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## New insights on Cu origin and fate from combined chemical extraction and $\delta^{65}\text{Cu}$ isotopic composition: Application to Cu transfers in a Mediterranean vineyard catchment

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Repeated use of Cu based fungicides (Bordeaux mixture:  $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$ ) to control vine downy has led to significant increase of Cu in vineyard soils. In Mediterranean catchments, brief and intense flood events can multiply stream discharge by up to 10 and are responsible for important soil leaching and therefore for high fluxes of Cu exported at the outlet of the catchment. In order to assess the origin and fate of Cu measured in the Baillaury catchment (South of France), combined sequential chemical extraction (SCE) and isotopic Cu compositions ( $\delta^{65}\text{Cu}$ ) approaches are proposed in this study. A cultivated vineyard soil (CV) and an abandoned one (AV) were sampled at different depths. River bed sediments (BS), suspended particulate matter (SPM) and river water were also collected during the flash flood event of February 2009. In the samples, Cu partitioning between residual and non residual fractions (dissolved with water, exchangeable, acido soluble, manganese oxides, amorphous and crystalline iron oxides, organic matter) was studied using a 7-steps SCE procedure. Data showed a more important residual fraction in AV soil (> 60%) than in CV soil, riverine BS and SPM (>25%). By normalizing Cu concentrations to those of the local bedrock using Fe, Sc and Ti as normalizers, enrichment factors (EF) were calculated revealing moderate to significant enrichments (EF > 2). Anthropogenic contributions in all samples were between 50 and 85 % attesting the impact of human activities on Cu content currently detected in the catchment. In non residual fractions of the samples, Cu showed the most important affinity for amorphous and crystalline Fe oxides (25-75%) and to a lesser extent for organic matter (5-10%).  $\delta^{65}\text{Cu}$  of bulk samples were similar to the bedrock and detailed isotopic investigations on SCE fractions of superficial CV and AV soils and SPM were therefore powerful to discriminate Cu origin and distribution. Copper in residual fractions of soils, BS and SPM is of natural origin because it has  $\delta^{65}\text{Cu}$  close to the local bedrock (0.07‰). In the surface horizon of the vineyard soil, copper has an isotopic ratio close to that ( $\delta^{65}\text{Cu} = -0.34$ ) of Cu fungicide.  $^{65}\text{Cu}$  is shown to have a preferential adsorption onto iron oxides. Cu transported in solution ( $\delta^{65}\text{Cu} = 0.31$ ‰) seemed to be associated with the dissolved fraction ( $\delta^{65}\text{Cu} = 0.26$ ‰) of SPM without the occurrence of any fractionation. Cu extracted from the organic matter fraction has negative isotopic values ( $\delta^{65}\text{Cu}$ : - 0.37‰ and -0.20‰ respectively in the cultivated soil and in the river suspended matters) showing that Cu from fungicide is bound to organic matter without or with slight isotopic fractionation. As a conclusion, combining a chemical sequential extraction with the isotopic measurements is a powerful tool to get a clearer insight of Cu distribution and mobility in the environment.