The fate of Cu-based pesticides in vineyard soils: A δ^{65}Cu case study on contrasting soil types

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Copper (Cu) based fungicides have been applied in European vineyards from the appearance of mildew in the late 19th century to the present day, particularly in organic viticulture. Even though its application is foliar, most of the Cu reaches the soil after being washed off or following leaf fall. As Cu accumulates in soils, the use of Cu based fungicides has strong ecotoxicological consequences.

On the basis of mineralogical, chemical and isotope analyses (δ^{65}Cu) in vineyard experiments, we show that Cu isotope ratios in pesticides differ strongly (-0.46 to 0.85 ‰) depending on Cu speciation and year of manufacture, making it difficult to trace Cu source in soils. Further, we present field data from vineyards in the Soave appellation area that have experienced long term Cu-based pesticide application. These soils develop on basaltic or calcareous substrate and sustain the same grape variety (i.e., Garganega). We report elevated Cu concentrations (up to 550 mg kg^{-1}) all along the soil profiles. Citrate extractability of Cu in soils decreases strongly with depth, suggesting an aging effect. A change in Cu speciation with soil depth as well as soil type is supported by changes in Cu isotope ratios. Cu isotopic signature of grapevine roots is similar to those of the corresponding topsoil horizons. Fractionation during Cu translocation to shoots is high ($\Delta^{65}Cu_{leaves\text{-}roots}$ = - 1.5 ‰). The magnitude of Cu isotope fractionation in plants appears to be correlated with photosynthetic activity. This study shows that stable Cu isotope fractionation is an efficient tracer of Cu biogeochemistry in vineyards.