δ65Cu isotope analysis to trace copper-based fungicides in contrasting vineyard soils

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Abstract

Copper-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. Thus, in this study, we investigate the use of Cu isotope ratios to trace the fate of Cu pesticides in vineyard soils.
We present mineralogical, chemical and isotope analyses (δ65Cu) on a series of Cu-based pesticides and soils from vineyard experiments in the Soave appellation area. These vineyard soils develop on either basaltic or calcareous substrate and have been long term treated with Cu pesticides. Copper contents are high (up to 550 mg kg-1) all along soil profiles and bioavailability (measured by citrate extractions) declines rapidly with depth.

Cu isotope ratios in pesticides differ strongly (from -0.46 to 0.85) depending on Cu speciation in pesticide and its year of manufacture. In vineyard soils, isotopic signatures differ by morphologic horizon and soil type indicating a speciation rather than a source control of δ65Cu ratios. This is supported by kinetic citrate extractions showing differences in isotope ratios between rapidly extracted Cu for the different soil types.
This study shows that stable Cu isotope fractionation is an efficient tracer of Cu biogeochemistry in vineyards and that the type of soil clearly influences Cu mobility and speciation.

Keywords: isotopes, Cu, soil, vine transfer, Cu, based fungicides, source tracers, process investigation

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