

## Comparison of soil, sediment and water sampling in a regional geochemical survey in the Spanish Pyrenees

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### Introduction

The varied purposes of geochemical surveys are well known. While exploration geochemistry surveys are carried out on a wide range of scales, surveys for other geochemical mapping purposes are often coarse scale. In this contribution we describe the result of a relatively high density sampling in the Spanish Pyrenees, whereby the efficiency of the different sample media: water, soil and stream sediments is compared.

In a selected region of some 1000 km<sup>2</sup> circa 300 locations were sampled. This area comprises the Pallaresa catchment extending from valleys in the south at 800 m to the crest line of the Pyrenees at 3100 m. The area is sparsely populated, with agricultural activities concentrating on cattle breeding and some crop growing. The geology of the area consists of greenschist facies slates, limestones, quartzites and micro-conglomerates of Paleozoic age. Variscan granodiorite complexes outcrop in the western and northern parts with a well developed contact aureole. Black shales and evaporites postdating the Variscan orogen are found in the south. Sedex type Pb-Zn deposits are also present and have been mined in the past.

### Methods

For the soils and stream sediments the -80 mesh fraction was analyzed after a hot hydrochloric acid (1:1) leach for the base metals and Li and Sr. Waters were analysed within 24 hours for Na, K, Ca, Mg, and SO<sub>4</sub>. Data interpretations are mainly based on basic statistics and cluster analysis (fuzzy c-means).

### Interpretations

Water results indicate influences such as snow melt in the higher regions, dolomitic vs calcitic composition, raised levels of sulphate due to pyrite oxidation, and leaching of evaporites. The stream sediments reflect the larger past mining activities, the black shales and locations with mafic rocks. Soil data gave similar results with somewhat higher concentrations due to grain size effects. The sample media used are very efficient in delineating geological and environmental phenomena in the Pallaresa basin. The results give reason to reconsider certain parts of the geological map and also suggests the delineation of Sr and Li rich regions within the evaporitic deposits.

## Dissolved Al, Fe, Mn, Cu, and Zn in surface and ground waters from the northern area of Okinawa Island

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Three rivers, six streams, stagnant water under the forest and ground water were studied in order to understand the level, sources and factors controlling the concentrations of Al, Fe, Mn, Cu, and Zn. The water samples were collected monthly for the period of one year (January to December 2002).

### Results and Discussion

The metals showed the solubility trend of Fe>Al>Mn>Zn>Cu with seasonal variation showing two patterns: Al, Cu and Zn were lowest during dry period whereas Fe and Mn showed reverse trend. During base flow, streams are mainly fed by spring water while in high flow season rain and soil contribute most of the solute. Hence the patterns may be interpreted as: Al, Cu, and Zn were derived from rain and soils while Fe and Mn were dissolved from the parent rock. Two rain samples analysed during the sample course had values up 227, 40, 2.8, 3 and 10ppb for Al, Fe, Mn, Cu, and Zn, respectively.

The spatial variability showed that stagnant water had the highest values of Fe, Al, Mn and Cu with concentrations 1056, 202, 269 and 2.3ppb, respectively while river contained higher concentrations of Fe and Mn than streams and ground water. The dissolved organic carbon content was also high in stagnant water than rivers, streams and ground water. Therefore the high values might be due to the influence of DOC through formation of organo-metal complexes. Our samples had relatively wide range of pH (4.65-7.73) for investigation of influence of pH on metals dissolution. pH did not clearly affect Fe but it did for Zn, Mn, Al and Cu.

### Conclusion

The level of metals in the water samples studied was relatively low, which suggest less pollution activities. The long-range transportation of polluted air deposited on the soil through precipitation might be the major pathway of Zn and Cu. The pH, and DO appear to be major controlling factors of the concentrations of the metals in the waters.