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Copper transfer dynamics during Mediterranean-type flash-floods (Baillaury River, Southwest of the Mediterranean coast of France)

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Mediterranean-type flow regime is characterized by brief and intense flow events multiplying the water discharge by up to ∼10. Consequently, the important soil leaching and storm runoff related to these events are responsible for high fluxes of pollutants exported to the outlet of the catchments.
In this study, we focus on the flash flood event of February 2009 in the small watershed of the Baillaury River in the South-West of the Mediterranean coast of France. Environmental monitoring has been conducted in this watershed within the framework of the CRUMED project in order to determine the pollutant impact on a marine coastal ecosystem. This river drains a steep of 18 km2 mainly covered by vineyards for centuries. Accordingly, considerable amounts of Cu were spread on soils through the common Bordeaux mixture treatment. The purpose of this work is to investigate the riverine behavior and transport of this anthropogenic Cu using sequential chemical extraction (SCE) and isotopic composition measurements.
Stream bed sediments (BS) and river suspended matters (SM) play a crucial role in the adsorption of heavy metals. Subsequently, during the flood event, BS at 3 different locations from the upstream to the outlet were sampled as well as one water sample at the outlet. SM were separated by centrifugation. Cu partitioning in different BS and SM (< 63μm) fractions was studied using the 7-steps SCE procedure developed by Leleyter and Probst (1999). This method was validated with comparison to the results obtained by total mineralization.
SCE are comparable for SM and BS indicating that Cu is mostly (>50%) adsorbed onto iron oxide fraction. A small fraction was associated with organic matter (5%) and the residual fraction accounts only for 30% of total Cu, 70% being controlled by non residual fractions.
Enrichment factors (EFs) were calculated for BS and SM by normalizing their concentrations to those of the local bedrock using different normalizers (Cs, Ti, Sc and Th). Calculated EFs reveal significant enrichments (> 4) of BS and SM as compared to the bedrock. Anthropogenic contribution to this enrichment is estimated to more than 75 % in all samples attesting that the Cu present in the river during these flood episodes is mainly due to agricultural practices.
Isotopic composition of Cu in the total BS and SM samples and in each extracted fraction of the SM was determined using MC-ICP-MS. Similar signatures (-0.1 <[U+F064]65Cu ‰ relative to NIST976 <0.1) were found for the total BS and SM samples. Considering the different fractions of the SM sample it appears that Cu associated to crystalline iron oxides exhibit the heaviest isotopic composition ([U+F07E]0.5‰ and the residual fraction presents an isotopic composition similar to that of the total sediment. Another result shows that dissolved Cu measured in the filtered water (0.22μm) has the same [U+F064]65Cu ([U+F07E]0.31‰ than Cu associated to the soluble fraction ([U+F07E]0.27‰ extracted by SCE. Further investigation is still required to better understand the origin of Cu associated to each fraction.
These results prove the important enrichment of Cu in BS and SM after centuries of vineyard treatments with the Bordeaux mixture. The Cu is mostly in non residual fractions; therefore the comprehension of its transfer dynamic is of great environmental interest in order to control its availability and toxicity for living organisms. This also means understanding its transfer dynamic in relation to its origin and its interaction with other molecules present in the water.

References

Leleyter, L. and Probst, J.L. 1999. Intl. J. Environ. Anal. Chem., 73 : 109-128.