ASSESSING TRACE ELEMENT DISTRIBUTION IN NATURAL TOP-SOILS WITH GEOLOGICAL MAPS: CATALONIA CASE STUDY

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INTRODUCTION

Baseline environmental geochemical data are necessary to inform policy and to provide a sound basis for land use purposes. Data on geochemical baselines are urgently needed in Europe, because environmental authorities are establishing levels for contaminants in soils (Darnley, 1995, Salminen et al., 2005).

Natural concentrations of elements in soils vary markedly between disparate areas. This is because soils are openend systems subjected to several factors (climate, organisms, topography, parent material, time and anthropogenic influence) (Adriano, 2001; Drever, 2003). Chemical and physical weathering of crustal rocks and soil formation processes involve mass transfer of material into or between parent material. However, it is expected that those soils that had not been significantly transported preserve to a certain extent the geochemical signature of the unweathered rocks that overlies. If this is true, geological maps can be a useful tool to predict trace element distribution in soils.

In this work we asses by the applicability of the previous reasoning comparing the trace element composition (As, Cd, Co, Cu, Mo, Ni, Pb, Sb, Sn, V, Tl, U and Zn) of 203 representative samples of the top-soil from Catalonia (NE Spain) with the geological map of Catalonia 1:250.000 scale.

SAMPLING AND ANALYTICAL PROCEDURES

Sampling points were chosen according to random systematic sampling (Gilbert, 1987) design planned by using Geographic Information Systems. Firstly, in order to place the natural sampling points, the territory object of this study was divided into 203 squared cells 13 km side (Fig. 1). In a first stage of the sampling design, one sampling point was placed randomly inside each cell. Sampling exclusion areas were defined around zones potentially affected by anthropogenic activities using the software ArcGIS and the cartographic layers provided by Departament de Medi Ambient and Institut Cartogràfic de Catalunya. The excluded areas and the associated buffer zones have been: industrial and urban areas (400 m), landfill sites (250 m), wet zones (0 m), major roads (200 m), secondary roads (50 m) and working and disused mining zones (100-50 m). Samples initially located inside an excluded zone were relocated.

Top-soil samples were taken from 5-10 cm to 30 cm depth, excluding material from the organic layer. First, surface vegetation, large roots and rock fragments were removed by hand and the top-soil samples were homogenized inside a plastic bag. Then the samples were transfered to a 500 ml plastic containers leaving the minimum volume of air.

Prior to analysis, samples were dried at 38ºC and were screened with a sieve shaker in order to discard the fraction > 2mm. Trace element concentration (As, Cd, Co, Cu, Mo, Ni, Pb, Sb, Sn, V, Tl, U and Zn) was determined by ICP-MS after microwave digestion with ultrapure HNO_3 and HF acids following the EPA (2000) guidances. Several isotopes were monitored in order to check for possible interferences. In addition, pH, humidity, loss on ignition, carbonate concentration and cation exchange capacity of soil were also determined.

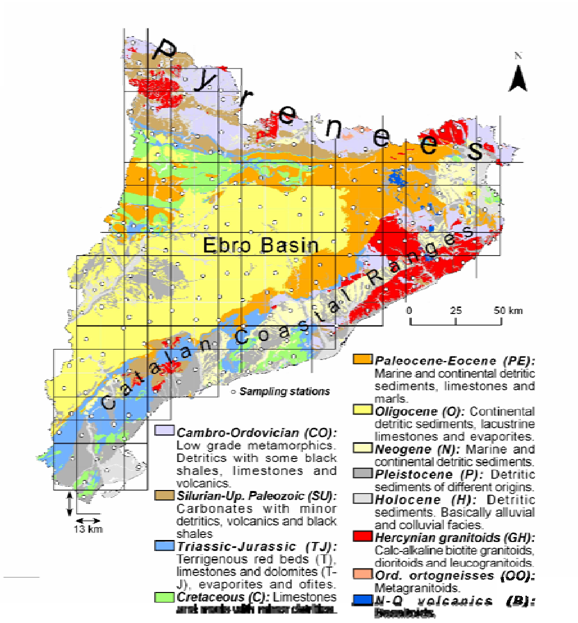

Figure 1 - Top-soil sampling design over a synthetic geological map derived from the geological map of Catalonia 1:250000 scale.

GEOLOGY OF CATALONIA: GEOLOGICAL UNITS ASSIGNMENT TO TOP-SOIL SAMPLES

Three main geologic domains can be distinguished in Catalonia: (i) the Central and Eastern sectors of the Southern limb of the Pyrenean Orogen that define the northern margin (ii) the Catalan Coastal Ranges that define the southeastern margin and (iii) the eastern sector of the Ebro Basin, closely linked to the structural development of the Pyrenean Orogen and the Catalan Coastal Range during the alpine orogenesis, that define the central domain (Fig. 1). Besides these three main domains it should also be mentioned the small basins developed in the Eastern Pyrenees (Cerdanya and Empordà) and the Catalan Coastal Ranges (Selva, Vallès-Penedès, Camp de Tarragona, Móra and Baix Ebre) which are linked to the extensional textonic regime and the magmatism that affects the Western Mediterranean since neogene times.

In this sector the Pyrenees present a complex structure involving a paleozoic basement composed of sedimentary, metamorphic and igneous rocks, and a cover which includes mesozoic and cenozoic sedimentary sequences deposited before and during the Pyrenean Orogen.

The Catalan Coastal Ranges are composed of Hercynian basement unconformably overlain by a sedimentary cover of Triassic to Cretaceous carbonates, terrigenous red beds, and evaporitic deposits.

The Paleozoic basement in both alpine units belong to a relatively external zone of the southern flank of the West European Hercynides. The deepest tectonic levels suffered low-pressure/high-temperature metamorphism linked to the Hercynian Orogen. Contemporaneously, large bodies of granitoids were emplaced at different structural levels as plutonic complexes.

In broad outline the fill of the eastern Ebro Basin consists of a thick pile of paleogene sedimentary rocks that can be grouped into coarse to fine-grained alluvial facies, fine grained alluvial lacustrine facies and marine facies composed by marls, limestones and calc-arenites.

The neogene basins are infilled basically by alluvial and transitional sediments. In the NE Catalonia there is a small volcanic (basaltic) province related to the development of these young extensional basins.

Quaternary deposits, cover heterogeneously Catalonia obscuring the bedrock geology. They range from soils and weathered bedrocks to sediments of alluvial, fluvial, colluvial, lacustrine, glacial, aeolian, coastal, estuarine and marsh origin. The distribution of such deposits in time and space is highly influenced by the quaternary climatic oscillations (glacial and interglacial periods).

The analysed top-soil samples were superimposed over the geological map of Catalonia 1:250.000 scale (Losantos et al., 2004). This map distinguishes 229 geologic units based on chronological and lithologic criteria. Each sample has been linked with a geologic unit according to its geographic position. Then, taking into account the geology of bedrock, the top-soil samples and the geologic units of the 1:250.000 geologic map, 20 representative geologic units were defined in order to analize the trace element distribution in Catalonia (Figures 1 and 5).

RESULTS AND DISCUSSION

As can be seen on the spider diagram (Fig. 2), the mean and the median Cd, Co Mo, Ni, Pb, Tl, V and Sn concentration of the top-soil from Catalonia are similar than the world average soil concentration proposed by Reimann & Caritat (1998). The average top-soil composition in Catalonia is slightly enriched into As and Sb and depleted into Cu, Sn i U with respect to the average for soils worldwide. The compositional range that define the mean and the median of the top-soils from Catalonia bears a resemblance to the compositional range that defines the mean and the median of the top soils from the whole of Europe according to Salminen et al. (2005).

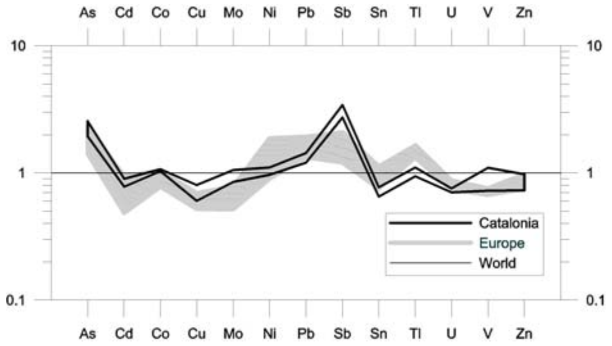

Figure 2 - World average soil normalized (Reimann & Caritat, 1998) trace element patterns of the mean and median composition of top soil from Catalonia (this study) and Europe (Salminen et al., 2005).

For each representative geologic unit mean, median, standard deviation, 90% percentile, maximum and minimum concentration values for trace elements were computed and the trace elements spatial distribution was assessed with dot and contour maps (Fig. 3).

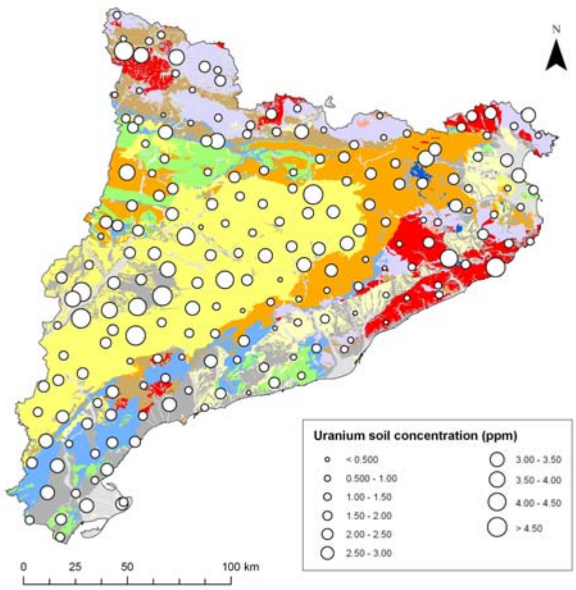

Figure 3 - Dot map of U of the top soil of Catalonia.

As can be seen in the case of U (Fig. 4), compositional ranges of the representative geologic units present an important scatter and there are considerable overlaps between them. However, trace element distributions obtained are comparable to the predictable compositional ranges of the geologic units from their characteristic lithotypes (Reimman and Caritat 1998; Drever, 2003; Adriano, 2001; Rudnick and Gao, 2003).

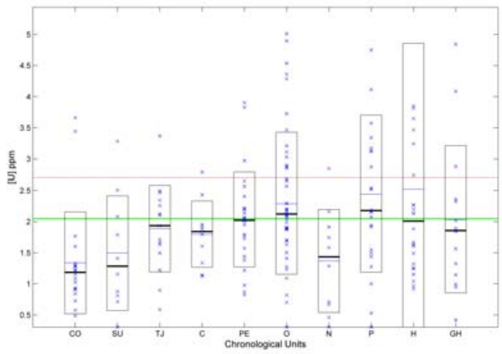

Figure 4 - Distribution of U in the different chronological units defined in the Figure 1. Mean (thin lines), median (thick lines) and standard deviation values (box limits) were represented for each chronological unit. Global mean value (thick) including all samples was also calculated. World average value (thin) was obtained from Reimann & Caritat (1998).

Figure 5 shows, in a schematic way, the relationships between the top-soil trace element concentration and the geology of bedrock. Briefly, it can be noticed that:

- Hercynian granitoids are depleted in As, Cd, Co, Cu, Mo, Ni and Sb and are enriched in Pb, Sn, Tl and U.
- Cambroordovician sequences are enriched into As, Co, Cu, Ni, Tl, V and Zn and are depleted in U. 3) Units composed by sedimentary rocks (mainly mesozoic and cenozoic) show closer concentrations to the median value of the whole dataset.
- Cartographic units enriched into carbonatic rocks don't show a different compositional pattern than the rest of sedimentary units.
- Unit LDM is slightly enriched in Cd.
- Unit DML is slightly depleted in Tl, V i Zn.
- Unit SE show lower concentration median values for Pb and Tl.
- Unit SLM have higher concentration mean values for Mo and Sb.
- Unit HM show concentration mean values closer to the median of the whole dataset.
- With the exception of U, units that define quaternary sediments show compositions close to the median of the whole dataset.

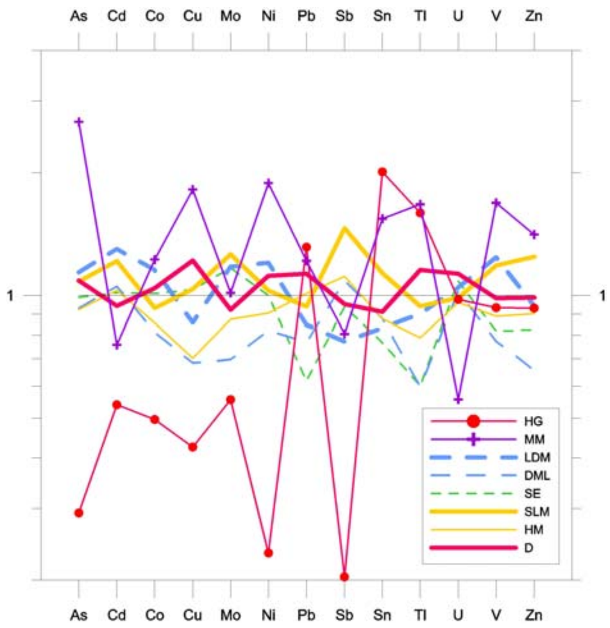

Figure 5 - Catalonia median soil normalized trace element patterns of soils of the different lithologic units. Hercynian granitoids (HG. Calc-alkaline biotite granitoids, mainly granodiorites ans monzogranites often bearing hornblende or muscovite, coexisting with small stocks of dioritoids and gabbroids). Metapelites and metasandstones (MM. Cambro-Ordovician without Upper Ordovician units, mainly low grade metamorphics). Limestones and/or dolomites (LDM. Devonian, Mesozoic and Eocene). Detritic sediments with marls and limestones (DML. Tertiary). Sedimentary rocks with evaporites (SE. Triassic and Oligocene). sandstones and lutites of mixed composition (SLM. Upper Ordovician, Upper Paleozoic and Tertiary). Heterogranular detritic sediments of mixed composition (HM. Tertiary). Drift sediments (D. Quaternary sediments).

Results indicate that indeed the trace element compositions of the top-soils are highly influenced by the lithotypes that overlay. This fact has permitted us to compute different trace element maps by means of representative geologic units derived from the geological map of Catalonia 1:250.000 scale. Area weighted mean values for a squared 5 km side cell layer have been computed from relevant statistic parameters (mean, median, 90th percentile,etc) of the geologic units defined using ArcGis 9.0. These weighted mean values were assigned to the centroid of each cell and a spline interpolation method was used to create trace element maps. Figure 6 show the results for the case of U mean values related to the geologic units from Fig. 1.

CONCLUSIONS

The analysis of the whole of the data reveals the dependence existing between the trace element composition of the top-soil and the geologic units. This relationship makes clear that geologic maps are useful and necessary tools to predict spatial trace elements distribution.

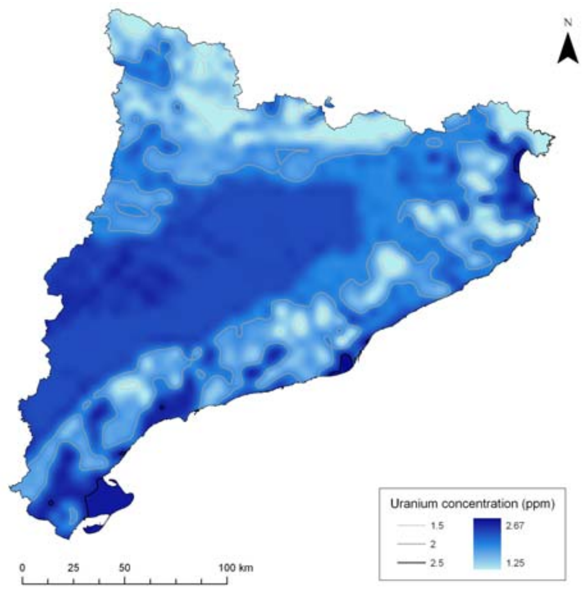

Figure 6 - Map of Uranium distribution in Catalonia.

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