Copper Stable Isotopes to Trace Copper Behavior in Vineyard Catchments and Connected Wetland Systems

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Copper (Cu) fungicides are typically used in vineyards resulting in Cu-contaminated soils. Cu may be released during rainfall-runoff events. Wetland can intercept Cu-contaminated runoff and immobilize metal released in effluents from industrial and agricultural areas. Cu stable isotope ratios ($\delta^{65}Cu$) are rarely applied to trace transport and transformation processes in polluted environments.

Here we used Cu stable isotopes to trace the behaviour of Cu in vineyard soils and in a wetland receiving runoff from the vineyard catchment (Alsace, France). Cu loads and stable isotope ratios were determined in runoff, suspended solids, as well as in wetland sediments and the vegetation. Surface soils were enriched in Cu due to large organic matter and carbonate content. $\delta^{65}Cu$ values of solid-bound Cu in runoff were lower than those of surface soils and Cu-fungicides ($\delta^{65}Cu \sim 0.00‰$).

The wetland retained >68% of dissolved and >92% of solid-bound Cu, which represented 84.4% of Cu in runoff. Dissolved Cu became depleted in ^{65}Cu when passing through the wetland ($\Delta\delta^{65}Cu_{inlet\text{-}outlet}$ from 0.03‰ to 0.77‰), reflecting Cu sorption to aluminium minerals and organic matter. The $\delta^{65}Cu$ values varied little in wetland sediments ($0.04 \pm 0.10‰$), in which >96% of the Cu mass was stored. During high-flow conditions, Cu outflowing the wetland became isotopically lighter, indicating the mobilization of reduced Cu(I)-species from the sediments and Cu reduction within the sediments.

Our results demonstrate that Cu stable isotope ratios may help tracing Cu behaviour at the catchment scale and in redox-dynamic environments, such as wetlands.