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# Approaching earth surface geochemical variability from representative samples of geological units: The Congost River basin case study

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## ARTICLE INFO

## ABSTRACT

Geochemical reference levels are necessary preliminary steps for appropriate environmental legislation, especially in the assessment of management of soil pollution and protection measures. The problem of establishing reference levels in areas with variable basic geology and anthropogenic pressure is addressed by characterising the geochemistry of 82 representative samples of the geologic materials of the Congost River basin (NE Iberia). The samples have been grouped in a system of 12 operative geochemical units comprising the entire area of the basin. The 'total' and 'partial' concentrations of 54 chemical elements have been determined. The geochemical variability has been discussed by means of statistical methodologies, diagrams and GIS techniques.

The analysed samples reveal that the composition of the Congost catchment is highly varied. The differences between the 'total' and 'partial' concentrations define complex patterns reflecting the mineralogy of samples. The results indicate that bedrock geology is the most important factor influencing the major and trace element distributions in the basin. Pb and Zn were observed to be enriched in units more exposed to pollution than their parent materials. In general, the defined operative geologic units are characterised by different major and trace element compositional ranges as a consequence of their lithological diversity. The fact that the samples have been linked to a system of regional geological units allows the geochemical comparison of materials from the Congost River basin with other reference materials from neighbouring areas, or worldwide. For such an approach, we have focused on the geochemistry of the Pleistocene detritic sediments. We close the study by proposing that a good way of expressing the geographic distribution of the geochemical variability of a region could be to apply geologic extrapolation of three representative statistics, an average value (the 50th percentile), a low value (the 25th percentile) and a high value (the 75th percentile). As an example, we present the Th maps, which permit the clear discussion of the Th distribution in the basin.

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## 1. Introduction

The Earth has a problem of historical contamination of soil due to the use and presence of dangerous substances in many agricultural, industrial and urban activities and the widespread use of motor vehicles. Though difficult to estimate, several studies demonstrate significant annual costs of European soil contamination in the range of 2.4–17.3 billion Euros per year (e.g., Commission of the European Communities, 2006). The relevant environmental authorities are establishing reference levels of the chemical elements that make up the Earth's surface at supranational, national and regional scales. These reference levels are generally based on statistical analysis of geochemical mapping datasets.

Geochemical mapping studies are necessary at different scales because the distribution of chemical elements on the Earth's surface is heterogeneous and discontinuous. This is a result of a large number of variables, such as the geological substratum, the geomorphological context, the natural superficial geological processes and anthropogenic activity (e.g., Appleton and Adlam, 2012; De Vos et al., 2006; Martínez-Lladó et al., 2008; Matschullat et al., 2000; Reimann and Caritat, 2005; Reimann and Garrett, 2005).

The composition of the different geological materials that define the Earth's surface changes from point to point. As a preliminary step, geological maps can be used to visualise such changes because in many cases the different lithologies that compose the crust can be distinguished from a geochemical point of view. Nevertheless, these three points should be considered: a) only some major elements are determinant variables to classify rocks, b) the elemental concentrations of a lithotype are variable and in many cases are better defined with a compositional range than a single average value and c) geological map units are usually composed of more than one lithotype.

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The sample media selected for a regional geochemical mapping should represent the composition of the surface environment and, thus, should be easily available. The most widely used media, because of their availability and representativity, are active stream sediment, regolith (including weathered rocks and saprolite), residual soils, flood-plain sediments and anthropogenic soils. The diversity of each sample
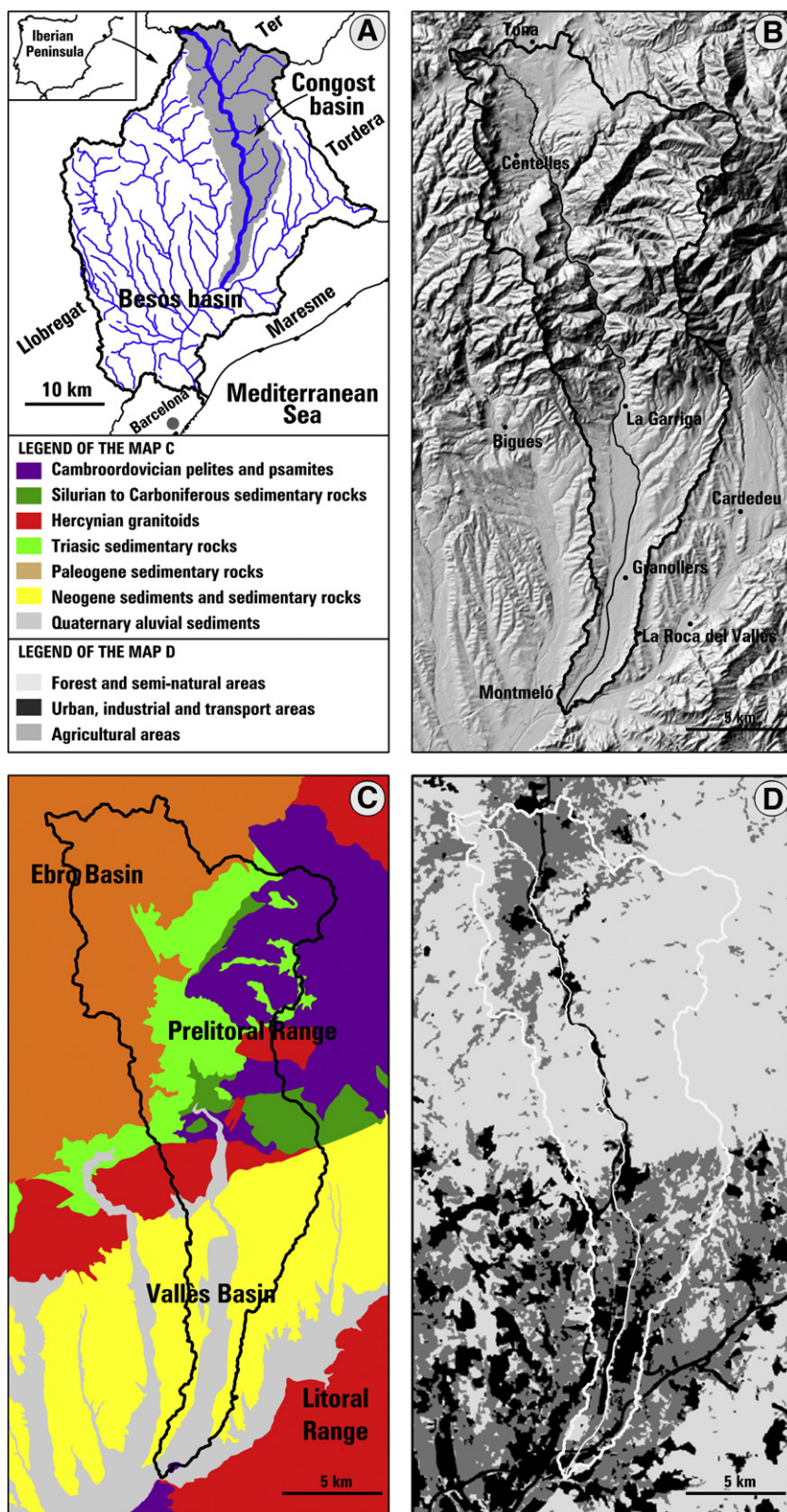


**Fig. 1.** A) Location of the Congost River basin. B) The shaded relief map of the Congost basin derived from the 15-m grid size digital terrain model of the Institut Cartografic de Catalunya. C) Regional geological map of the Congost basin derived from the 1:50,000 digital geological map of Catalonia from the Institut Geològic de Catalunya. D) Land cover map of the Congost basin derived from the Centre de Recerca Ecològica i Aplicacions Forestals.

medium is closely related to certain inherent characteristics. Active stream sediment and floodplain sediment samples are representative of the average geochemical composition of the entire catchment basin above the sampling site. Residual soil and regolith are essentially the product of the weathering of the underlying rocks; consequently, such samples are representative of a very restricted area, and neighbouring samples may differ considerably from each other. In areas where the original natural surface has been extensively remodelled by human activities, the sample media used are anthropogenic soils. It is important to emphasise that the Earth's surface is exposed, to a greater or lesser extent (especially since the start of the Industrial Revolution in the 18th century), to urban, industrial, agricultural and other anthropogenic activities which do change the composition of the environment. Even in areas of little anthropogenic activity, surficial samples can be influenced by environmental pollution. In some cases, an effective strategy to minimise the anthropogenic influence is to collect deep samples such as subsoils (i.e., below 25 cm deep).

For a compositionally homogeneous parent material, the composition of the derived soils and sediments can present high variability due to of differential weathering, erosion, denudation, transport and deposition. This geochemical differentiation, from parent material to soil and sediment, depends on the nature and chemistry of the weathered material. Furthermore, the interaction of superficial deposits with the atmosphere, the hydrosphere and the biosphere varies from place to place. For any given study area, the analysis of representative fresh samples of the geologic cartographic units is a key factor in understanding such surficial geochemical processes. Sampling strategies guided by geological knowledge allow such an exhaustive analysis of the data and contrast with a random sampling strategy, which gives a priori more neutral values.

Aside from the typology of the geologic material sampled, the utility of a geochemical mapping study applied to a particular environmental problem is conditioned by other factors such as the boundaries of the study area, the sampling protocol, the sample fraction to be analysed and the analytical method being used (e.g., Albanese et al., 2008; Darnley et al., 1995; Johnson and Ander, 2008; Salminen and Tavarnien, 1997; Salminen et al., 2005; Tarvainen and Kallio, 2002).

Depending on the objective in view, the geographic limits of geochemical mapping surveys could be administrative boundaries, cartographic grids, geological units or physiographic domains (e.g., catchment basins).

The reference geochemical concentrations of a specific site may vary depending on the limits of the geochemical mapping survey. This is because the geochemistry of a specific area of the Earth's surface is influenced by processes that take place outside the study area.

As far as possible, each sample should be homogeneous. This can be achieved by different sampling strategies, each of which will influence the results. For example, in some geochemical soil studies, inhomogeneities are minimised by assembling each sample from a composite of various sub-samples (usually three to five) collected from pits located at a variable minimum distance (5 to 20 m).

As well as the homogeneity of the whole sample, it should be considered that the composition of the different components is not necessarily similar. For several reasons, in some cases just a fraction of the sample is analysed. For instance, as regards sediment and soil samples, often only the <2 mm fraction is analysed. It is evident that the grain size analysed is going to have a basic influence on the average background values obtained.

Several analytical methods are available for regional geochemical mapping, depending on the final objective. Total analysis (by X-ray fluorescence, instrumental neutron activation or inductively coupled plasma after total digestion) gives absolute element concentrations and a true picture of the natural relationships of elements in the sample analysed. For many practical purposes, however, methods based on a partial leach, in which only a soluble part of the element is extracted and measured, are preferred. Examples of partial leaching are the *aqua regia* attack, giving, as a result, the extractable element concentration, or the EDTA attack, giving, as a result, the bioavailable element concentration. Therefore, it is very important that the method of analysis is considered when comparing geochemical reference values.

In this paper, we present a geochemical mapping survey of the Congost River catchment basin (NE of Iberia Peninsula) to highlight the major and trace element compositional variabilities of the geological materials of the basin, with average and confidence interval values. In
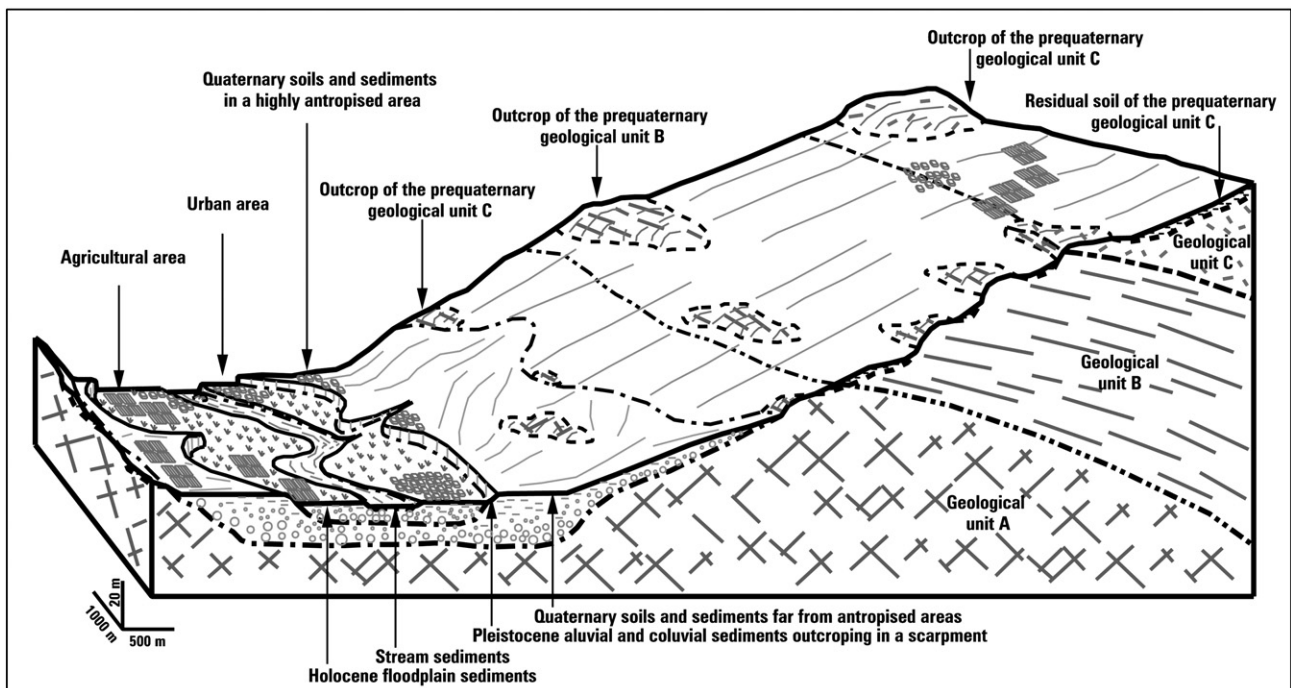


Fig. 2. Conceptual model of a sector of the study area, based on Salminen et al. (2005) and Strahler (1969), showing the different types of geological materials that constitute the ground surface.

order to do so, our methodology was based following considerations: a) a sampling survey guided by knowledge of the geology and land use of the study area, b) the analysis of representative samples of the different geological materials that constitute the ground of the basin (i.e., rocks, sediments and soils) and c) the determination of the total and partial (*aqua regia* digestion) concentrations of 56 elements.
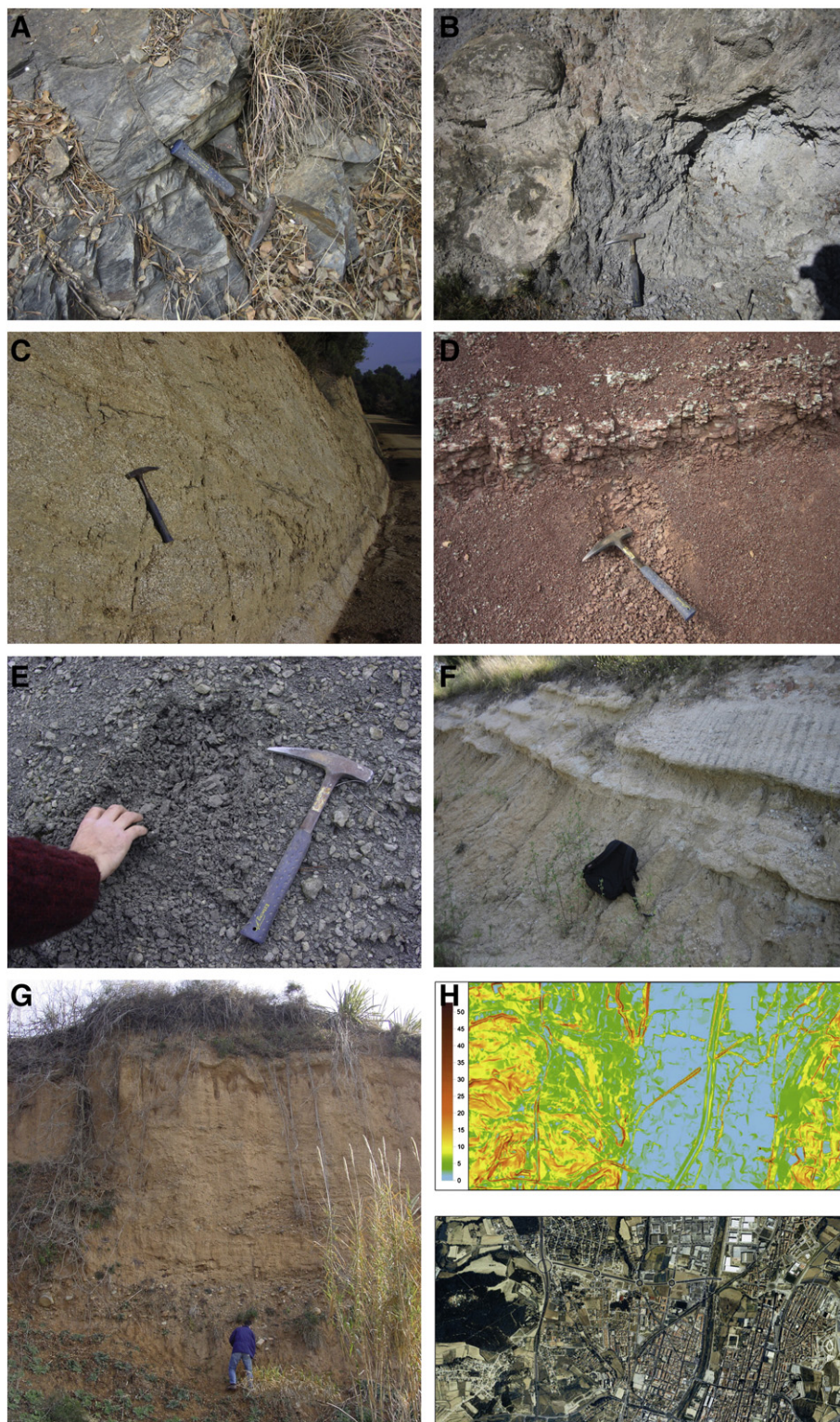


**Fig. 3.** Representative details of the sampled geological units: A) pelitic slates of the CO unit, B) Silurian massive limestones and very deformed black shales (unit SDC), C) weathered grano-diorite (unit G) outcropping in a road slope, D) lutites from Buntsandstein facies of the T unit, E) Eocene grey marls of the P unit, F) Tortonian unconsolidated lutites with intercalations of arkosic sandstones of unit N, G) Pleistocene sediments (P unit) outcropping in a 10-m high escarpment defining the boundary of the Congost River Holocene floodplain (QH), and H) slope map (top image) and orthophotograph (bottom image) showing a highly urbanised area of the Congost River Holocene floodplain.

## 2. Study area

The Congost River, located in the northeastern portion of the Iberian Peninsula, is a tributary of the Besòs River, which reaches the Mediterranean Sea at the north side of the Barcelona metropolitan area (Fig. 1). The Congost River has a catchment area of 225 km²; from north to south, it crosses three main morphodynamic units: the eastern margin of the Ebro Basin, the Prelitoral Range and the Vallès Basin (IGC-ICC, 2010; Roca et al., 1999).

The Ebro Basin represents the foreland basin of the Pyrenees, the Catalan Coastal Ranges and the Iberian Cordillera (López-Blanco, 2002). The part of the Ebro Basin that belongs to the Congost River basin is composed of Paleogene rocks, including sandstones, mudrocks, conglomerates, marls and limestones.

The Prelitoral Range is a relatively high SW–NE relief area which is a part of the NW flank of the Catalan Coastal Ranges (Gaspar-Escribano et al., 2004; Roca et al., 1999). In the transect of the Congost River, the Prelitoral Range includes a sedimentary cover of Triassic red beds and carbonate rocks, overlying a basement of highly deformed metamorphic and sedimentary Paleozoic rocks and Hercynian granitoids.

The Vallès Basin defines a SW–NE oriented lowland related to the Neogene opening of the western Mediterranean Sea (Cabrera and Calvet, 1996). In the Vallès Basin, the ground under the Congost River basin is primarily composed of Miocene alluvial sediments derived from the erosion of the Catalan Coastal Ranges.

The footslopes of the Congost River basin are often covered by thin alluvial and colluvial Pleistocene deposits. In its lower course, the river defines a Holocene floodplain infilled by alluvial deposits.

The land use map in Fig. 1 shows that a relevant percentage of the southern half of the basin is covered by anthropogenic areas. This zone, which is concentrated around the city of Granollers, hosts approximately 100,000 inhabitants and belongs to the metropolitan area of Barcelona. This highly anthropised zone has been subjected historically to intense agricultural activity. In our days, it is part of one of the main industrial areas of Southern Europe, and it is crossed by a great number of important roads that connect eastern Spain with the rest of Europe. Towards the north, the anthropisation decreases and is concentrated in the alluvial valley of the Congost River. In the Ebro basin, where the study area defines a relatively flat highland, there is an extensive agricultural use of the land and an important farming industry.

The Congost River basin is fully covered by the geochemical atlas of Spain, recently published (Locutura, 2012). This excellent survey, which addresses the total concentration (63 elements) as well as the partial concentration (59 elements) of Spain's surficial materials, follows the same methodology developed for the geochemical atlas of Europe (Salminen et al., 2005). The sampling density for soils and stream sediments in this survey is greater than 1 sample/100 km². In the Congost area, there is approximately one sample of soil and one sample of stream sediment per 20 km². Previous geochemical studies have covered the Congost catchment. Martínez-Lladó et al. (2008) refer to the spatial distribution (1 sample/13 km²) of As, Be, Cd, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, Tl, U, V and Zn in soils of Catalonia. Bech et al. (2008, 2011) estimated the spatial distribution (1 sample/5 km²) of Cr, Ni, Cu, Al, Ba, Pb, Ti and V in soils of the Barcelona Province.

## 3. Methodology

We have collected 82 representative samples of the rocks, sediments and topsoils that compose the ground of the Congost catchment. The sampling survey has been guided by a detailed lithological synthesis study of the geological units of the geological map of Catalonia (1:50,000 scale) which can be found in the Congost River basin and surrounding area. As a result of the lithological synthesis, we have decided that, on the surface, the Congost River basin can be compartmentalised into 12 main operative geochemical units. Fig. 2 shows a conceptual model of the study area based on Salminen et al. (2005) and Strahler (1969). It schematically indicates the types of the geochemical units selected. These are the 12 operative geochemical units:

CO — Cambroordovician pelites and psammites. Includes samples of slates, phyllites and hornfels.

SDC — Complex lithological unit that primarily includes Silurian black shales and limestones, Devonian limestones and marls and Carboniferous shales and sandstones.

G — Hercynian granitoids of the Catalan Coastal Ranges, essentially granodiorites, in many cases weathered.

T — Triassic red mudstones and sandstones of the Buntsandstein facies; and limestones, marls, red mudrocks and sandstones of the Muschelkalk facies.

P — Paleogene sedimentary rocks of the Ebro Basin foreland, including continental mudstones and sandstones and marine sandstones, marls and limestones.

PS — Topsoils over the P unit (mud and sand fraction).

N — Neogene moderately consolidated sandstones and lutites of the Vallès Basin.

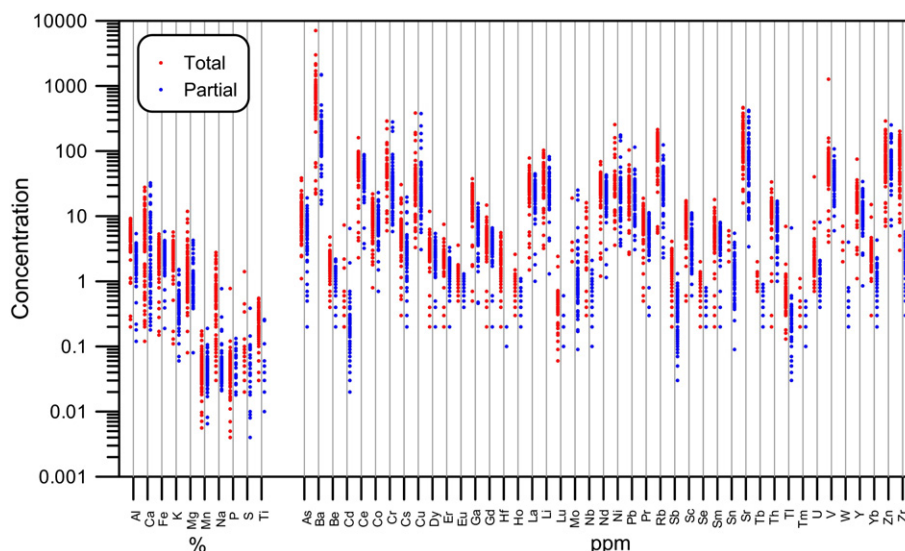NS — Topsoils over the N unit (mud and sand fraction).



**Fig. 4.** Box-plot of major and trace element concentration values for totally and partially digested samples.

**Table 1**

Descriptive statistics of the total digestion analysis. The table includes the median and 90th-percentile compositions of the stream sediments of Europe (Median-StS and Pctl90-StS respectively) obtained by the Geochemical Baseline Mapping Programme (Salminen et al., 2005), and the average composition of the upper crust recommended by Rudnick and Gao, 2003.

| Element | Unit | Count | D.L. | N.S. < D.L. | Min | Pctl 10 | Pctl 25 | Pctl 40 | Median | Pctl 60 | Pctl 75 | Pctl 90 | Max | Mean | Std. Dev. | Median-StS | Pctl90-StS | Upper crust |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As | ppm | 82 | 0.5 | 9 | <0.5 | 1.0 | 5.0 | 8.0 | 9.5 | 10.0 | 14.0 | 19.5 | 38.5 | 10.0 | 7.5 | 6 | 22 | 4.8 |
| Ba | ppm | 82 | 1 | 0 | 22 | 310 | 453 | 581 | 677 | 770 | 921 | 1231 | 7100 | 808 | 852 | 370 | 644 | 628 |
| Be | ppm | 82 | 0.1 | 3 | <0.1 | 0.9 | 1.4 | 1.6 | 1.8 | 1.9 | 2.2 | 2.8 | 4.8 | 1.8 | 0.8 | 1.4 | 3.9 | 2.1 |
| Cd | ppm | 82 | 0.1 | 45 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.3 | 0.5 | 7.3 | 0.3 | 0.8 | 0.29 | 0.82 | 0.09 |
| Ce | ppm | 82 | 0.1 | 0 | 2.3 | 27.9 | 46.4 | 56.6 | 60.6 | 67.1 | 74.0 | 84.0 | 161.0 | 59.5 | 25.2 | 65.1 | 135 | 63 |
| Co | ppm | 82 | 0.1 | 0 | 0.8 | 3.9 | 6.7 | 8.1 | 8.7 | 9.5 | 11.1 | 15.1 | 22.0 | 9.1 | 4.2 | 8 | 21 | 17.3 |
| Cr | ppm | 82 | 1 | 43 | 6 | 12 | 36 | 48 | 53 | 60 | 86 | 128 | 291 | 71 | 66 | 64 | 139 | 92 |
| Cs | ppm | 82 | 0.05 | 0 | 0.30 | 2.30 | 4.05 | 5.10 | 5.55 | 6.05 | 7.25 | 9.05 | 30.50 | 6.30 | 4.50 | 3 | 10 | 4.9 |
| Cu | ppm | 82 | 0.2 | 0 | 3.2 | 9.6 | 18.0 | 24.6 | 26.2 | 29.2 | 39.6 | 55.4 | 385.0 | 37.8 | 50.2 | 17 | 38 | 28 |
| Dy | ppm | 82 | 0.1 | 0 | 0.2 | 2.1 | 2.7 | 3.1 | 3.3 | 3.6 | 3.8 | 4.3 | 11.9 | 3.3 | 1.5 | 4.45 | 8.65 | 3.9 |
| Er | ppm | 82 | 0.1 | 0 | 0.2 | 1.2 | 1.7 | 1.9 | 2.1 | 2.2 | 2.5 | 2.8 | 7.5 | 2.1 | 1.0 | 2.6 | 5.35 | 2.3 |
| Eu | ppm | 82 | 0.05 | 7 | <0.05 | 0.5 | 0.8 | 0.9 | 1 | 1.1 | 1.3 | 1.6 | 3.6 | 1.05 | 0.50 | 0.99 | 1.79 | 1 |
| Ga | ppm | 82 | 0.1 | 0 | 0.5 | 8.5 | 12.2 | 16.5 | 18.0 | 19.3 | 22.2 | 25.7 | 37.6 | 17.5 | 7.8 | 12 | 20 | 17.5 |
| Gd | ppm | 82 | 0.1 | 0 | 0.2 | 2.4 | 3.7 | 4.4 | 4.7 | 5.0 | 5.4 | 6.4 | 14.8 | 4.6 | 2.1 | 4.88 | 9.69 | 4 |
| Hf | ppm | 82 | 0.1 | 3 | <0.1 | 0.4 | 1.0 | 1.4 | 1.8 | 2.1 | 2.7 | 4.0 | 5.6 | 2.0 | 1.3 | 8.11 | 23 | 5.3 |
| Ho | ppm | 82 | 0.1 | 5 | <0.1 | 0.4 | 0.6 | 0.7 | 0.7 | 0.8 | 0.9 | 1.0 | 2.6 | 0.7 | 0.3 | 0.89 | 1.77 | 0.83 |
| La | ppm | 82 | 0.1 | 0 | 1.5 | 14.3 | 24.3 | 28.2 | 32.0 | 33.8 | 37.6 | 42.5 | 78.2 | 30.4 | 13.1 | 31.1 | 63.2 | 31 |
| Li | ppm | 82 | 0.5 | 0 | 3.0 | 13.5 | 29.0 | 36.0 | 39.5 | 41.5 | 47.5 | 61.5 | 103.0 | 40.0 | 19.0 | 20.8 | 63.7 | 24 |
| Lu | ppm | 82 | 0.1 | 8 | <0.1 | 0.1 | 0.3 | 0.4 | 0.4 | 0.5 | 0.6 | 0.7 | 2.4 | 0.4 | 0.3 | 0.38 | 0.79 | 0.31 |
| Mo | ppm | 82 | 1 | 73 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 3 | 19 | 1 | 3 | 0.6 | 1.46 | 1.1 |
| Nb | ppm | 82 | 0.1 | 59 | <0.1 | <0.1 | <0.1 | <0.1 | 0.4 | 1.3 | 3.4 | 10.1 | 16.1 | 2.9 | 4.7 | 13 | 21 | 12 |
| Nd | ppm | 82 | 0.1 | 0 | 1.2 | 13.6 | 22.7 | 27.0 | 28.6 | 32.0 | 35.7 | 40.4 | 68.8 | 28.6 | 12.1 | 27.6 | 58.4 | 27 |
| Ni | ppm | 82 | 0.5 | 43 | 3.5 | 10.0 | 20.0 | 22.5 | 26.0 | 29.5 | 41.5 | 93.0 | 255.0 | 42.0 | 49.0 | 23 | 59 | 47 |
| Pb | ppm | 82 | 0.5 | 0 | 2.5 | 10.5 | 14.5 | 22.5 | 24 | 25.5 | 32 | 41.5 | 104 | 25.5 | 15.0 | 21 | 51 | 17 |
| Pr | ppm | 82 | 0.1 | 0 | 0.5 | 3.8 | 6.7 | 7.7 | 8.7 | 8.9 | 10.3 | 12.2 | 18.8 | 8.3 | 3.5 | 7 | 15 | 7.1 |
| Rb | ppm | 82 | 0.2 | 0 | 5.4 | 41.4 | 81.6 | 96 | 108 | 120.8 | 139.4 | 158.8 | 214 | 105.2 | 46.0 | 70 | 133 | 84 |
| Sb | ppm | 82 | 0.1 | 5 | <0.1 | 0.2 | 0.6 | 0.9 | 1.1 | 1.3 | 1.7 | 2.3 | 4.1 | 1.2 | 0.9 | 0.64 | 2.1 | 0.4 |
| Sc | ppm | 82 | 0.1 | 0 | 0.5 | 3.7 | 6.4 | 7.9 | 8.8 | 9.8 | 11.4 | 14.5 | 17.3 | 8.9 | 4.1 | | | 14 |
| Se | ppm | 82 | 0.1 | 3 | <0.1 | 0.2 | 0.4 | 0.5 | 0.6 | 0.7 | 0.9 | 1.1 | 2.0 | 0.7 | 0.4 | | | 0.09 |
| Sm | ppm | 82 | 0.1 | 0 | 0.2 | 2.7 | 3.9 | 4.7 | 5.1 | 5.8 | 6.9 | 9.0 | 18.0 | 5.6 | 3.0 | 5.2 | 11 | 4.7 |
| Sn | ppm | 82 | 1 | 33 | <1 | <1 | <1 | <1 | 2 | 2 | 3 | 3 | 6 | 2 | 1 | 2.1 | 8.76 | 2.1 |
| Sr | ppm | 82 | 0.2 | 0 | 16.0 | 55.8 | 82.7 | 101.0 | 121.0 | 142.0 | 182.0 | 271.4 | 468.0 | 147.6 | 96.6 | 124 | 327 | 320 |
| Tb | ppm | 82 | 0.5 | 69 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 1.0 | 2.0 | 0.5 | 0.5 | 0.77 | 1.47 | 0.7 |
| Th | ppm | 82 | 0.1 | 0 | 0.2 | 4.8 | 9.8 | 11.4 | 12.2 | 13.1 | 14.6 | 16.9 | 33.5 | 11.8 | 5.5 | 10 | 21 | 10.5 |
| Tl | ppm | 82 | 0.05 | 3 | <0.05 | 0.30 | 0.45 | 0.60 | 0.60 | 0.65 | 0.75 | 0.95 | 7.00 | 0.70 | 0.75 | 0.37 | 0.83 | 0.9 |
| Tm | ppm | 82 | 0.1 | 6 | <0.1 | 0.2 | 0.2 | 0.3 | 0.3 | 0.3 | 0.4 | 0.4 | 1.1 | 0.3 | 0.1 | 0.39 | 0.79 | 0.3 |
| U | ppm | 82 | 0.1 | 1 | <0.1 | 1.2 | 1.7 | 1.9 | 2.0 | 2.2 | 2.7 | 3.4 | 40.1 | 2.7 | 4.3 | 2 | 6 | 2.7 |
| V | ppm | 82 | 1 | 0 | 4 | 30 | 39 | 51 | 59 | 69 | 76 | 94 | 1270 | 74 | 137 | 62 | 123 | 97 |
| W | ppm | 82 | 1 | 72 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 2 | 7 | 1 | 1 | 1.24 | 3.53 | 1.9 |
| Y | ppm | 82 | 0.1 | 0 | 1.1 | 11.2 | 13.5 | 16.2 | 17.4 | 18.4 | 20.5 | 23.7 | 75.0 | 17.7 | 9.1 | 24.9 | 44.6 | 21 |
| Yb | ppm | 82 | 0.1 | 3 | <0.1 | 1.4 | 2.0 | 2.5 | 2.7 | 2.9 | 3.4 | 3.9 | 15.1 | 2.8 | 1.9 | 2.48 | 5.16 | 1.96 |
| Zn | ppm | 82 | 0.5 | 0 | 7.0 | 33.0 | 51.5 | 64.0 | 70.0 | 75.5 | 100.5 | 140.0 | 289.0 | 79.0 | 49.5 | 71 | 164 | 67 |
| Zr | ppm | 82 | 1 | 0 | 3 | 21 | 38 | 50 | 65 | 78 | 95 | 133 | 202 | 71 | 44 | 386 | 992 | 193 |
| Al | % | 82 | 0.01 | 0 | 0.20 | 2.82 | 3.73 | 4.93 | 5.18 | 5.47 | 6.17 | 8.00 | 9.26 | 5.08 | 2.14 | 5.51 | 8.52 | 8.15 |
| Ca | % | 82 | 0.01 | 0 | 0.12 | 0.35 | 1.06 | 2.85 | 3.89 | 5.85 | 9.29 | 15.78 | 27.80 | 6.37 | 6.83 | 1.74 | 13.21 | 2.56 |
| Fe | % | 82 | 0.01 | 0 | 0.15 | 1.27 | 1.94 | 2.35 | 2.52 | 2.74 | 3.24 | 4.05 | 5.34 | 2.58 | 1.09 | 2.50 | 5.00 | 3.53 |
| K | % | 82 | 0.01 | 0 | 0.11 | 1.46 | 2.15 | 2.46 | 2.65 | 2.89 | 3.09 | 3.80 | 5.70 | 2.59 | 1.01 | 1.68 | 2.70 | 2.32 |
| Mg | % | 82 | 0.01 | 0 | 0.08 | 0.53 | 0.66 | 0.82 | 1.10 | 1.31 | 1.77 | 3.22 | 11.90 | 1.66 | 1.90 | 0.7 | 2.0 | 1.49 |
| Mn | % | 82 | 0.0001 | 0 | 0.0056 | 0.0223 | 0.0321 | 0.0429 | 0.0493 | 0.0537 | 0.0628 | 0.0825 | 0.1720 | 0.0522 | 0.0301 | 0.0600 | 0.1570 | 0.08 |
| Na | % | 82 | 0.01 | 0 | 0.03 | 0.07 | 0.20 | 0.44 | 0.60 | 0.69 | 0.85 | 1.83 | 2.79 | 0.70 | 0.65 | 0.59 | 1.85 | 2.43 |
| P | % | 82 | 0.001 | 2 | <0.001 | 0.016 | 0.025 | 0.035 | 0.039 | 0.044 | 0.054 | 0.072 | 0.776 | 0.050 | 0.084 | 0.056 | 0.140 | 0.06 |
| S | % | 82 | 0.01 | 34 | <0.01 | <0.01 | <0.01 | <0.01 | 0.02 | 0.03 | 0.04 | 0.07 | 1.41 | 0.06 | 0.17 | | | 0.0062 |
| Ti | % | 82 | 0.01 | 4 | <0.01 | 0.08 | 0.16 | 0.20 | 0.23 | 0.27 | 0.31 | 0.41 | 0.55 | 0.24 | 0.13 | 0.37 | 0.62 | 0.38 |

QP  Sandy and muddy Pleistocene alluvial and colluvial sediments.
QPS  Topsoils over the QP unit (mud and sand fraction).
QH  Sandy and muddy surficial sediments of the Holocene Congost alluvial floodplain.
SS  Stream sediments (mud and sand fraction) of the Congost River mainstream.

The photo gallery in Fig. 3 shows some representative field details of the geological units sampled. We have avoided sampling coarse-grained materials (e.g., gravels or conglomerates) to prevent problems related to representativity. The weathering grade of the samples of the different rock units (CO, SDC, G, T, P, N) is variable (from I to V according to the scale proposed by Brown, 1981). The CO, SDC, G, T, P, N and QP samples derive from unpolluted outcropping areas. The samples of the units PS, NS, QPS, QH and SS are surficial deposits within a depth range from 0 to 25 cm (excluding material from the organic layer where present)

exposed to diffuse pollution, and they can include material related to anthropogenic activities.

The sample preparation and the sample analysis were performed at the Actlabs Laboratories. All samples were crushed, if necessary, and were pulverised to a grain size <0.063 mm with a mild steel before being submitted to the laboratory analyses.

We have determined the 'total' and the 'partial' concentrations of 54 elements: Al, As, Ba, Be, Br, Ca, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Hf, Ho, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, P, Pb, Pr, Rb, S, Sb, Sc, Se, Sm, Sn, Sr, Tb, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn and Zr.

The 'total' concentrations were determined by combining instrumental neutron activation analysis and inductively coupled plasma mass spectrometry analysis after 4-acid digestion (hydrochloric, nitric, perchloric and hydrofluoric). According to the technical specifications of the laboratory, although it is a very vigorous digestion, certain minerals (barite, gahnite, chromite and cassiterite) may not go into solution.

**Table 2**
Descriptive statistics of the partial digestion analysis.

| Element | Unit | Count | D.L. | N.S. < D.L. | Min | Pctl 10 | Pctl 25 | Pctl 40 | Median | Pctl 60 | Pctl 75 | Pctl 90 | Max | Mean | Std. Dev. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| As | ppm | 66 | 0.1 | 7 | <0.1 | 0.2 | 2.2 | 4.4 | 5.1 | 6 | 8.3 | 10.1 | 19.1 | 5.4 | 4.1 |
| Ba | ppm | 66 | 0.5 | 0 | 15.5 | 49.0 | 100.0 | 142.0 | 162.0 | 180.0 | 203.5 | 313.0 | 1490.0 | 206.5 | 246.5 |
| Be | ppm | 66 | 0.1 | 2 | <0.1 | 0.4 | 0.7 | 0.9 | 0.9 | 1.2 | 1.3 | 1.6 | 2.2 | 1.0 | 0.5 |
| Cd | ppm | 66 | 0.01 | 0 | 0.02 | 0.04 | 0.07 | 0.12 | 0.15 | 0.17 | 0.25 | 0.40 | 6.50 | 0.30 | 0.82 |
| Ce | ppm | 66 | 0.01 | 0 | 3.21 | 22.00 | 35.23 | 47.60 | 49.35 | 57.00 | 62.98 | 70.35 | 88.20 | 49.24 | 20.08 |
| Co | ppm | 66 | 0.1 | 0 | 0.7 | 3.7 | 5.8 | 7.0 | 7.5 | 8.3 | 9.8 | 13.2 | 23.0 | 8.2 | 4.0 |
| Cr | ppm | 66 | 0.5 | 0 | 6 | 11 | 19 | 24.5 | 27.5 | 32 | 41.5 | 71 | 281 | 40.5 | 47.5 |
| Cs | ppm | 66 | 0.02 | 0 | 0.20 | 0.90 | 1.46 | 2.10 | 2.28 | 2.68 | 3.12 | 4.74 | 19.60 | 3.10 | 3.38 |
| Cu | ppm | 66 | 0.01 | 0 | 3.08 | 11.05 | 17.80 | 21.50 | 25.35 | 27.90 | 35.13 | 61.85 | 377.00 | 39.94 | 57.67 |
| Dy | ppm | 66 | 0.1 | 0 | 0.2 | 1.3 | 1.8 | 2.3 | 2.5 | 2.7 | 2.9 | 3.9 | 5.4 | 2.5 | 1.0 |
| Er | ppm | 66 | 0.1 | 1 | <0.1 | 0.6 | 0.8 | 1.0 | 1.1 | 1.3 | 1.5 | 2.0 | 3.3 | 1.2 | 0.6 |
| Eu | ppm | 66 | 0.1 | 4 | <0.1 | 0.4 | 0.6 | 0.7 | 0.8 | 0.8 | 0.9 | 1.1 | 1.3 | 0.7 | 0.3 |
| Ga | ppm | 66 | 0.02 | 0 | 0.46 | 2.5 | 4.62 | 6 | 6.72 | 7.26 | 8.88 | 10.74 | 15.7 | 6.80 | 3.14 |
| Gd | ppm | 66 | 0.1 | 0 | 0.2 | 2.1 | 3.125 | 3.7 | 4 | 4.2 | 4.6 | 5.45 | 6.6 | 3.9 | 1.3 |
| Hf | ppm | 66 | 0.1 | 62 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.1 | <0.1 |
| Ho | ppm | 66 | 0.1 | 3 | <0.1 | 0.2 | 0.3 | 0.4 | 0.4 | 0.5 | 0.6 | 0.7 | 1.1 | 0.5 | 0.2 |
| La | ppm | 66 | 0.5 | 0 | <0.5 | 11.0 | 18.0 | 23.5 | 25.0 | 27.0 | 31.5 | 35.5 | 45.0 | 24.5 | 10.0 |
| Li | ppm | 66 | 0.1 | 0 | 1.3 | 15.2 | 23.8 | 28.3 | 31.3 | 33.0 | 36.3 | 54.7 | 82.2 | 32.2 | 15.8 |
| Lu | ppm | 66 | 0.1 | 41 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.2 | 0.6 | 0.1 | 0.1 |
| Mo | ppm | 66 | 0.01 | 1 | <0.01 | 0.28 | 0.49 | 0.72 | 0.85 | 1.05 | 1.43 | 3.19 | 25.10 | 2.06 | 4.42 |
| Nb | ppm | 66 | 0.1 | 30 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.3 | 0.7 | 1.0 | 2.1 | 0.4 | 0.5 |
| Nd | ppm | 66 | 0.02 | 0 | 1.14 | 11.24 | 17.4 | 21.7 | 23.44 | 25.6 | 29.28 | 33.34 | 43 | 23.20 | 9.24 |
| Ni | ppm | 66 | 0.1 | 0 | 3.5 | 8.8 | 18.1 | 20.6 | 22.0 | 24.1 | 32.0 | 46.6 | 177.0 | 30.2 | 32.0 |
| Pb | ppm | 66 | 0.01 | 0 | 3.08 | 7.40 | 10.20 | 16.50 | 18.60 | 20.20 | 27.48 | 33.85 | 115.00 | 21.15 | 16.04 |
| Pr | ppm | 66 | 0.1 | 0 | 0.3 | 2.9 | 4.6 | 5.8 | 6.4 | 7.0 | 7.8 | 9.1 | 11.3 | 6.2 | 2.5 |
| Rb | ppm | 66 | 0.1 | 0 | 2.3 | 10.4 | 19.6 | 26.3 | 32.7 | 36.1 | 44.0 | 56.5 | 124.0 | 33.8 | 21.1 |
| Sb | ppm | 66 | 0.02 | 2 | <0.02 | 0.06 | 0.12 | 0.24 | 0.32 | 0.38 | 0.52 | 0.74 | 1.3 | 0.4 | 0.3 |
| Sc | ppm | 66 | 0.1 | 2 | <0.1 | 1.6 | 2.5 | 3.3 | 3.9 | 4.6 | 5.3 | 8.3 | 11.2 | 4.3 | 2.5 |
| Se | ppm | 66 | 0.1 | 2 | <0.1 | 0.2 | 0.3 | 0.3 | 0.4 | 0.4 | 0.5 | 0.6 | 0.8 | 0.4 | 0.2 |
| Sm | ppm | 66 | 0.1 | 0 | 0.2 | 2.3 | 3.6 | 4.3 | 4.7 | 5.1 | 5.5 | 6.6 | 8.0 | 4.6 | 1.7 |
| Sn | ppm | 66 | 0.05 | 0 | 0.10 | 0.45 | 0.85 | 1.20 | 1.30 | 1.45 | 1.85 | 2.65 | 5.45 | 1.50 | 1.00 |
| Sr | ppm | 66 | 0.5 | 0 | 3.5 | 12.0 | 21.0 | 39.0 | 48.0 | 73.5 | 101.5 | 185.5 | 422.0 | 84.5 | 92.5 |
| Tb | ppm | 66 | 0.1 | 3 | <0.1 | 0.3 | 0.4 | 0.5 | 0.5 | 0.5 | 0.6 | 0.7 | 0.9 | 0.5 | 0.2 |
| Th | ppm | 66 | 0.1 | 1 | <0.1 | 2.9 | 4.9 | 6.3 | 7.1 | 8.2 | 9.4 | 12.5 | 17.0 | 7.4 | 3.8 |
| Tl | ppm | 66 | 0.02 | 1 | <0.02 | 0.06 | 0.14 | 0.18 | 0.20 | 0.22 | 0.28 | 0.38 | 6.60 | 0.30 | 0.80 |
| Tm | ppm | 66 | 0.1 | 27 | <0.1 | <0.1 | <0.1 | <0.1 | 0.1 | 0.2 | 0.2 | 0.3 | 0.5 | 0.1 | 0.1 |
| U | ppm | 66 | 0.1 | 0 | 0.4 | 0.6 | 0.6 | 0.8 | 0.8 | 0.9 | 1.0 | 1.5 | 8.1 | 1.0 | 1.0 |
| V | ppm | 66 | 1 | 1 | <1 | 18 | 27 | 36 | 39 | 41 | 49 | 61 | 108 | 40 | 19 |
| W | ppm | 66 | 0.1 | 49 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | 0.5 | 4.0 | 0.2 | 0.5 |
| Y | ppm | 66 | 0.01 | 0 | 0.85 | 6.56 | 9.28 | 11.00 | 12.50 | 14.10 | 15.68 | 20.35 | 34.10 | 12.84 | 5.89 |
| Yb | ppm | 66 | 0.1 | 2 | <0.1 | 0.3 | 0.5 | 0.6 | 0.8 | 0.9 | 1.1 | 1.5 | 4.3 | 0.9 | 0.6 |
| Zn | ppm | 66 | 0.1 | 0 | 7.1 | 34.2 | 51.2 | 59.2 | 66.0 | 69.8 | 87.4 | 136.5 | 252.0 | 75.1 | 43.0 |
| Zr | ppm | 66 | 0.1 | 0 | 0.3 | 0.7 | 0.8 | 1.4 | 1.8 | 2.2 | 2.9 | 4.0 | 5.8 | 2.1 | 1.4 |
| Al | % | 66 | 0.01 | 0 | 0.12 | 0.92 | 1.43 | 1.98 | 2.15 | 2.34 | 2.85 | 3.42 | 5.41 | 2.15 | 0.99 |
| Ca | % | 66 | 0.01 | 0 | 0.18 | 0.42 | 0.89 | 1.65 | 3.04 | 4.73 | 7.88 | 15.40 | 32.40 | 5.86 | 7.43 |
| Fe | % | 66 | 0.01 | 0 | 0.19 | 1.39 | 1.94 | 2.32 | 2.53 | 2.65 | 3.11 | 3.70 | 5.84 | 2.52 | 0.98 |
| K | % | 66 | 0.01 | 0 | 0.06 | 0.17 | 0.27 | 0.34 | 0.42 | 0.48 | 0.57 | 0.81 | 1.52 | 0.46 | 0.30 |
| Mg | % | 66 | 0.01 | 1 | 0.08 | 0.48 | 0.56 | 0.73 | 0.88 | 1.09 | 1.33 | 2.29 | 11.50 | 1.28 | 1.53 |
| Mn | % | 66 | 0.0001 | 0 | 0.0065 | 0.0221 | 0.03145 | 0.0383 | 0.04295 | 0.0478 | 0.0552 | 0.0678 | 0.19 | 0.0470 | 0.0268 |
| Na | % | 66 | 0.01 | 0 | 0.02 | 0.03 | 0.03 | 0.04 | 0.05 | 0.05 | 0.06 | 0.08 | 0.77 | 0.06 | 0.10 |
| P | % | 66 | 0.001 | 40 | 0.018 | 0.023 | 0.033 | 0.036 | 0.042 | 0.056 | 0.074 | 0.111 | 0.133 | 0.057 | 0.034 |
| S | % | 66 | 0.001 | 40 | 0.004 | 0.010 | 0.025 | 0.039 | 0.053 | 0.056 | 0.091 | 0.105 | 0.386 | 0.067 | 0.075 |
| Ti | % | 66 | 0.01 | 46 | <0.01 | <0.01 | 0.01 | 0.03 | 0.03 | 0.04 | 0.04 | 0.09 | 0.26 | 0.05 | 0.07 |

Other minerals including zircon, sphene and magnetite may not be totally dissolved. Most other silicates will be dissolved, but some elements will be erratically volatilised, including Si, As, Sb, Cr and U. This method cannot be used for accurate determinations of the rare earth elements Nb, As, Sb, Sn, Hf, Cr and Si. In total, 82 samples (8 from CO, 7 from SDC, 9 from G, 12 from T, 9 from P, 5 from PS, 6 from N, 2 from NS, 5

from QP, 8 from QPS, 6 from QH and 5 from SS) and 18 replicates were analysed using the 'total' method, which has the commercial code Ultratrace3.

The 'partial' concentrations were determined by inductively coupled plasma mass spectrometry and inductively coupled plasma atomic emission spectrometry after *aqua regia* digestion. This digestion leaches
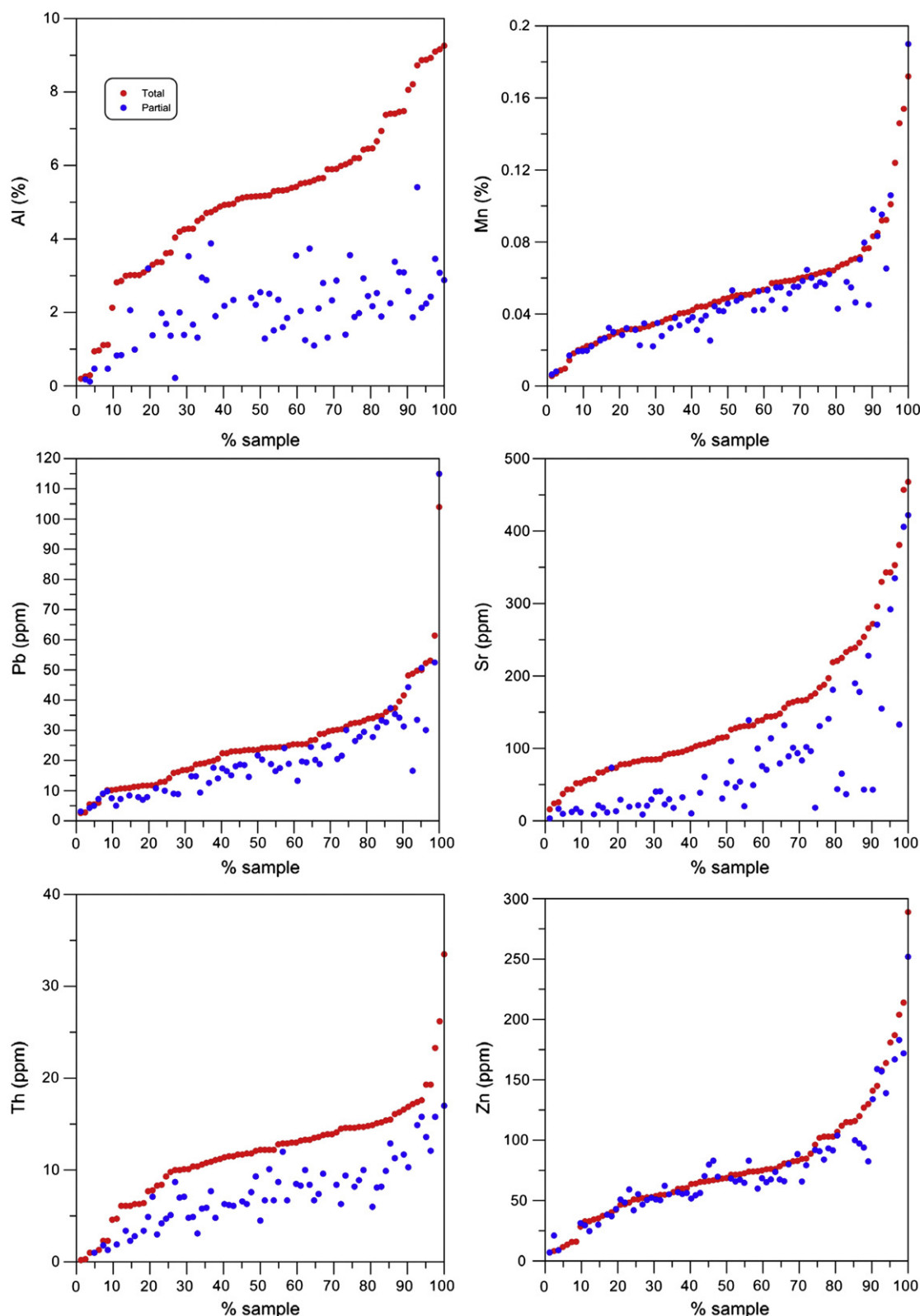


Fig. 5. Cumulative distribution plots for Al, Mn, Pb, Sr, Th and Zn total and partial concentrations.

sulphides, some oxides and some silicates. Mineral phases that are hardly attacked, if at all, include barite, zircon, monazite, sphene, chromite, gahnite, garnet, ilmenite, rutile and cassiterite. The remaining silicates and oxides are only slightly to moderately attacked, depending on the degree of alteration. A total of 66 samples (5 from CO, 4 from SDC, 8 from G, 6 from T, 8 from P, 4 from PS, 6 from N, 2 from NS, 4 from QP, 8 from QPS, 6 from QH and 5 from SS) were analysed using the 'partial' method, which has the commercial code Ultratrace2.

## 4. Results and discussion

The 'total' and the 'partial' element concentration analyses are shown in Fig. 4, and Tables 1 and 2. They present statistical data from the analytical results. The results obtained by both methods define wide compositional ranges of major and trace elements. A significant aspect of this variability is that the ratio between the 75th and 25th percentiles (the intermediate 50% of values) is often greater than 1.5 and in some cases, exceeds 2 (e.g., the As, Ba, Sr, Zr, Ca and Na concentrations obtained by both analytical methods). Since the analysed samples are representative of the different geological materials that compose the ground surface of the study area, it can be considered that, such variability could be attributed to the lithological, geomorphological and anthropogenic diversities of the region.

In order to compare better results with reference values, we have included in Table 1 the median and 90th-percentile compositions of the stream sediments of Europe obtained by the Geochemical Baseline Mapping Programme (Salminen et al., 2005) and the average composition of the upper crust recommended by Rudnick and Gao, 2003. Focusing on the 'total' compositions, it should be noted that, on average, the studied samples are enriched in Ca with respect to the stream sediments of Europe and the upper crust reference compositions. This average calcium enrichment can be explained by the relative abundance of samples of carbonate rocks in the SDC, T and P units. The average obtained

compositions of the other major elements do not differ significantly from the reference compositions. Most trace element average compositions are similar to the reference compositions or at least do not differ significantly. The most significant differences are the low average concentrations of Hf, Zr and Nb. We attribute these differences to incomplete dissolution of zircon- and Nb-rich phases during the four-acid attack digestion process. The remaining differences, as discussed below, can be attributed to geochemical peculiarities of the study area and to sampling biases.

By using the percentiles of Tables 1 and 2 as a reference, it can be noticed that, in general, the concentrations obtained by the 'total' method are higher than those obtained by the 'partial' method. The cumulative distribution plots in Fig. 5 allow a more detailed analysis of some of these concentration differences because they allow comparisons of the 'total' and 'partial' concentrations of each sample. In the case of Al, it can be observed that the difference between 'total' and 'partial' compositions broadly increases in the Al-rich samples. These samples are rich in feldspar and micas, which are insoluble to aqua regia attack. In the case of Pb and Th, leaving aside the extreme values, it can be seen that the difference between 'total' and 'partial' compositions remains roughly constant. Th is considerably more insoluble with aqua regia digestion than Pb. Except for a few samples, for Mn and Zn, the aqua regia attack can be considered a total digestion. The Sr cumulative distribution plot defines a complex pattern, suggesting the presence of different proportions of carbonates that may be completely dissolved after aqua regia digestion and of insoluble feldspar.

Fig. 6 presents the distribution maps of Pb and Th 'total' concentrations, as a revealing example of the spatial variability of the obtained compositions. The samples were grouped into discrete classes limited by the percentiles 10, 25, 40, 60, 75 and 90. The Pb dot map reveals that those samples richer in Pb are located specifically in the southern half of the basin, the area with high urban and industrial activity. In the case of Th, the southern samples define a heterogeneous Th
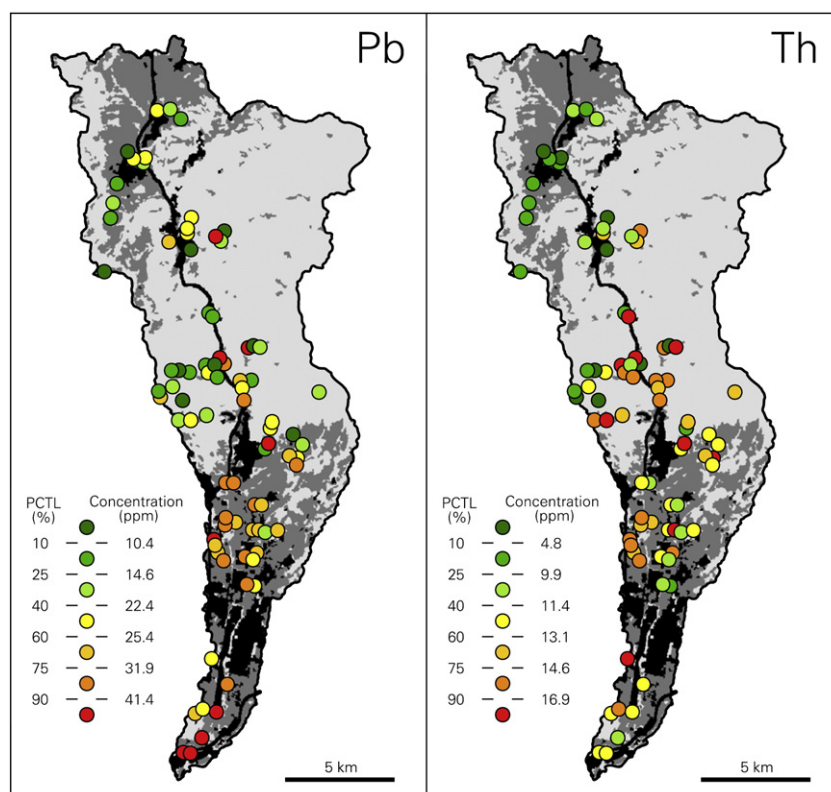


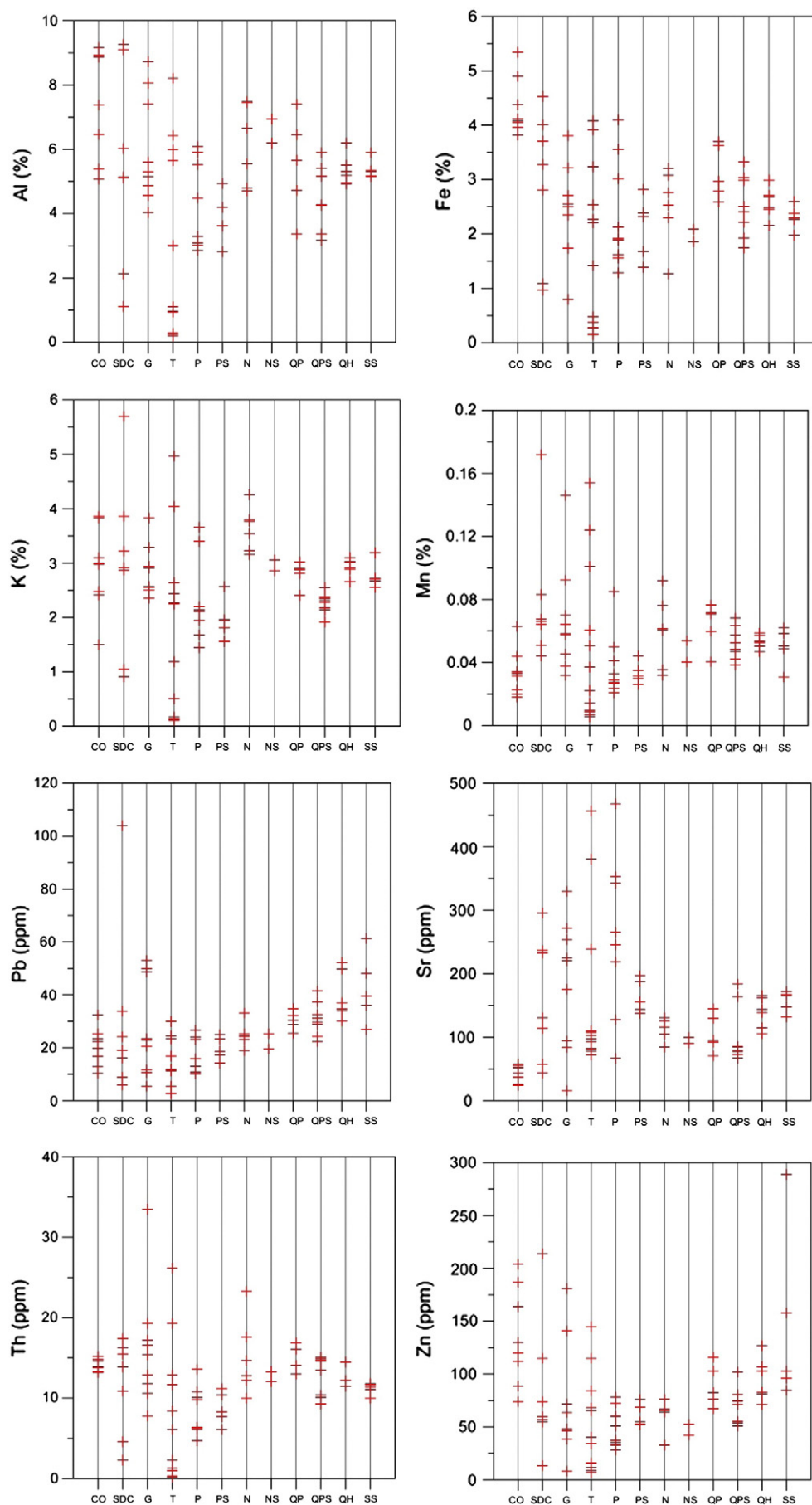**Fig. 6.** Dot maps for Pb and Th total concentrations.

**Fig. 7.** Al, Fe, K, Mn, Pb, Sr, Th and Zn total concentration distributions in the operative geological units of the Congost catchment.

distribution, and the higher concentrations being located in the central part of the basin, an area with low anthropogenic activity and with a geological ground composed primarily of Paleozoic rocks. In both cases, the lowest Pb and Th concentrations are located in the North and the mid-West of the study area, the Ebro Basin.

To more exhaustively study the geochemistry of the Congost River basin, Fig. 7 shows the Al, Fe, K, Mn, Pb, Sr, Th and Zn 'total' compositions grouped by the operative geological units described in the methodology section. The most representative ideas that emerge from the analysis of these graphs are:

a) The CO unit compared to the rest of the units is characterised by its high Al (>5%) and Fe (>3.5%) concentration, an intermediate K concentration (between 1.5 and 4%) and a relatively low Mn concentration (<0.065%). For trace elements, it should be noted that the CO unit in relative terms is depleted in Sr, enriched in Th and shows a wide range of Zn and Pb levels.

b) The SDC unit, in general, defines wider compositional ranges than the CO unit. This variability results from the lithological heterogeneity of the SDC unit. It is worth noting that the SDC unit includes limestones, shales and sandstones. There is one SDC sample with an anomalously high Pb concentration which should be related to the presence of sulphide ores.

c) The G unit, which is broadly a lithologically homogeneous unit, presents a considerable variability in major and trace element compositions. This variability can be attributed to petrogenetic processes. For example, the sample with the highest Th composition (33.5 ppm) corresponds to a leucogranite dike, which can be interpreted as a body of magmatic rocks derived from the crystallisation of residual magma. Apart from the lithotypes, the geochemical variability of the G could also be conditioned by different grades of weathering.

d) The T unit, which, like the SDC unit, includes detritic and carbonatic rocks, includes a wide range of compositions. This unit is outstanding for the presence of carbonatic rocks depleted in Al, Fe, Mn, K, Zn and Th and enriched in Sr.

e) The P unit, which also includes detritic and carbonatic rocks, generally presents a lower geochemical variability than the T unit.

f) The compositional ranges defined by the N and QP units, which are essentially composed of detritic sediments, are intermediate and can be compared with the compositions of their parent materials (CO, SDC, T and P units). Generally speaking, the Neogene sediments are richer in K and poorer in Fe than Pleistocene sediments. These differences could be interpreted as a significant change in configuration of the source area of sediments from the Miocene to the Pleistocene.
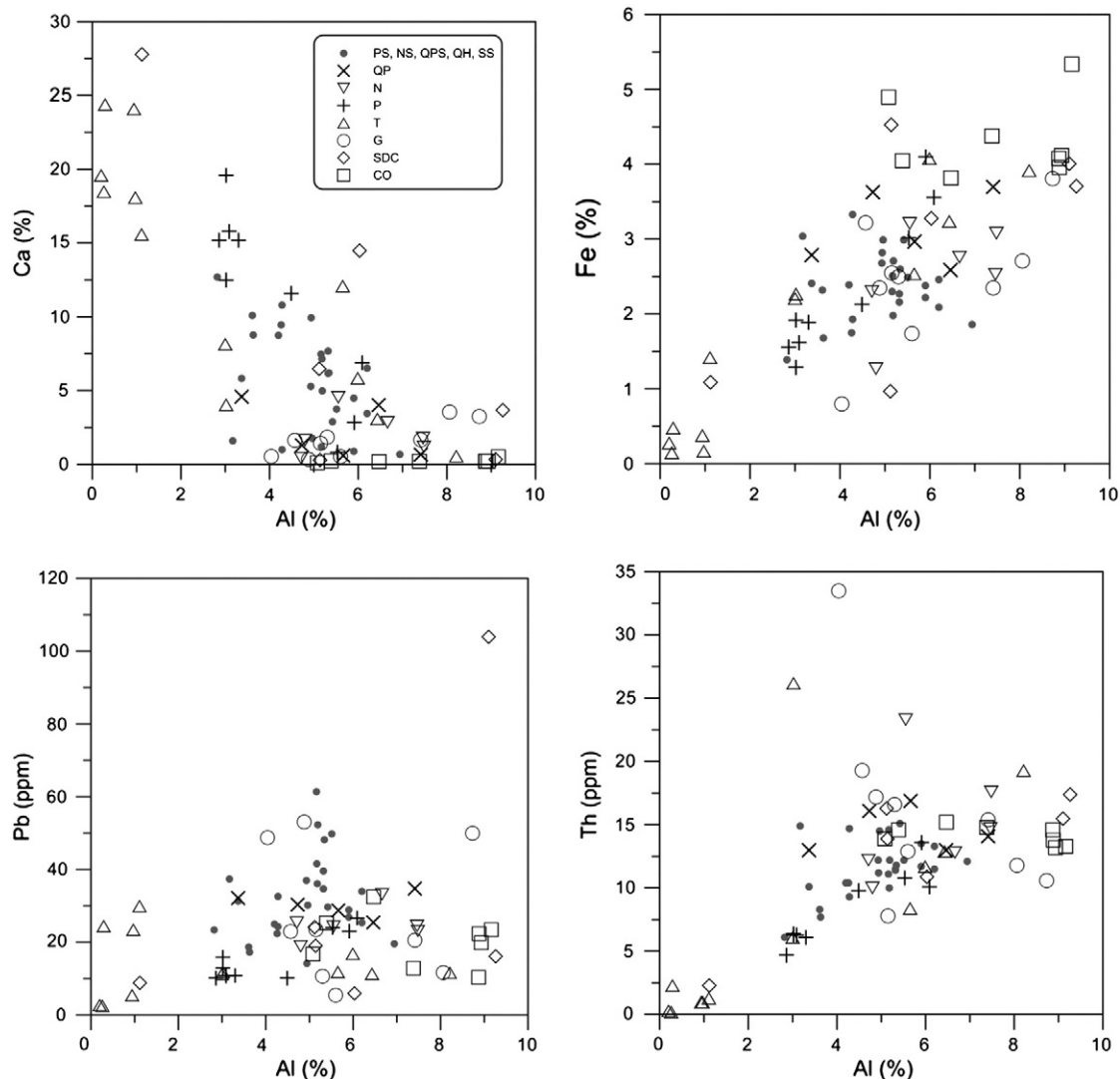


**Fig. 8.** Al versus Ca, Fe, Pb and Th (total concentration) diagrams of the geological units QP, N, P, T, G, SDC and CO and the superficial units PS, NS, QPS, QH and SS.

**Table 3**

Major element and trace element total concentrations of representative samples of the geological units (CO, SDC, G, T, P, N, QP) and median total concentrations of the surficial units (PS, NS, QPS, QH and SS) of the Congost Riber basin.

| Sample | C18 | C72 | C19 | C36 | C20 | C32 | C5 | C1 | C4 | C42 | C45 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Unit | CO | CO | SDC | SDC | SDC | G | G | T | T | T | P |
| Lithotype | Pelite | Psammite | Limestone | Black shale | Sandstone | Granodiorite | Weathered granodiorite | Limestone | Mudstone | Sandstone | Continental sandstone |
| As (ppm) | 4.9 | 7.2 | 35.5 | <0.5 | 14.1 | <0.5 | <0.5 | 1.1 | 20.7 | 5.6 | 19.7 |
| Ba (ppm) | 998 | 1150 | 196 | 1520 | 1070 | 713 | 561 | 22 | 429 | 646 | 770 |
| Be (ppm) | 2.4 | 1.6 | 0.9 | 4.8 | 2.8 | 1.8 | 2.0 | <0.1 | 2.4 | 1.2 | 1.8 |
| Cd (ppm) | <0.1 | 0.4 | <0.1 | <0.1 | 0.6 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Ce (ppm) | 84.1 | 13.3 | 27.7 | 98.8 | 71.9 | 42.9 | 46.4 | 2.3 | 67.4 | 161.0 | 63.5 |
| Co (ppm) | 15.2 | 12.0 | 7.8 | 2.6 | 12.4 | 6.1 | 6.6 | 0.8 | 11.7 | 5.5 | 10.0 |
| Cr (ppm) | 79 | 97 | 10 | 100 | 93 | 135 | 9 | 8 | 80 | 65 | 58 |
| Cs (ppm) | 6.40 | 3.80 | 3.27 | 16.10 | 7.90 | 2.50 | 3.50 | 0.30 | 11.40 | 8.55 | 7.30 |
| Cu (ppm) | 180.0 | 94.4 | 20.4 | 6.1 | 28.3 | 193.0 | 4.6 | 6.6 | 26.9 | 5.8 | 33.3 |
| Dy (ppm) | 4.2 | 2.2 | 2.5 | 11.9 | 4.2 | 3.2 | 3.7 | 0.2 | 3.6 | 5.2 | 3.5 |
| Er (ppm) | 2.5 | 1.7 | 1.7 | 7.5 | 2.9 | 2.5 | 2.8 | 0.2 | 2.1 | 2.6 | 2.4 |
| Eu (ppm) | 1.5 | 1.1 | 0.6 | 3.6 | 1.4 | 1.0 | 1.0 | <0.2 | 1.1 | 1.8 | 1.0 |
| Ga (ppm) | 25.7 | 24.3 | 6.9 | 24.6 | 31.9 | 22.1 | 20.8 | 1.8 | 19.8 | 10.9 | 18.6 |
| Gd (ppm) | 7.1 | 2.2 | 2.9 | 14.8 | 6.1 | 3.3 | 4.4 | 0.2 | 5.3 | 9.7 | 4.6 |
| Hf (ppm) | 2.1 | 4.8 | 1.2 | 1.2 | 1.3 | 2.8 | 0.9 | <0.1 | 2.8 | 5.6 | 0.2 |
| Ho (ppm) | 0.9 | 0.5 | 0.5 | 2.6 | 1.0 | 0.8 | 0.9 | <0.1 | 0.8 | 1.0 | 0.8 |
| La (ppm) | 41.7 | 5.1 | 17.7 | 55.9 | 38.3 | 14.1 | 21.3 | 1.5 | 34.8 | 78.2 | 33.2 |
| Li (ppm) | 43.7 | 31.8 | 12.3 | 20.5 | 87.6 | 27.9 | 47.2 | 5.1 | 57.9 | 27.2 | 40.2 |
| Lu (ppm) | 0.5 | 0.6 | <0.1 | 1.7 | 0.7 | 0.5 | 0.4 | <0.1 | 0.2 | 0.6 | 0.5 |
| Mo (ppm) | <1 | <1 | 1 | 10 | <1 | 3 | <1 | <1 | 2 | 2 | <1 |
| Nb (ppm) | <0.1 | 16.0 | <0.1 | 1.0 | <0.1 | 9.7 | 0.3 | 0.5 | 1.0 | 1.5 | <0.1 |
| Nd (ppm) | 41.6 | 7.9 | 15 | 61.7 | 39.4 | 14.2 | 21.9 | 1.2 | 32.1 | 68.8 | 30.6 |
| Ni (ppm) | 42.7 | 37.2 | 10.5 | 20 | 49.2 | 21.4 | 3.6 | 8.6 | 30.5 | 25 | 40.5 |
| Pb (ppm) | 22.4 | 32.5 | 33.9 | 24.2 | 104.0 | 10.7 | 20.6 | 2.6 | 16.9 | 11.8 | 24.1 |
| Pr (ppm) | 12.8 | 2.3 | 4.1 | 15.7 | 12.2 | 4.4 | 7.0 | 0.5 | 8.8 | 18.8 | 9.7 |
| Rb (ppm) | 214.0 | 82.7 | 49.2 | 126.0 | 145.0 | 105.0 | 123.0 | 5.5 | 147.0 | 106.0 | 126.0 |
| Sb (ppm) | 0.2 | 0.4 | 3.2 | 0.9 | 1.4 | 0.2 | <0.1 | 0.2 | 4.1 | 2.0 | 2.3 |
| Sc (ppm) | 14.2 | 14.5 | 4.9 | 17.3 | 16.6 | 8.5 | 9.5 | 0.5 | 10.4 | 6.9 | 9.4 |
| Se (ppm) | 1.1 | 0.7 | 0.2 | 2.0 | 0.5 | 0.9 | 0.9 | 0.5 | 0.7 | 0.5 | 0.5 |
| Sm (ppm) | 6.7 | 3.9 | 2.8 | 18.0 | 6.5 | 4.5 | 4.5 | 0.2 | 6.6 | 13.6 | 4.8 |
| Sn (ppm) | <1 | 3 | <1 | <1 | <1 | 2 | <1 | <1 | 3 | <1 | <1 |
| Sr (ppm) | 37.3 | 25.8 | 237 | 114 | 43.6 | 176 | 221 | 72.3 | 81.7 | 78.3 | 66.8 |
| Tb (ppm) | <0.5 | 1.2 | <0.5 | 2.0 | 1.3 | <0.5 | <0.5 | <0.5 | <0.5 | 1.3 | <0.5 |
| Th (ppm) | 13.8 | 15.2 | 4.6 | 16.3 | 15.5 | 16.6 | 15.4 | 0.2 | 11.7 | 26.2 | 10.8 |
| Tl (ppm) | 1.29 | 0.68 | 0.30 | 1.84 | 0.80 | 0.65 | 0.62 | <0.05 | 0.64 | 0.53 | 0.62 |
| Tm (ppm) | 0.4 | 0.3 | 0.2 | 1.1 | 0.4 | 0.4 | 0.4 | <0.1 | 0.3 | 0.4 | 0.3 |
| U (ppm) | 3.0 | 2.0 | 0.9 | 40.1 | 2.8 | 1.7 | 1.0 | 2.1 | 2.0 | 4.1 | 3.4 |
| V (ppm) | 64 | 111 | 39 | 1270 | 76 | 51 | 38 | 5 | 94 | 42 | 36 |
| W (ppm) | 3 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| Y (ppm) | 20.6 | 7.4 | 18.0 | 75.0 | 22.3 | 20.0 | 22.8 | 1.1 | 18.3 | 23.1 | 19.7 |
| Yb (ppm) | 3.7 | 3.3 | 1.5 | 9.7 | 4.0 | 2.9 | 2.7 | <0.2 | 2.4 | 4.7 | 2.8 |
| Zn (ppm) | 130.0 | 164.0 | 57.1 | 13.6 | 214.0 | 38.5 | 48.4 | 7.0 | 68.2 | 16.0 | 60.1 |
| Zr (ppm) | 84 | 165 | 48 | 91 | 61 | 87 | 27 | 3 | 97 | 202 | 21 |
| Al (%) | 8.88 | 6.47 | 2.13 | 5.12 | 9.10 | 5.30 | 7.41 | 0.26 | 5.99 | 3.02 | 5.53 |
| Ca (%) | 0.24 | 0.20 | 24.80 | 6.49 | 0.35 | 1.85 | 1.67 | 18.50 | 5.86 | 4.06 | 0.83 |
| Fe (%) | 3.96 | 3.82 | 2.81 | 0.97 | 4.01 | 2.50 | 2.35 | 0.15 | 4.08 | 2.27 | 3.02 |
| K (%) | 3.86 | 1.50 | 1.05 | 3.86 | 3.22 | 2.36 | 3.29 | 0.11 | 4.97 | 2.27 | 2.11 |
| Mg (%) | 0.81 | 0.76 | 0.57 | 1.78 | 1.53 | 0.77 | 0.66 | 11.90 | 2.30 | 0.17 | 0.98 |
| Mn (%) | 0.0440 | 0.0200 | 0.0509 | 0.0676 | 0.0442 | 0.0378 | 0.0642 | 0.0056 | 0.0570 | 0.1240 | 0.0411 |
| Na (%) | 0.29 | 0.72 | 0.20 | 0.06 | 1.16 | 2.54 | 1.95 | 0.04 | 0.10 | 0.07 | 0.11 |
| P (%) | 0.054 | 0.052 | 0.015 | 0.776 | 0.054 | 0.039 | 0.045 | 0.004 | 0.037 | 0.067 | 0.032 |
| S (%) | <0.01 | <0.01 | 1.41 | 0.02 | <0.01 | <0.01 | <0.01 | 0.02 | 0.02 | <0.01 | 0.02 |
| Ti (%) | 0.20 | 0.48 | 0.12 | 0.03 | 0.16 | 0.26 | 0.16 | <0.01 | 0.33 | 0.47 | 0.13 |

**Table 3** (*continued*)

| Sample | C46 | C31 | C82 | C49 | C67 | C12 | C68 | MedianPS | MedianaNS | MedianQPS | MedianQH | MedianSS |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Unit | P | P | P | N | N | QP | QP | PS | NS | QPS | QH | SS |
| Lithotype | Continental mudstone | Marine marl | Marine sandstone | Sandy sediment | Muddy sediment | Sandy sediment | Muddy sediment | Topsoil | Topsoil | Topsoil | Floodplain sediment | Stream sediment |
| As (ppm) | 21.0 | 5.9 | 3.6 | 4.3 | 13.4 | 14.2 | 14.0 | 9.5 | 7.8 | 14.5 | 9.8 | 8.6 |
| Ba (ppm) | 437 | 428 | 483 | 660 | 990 | 1050 | 455 | 440 | 710 | 512 | 880 | 745 |
| Be (ppm) | 2.6 | 1.8 | 1.0 | 2.2 | 1.9 | 2.0 | 2.2 | 1.3 | 1.6 | 1.7 | 1.7 | 1.5 |
| Cd (ppm) | <0.1 | 0.2 | <0.1 | 0.2 | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.3 | 0.3 |
| Ce (ppm) | 66.5 | 48.3 | 35.1 | 72.7 | 71.5 | 78.0 | 78.1 | 58.3 | 50.9 | 73.2 | 67.9 | 60.0 |
| Co (ppm) | 13.5 | 8.5 | 4.7 | 8.2 | 11.0 | 11.1 | 10.0 | 7.6 | 5.8 | 9.5 | 9.1 | 8.5 |
| Cr (ppm) | 50 | 49 | 26 | 20 | 62 | 45 | 52 | 52 | 22 | 46 | 47 | 64 |
| Cs (ppm) | 19.00 | 6.20 | 4.00 | 6.30 | 5.50 | 7.90 | 7.30 | 5.40 | 5.70 | 5.50 | 6.00 | 6.60 |
| Cu (ppm) | 30.2 | 17.5 | 72.0 | 25.5 | 29.5 | 25.7 | 46.3 | 23.2 | 20.3 | 24.5 | 33.8 | 44.0 |
| Dy (ppm) | 3.2 | 2.7 | 2.1 | 4.5 | 3.6 | 3.5 | 4.3 | 2.6 | 3.3 | 3.6 | 3.4 | 3.6 |
| Er (ppm) | 1.8 | 1.9 | 1.4 | 3.1 | 2.5 | 2.2 | 2.7 | 1.6 | 2.4 | 2.0 | 2.1 | 2.1 |
| Eu (ppm) | 1.1 | 0.9 | 0.6 | 0.9 | 1.1 | 1.6 | 1.2 | 0.9 | 0.8 | 1.3 | 0.9 | 0.9 |
| Ga (ppm) | 21.0 | 15.4 | 9.3 | 21.5 | 15.8 | 18.2 | 19.1 | 11.8 | 18.1 | 17.0 | 16.4 | 15.9 |
| Gd (ppm) | 4.7 | 3.7 | 2.7 | 6.2 | 4.8 | 5.2 | 5.8 | 4.1 | 4.1 | 5.1 | 5.1 | 5.3 |
| Hf (ppm) | 2.5 | 4.7 | 0.9 | 0.5 | 0.4 | 4.0 | 1.6 | 2.1 | 0.7 | 2.5 | 2.1 | 1.8 |
| Ho (ppm) | 0.6 | 0.6 | 0.5 | 1.1 | 0.9 | 0.7 | 1.0 | 0.6 | 0.8 | 0.7 | 0.8 | 0.7 |
| La (ppm) | 36.0 | 26.4 | 18.6 | 35.2 | 35.4 | 36.7 | 39.5 | 32.2 | 26.7 | 37.8 | 35.8 | 31.2 |
| Li (ppm) | 55.7 | 47.6 | 27.9 | 48.5 | 38.0 | 47.3 | 48.4 | 35.9 | 42.2 | 37.1 | 39.9 | 43.4 |
| Lu (ppm) | 0.4 | 0.4 | 0.2 | 0.5 | 0.5 | 0.7 | 0.5 | 0.3 | 0.4 | 0.5 | 0.4 | 0.4 |
| Mo (ppm) | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 2 |
| Nb (ppm) | <0.1 | 11.9 | 4.8 | <0.1 | <0.1 | <0.1 | <0.1 | 3.7 | 4.0 | <0.1 | 0.4 | 4.7 |
| Nd (ppm) | 30.7 | 23 | 17 | 34.9 | 31.9 | 36.1 | 38.1 | 28.2 | 24.3 | 35.1 | 32.7 | 30.5 |
| Ni (ppm) | 30.5 | 27.1 | 20.3 | 11.4 | 28 | 10 | 32 | 23.3 | 8.3 | 24.2 | 24.1 | 25.6 |
| Pb (ppm) | 26.7 | 10.2 | 10.2 | 24.5 | 33.2 | 28.8 | 25.5 | 18.7 | 22.5 | 30.5 | 35.8 | 39.6 |
| Pr (ppm) | 8.3 | 7.3 | 5.6 | 11.0 | 10.4 | 9.5 | 12.2 | 7.7 | 7.7 | 9.7 | 8.9 | 9.0 |
| Rb (ppm) | 187.0 | 90.9 | 70.7 | 173.0 | 134.0 | 108.0 | 142.0 | 92.4 | 134.0 | 93.2 | 109.0 | 118.0 |
| Sb (ppm) | 2.7 | 1.1 | 0.7 | 0.3 | 1.3 | 2.5 | 1.5 | 1.0 | 0.4 | 1.6 | 1.5 | 1.9 |
| Sc (ppm) | 11.1 | 8.4 | 4.5 | 9.9 | 9.7 | 10.8 | 9.0 | 6.7 | 7.1 | 8.3 | 8.7 | 7.7 |
| Se (ppm) | 0.2 | 1.2 | 0.8 | 1.0 | 0.4 | 0.5 | 1.0 | 0.8 | 0.4 | 0.6 | 0.6 | 0.6 |
| Sm (ppm) | 6.0 | 4.0 | 1.3 | 5.0 | 4.7 | 9.3 | 5.2 | 5.6 | 3.8 | 7.0 | 7.0 | 5.6 |
| Sn (ppm) | 4 | 3 | <1 | <1 | <1 | 3 | <1 | 2 | 2 | 3 | 3 | 4 |
| Sr (ppm) | 246 | 343 | 266 | 116 | 84.6 | 95.4 | 130 | 156 | 95.2 | 81.9 | 141.5 | 166 |
| Tb (ppm) | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | <0.5 | 0.9 | 1.2 | 0.8 | <0.5 |
| Th (ppm) | 10.1 | 9.8 | 4.7 | 14.7 | 12.8 | 16.9 | 13.0 | 8.3 | 12.7 | 14.0 | 12.2 | 11.4 |
| Tl (ppm) | 0.94 | 0.32 | 0.33 | 0.70 | 0.76 | 0.69 | 0.73 | 0.44 | 0.70 | 0.57 | 0.59 | 0.58 |
| Tm (ppm) | 0.3 | 0.3 | 0.2 | 0.4 | 0.4 | 0.3 | 0.4 | 0.2 | 0.4 | 0.3 | 0.3 | 0.3 |
| U (ppm) | 3.3 | 2.2 | 1.9 | 1.9 | 2.3 | 2.3 | 2.6 | 1.9 | 1.3 | 1.8 | 1.9 | 2.1 |
| V (ppm) | 94 | 70 | 37 | 48 | 26 | 86 | 34 | 61 | 52 | 68 | 67 | 65 |
| W (ppm) | <1 | 2 | <1 | 7 | <1 | <1 | <1 | <1 | <1 | <1 | 2 | <1 |
| Y (ppm) | 16.6 | 14.4 | 11.2 | 28.5 | 19.7 | 17.9 | 23.2 | 14.0 | 20.0 | 17.2 | 18.6 | 18.1 |
| Yb (ppm) | 2.4 | 2.2 | 1.4 | 3.0 | 2.8 | 4.1 | 3.0 | 2.4 | 2.4 | 3.4 | 2.8 | 2.6 |
| Zn (ppm) | 72.6 | 60.4 | 28.4 | 65.8 | 66.9 | 76.2 | 67.5 | 54.8 | 47.5 | 72.8 | 92.9 | 103.0 |
| Zr (ppm) | 85 | 154 | 34 | 24 | 20 | 141 | 54 | 74 | 24 | 88 | 73 | 61 |
| Al (%) | 6.09 | 4.49 | 2.86 | 7.46 | 6.66 | 5.66 | 6.46 | 3.63 | 6.57 | 4.28 | 5.25 | 5.32 |
| Ca (%) | 6.90 | 11.60 | 15.20 | 1.78 | 2.85 | 0.61 | 4.03 | 9.94 | 2.06 | 2.24 | 5.13 | 6.21 |
| Fe (%) | 3.56 | 2.13 | 1.56 | 2.53 | 2.76 | 2.97 | 2.59 | 2.32 | 1.97 | 2.46 | 2.58 | 2.30 |
| K (%) | 3.66 | 2.14 | 1.45 | 3.80 | 3.16 | 3.02 | 2.90 | 1.95 | 2.96 | 2.29 | 2.97 | 2.71 |
| Mg (%) | 4.19 | 2.61 | 2.78 | 1.27 | 0.66 | 0.69 | 1.04 | 1.58 | 0.71 | 0.58 | 1.22 | 1.56 |
| Mn (%) | 0.0499 | 0.0289 | 0.0275 | 0.0604 | 0.0762 | 0.0766 | 0.0716 | 0.0316 | 0.0472 | 0.0506 | 0.0531 | 0.0506 |
| Na (%) | 0.12 | 0.42 | 0.22 | 0.72 | 0.73 | 0.67 | 0.56 | 0.38 | 1.08 | 0.51 | 0.81 | 0.71 |
| P (%) | 0.016 | 0.037 | 0.025 | 0.043 | 0.027 | 0.033 | 0.045 | 0.050 | 0.024 | 0.027 | 0.057 | 0.078 |
| S (%) | 0.03 | 0.34 | 0.10 | <0.01 | <0.01 | 0.02 | <0.01 | 0.05 | 0.01 | 0.03 | 0.03 | 0.07 |
| Ti (%) | 0.29 | 0.27 | 0.16 | 0.18 | 0.10 | 0.39 | 0.11 | 0.23 | 0.22 | 0.33 | 0.28 | 0.27 |

g) The compositions of the topsoil units PS, NS and QPS are broadly similar, or at least comparable, with the compositions of those units providing their parent material (P, N and QP, respectively). It's worth noting the existence of some topsoil samples with a relatively high Pb concentration that could be related to pollution.

h) Some Holocene fluvial sediments (QH unit) and stream sediments (SS unit) also present high Pb and Zn concentrations, probably as a consequence of anthropogenic activities. The Al, Fe, K, Mn, Sr and Th compositional ranges of QH and SS units are intermediate in relation to the whole of their potential natural parent materials.

Fig. 8 comprises a selection of binary diagrams to show and compare the general aspects of chemical variations within and between units. We note that, overall, the concentrations of Al and Ca define a negative correlation, whereas the concentrations of Al and Fe broadly define a positive correlation. There is no clear relationship between Al and Pb in CO, SDC, G, T, P, N and QP. Nevertheless, the Al–Pb diagram underlines the existence of topsoils (PS, NS, QPS) and Holocene sediments (QH and SS) enriched in Pb with respect to the majority of the samples, representative of their natural parent materials. Leaving aside samples with more than 20 ppm, the Th compositions of CO, SDC, G, T, P, N and QP show a definite positive correlation with Al. The Quaternary surficial materials broadly also define similar trends.

Graphics of Figs. 7 and 8 show that geological units CO, SDC, G, T, P, N and QP present a significative compositional variability. These units can be considered as lithostratigraphic (SDC, T, P, N, QP) or lithodemic (CO and SDC) units, and, thus, composed of unpolluted rocks and sediments. This is not the case of those units of surficial deposits PS, NS, QPS, QH and SS, that can include materials related to anthropogenic activities. The geochemical variability of the CO, SDC, G, T, P, N and QP units relates to natural processes (igneous, metamorphic, sedimentary and weathering). Therefore, an important step, to explain the geochemical variability of these geological units, could be, indeed, to determine the representative reference geochemical compositions of main lithotypes. According to the geology of the study area, the main representative lithotypes of the Congost River basin are: CO pelite, CO psammite, SDC limestone, SDC black shale, SDC sandstone, G granodiorite, G weathered granodiorite, T limestone, T mudstone, T sandstone, P continental mudstone, P continental sandstone, P marine marl, P sandstone, N sandy sediment, N muddy sediment, QP sandy sediment and QP muddy sediment. Table 3 presents the major element and trace element 'total' concentrations of these lithotype representative samples.

The lithotype compositions of Table 3 were selected after a thorough revision and analysis of geochemical results and sample descriptions. As expected, the reference compositions highlight the presence of remarkable geochemical differences and affinities between the representative lithotypes. An interesting fact revealed by Table 3 is that the reference composition of the same lithotype may change in considerable ways, depending on the unit. For instance, the SDC limestone is enriched in As, Ba, Cu or Zn as regards the T limestone.

Compositions of reference lithotypes can be used to estimate intermediate compositions of materials of geological units. In any case, it should be considered that the geochemical variability of each litotype could be remarkable. Furthermore, the composition of samples of Table 3 could not be considered as pure end member. To fully understand the major and trace element variabilities of each litotype a bigger number of samples is required, as well as specific petrologic studies, which go beyond the scope of this research.

We are fully aware of our limitations. Yet, by disposing of the 'total' as well as the 'partial' concentration of elements in a sample we better understand the surfial chemical fractioning processes which influence geological materials. As an example, Fig. 9 compares the K, Sr and Th 'total' and 'partial' concentrations of different samples of geological units in order to make clear, in a certain way, the environmental availability of these elements. From the analysis of the graph it seems
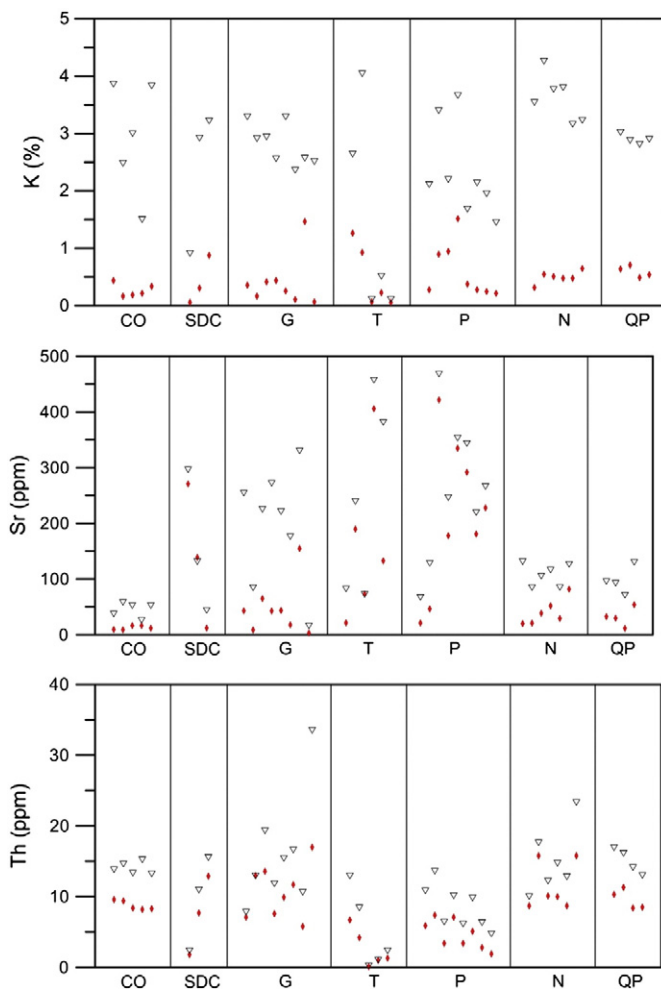


**Fig. 9.** Comparison of the K, Sr and Th total and partial concentrations of the samples of the geological units.

obvious that: i) for potassium, the ratio between the 'total' concentration and the 'partial' concentration in most samples is higher than two; ii) for thorium, the ratio reaches, generally, from 1.2 to 2, with no significative differences between geological units; and iii) for strontium, the ratio varies from near 1 (carbonate-rich samples of the SDC, T and P units) to over 4 (granitoids of the G unit).

Table 3 incorporates the median total concentrations of the units of surficial deposits PS, NS, QPS, QH and SS. The median compositions of the PS, NS and QPS topsoil units are broadly intermediate as regards the reference compositions of the geological units P, N and QP, respectively, that is, their prevailing underlying geochemical environment. The median composition of the floodplain sediments (QH unit) and stream sediments (SS unit) is compatible with the representative compositions of the geological units that define the source area of sediment of the Congost River basin.

It is quite clear that the natural surficial processes that occur in the basin – such as weathering, erosion, transportation and deposition – imply a certain chemical fractionation (e.g., particle sorting or elemental solubility) between surficial deposits and their parent material. Nevertheless, it was previously mentioned the existence of some Pb and Zn-rich concentrations related to environmental pollution. Despite these facts, the analysis of available data suggests that natural chemical fractionation is not so significant, and that, letting aside Pb and Zn concentrations, the anthropogenic influence is hard to identify. As a result, the median compositions of the surficial deposit units PS, NS, QPS, QH and SS could be used as orientative reference values
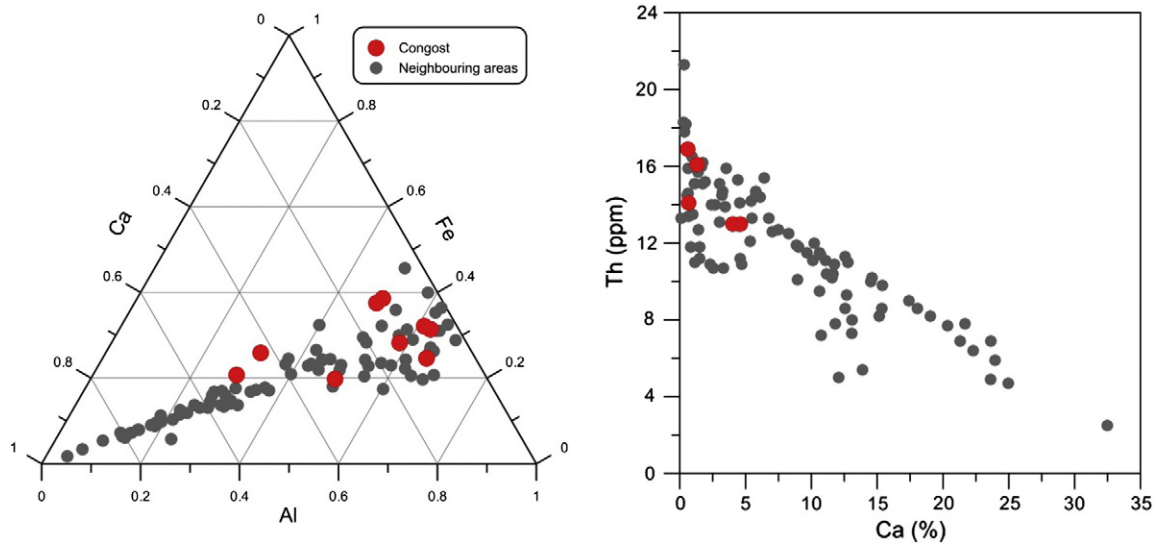
**Fig. 10.** Ca–Fe–Al and Ca–Th diagrams comparing the QP samples from the Congost River basin (total concentration) with other representative samples of Pleistocene sediments from neighbouring river basins.

to address specific studies. We are well aware that only a limited number of samples per unit have been analysed. In this sense, we do recommend that these median compositions should be used with caution. Additional sampling is, therefore, required to determine hard reference values.

The study of the origin of the geochemical variability of each lithotype requires a much more detailed approach, which exceeds the objectives of this work. However, the fact that the samples have been linked to a system of regional geological units allows us to compare, from a geochemical point of view, the Congost River basin materials with other reference materials from neighbouring areas and around the world.

In this sense, in Fig. 10, the QP 'total' compositions from the Congost catchment are compared with the compositions of representative samples of Pleistocene deposits (lutitic and sandy sediments) of the neighbouring areas. The reference compositions derive from several

technical documents of the Institut Geològic de Catalunya related to the geology of the catchment basins of Besòs, Maresme, Barcelona and Llobregat (see Fig. 1A). The ternary diagram Ca–Al–Fe shows that the Pleistocene sediments of this sector of the NE Iberian Peninsula define an Al/Fe relationship of approximately 0.6, which broadly remains constant for any Ca concentration. We attribute the high Ca variation to the lithological composition of the source area of the sediments, as well as to the presence of powder, nodular or concretionary carbonates related to pedogenetic processes. The QP samples from the Congost catchment match this regional Ca–Fe–Al trend, mainly with a Ca/(Ca + Fe + Al) ratio lower than 0.50. Trace elements also reveal some interesting relationships. For example, the Ca-Th diagram of Fig. 10 shows that the Th concentration of the Pleistocene sediments is clearly inversely proportional to the Ca concentration.

The compositions of the analysed samples reveal that the composition of the Congost catchment is highly varied. There are several
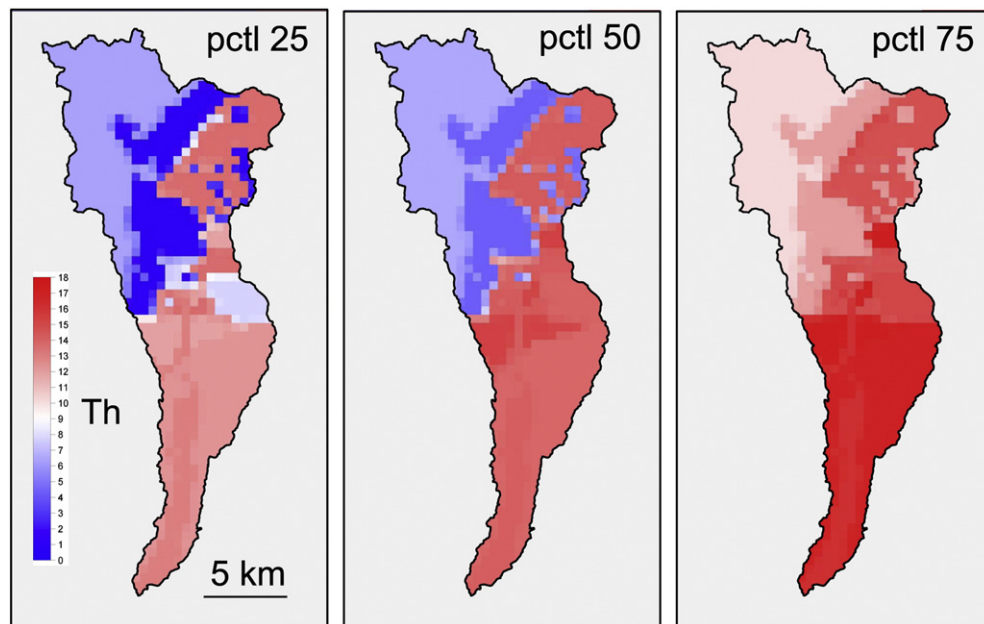


**Fig. 11.** Th concentration distributions of the Congost catchment obtained by assigning representative percentile concentrations (25, 50 and 75) to the units (CO, SDC, G, T, P, N, QP) of the geological map of Fig. 1. The concentrations are presented after interpolation with a 500-m grid size weighted area.

methods to map the spatial variation of geochemical data, and kriging and other interpolation methods have been extensively used. Interpolation between sample sites is likely to give a false impression of the variability of elements. Geological maps can be used to extrapolate the geochemical results for the whole of the Congost River basin. We must remember that sampling was guided by the regional geology of the study area. However, as shown, for example, by the diagrams in Fig. 7 and Table 3, the operative geological units present high geochemical variabilities and, often, the computed average compositions are not representative of the lithotypes that compose the unit. Therefore, to assign a single average value for the whole unit is fully unreasonable. This occurs, for example, in the T unit, which includes a wide range of carbonate and detrital rocks. In the case of Th, the 'total' concentration of the T samples varies from 0.2 to 26.2 ppm, the mean is 4.2 ppm, the standard deviation 8.13 ppm and the median 7.56 ppm. Carbonate rocks have a Th concentration <4 ppm and the detritic rocks >5 ppm.

A way of overcoming this high variability could be to substitute the model of geologic units by another model uses more lithologically homogeneous units. Most often, such changes, even if possible, are not economically feasible, considering the high density of sampling and geological mapping required. For geological units composed of cyclic or heterogeneous sequences including wide lithological spectra, such subdivision is absolutely impossible. Samples of surface materials (e.g., stream sediments or soils) can be used to predict the average composition of geological units, but it must be remembered that these samples may be affected by anthropogenic pollution. In addition to this, when surface material samples are attributed to geological map units, the influence of materials of the neighbouring geological units (e.g., hillwash deposits) must be considered.

An effective way to express the geographic distribution of the geochemical variability of a region can be achieved using an estimate of the average concentration bounded by a confidence interval. For many purposes, the 25th, 50th and 75th percentiles are useful reference values to depict geochemical variability. The maps obtained in such a form, after geologic extrapolation of these three percentiles offer a clear visualisation of the geochemical variability. As an example, in Fig. 11, we present the Th distribution in the Congost River basin using the geological map from Fig. 1. This geological map, which includes the CO, SDC, G, T, P, N and QP units, has been elaborated from a synthesis of the digital geological map of Catalonia at a 1:50,000 scale. For each geochemical map, the Th concentration distributions have been obtained by extrapolation of the corresponding percentile concentrations (25, 50 and 75) of the units. The concentrations are presented after a 500-m grid size weighted area interpolation. The compositions of units of surficial materials (PS, NS, QPS, QH and SS) have not been incorporated, to avoid the possible influence of anthropogenic and hillwash deposits. Thus, by using this method one can represent the overall distribution, in natural conditions, of any one of the other 56 elements analysed.

Considered as a whole, the three maps of Fig. 11 allow a thorough reading of the Th distribution in the whole of the Congost catchment. In the northwest, in the Ebro Basin, the Th concentration is rather constant and relatively low, below 10 ppm. Southwards, in the areas composed of T and SDC materials, the Th concentration shows high variability. And, last, the eastern margin, which is composed of pelites, and the southern half of the basin, which is composed of granitoids and Neogene and Pleistocene sediments, are characterised by a relatively high concentration of Th, above 10 ppm.

## 5. Conclusions

This paper has dealt with the geochemical variability of geological materials (rocks, sediments and soils) of the Congost River basin. In order to do so, we have defined a system of twelve geological operative units, which, all together, constitute the surface and near-surface of the study area. Seven of these units (CO, SDC, G, T, P, N and QP) can be considered as volumes of unpolluted geologic materials, by the fact of sharing enough characteristics (such as composition, areal extent, age, and (or) genesis). In such a way it can be considered as single entities. The remaining five units (PS, NS, QPS, QH and SS) represent surficial deposits that can include anthropogenic material. For each of those units a set of representative samples has been selected, and, at the same time, the 'total' and 'partial' concentrations of 56 chemical elements have been determined. The type of data base created has enabled us to carry on a thorough analysis of the earth surface geochemical variability for the whole basin. For each unit we have established several 'total' reference compositions and we have assessed their variability. The most relevant findings of our analysis are:

a) Bedrock geology should be considered the most important factor influencing the major and trace element distributions in the whole basin.

b) The geologic units CO, SDC, G, T, P, N and QP are characterised by different major and trace element compositional ranges, as a result of their lithological diversity and weathering grades.

c) To a considerable extent, the major and trace element compositions of the surficial deposits PS, NS, QPS, QH and SS are compatible with those of their parent geological materials. A considerable number of samples show relatively high concentrations of Pb and Zn, suggesting, thus, environmental pollution.

d) Differences between the 'total' and 'partial' concentrations define complex patterns related to the mineralogy of samples.

Our approach enables us to express the geographic distribution of the geochemical variability of a region by applying geologic extrapolation of three representative statistics of the units. That is, an average value (the 50th percentile), a low value (the 25th percentile) and a high value (the 75th percentile). The Th maps of Fig. 11 are a representative example of this cartographic method. These maps permit a clear discussion of the Th distribution in the Congost River basin. It is important to underline that this kind of maps does not take into consideration the units of surface deposits (PS, NS, QPS, QH and SS) which may be contaminated and, therefore, it should be expected that they represent the distribution of elements under natural conditions.

The geochemical results are insufficient to analyse, in depth, all processes that determine the geochemical variability of operative geological units (both inside each unit and among them). We consider that, for a better understanding of these processes many more samples are needed, as well as specific petrologic studies, which go beyond the scope of this research. In any case, it should be underlined that samples are linked to a system of regional geological units that do allow geochemical comparison of materials of the Congost River basin with other reference materials from neighbouring or remote areas. The example of the Pleistocene sediments, as shown in Fig. 10, gives clear evidence of this interesting possibility.

Standard regional geochemical mapping studies based on the analyses of stream sediments and soils (e.g., Darnley et al., 1995; Locutura, 2012; Salminen et al., 2005) provide background compositions. These studies also represent, as well, an important quantitative base on which local investigations can be built. In our opinion, without moving from the far field, such standard regional geochemical studies based on a random sampling strategy can be complemented with the analyses of additional samples representative of the primary earth materials of the area, taking into consideration the geology and land use of the area. These complementary samples, as shown in this research, allow a more exhaustive analysis of the geochemical composition of the ground, and, thus, can assist professionals and the general public to address particular environmental and economic problems.

This kind of 'geologically oriented' regional geochemical study, that we have developed in the Congost River basin, can be implemented in other areas of the world where there is substantial knowledge of the

regional geology and little or insufficient data about the chemical composition of the surficial geology. Regardless of the economic infrastructure and the logistics required for any geochemical survey, the method that we propose requires a reference geological map and a good knowledge of the regional geology (lithological and genetic) and the land use of the study area.

## Acknowledgements

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