Hydrological and geochemical control of metals in a rural catchment (NW Spain)

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Accurate information on metals in rivers draining rural catchments is very limited. Metals in surface waters come from natural as well as anthropogenic sources such as applications of manure and fertilizers from agricultural activities. Dissolved and particulate concentrations of metals (Al, Fe, Mn, Cu and Zn), suspended sediments, and dissolved organic carbon were monitored over 3 year period (October 2005 to September 2008) at the outlet of the Mero River headwater catchment (NW Spain), which is dominated by agriculture and forest activities. Water samples were collected automatically (ISCO 6712FS) at the catchment outlet at irregular intervals, depending on the discharge rate, during rainfall events. Manual sampling was also undertaken at two week intervals during baseflow conditions. Determinations of metals were performed by ICP-MS.

Metals were predominantly in particulate phase during baseflow and runoff events. At baseflow, the mean particulate and dissolved contents presented the following order of abundance: Fe> Al > Mn> Zn > Cu. During events particulate phase followed the same order of abundance, but in dissolved form the order of abundance changed: Fe > Al > Zn ~ Mn ~ Cu.

Particulate Al, Fe and Mn followed the same pattern along the year, which was characterized by different peak concentrations related with the amount of suspended sediment. Therefore, the transport of these metals was intimately linked to sediment in the runoff, indicating a soil erosion-associated metal transport.

Although particulate Cu and Zn showed different peak concentrations along the year, these peaks are not always according peak concentrations in suspended sediments. This pattern provides an idea about the main source of these compounds. The first group, originate mainly from the washing of the materials that make up the soils of the catchment, while the main source of Cu and Zn is the application of fertilizers, especially slurry, in the agricultural fields at the catchment. Dissolved concentrations showed less variability along these three years for Fe and in particulate form for Mn.

Particulate and dissolved metal concentrations also showed variations as a function of river discharge, concentrations were similar to baseline values at the beginning of the event and mostly increased during the event. This illustrate that the runoff events are the driving factor on heavy metals losses, since annual flux of metals were strongly dominated by runoff events.

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