were used. This calculation of the geochemical baseline was done by adding the standard deviation to the background level (geometric mean). These were obtained by applying the statistical method proposed in ISO/DIS 19258 (2005). This approach is the simplest for calculating baseline values, although other methods can be used (e.g. using median or regression equations).

The results from statistical analysis of the uranium content in the soils of western Salamanca Province can be seen in Table 2. The average concentration of uranium obtained in the soils developed from slate is 65.3 mg kg<sup>-1</sup> and the baseline is 62.0 mg kg<sup>-1</sup>. In soils developed from granites, the corresponding concentrations are 28.0 and 28.4 mg kg<sup>-1</sup>, respectively. Also in Table 2, is a comparison of these results with those in the literature of uranium concentrations obtained worldwide.

The geochemical baselines of uranium in the natural soils of western Salamanca Province, present values much higher than the mean values found in the earth's crust and soils in other parts of the world (Taylor, 1996; Turekian and Wedepohl, 1961; Taboada et al., 2006; Kabata-Pendias and Pendias, 2001). However, values similar to those obtained in soils from granite (>20 mg kg<sup>-1</sup>) were obtained in Spodosols from the USA (Morton et al., 2001).

In the Geochemical Atlas of Spain three maps of the spatial distribution of uranium are presented: in sediments or rocks, in the soil surface horizons and in the lower soil horizons (Fig. 5). Among them were several geochemical anomalies with concentrations much higher than the geochemical background. These areas in the Salamanca Province have been the major producers of uranium in Spain in the last 70 years. Indeed, these areas show much potential for continued uranium mining, given the richness of the natural deposits in the region.

The background levels and ranges of the values reported in the

**Table 2**

Statistical analysis of uranium content in surface horizons of the soils developed on slates and granites and proposal of geochemical baseline ("mg" - geometric mean and "ds" - standard deviation); in bedrock and solum horizon.

Soils on slates	Uranium mg kg <sup>-1</sup>	Soils on granites	Uranium mg kg <sup>-1</sup>	Uranium (Solum) mg kg <sup>-1</sup>	Uranium (Bedrock) mg kg <sup>-1</sup>
Mean	65.3	Mean	28.0	53.1	51.2
Dev. Stand.	26.7	Dev. Stand.	12.9	28.7	27.5
Geometr.mean	58.7	Geometr. mean	25.0	44.4	43.7
Dev. Stand. Geometr.	1.7	Dev. Stand. Geometr.	1.7	—	—
Median	76.3	Median	28.3	46.0	41.1
Kurtosis	-1.23	Kurtosis	-1.33	-1.40	-1.50
Minimum	20.0	Minimum	11.2	11.2	13.5
Maximum	102.0	Maximum	49.4	102.0	96.5
Geochemical baseline proposal (mg + 2ds)	62.0	Geochemical baseline proposal (mg + 2ds)	28.4	—	—
Average in the Earth's crust (Taylor, 1996)	2.7	Average in the Earth's crust (Taylor, 1996)	2.7	—	—
Average on slates (Turekian and Wedepohl, 1961)	3.7	Average in granitic rocks (Turekian and Wedepohl, 1961)	3.0	—	—
Average in soils (Kabata-Pendias and Pendias, 2001)	0.79 to 11	Average in granitic rocks of the NW of Spain (Taboada et al., 2006)	5.3 to 27.7	—	—

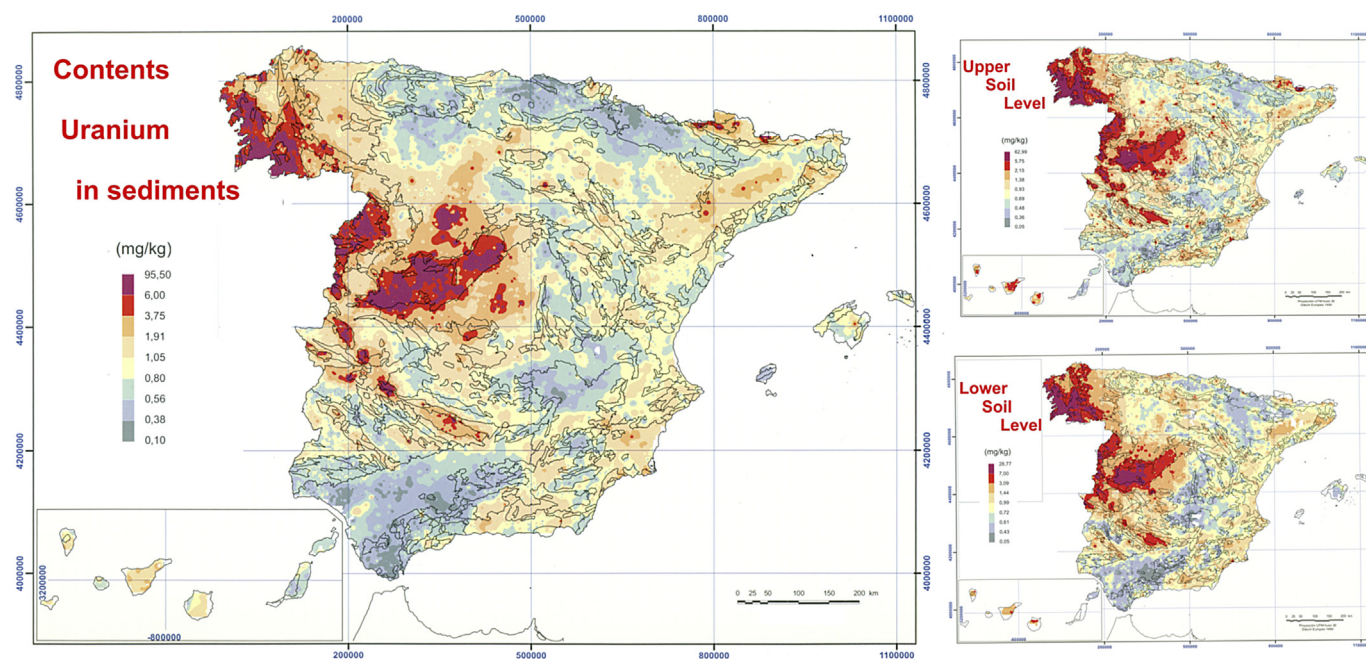


Fig. 5. Distribution of uranium in sediments (left) and soils of the Iberian Peninsula (right) (Geochemical Atlas of Spain, Locutura et al., 2012).

cartography of the Geochemical Atlas of Spain (Locutura et al., 2012) were as follows. The reported background level (median) of the sediments was  $2.6 \text{ mg kg}^{-1}$  and the range was  $0.05\text{--}97.5 \text{ mg kg}^{-1}$ . At the bottom of the upper horizons of soils, the median was  $2.9 \text{ mg kg}^{-1}$  and the range was  $0.05\text{--}65.9 \text{ mg kg}^{-1}$ . At the bottom of the lower horizons of soils, the median was  $2.8 \text{ mg kg}^{-1}$  and the range  $0.05\text{--}28.8 \text{ mg kg}^{-1}$ .

In the northwest part of the Iberian Peninsula (Galicia), in the Central System, and in the west of Extremadura and Salamanca Provinces (western Spain); the highest uranium concentrations are found; the highest of which are very close to the maximum values reported.

The geochemical baselines of uranium in the natural soils of western Salamanca Province have values well above the background levels obtained in Spain (Locutura et al., 2012), but are within the ranges existing in the Central System, and in the north-western and western parts of the Iberian Peninsula.

In the present study, samples of the C-horizon (soil bedrock) were used to determine the 'natural geological background level' to avoid the influence of soil formation processes and human influence. The values selected were the median statistics (Table S1); the same method followed in the Geochemical Atlas of Spain (Locutura et al., 2012).

This level of background or other concentration of uranium in granitic rock was of the same order of magnitude as the average content obtained ( $24.4 \pm 4.7 \text{ mg kg}^{-1}$ ) in calcoalkaline granites from NW Spain (Taboada et al., 2006).

In addition, a statistical analysis was carried out in this study, using the data of the most superficial and underlying horizons of all soils. These data were treated separately. The most superficial horizons (solum) are those that, logically, must contain the contributions due to the processes of soil formation and anthropogenic processes, while the underlying horizon represents the lithogenic contributions. As can be seen in Table 2, there is a small difference

in the statistics of uranium concentrations between the surface horizons (median value  $45.9 \text{ mg kg}^{-1}$ ) and the parent rock (median  $41.1 \text{ mg kg}^{-1}$ ).

### 3.3. Assessment of environmental risks: pollution rates

Higher concentrations of uranium occur in the surface horizons, which logically must contain the results of anthropogenic contributions. The underlying horizons should represent the distinctly lithogenic contributions. Therefore, it is logical to think that there may be a weak or diffuse contamination of natural soils, located more or less distantly from the mineral deposits, in this region of western Salamanca Province (Spain).

The contribution of uranium to the geological character of the natural environment mainly comes from the weathering and mineralisation of uranium-bearing rock, and from the anthropogenic impacts of mining operations and the application of phosphate fertilizers.

Keep in mind that radionuclides can be transported by wind. Their weight and the climatic conditions determine their deposition on the ground. In addition, heavy rains can bring radioactive particles to the ground from the atmosphere. Soils possess sorbent and complexing capabilities that contribute to the immobilisation of radionuclides (Gravilescu et al., 2009).

For these reasons, we aimed to verify the possible existence of contamination in these natural soils using two contamination indexes: Pollution Factor and Geo-accumulation Index.

The contamination factor is  $Pi = Ci/Bi$ , where 'Ci' is the measured concentration of the pollutant and 'Bi' is the natural background level (Table S2).

According to the results of this pollution factor, three categories were established: low pollution ( $Pi < 1$ ), moderate pollution ( $1 = Pi < 3$ ), and high pollution ( $3 = Pi \geq 6$ ). These data show that 43.5 and 50% of the studied soil samples from slates and granites, respectively, had a low level of contamination and that 56.5 and 50% had a moderate level of contamination.

The Geo-accumulation Index (Igeo) is calculated from (eq. (1)):

$$I_{geo} = \log_2 (Ci / 1.5 Bi) \quad (1)$$

Where 'Ci' is the measured concentration of 'i' in the soil and 'Bi' is the background level of the 'i' metal. The factor 1.5 is used to correct possible variations in background values for a given metal in the environment (Table S3). The resulting values are classified as non-contaminated ( $I_{geo} < 0$ , Class 0); then, from mildly contaminated ( $0 = I_{geo} < 1$ , Class 1); to moderately contaminated ( $1 = I_{geo} < 2$ , Class 2); to strongly contaminated ( $2 = I_{geo} < 3$ , Class 3); and strongly contaminated ( $3 = I_{geo} < 4$ , Class 4). From here, the classification proceeds from heavily contaminated ( $4 = I_{geo} < 5$ , Class 5) to extremely contaminated ( $I_{geo} \geq 5$ , Class 6). The calculated Igeo for uranium allowed us to evaluate the level of contamination of this element in the study area and to calculate the percentage of pollution (Igeo). Considering Igeo, it can be seen that 100% and 83.3% of the slate and granite soil samples, respectively, correspond to soils not contaminated by uranium, and that 16.7% of the soils from granites are considered to be either non-contaminated or moderately contaminated.

### 3.4. Uranium in the soils located in the proximities to the mining sites

Extraction of uranium minerals results in the production of tailings and large volumes of rock waste with remaining low-grade minerals. One of the objectives of this work was to calculate the spatial distribution of uranium content in all soils of the studied

region. In addition to sampling natural soils in areas adjacent to, but beyond influence by the mining sites, sampling was also conducted of the soils located within the influence (i.e. near the tailings and mineralised tailings) of five abandoned mine sites. The deposits exhibited two different types of mineralisation:

1) Intragranite mineralisation: This type is typical of the Villar de Peralonso deposit, consisting of a network of quartz reefs, inside a sericitised two-mica leucogranite. It is very tectonised, especially in areas close to contact with a formation of metamorphic rocks. It corresponds to a mineral deposit of the 'stockwork' type, which extends to the northeast, where the mineral uraniferous is distributed irregularly.

The granite is somewhat porphyritic, with feldspathic phenocrysts very irregularly distributed. The biotite is small and of small size. It is distributed homogeneously and seems to keep a certain sub-horizontal orientation that would mark a foliation. Muscovite is very abundant and occurs in plaques of variable size, sometimes up to 1 cm, which are always disordered.

The contact metamorphic rocks appear immediately to the south of the deposit, forming a narrow band, interspersed between granites. Predominantly they are mica schists, metapsamitas and feldspathic paragneises, with sandstones and even quarcitic intercalations. Calcosilicate levels of centimeter to decimetric thickness are also found. These materials are azoic, but are considered to be of a Precambrian-Lower Cambrian age. They are affected by metamorphism, which effect reaches even the point of migmatization.

The primary mineral associations are of quartz, coffinite, some pitchblende, fluorite, pyrite and other sulphides (marcasite and pyrite). The paragenesis corresponds to a 'uraniferous epithermal deposit', which abound in European variscan granitic areas (Arribas, 1964).

2) Mineralisations embedded in metamorphic rocks: The fields studied in Alameda de Gardón, Villavieja de Yeltes, Villar de Yegua, and Carpio de Azaba are of this type. It should be noted that the Saelices el Chico Mine was the largest of its kind and the most important in Spain (Both et al., 1994), but in the present work, the soils in its vicinity were not studied. This is because it was recently restored, and all the mining waste covered with a layer of sandstone and a layer of soil. In general, there are schistous slates, with some organic content, generally located very close to the contact with the granites. Due to the proximity of the deposits with the areas of contact with the granitic rocks, the meta-sediments are more or less affected by the thermal metamorphism auras. These are embedded filonian mineralizations, in the zones of fractures, and breccias within the meta-sediments of the Lower Palaeozoic Schist-Greywacke Complex. These mineralisations were formed in filaments of millimetre to centimetre size, of quartz, pitchblende, and coffinite that cross irregularly to the slates. These, in turn, contain secondary uranium mineral discharges in the zones of superficial oxidation. The primary mineralisation is by carbonates, adularia, pitchblende, coffinite, and marcasite, with a series of accessory minerals such as quartz, galena, esphalerite, chalcopyrite, and fluorite. The mineralisations of these deposits are generally located in the pelitic sections, many of them markedly ampelitic (Arribas et al., 1983; Martín Izard, 1986).

In these five mineral deposits located in western Salamanca Province, 93 samples were collected to determine the U-content in the soil surface horizon. The mean concentration of U in the soil samples of each reservoir was as follows:  $207.2 \text{ mg kg}^{-1}$  in Villar de



la Yegua, 229.6 mg kg<sup>-1</sup> in Carpio de Azaba, 260.0 mg kg<sup>-1</sup> in Villavieja de Yeltes, 291.3 mg kg<sup>-1</sup> in Alameda de Gardón, and 542.4 mg kg<sup>-1</sup> in Villar de Peralonso.

3.5. Spatial distribution of uranium content in natural soils

The IDW (weighted inverse distance) interpolation method allowed us to predict the spatial distribution of the uranium concentration in non-sampled locations from the values collected in the field work samples, so that the nearest values present a better correlation and similarity than those that were further away.

The mapping of the uranium concentration of the natural soils (background level) of the studied region (Fig. 6), shows that the highest concentrations were located in the horizons of the soils developed from slates (profiles 1, 11, 12 and 13), with concentrations between 81.8 and 85.8 mg kg<sup>-1</sup> and located in the vicinity of the populations of Alameda de Gardón and Fuenteguinaldo. However, the soils with the lowest uranium concentrations were

located in the natural soils developed on granite-green-coloured zones (profiles 7 and 16), with concentrations between 14.4 and 19.7 mg kg<sup>-1</sup> and located close to Villar de Ciervo and Villar de Peralonso. It should be noted that, unlike natural soils, the highest concentration of uranium (542.4 mg kg<sup>-1</sup>) measured in the region occurred in the soils in the vicinity of the uranium deposits located on granite, in the area of Villar de Peralonso. In the deposits located on slate, the concentration of uranium in the soils was between 207.2 and 291.3 mg kg<sup>-1</sup>.

3.6. Distribution of uranium in horizons A, B, and C of soil profiles

In the soils on granites and slates of the western Salamanca Province, the average concentration of uranium (Table S4) increased in the B-horizons (Bw and Bt) and decreased in the A-horizon. As can be seen in Table 2, there is a small difference in the uranium concentrations between the surface horizons (median 46.0 mg kg<sup>-1</sup>) and the parent rock (median 41.1 mg kg<sup>-1</sup>).

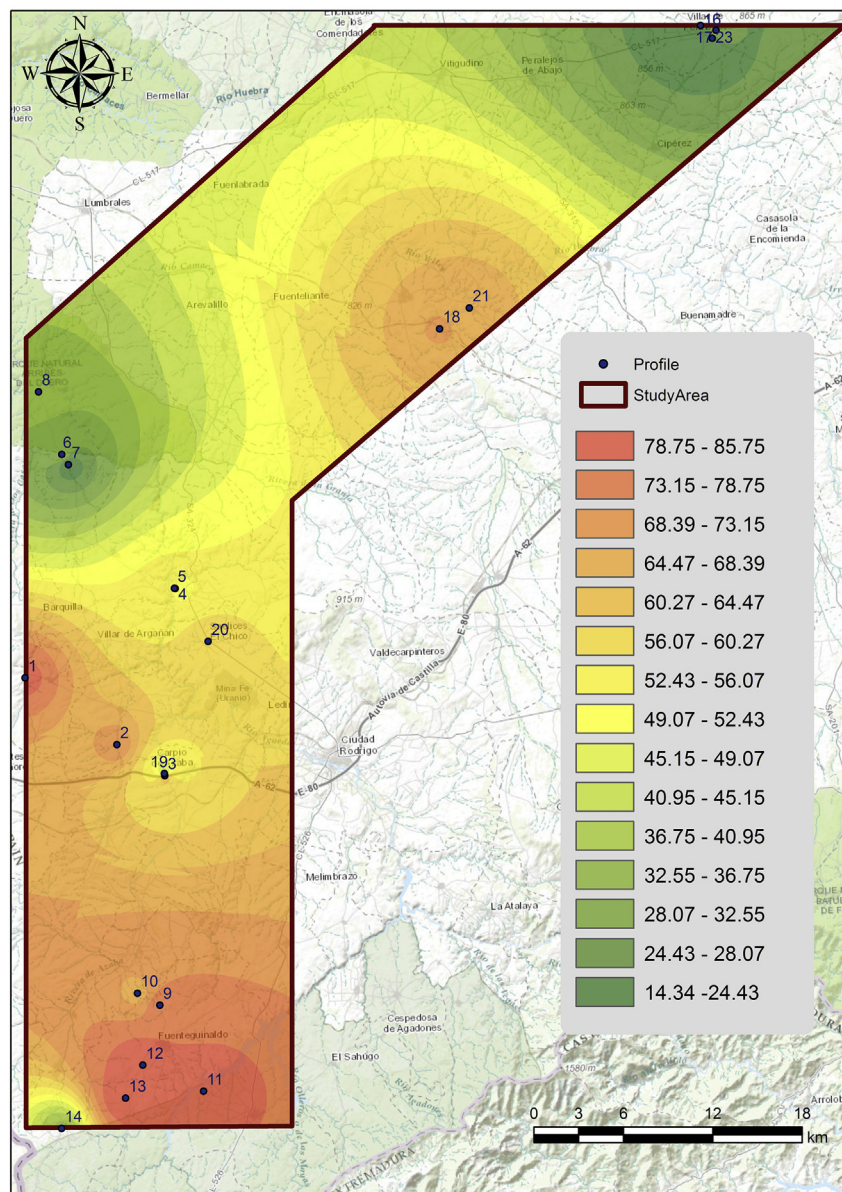


Fig. 6. Spatial distribution of uranium content in the natural soils of western Salamanca province.

Uranium enrichment occurred in the horizons with the highest clay content (Bw and Bt horizons), with enrichments up to two times higher than in the mother rock. Uranium distribution profiles with depth suggest that uranium is leached from the soil surface by rainwater and accumulates in lower horizons with higher clay content. This could be considered a natural attenuation of possible impacts from uranium-sourced ionizing radiation in the environment.

The depth distribution of uranium, along the predominant profiles (Inceptisols and Alfisols) of soils of western Salamanca Province (Fig. 7), is similar to or coincident with the clay distribution and the cation exchange capacity. That is, the uranium content increases in the B-horizon of the soils, and the highest concentrations of uranium occur in the Bt-horizon of the Alfisols. However, in Entisols, the content of trace elements with depth is highly variable. In some soils, the uranium content is higher in the A-horizon than in the C, but in other Entisols, the opposite occurs (higher in the C-horizon). The organic matter content, absorption of uranium by plants and the existence or non-existence of ‘allochthonous’ surface horizons (i.e. the presence of a lithological discontinuity), have great influence on the distribution.

The similarity between the depth distributions of the clay content of the soil and the uranium concentration can be explained as follows. The uranium filtration through the most sandy, porous, and aerated horizons of the soil, such as the A-horizon, is consistent with the geochemical behaviour of this element (more stable under oxidizing conditions as U (VI) than in the U (IV) form). The primary abiotic and biological processes that transport uranium into the soil are oxidation-reduction reactions that convert U (VI), which is

soluble, into U (IV), which is insoluble. The conditions of higher porosity and aeration of the soil surface horizons allow the oxidation of uranium from U (IV) to U (VI) and thus increase its solubility and potential for leaching. U (VI) forms the uranyl anion ( $UO_2^{2+}$ ) and this ion forms water-soluble complexes (depending on pH). U (IV) is very insoluble and generally forms uraninite ( $UO_2$ ). Within the pH range 4.0–7.5, the pH range of most soils, U (VI) exists mainly in hydrolysed forms (Coward and Burnett, 1994; Barnett et al., 2000). The increase of the uranium concentrations in the Bt-horizons suggests the existence of leaching from the most superficial horizons and their accumulation and immobilisation in the illuvial horizon. This occurs by adsorption to clay minerals, iron oxides and iron hydroxides, or by direct uranium precipitation in the form of oxides. In addition, redox conditions may vary in the deep profile horizons (with higher moisture retention). The leaching is slower in the deep horizons of the soil due to slower drainage, and this increases the average residence time (Murakami et al., 1997; Turner et al., 1996; Hudson et al., 1999).

#### 4. Conclusion

The natural soils of western Salamanca Province (Spain) developed from granite rock and slates, and have high concentrations of uranium. These values are higher than the mean values obtained for the earth’s crust worldwide, especially in soils developed on slates. When calculating the ‘natural geological background level’ of the soils developed from slates, a value of  $71.2 \text{ mg kg}^{-1}$  was obtained, and for soils from granites it was  $29.8 \text{ mg kg}^{-1}$ .

Using two contamination indexes (Pollution Factor and Geo-

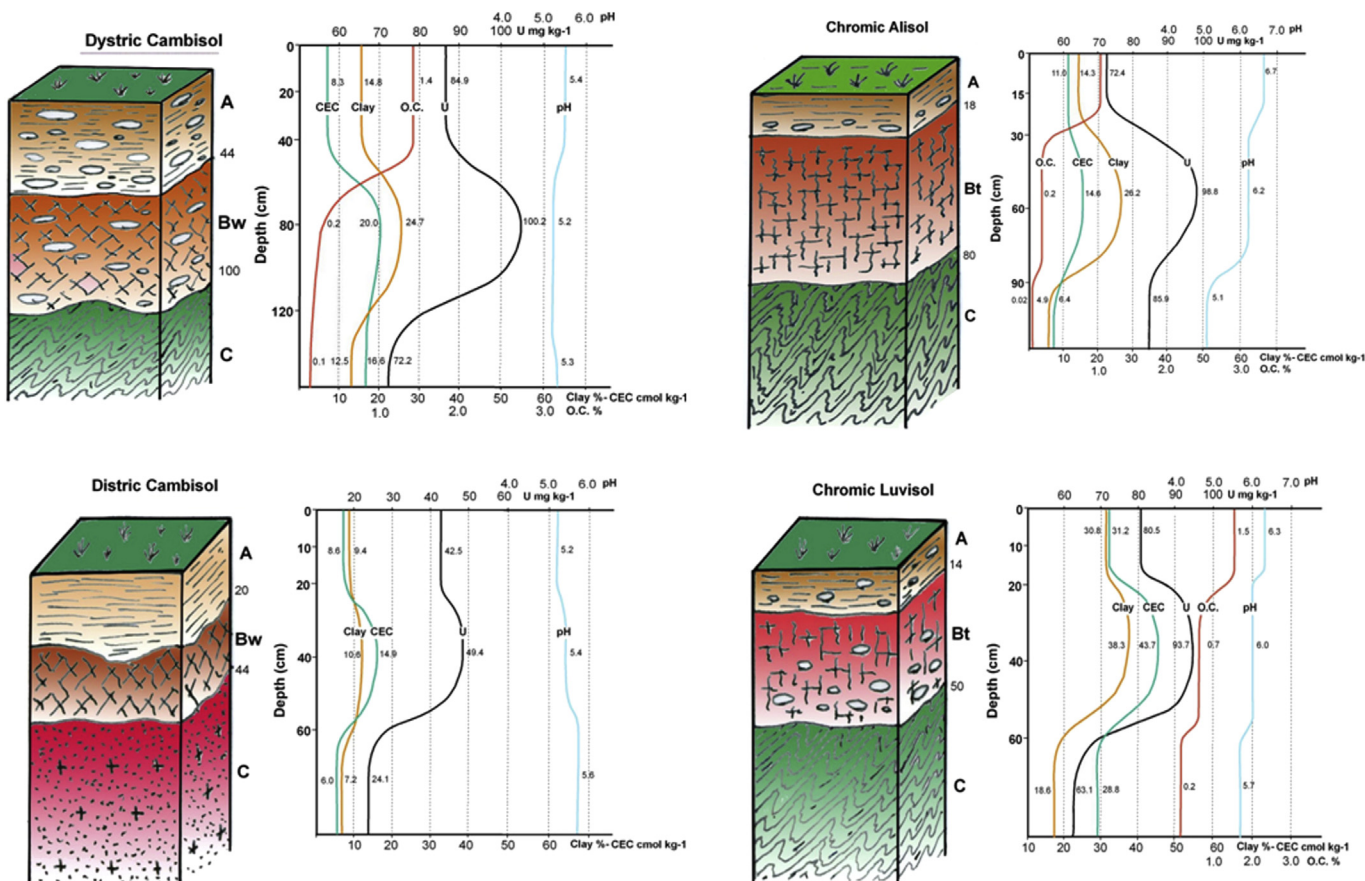


Fig. 7. Distribution of the uranium content in depth, along the profile, in the Cambisols and Luvisols/Alisols of the W of the province of Salamanca.

accumulation Index), the degree of contamination caused by mining activities in the soils located to the west of Salamanca Province (Spain) was calculated. The values obtained from these indices indicate that in the natural soils, between 16.7 and 56.5% of the samples studied had moderately diffuse pollution. These contributions of uranium, generally geogenic and anthropogenic, to the natural environment of this region may come from the weathering of rocks, mineralisation and mining.

The spatial distribution of uranium content in natural soils shows that the highest uranium contents are located in the horizons of the soils developed on slates.

The vertical distribution of uranium, along the horizons of the soil profiles, shows a tendency to accumulate in the horizons with higher clay content (Bw and Bt horizons), through the processes of weathering and leaching from the surface of the floor.

Due to the high concentration of uranium in the areas close to the abandoned mining facilities in this region, it is proposed to carry out environmental restoration. First, 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.

Radiological impact is the main effect from uranium mines and, to be successful with restoration measures, the concentration of uranium in soils and mining wastes should be evaluated.

## Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.envpol.2018.01.038>.

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