

## Storage of metals in active stream sediments from mountainous rivers: a case study in the River Douro basin (North Portugal)

<sup>a</sup>Reis A R, <sup>b</sup>Parker A, <sup>a</sup>Alençã A

The study area is located in the transboundary River Douro basin (northern Portugal); it comprises the River Corgo fluvial network, which drains a meso-scale rural catchment with an area of 295 km<sup>2</sup>, underlain by crystalline rocks, in a temperate climate. The results reported in this study derive from a geochemical survey of active fluvial sediments, with the aim of characterising the spatial and temporal distribution of the contents of Cd, Co, Cr, Ni, Cu, Zn, Pb, Fe and Mn, in a basin with mountainous features. To assess possible different origins of metals (natural vs. anthropogenic), and their potential availability, a sequential chemical approach was used (modified BCR procedure). Multivariate data analysis (PCA) was used to assist the interpretation of datasets.

The results show that, on the one hand, the metal contents distribute among all the geochemical phases studied. For the most relative labile fractions the reducible fraction is the most significant. The element-partitioning among geochemical phases indicates: a) Co and Mn are transported in greater proportions in the most labile fraction, as exchangeable ions, as well as important proportions of Ni, Zn and Cu; b) Cd and Pb associate preferentially with the hydroxides of Fe and Mn; c) Cr and Cu are also transported by the organic phase; d) the residual phase transport important proportions of Cr, Ni, Zn, Cu, Fe

and Pb. The higher concentrations of Cu, Zn and, in particular, Pb, in the most labile fractions, which are higher where the total contents are also higher (and not concomitant with a correspondent increase in the residual fraction), suggest an important contribution of anthropogenic activities to the total contents of these elements in the sediments. Chromium and Ni are the main metals from a lithological source, with relatively higher contents in the residual fraction, and the lowest in the most mobile fractions.

On the other hand, the spatial distribution pattern of metal contents in the mobile and semi-mobile fractions (available + reducible + oxidisable), shows that, in general, higher contents of metals in the most mobile fractions occur along the main courses of the major tributaries, in particular in the flatter reaches.

The patterns of occurrence and distribution of metals through the hydrological year show, in general, that the relative contents associated with the potentially available fraction increase during the period of low flow, which extends from April to September. The relative contents in the residual fraction decreases after the influence of the first autumn rain and then similar contents between sampling campaigns are registered; Cr and Ni are an exception, showing an increase in the samples from stages of low flow.

<sup>a</sup> Department of Geology, University of Trás-os-Montes e Alto Douro, Vila Real, Portugal; Center for Geophysics from the University of Coimbra, Coimbra, Portugal (anarreis@utad.pt)

<sup>b</sup> Soil Research Group, School of Human and Environmental Sciences, University of Reading, Reading, UK