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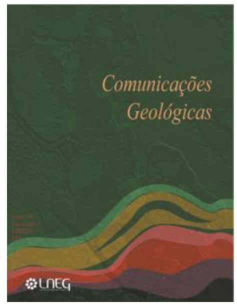
Distribution of naturally radioactive elements (U, Th and K) in grazing land soils of the Iberian Peninsula compared with total natural radiation



Distribuição de elementos naturalmente radioativos (U, Th e K) em solos de poisio na Península Ibérica em comparação com a radiação natural total

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Artigo original
Original article

Abstract: The present study focus on the samples collected in the Iberian Peninsula in 239 locations, of land under permanent grass cover ("grazing land" - Gr, topsoil 0-10 cm) of the European Atlas of Agricultural and Grazing Land (GEMAS). The objective was to test the differences between natural radionuclides in grazing land soils and its distribution in total and partial extraction and in comparison, with total natural radioactivity. High natural radiation areas of the Iberian Peninsula are coincident with the distribution of the U, Th and K analysed by XRF. The regression exercise done for the Iberian Peninsula allow a better understanding of which variables influence U distribution in this kind of soils. The results show that, although uranium presence in soils is more important to understand hazard and economical potential of radionuclides, the differences between analytical methods (total analysis - XRF and aqua regia extraction) that occur in potassium were the most important remark of the study.

Keywords: Iberian Peninsula, uranium, thorium, potassium, grazing land soils.

Resumo: O presente estudo consiste na comparação da distribuição entre os radionuclídeos nos solos superficiais de poisio (0-10 cm), amostrados no âmbito do projeto GEMAS - European Atlas of Agricultural and Grazing Land em 239 pontos de amostragem na Península Ibérica. Estes valores são comparados entre si e em relação ao método analítico e ainda a sua relação com a radioatividade natural. As áreas da Península Ibérica que apresentam uma maior radioactividade natural coincidem com a distribuição do U, Th e K analisados por XRF. As regressões apresentadas para a Península Ibérica possibilitaram o melhor conhecimento acerca das variáveis que influenciam a distribuição do urânio nos solos analisados. Os resultados mostram que apesar do urânio ser o mais importante entre os elementos que são naturalmente radioativos e a sua distribuição ser de grande importância, tanto em termos de potencial perigosidade como potencial económico, o principal registo deste estudo foi a diferença entre os métodos analíticos utilizados (XRF e aqua regia) relativamente ao potássio.

Palavras-chave: Península Ibérica, urânio, tório, potássio, solos de poisio.

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1. Introduction

The European Chemicals Regulation REACH (Registration, Evaluation and Authorisation of Chemicals) implemented in 2007, required new harmonized data from organizations to provide reliable studies on risk assessment for food production safety. In order to obtain consistent data, Eurometaux contracted the Geological Surveys of Europe through the Geochemical Expert Group (GEG) of the EuroGeoSurveys to produce this data. The result of this contract was the Project GEMAS, an Atlas of Agricultural and Grazing Land of (continental) Europe (Reimann *et al*., 2014). Because of the great amount of data produced by the project GEMAS, it is possible to use this data in transnational studies and with different objectives. The low density sampling proved to reduce local noise, providing information of important events, which is not visible at higher resolutions.

Exploration of naturally radioactive elements was extensively carried out in the past but only at local or regional scales and the natural background variations must be understood. The present study shows the Iberian image of U, Th and K in sampled undisturbed soils (at least for some years) based on GEMAS project data for all Europe. Multiple regression analysis was performed to test the differences between natural radionuclides in superficial soils and its distribution in total and partial extraction in comparison with total natural radioactivity.

2. Materials and methods

Samples were collected in the Iberian Peninsula in 239 locations (Fig.1), from land under permanent grass cover ("grazing land" - Gr, topsoil 0-10 cm). The GEMAS project contemplates a sampling density of 1 composite sample/2500 km^2 (50 x 50 km grid), essentially all taken in the autumn 2008. All samples were sieved to <2 mm and ground to less than 63 µm in a central laboratory (Geological Survey of the Slovak Republic) for analysis by wavelength dispersive X-ray fluorescence spectrometry (WD-XRFS) using PANalytical PW2400 and AXIOS WD-XRFs, with Cr and Rh anode X ray tubes, respectively, at the German Geological Survey. The same elements were analyzed at ACME Lab (Canada) by ICP-MS after extraction by aqua regia (AR). A weight of 15 g of the sieved mineral soil samples (<2 mm) were digested in 90 ml aqua regia and leached for one hour in a hot (95 ºC) water bath. As Kisser (2005) discusses, the AR method is more likely an extraction procedure than a digestion. Chemical Index of Alteration, corrected with apatite and calcite (CIA %; Nesbitt and Young, 1982), normalized sand, silt and clay, CEC (meq), pH ($CaCl_2$), TOC (wt %), P (mg/kg) were also determined. The projects field manual and three quality control reports can be downloaded from the internet (http://www.ngu.no/).

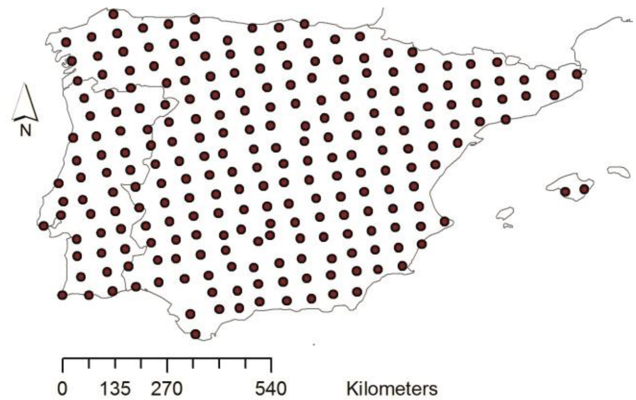

Fig. 1. Grazing land soil sampling locations in the Iberian Peninsula.

Fig. 1. Localização da amostragem de solos de pousio na Península Ibérica.

Sampled soils were related with the source parent material (PM) to which were given different significance levels. PM was classified in the following groups adapted from Günther (2013) and adjusted to the substrate of the Iberian Peninsula: other: undefined parent material; quartz: SiO_2>75 % (quartzites, coarse sandy deposits); org: TOC>5 %; green: greenstones, ophiolites etc.; chalk: calcareous rocks; granite: granite; schist: schist. In each agricultural sampling site the PM was registered and since in the Iberian Peninsula the grazing land samples were collected in the same lithologies as the agricultural sites, the same categorization is used in this study.

A multiple regression analysis was performed using as predictors the U, Th and K, each at a time, using stepwise regression both for total concentrations determined by XRF and also by ICPMS (aqua regia (AR)) using STATISTICA 12.0 (StatSoft).

The set of studied variables were chosen by the affinity with felsic igneous parent rocks, where radionuclides have, in general, higher concentrations. This was tested by Principal Components Analysis. The selected variables were Al, Ce, Cs, Fe, Hf, K, La, Pb, Rb, Sc, Si, Sn, Th, U, Y and Zr.

For the Multiple Regression Analysis (MRA) parent material were coded as: zero for "other"; one for "chalk"; two for "green+schist"; six for "granite+quartz+org". This grouping of PM's was based in the affinity of U, Th and K to these parent materials.

Data were log transformed because apart from grain size distribution (sand, silt and clay) that were normally distributed populations and Si, Al and pH in total analysis (XRF) that were bimodal distributed populations, the rest of the elements were close to lognormal distribution.

3. Results and discussion

The geochemical distribution of U, Th and K in the grazing land soils of the Iberian Peninsula is mainly controlled by lithology, element mobility, and redox conditions (Fig. 2). The three radionuclides are preferentially included in igneous rocks minerals, especially U and Th (Killeen, 1979). The mobility of U in superficial environment is governed by the formation of the uranyl ion UO_2^{2+}, which is responsible for its solubility in a wide range of soil pH. Its immobilization as uranyl ion (UO_2^{2+}) depends on the formation of soluble phosphates, vanadates, arsenates and carbonates or oxide precipitates, and by adsorption on clay minerals and organic matter (Finch and Murakami, 1999).

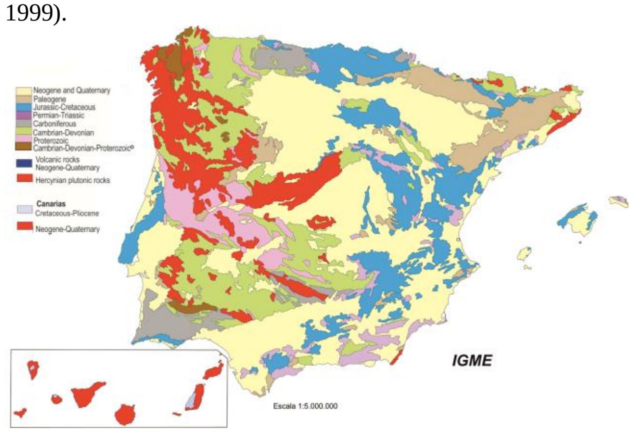

Fig. 2. Geological sketch of the Iberian Peninsula.

Fig. 2. Esboço geológico da Península Ibérica.

This is patent in general when the anomalous area is greater than the most probable source, the granitic intrusion or adjacent metasediments (Fig. 2), meaning it is displaced from the source. Comparing partial extraction AR and total analysis XRF, the latter, a total analysis, seems to better depict the anomaly source related with the parent material (Fig. 3b).

Thorium, although having similar host primary mineralogy as U, in the superficial environment only appears in the tetravalent state which decreases its mobility because it is readily adsorbed and not easily oxidized and mobilized. Its distribution is fairly limited to the variscan intrusive granites of the Peninsula (Fig. 3c and d).

In general, K distribution is related with the felsic igneous parent rock, but this is only visible using total concentrations (Fig. 3d). When aqua regia extraction analyzed samples are displayed on the map a different feature appears especially in the northern part of the Betic Belt in southern Spain (Fig. 3c), an area of evaporitic sedimentation (Locutura *et al.*, 2012). The K element can be hosted, apart from the rock forming silicate minerals, by sulfates or chlorides.

To verify if distribution of the radionuclides depends on the analytical method, predictors of U, Th and K were determined, using independent variables (Fig. 4). The variables used were selected by their affinity to felsic rocks; those not used in the regression were either not introduced or introduced with no significant importance.

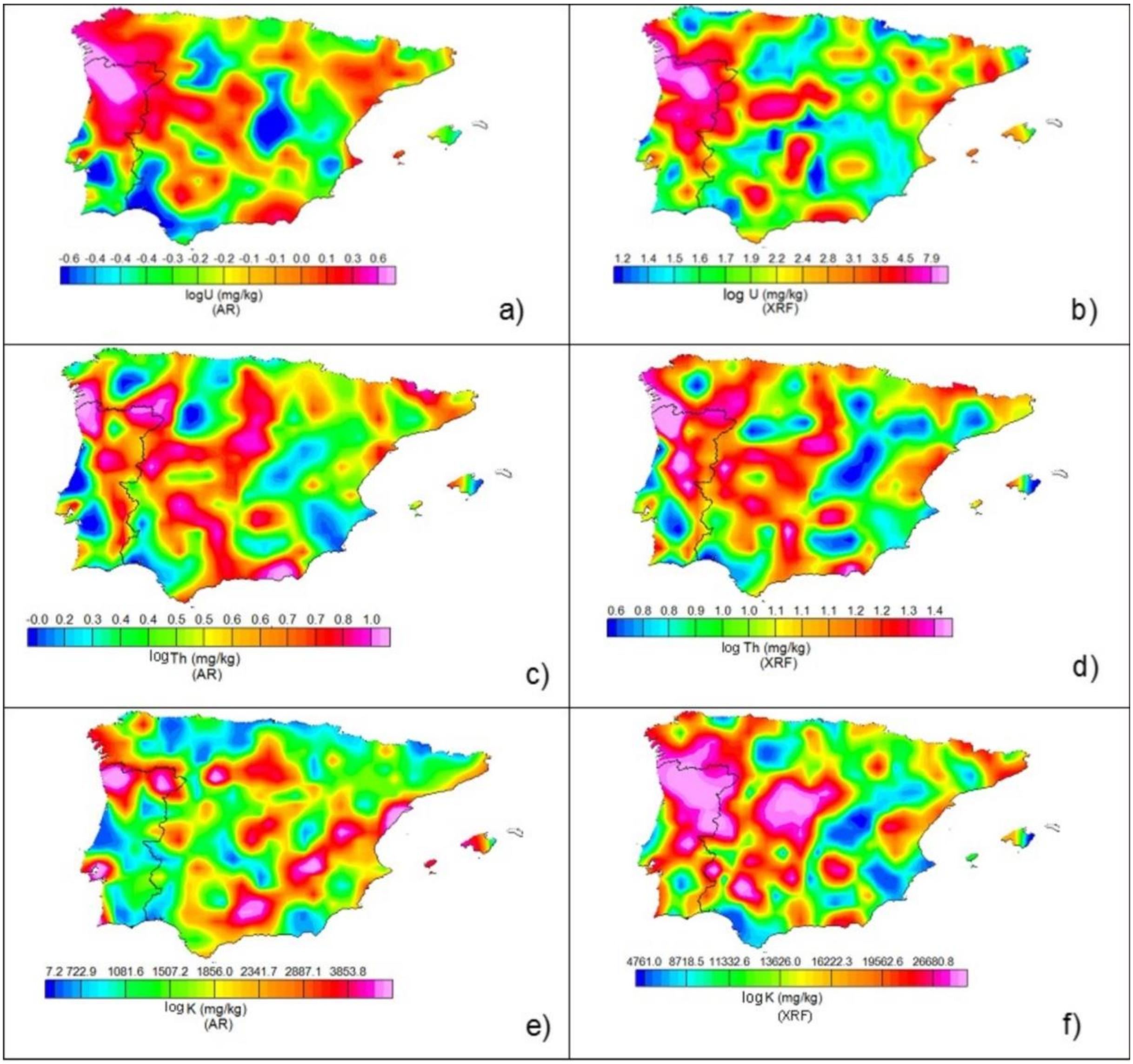

Fig. 3. U, Th and K concentrations of sampled grazing land soils in Iberian Peninsula: a) U analysed by ICM-MS-aqua regia; b) U analysed by XRF; c) Th analysed by ICM-MS-aqua regia; d) Th analysed by XRF; e) K analysed by ICM-MS-aqua regia; f) K analysed by XRF.

Fig. 3. Concentrações de U, Th e K das amostras de solos de poisio na Península Ibérica: a) U analisado por ICP-MS-aqua regia; b) U analisado por XRF c) Th analisado por ICP-MS-aqua regia; d) Th analisado por XRF e) K analisado por ICP-MS-aqua regia; f) K analisado por XRF.

The differences in coefficient of determination (R2 adjusted) for U by analytical method may be justified by the lower variability of data observed by XRF, due to the higher detection limit and elements interference. The elements introduced in the model correspond, in XRF, to elements obtained from accessory minerals where U and Th were introduced in the late stages of crystallization, resistant to erosion but also in the superficial materials, resulting from the weathering of granitic rocks into clay material (Fig.4b, d). On the other hand, the parameters introduced in the predictive U by aqua regia, delimit more pronouncedly a surrounding area of mobilized elements that can also be related with the compounds formed by uranyl (Fig. 4a). The case of K reveals the differences between analytical methods (Fig. 5). Extraction of K by aqua regia allows isolating that K from sedimentary formations in Spain, more easily extractable while XRF analysis continues to exhibit the granitic origin. The total natural gamma radioactivity signature of Portugal and Spain is available at national basis (Batista *et al.*, 2013; Suárez *et al*., 2000) with 840,000 and 1,500,000 radiometric measurements respectively (Fig. 6). Total natural radiation is higher in Variscan granitic intrusions and the predicted U and Th (XRF and AR) and K (XRF) shows consistency with the radiometric distribution in the Iberian Peninsula (Fig. 6). This must be due to the fact that the variables used to predict radionuclides concentrations reduced the effect of dispersion of the anomalies, an outcome that was present in the U observed (AR) (Fig. 3a). Predicted K (AR) is not well depicted in the radiometry map. This extraction does not show the totality of K in the samples and therefore, the resistant granite related minerals (Fig. 5a).

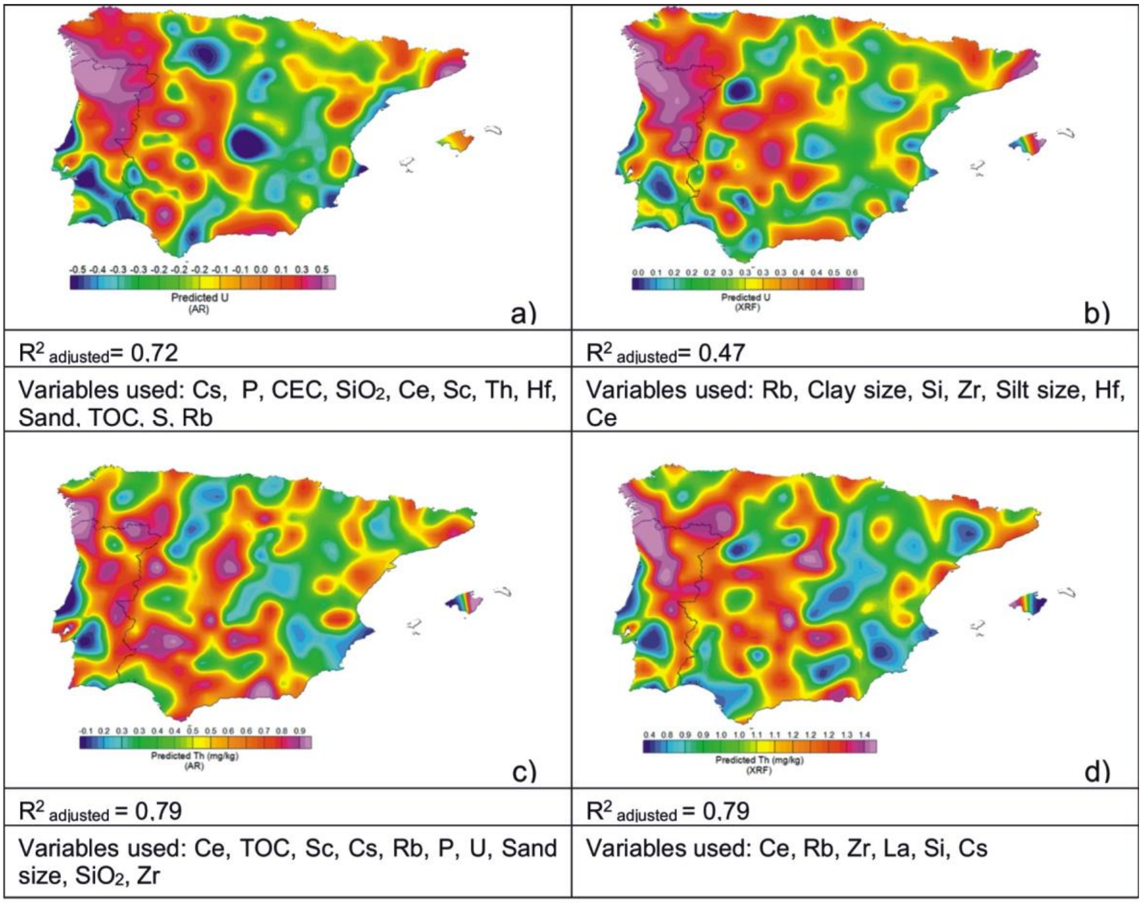

Fig. 4. U and Th prediction maps: a) predictive U (AR); b) predictive U (XRF); c) predictive Th (AR); d) predictive Th (XRF). Variables used to construct the predictive maps are in order of importance.

Fig. 4. Mapas de estimação para U e Th: a) U (AR) estimado; b) U(XRF) estimado; c) Th (AR) estimado; d) Th (XRF) estimado. As variáveis usadas para contruir os mapas de estimação encontram-se por ordem de importância.

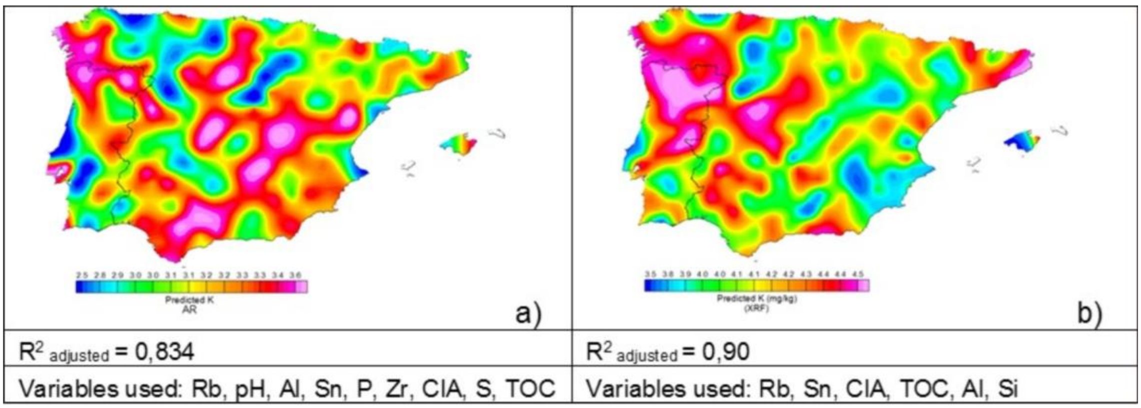

Fig. 5. K prediction maps: a) predictive K (AR; b) predictive K (XRF). Variables used to construct the predictive maps are in order of importance.

Fig. 5. Mapas de estimação para K: a) K (AR) estimado; b) K (XRF) estimado. As variáveis usadas para contruir os mapas de estimação encontram-se por ordem de importância.

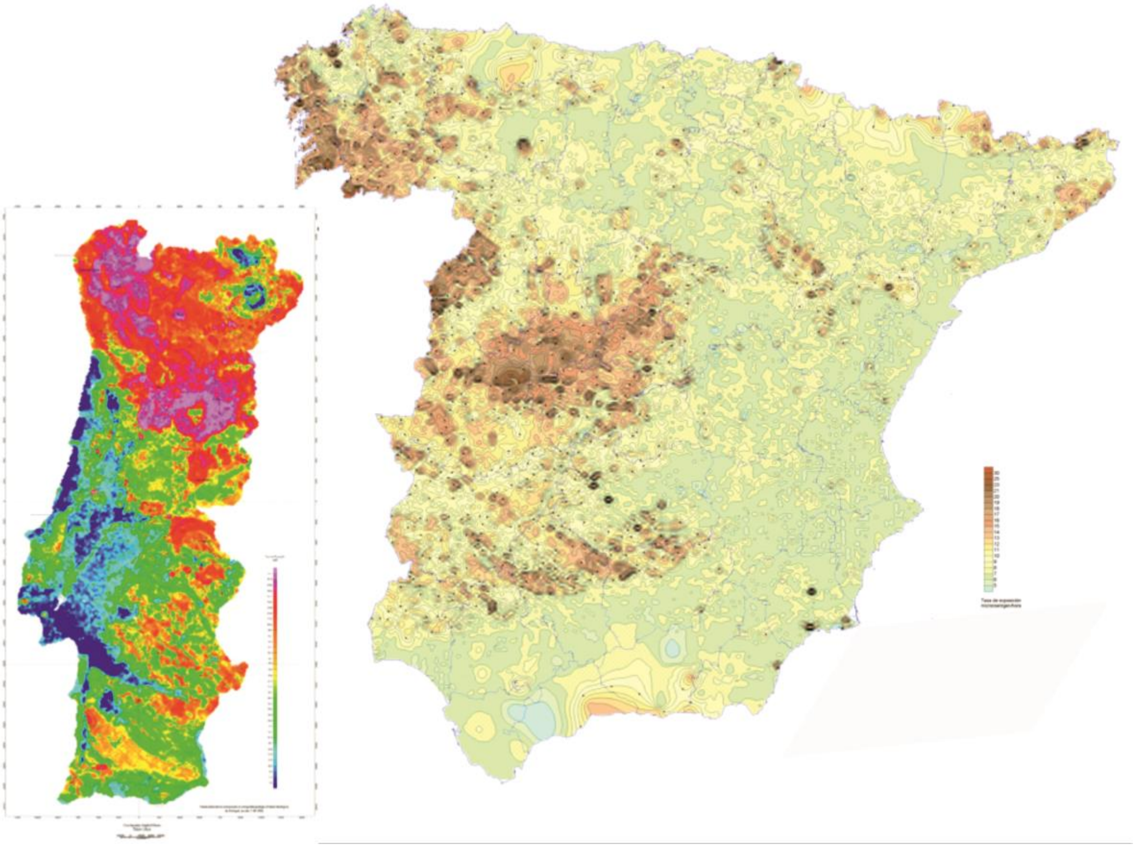

Fig. 6. Total natural radioactivity in the form of exposure rate: a) Portugal total count (nG/h) (Batista *et al*., 2013) and b) Spain total count (µR/h) (Suárez *et al*., 2000).

Fig. 6. Radioactividade natural total na forma de taxa de exposição: a) contagens totais para Portugal (nG/h) (Batista *et al*., 2013) e b) contagens totais para Espanha (µR/h) (Suárez *et al*., 2000).

4. Conclusions

Although U distribution in soils is a major issue to understand hazard and economical potential, the differences between analytical methods in K distribution were a relevant result. Naturally high radioactive areas of the Iberian Peninsula are well represented using the XRF method maps, but the two methods applied show the different grouping between more mobile and easily extractable elements and those included in the more weathering resistant minerals. The regression exercise undertaken for the Iberian Peninsula allowed a better understanding of which variables influence U, Th and K distribution and the use of independent variables allows understanding the natural associations of radionuclides. While for U and Th mobility is vastly controlled by the oxidation state, for K the analytical method used is a key factor. These results are in line with those from more densely sampled campaigns, as in Spain, or from total gamma radiation mapping in the Peninsula. A similar exercise could be applied to the European data available at the GEMAS project.

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