



Copper in soil fractions and runoff in a vineyard catchment: Insights from copper stable isotopes



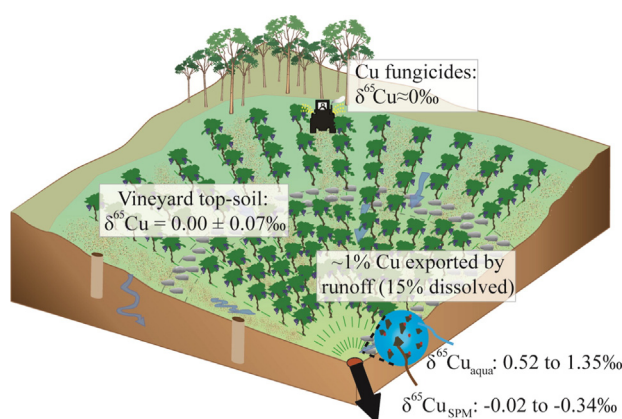
Izabella Babcsányi, François Chabaux, Mathieu Granet, Fatima Meite, Sylvain Payraudeau, Joëlle Duplay, Gwenaël Imfeld*

Laboratoire d'Hydrologie et de Géochimie de Strasbourg (LHyGeS), Université de Strasbourg/EOST, CNRS, 1 rue Blessig, 67084 Strasbourg Cedex, France

HIGHLIGHTS

- We investigated Cu sorption processes in vineyard soils and runoff transport.
- Cu export by runoff from the catchment accounted for 1% of the applied Cu mass.
- $\delta^{65}\text{Cu}$ values differed between the particle-size soil fractions.
- The clay soil fraction controlled sorption and runoff export of Cu fungicides.
- Cu stable isotopes enabled to trace Cu distribution in soils and runoff transport.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 11 December 2015

Received in revised form 26 February 2016

Accepted 7 March 2016

Available online xxxx

Editor: F.M. Tack

Keywords:

Fungicides

Clay

Particle-size fraction

Heavy metal

Sorption

Transport

ABSTRACT

Understanding the fate of copper (Cu) fungicides in vineyard soils and catchments is a prerequisite to limit the off-site impact of Cu. Using Cu stable isotopes, Cu retention in soils and runoff transport was investigated in relation to the use of Cu fungicides and the hydrological conditions in a vineyard catchment (Rouffach, Haut-Rhin, France; mean slope: 15%). The $\delta^{65}\text{Cu}$ values of the bulk vineyard soil varied moderately through the depth of the soil profiles (-0.12 to $0.24\text{‰} \pm 0.08\text{‰}$). The values were in the range of those of the fungicides (-0.21 to 0.11‰) and included the geogenic $\delta^{65}\text{Cu}$ value of the untreated soil (0.08‰). However, $\delta^{65}\text{Cu}$ values significantly differed between particle-size soil fractions ($-0.37 \pm 0.10\text{‰}$ in fine clays and $0.23 \pm 0.07\text{‰}$ in silt). Together with the soil mineralogy, the results suggested Cu isotope fractionation primarily associated with the clay and fine clay fractions that include both SOM and mineral phases. The vegetation did not affect the Cu isotope patterns in the vineyard soils. Cu export by runoff from the catchment accounted for 1% of the applied Cu mass from 11th May to 20th July 2011, covering most of the Cu use period. 84% of the exported Cu mass was Cu bound to suspended particulate matter (SPM). The runoff displayed $\delta^{65}\text{Cu}$ values from 0.52 to 1.35‰ in the dissolved phase ($<0.45 \mu\text{m}$) compared to -0.34 to -0.02‰ in the SPM phase, indicating that clay and fine clay fractions were the main vectors of SPM-bound Cu in runoff. Overall, this study shows that Cu stable isotopes may allow identifying the Cu distribution in the soil fractions and their contribution to Cu export in runoff from Cu-contaminated catchments.

© 2016 Elsevier B.V. All rights reserved.

* Corresponding author at: Laboratory of Hydrology and Geochemistry of Strasbourg (LHyGeS), University of Strasbourg/EOST and CNRS, 1 rue Blessig, 67084 Strasbourg Cedex, France.
E-mail address: imfeld@unistra.fr (G. Imfeld).

1. Introduction

Copper (Cu) is a trace element that can adversely impact soil biota and fertility when released to the environment (Komarek et al., 2010). Cu accumulates in vineyard soils due to its long-term use as Cu fungicides since the end of the 19th century (EC/889/2008; MacKie et al., 2012; Rusjan et al., 2007). Vineyards with steep slopes are generally prone to soil erosion, transporting Cu to downstream aquatic ecosystems and increasing their vulnerability to Cu due to its potential toxicity towards organisms (El Azzi et al., 2013; Fernández-Calviño et al., 2008a; Flemming and Trevors, 1989). However, knowledge of the fate and transport processes of anthropogenic Cu in the soils from agricultural catchments, as well as the ability to predict the off-site impact of Cu remains scarce.

Complementarily to traditional methods such as mass balances or sequential extractions, the fate and transport of anthropogenic Cu in the environment can be studied using stable Cu isotopes ($^{65}\text{Cu}/^{63}\text{Cu}$) (Babcsányi et al., 2014; Bigalke et al., 2013; Bigalke et al., 2010a; El Azzi et al., 2013; Fekiacova et al., 2015; Pérez Rodríguez et al., 2013; Petit et al., 2013; Thapalia et al., 2010). Cu isotope fractionation was observed during Cu adsorption onto Fe and Al oxy(hydr)oxides (Balistrieri et al., 2008; Pokrovsky et al., 2008), clay minerals (Li et al., 2015), as well as oxidation-reduction (Ehrlich et al., 2004; Zhu et al., 2002), uptake by plants (Jouvin et al., 2012; Ryan et al., 2013) or microorganisms (Navarrete et al., 2011), precipitation as Cu mineral phases (Ehrlich et al., 2004; Maréchal and Sheppard, 2002), and complexation with organic matter (Bigalke et al., 2010b; Ryan et al., 2014). In vineyard soils, Cu fungicides can sorb to clays, iron (Fe), manganese (Mn) and aluminum (Al) oxy(hydr)oxides, carbonates, (co)precipitate with secondary minerals and complex with soil organic matter (SOM) (Komarek et al., 2010). SOM efficiently sorbs Cu, while dissolved organic matter

(DOM) complexes with Cu and maintains it in solution, thus favoring its mobilization by rainfall (Komarek et al., 2010). Off-site export of Cu in vineyards was recently evaluated using Cu isotope analysis (El Azzi et al., 2013). Cu was found in rivers mainly associated with Fe oxy(hydr)oxides in the suspended particulate matter (SPM) (El Azzi et al., 2013). The SPM-bound Cu was found to be isotopically lighter compared to the dissolved Cu, which may be related to isotopically heavier Cu associated with DOM in the dissolved phase (El Azzi et al., 2013; Vance et al., 2008). However, the distribution of Cu in particle-size fractions (i.e., sand, silt, clay) can also influence Cu mobilization from the soil during rainfall-runoff events (Roussiez et al., 2013; Wang et al., 2014). Cu can accumulate in the coarse particulate SOM (Besnard et al., 2001; Parat et al., 2002) as well as in finer soil particles that are preferentially mobilized by runoff (Di Stefano and Ferro, 2002). However, knowledge of the effect of pedogenetic processes on the metal isotopic signature in soils is scarce, and the Cu isotope distribution in the particle-size fractions of the soil and in runoff is currently unknown.

Therefore, we hypothesized that Cu isotopes can be used to discriminate anthropogenic from geogenic Cu, and to evaluate Cu distribution in particle-size fractions of agricultural soils as well as Cu export during rainfall-runoff events. We combined a Cu mass balance approach, particle-size separation of bulk vineyard soils, mineralogical and Cu isotope analysis in a vineyard catchment (Rouffach, Haut-Rhin, France) to investigate i) the retention and distribution of Cu in particle-size fractions of the vineyard soil, and ii) the mobilization and transport by runoff of the dissolved and SPM-bound Cu in relation to Cu-fungicide use and rainfall patterns. To achieve this, the $\delta^{65}\text{Cu}$ values of the Cu-fungicides, $^{65}\text{Cu}/^{63}\text{Cu}$ fractionation upon Cu retention and distribution in the soils, and Cu transport in runoff were evaluated during the period of Cu fungicide use (May to July).

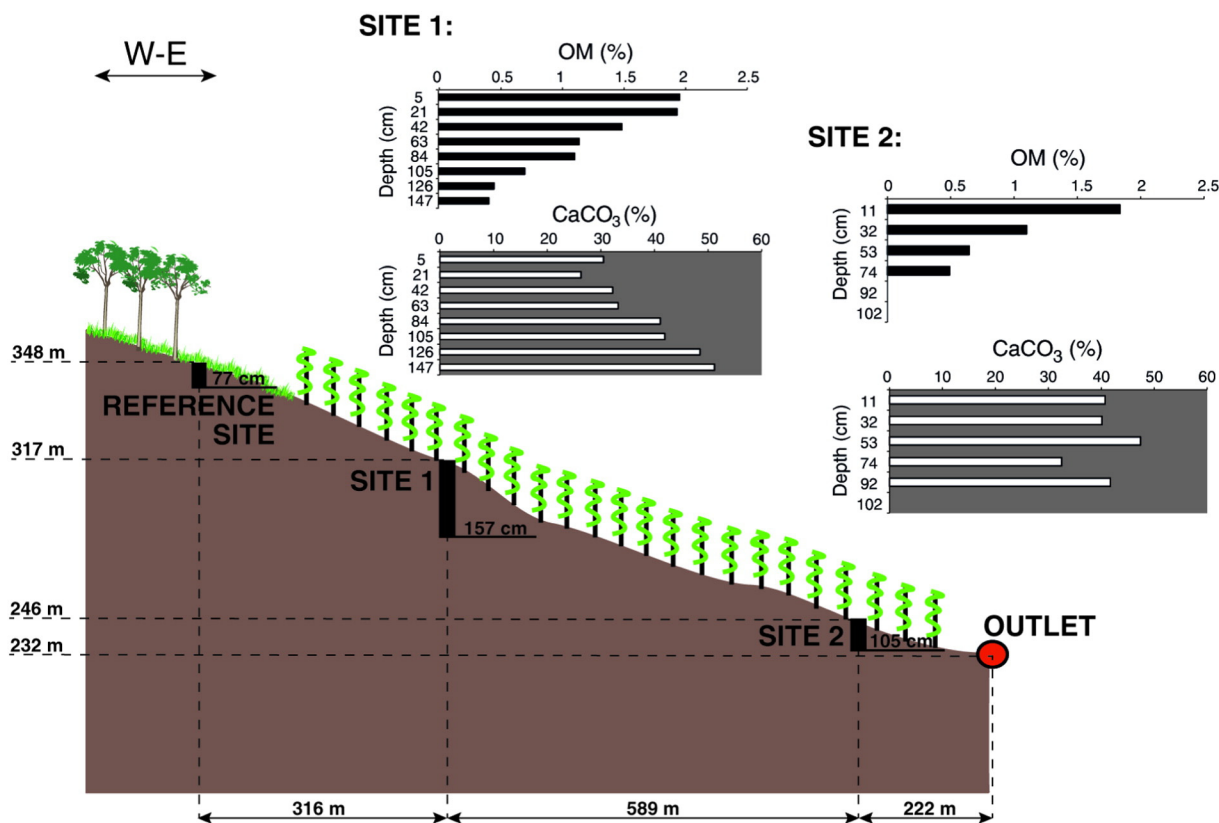


Fig. 1. Schematic cross-section of the vineyard catchment at Rouffach (Haut-Rhin, France) and location of the soil profiles (sites 1 and 2) and the reference site. The depth variation of the carbonate (CaCO_3) and the organic matter (OM) concentrations under weeded inter-rows are provided for sites 1 and 2.

Download English Version:

<https://daneshyari.com/en/article/6322436>

Download Persian Version:

<https://daneshyari.com/article/6322436>

[Daneshyari.com](https://daneshyari.com)