



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



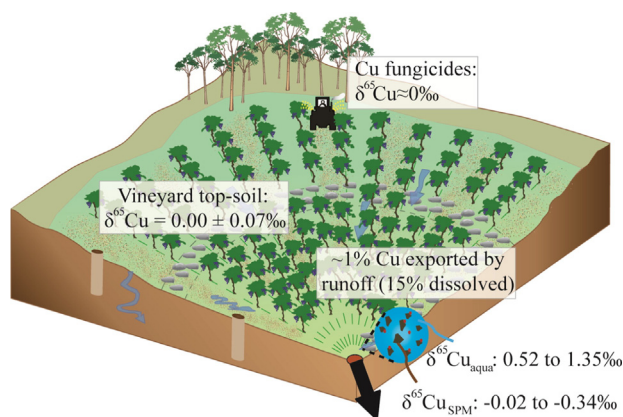
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HIGHLIGHTS

- 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



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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.

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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 (⁶⁵Cu/⁶³Cu) (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, ⁶⁵Cu/⁶³Cu 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).

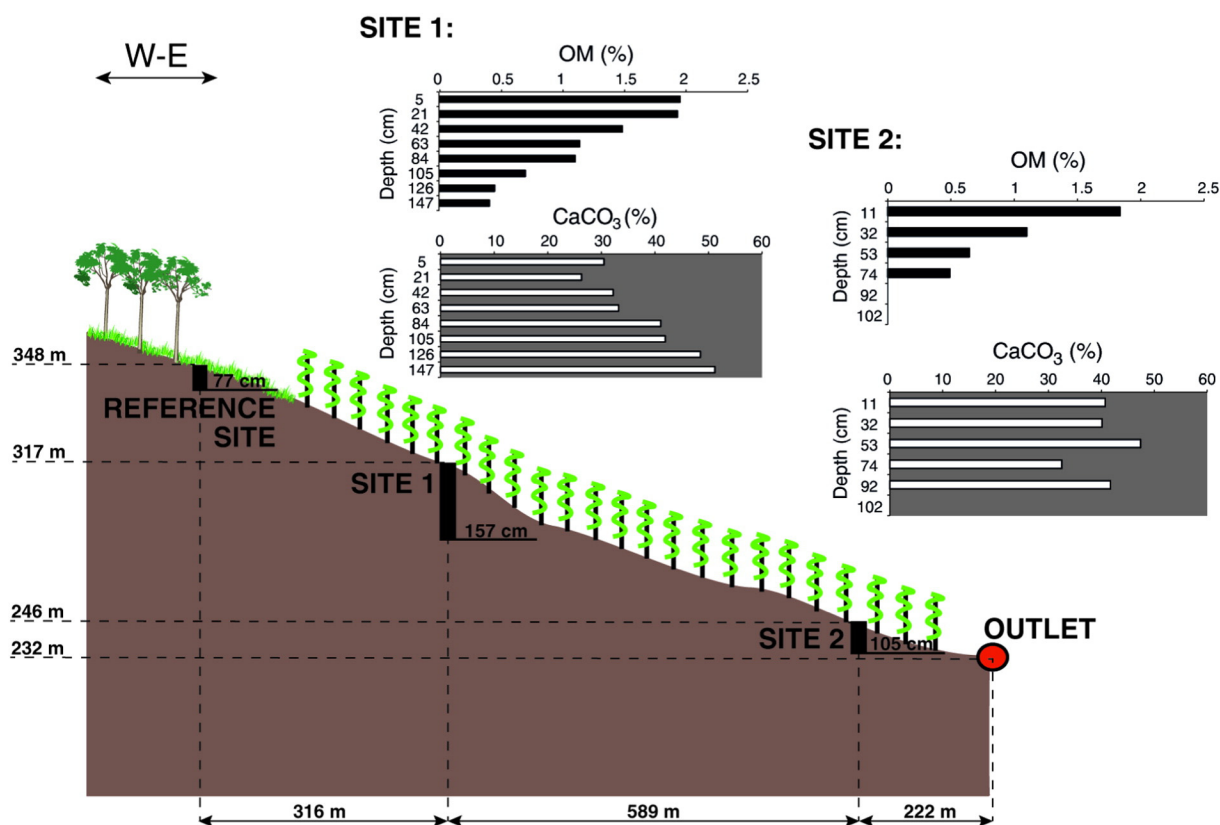


Fig. 1. Schematic cross-section of the vineyard catchment at Rouffach (Haut-Rhin, France) and location of the soil profiles (sites 1 and 2) and the reference site. The depth variation of the carbonate (CaCO₃) and the organic matter (OM) concentrations under weeded inter-rows are provided for sites 1 and 2.

2. Materials and methods

2.1. Study catchment and soils

The study site is a 42.7 ha vineyard catchment situated in the Alsatian foothills (47°57'9 N, 07°17'3 E) (Grégoire et al., 2010). The catchment has a mean slope of 15%. The catchment is mainly occupied by vineyards (59%, i.e. 25.3 ha), forests and pasture (29%), grassed strips and ditches (7%), as well as roads and paths (5%). Roads and paths represent the principal route of water flow in this catchment (Lefrancq et al., 2013).

The rainfall was monitored by a meteorological station located in the catchment (Lefrancq et al., 2013). Rainfall between May and July averaged 187 ± 64 mm (1998–2011) and was 157 mm during the study period (from 11th May to 20th July). The mean runoff coefficient in the catchment was 1.61% during the study period. The rainfall-runoff events do not generate a permanent stream in the catchment. Discharge at the catchment's outlet is driven by Hortonian overland flow. The road network mainly contributes to the discharge during low rainfall intensity (i.e. >6 mm h⁻¹) (Lefrancq et al., 2014), while the vineyard plots contribute when the rainfall intensity overcomes the saturated hydraulic conductivity (i.e. 58 mm h⁻¹ ± 50 , $n = 48$) (Tournebize et al., 2012). The saturated hydraulic conductivity can be reduced by one order of magnitude on plots when top soil sealing appears. Overland flow on plots is reduced by grass strips of 2 to 3 m width at the plot edges (Lefrancq et al., 2014). Hortonian overland flow prevails, as indicated by fast hydrological response to rainfall events (i.e. 6 to 12 min between rainfall and runoff peaks) and fast recession period (<1 h) with total discharge cessation at the outlet. The contribution of baseflow is thus unlikely as steep slopes (i.e. 15%), with high vertical saturated hydraulic conductivity prevent downslope lateral flow on saturated zones.

The soils are calcareous clay loam with a soil bulk density of 1.4 g cm⁻³ developed on a loess basement (Tournebize, 2001). The main soil types of the catchment are Cambisol (Hypereutric Clayic) (site 1) and Haplic Cambisol (Calcaric Siltic) (site 2) (Duplay et al., 2014). The vineyard plots are permanently covered by grass in every second inter-row to limit soil erosion, and weeded inter-rows are ploughed to a depth of 15 cm to enhance water infiltration. The grass cover was implemented 3 to 4 years after the planting of vines. Vine growing started in 1973 on site 1 (previously grassland) and in 1962 on site 2 (Fig. 1). The width between grass-covered vine inter-rows is 170 cm on site 1 (as for 77% of the catchment's area), 240 cm at site 2, while the width between weeded inter-rows is 140 cm. Surface soils on site 1 have less carbonates, and slightly higher OM compared to site 2 (Fig. 1 and Table S.1). Soil minerals mainly consisted of calcite, quartz, and minor amounts of feldspars, dolomite and clay minerals (Table S.2) (Duplay et al., 2014). The A horizon extends until 30–45 cm depth, the B horizon until 80–100 cm, and the C horizon until the bedrock (loess) situated at ~ 210 cm.

2.2. Cu fungicide applications

Cu fungicide applications were estimated based on surveys addressed to the wine producers of the catchment. Cu was sprayed directly on the vine canopy to combat downy mildew (*Plasmopara viticola*) (MacKie et al., 2012). Cu fungicides were applied almost on all vineyards ($>97\%$) in the catchment from May to August in quantities of 2.2 ± 0.3 kg (of the fungicide preparation) ha⁻¹ y⁻¹ (2008–2011) in the forms of Cu-sulfate (Bordeaux mixture, CuSO₄ + Ca(OH)₂), Cu-oxide (Cu₂O), Cu-hydroxide (Cu(OH)₂) and Cu-oxchloride (3Cu(OH)₂·CuCl₂). Application rates of the Cu-fungicides ranged from 0.09 to 1.50 kg ha⁻¹ in 2011, depending on the vine-producers and the type of Cu-fungicide. The study was performed from 11th May to 20th July 2011, covering most of the Cu application period and corresponding to 63% of the annual application of Cu. The input of atmospheric Cu to the catchment (~ 83 g) was $\leq 0.5\%$ of the

mass of applied Cu fungicides during the study period (Chabaux et al., 2005) (Table 1).

2.3. Soil and runoff collection

Two soil cores were collected using a hand auger down to a depth of 157 cm at site 1, and a depth of 105 cm at site 2 (Fig. 1). The depth resolution of the soil sampling ranged from 10 to 20 cm. Eight soil samples were collected at site 1, and six at site 2. The Cu isotope ratios of six samples at site 1 and five samples at site 2 were measured. The physico-chemical characteristics of the soil samples are summarized in the Table S.1 and described elsewhere (Duplay et al., 2014). Four surface (0–18 cm) and near surface (36–54/30–42 cm) soil samples were also collected under grass-covered inter-rows at sites 1 and 2 for chemical composition and Cu isotope analyses, and stored in polyethylene bags. In addition, composite topsoil samples (0–5 cm) were collected along three transects across the catchment (~ 50 g bags of soil were collected each dozen of vine-rows, corresponding to a distance of 15 to 20 m) and pooled to one composite sample per sampling date on 6th April, 11th May and 8th June 2011. A reference soil was collected in the forested area of the catchment (Fig. 1), which was never cultivated, for comparison with the vineyard soils from sites 1 and 2. The reference soil was sampled at 70 cm, close to the bedrock and served for quantifying the geogenic Cu.

The water discharge at the catchment outlet, consisting in a constructed ditch, was continuously monitored using a bubbler flow module (Hydrologic, Canada) combined with a Venturi channel. Flow-proportional samples of runoff water were collected during each runoff event (300 mL every 3 m³) using a 4010 Hydrologic automatic sampler (Hydrologic, Canada) (Maillard and Imfeld, 2014), and samples were combined weekly into a single composite sample. Samples were refrigerated during sampling and placed on ice during transport to the laboratory.

2.4. Sample preparation and analysis

Soil samples were air-dried at 20 °C and sieved (2 mm). Dried samples were powdered using an agate disk mill (<100 μm) prior to alkaline fusion and total dissolution by acids for chemical composition

Table 1

Estimates of annual inputs of elemental Cu, seasonal Cu fluxes (from 11th May to 20th July 2011) and Cu stocks in the upper soil and the grass biomass of the vineyard catchment (Rouffach, France; 42.7 ha, of which 25.3 ha of vineyards).

Stock in the catchment soil (top 5 cm) ^a	[kg]	1800
Stock in vineyard soils (top 5 cm)	[kg]	1670
Stock in the grass biomass of vineyards ^b	[kg]	5.2
Initial stock in the vineyard topsoils (top 5 cm) ^c	[kg]	200
Accumulation rate in the vineyard topsoils (top 5 cm) ^d	[kg ha ⁻¹ year ⁻¹]	1.2
Amount of applied Cu fungicides	[kg]	16.5
Rate of Cu fungicides' application	[kg ha ⁻¹ year ⁻¹]	1.24
Atmospheric input ^e	[kg ha ⁻¹ year ⁻¹]	6×10^{-3}
SPM-bound export by runoff	[kg ha ⁻¹ season ⁻¹]	3×10^{-3}
Dissolved export by runoff	[kg ha ⁻¹ season ⁻¹]	5×10^{-4}

^a Estimated based on the mean Cu concentration in vineyard top-soil samples (top 5 cm of the soils sampled along three transects in the catchment) and the Cu concentration of the (uncultivated) reference soil (top 5 cm).

^b Estimated based on the mean Cu concentrations in the aerial part of the grass (22.8 mg kg⁻¹) and the root following Cu applications (44.3 mg kg⁻¹) (Duplay et al., 2014), a shoot to root biomass ratio of 1.75 (Bolinder et al., 2002) and a maximum dry grass biomass of 6.7 t ha⁻¹ (Tournebize, 2001).

^c Estimated based on the Cu concentrations in the (uncultivated) reference soil.

^d Estimated based on the initial stock in the vineyard top-soils (top 5 cm) and the actual stock in the vineyard soils (top 5 cm) over the 50 years period of vine growing.

^e Estimated based on the mean Cu concentration of the rainwater in the Alsatian basin (Chabaux et al., 2005) and the annual rainfall depth in the catchment in 2011 (502 mm).

analysis (Dequincey et al., 2006). The geological standards BCR-2 (US Geological Survey, Reston, VA, USA) and CRM-7003 (Analytika, Prague, Czech Republic) were used to quantify the Cu recovery following acid digestion, which was always >97%. Soil physico-chemical characteristics including the soil organic matter content (by loss on ignition) were determined as previously described (Duplay et al., 2014).

A composite topsoil (0–5 cm) sampled on 8th June, a weeded topsoils at site 1 (0–10 cm) and at site 2 (0–21 cm) as well as the reference soil were selected to determine the Cu distribution among particle size fractions (i.e., sand, silt, clay and fine clay) and analyzed in duplicate. Approximately 20 g of sieved soil (<2 mm) were suspended in 200 mL of 18.2 MΩ water (Millipore, Billerica, MA, USA) and disaggregated by high intensity sonication as described previously (see the SI for the detailed protocol) (Genrich and Bremner, 1974). Mineral phases present in bulk soil and particle-size fractions were identified by X-ray diffraction (XRD) (Bruker D5000, Karlsruhe, Germany) (Duplay et al., 2014).

The runoff water samples were filtered using a 0.45 μm cellulose acetate membrane (Millipore) and the filtrate (named below ‘dissolved phase’) was acidified to pH ~ 2 using double-distilled nitric acid. Hydrochemical analyses were performed as described elsewhere (Lucas et al., 2010).

2.5. Cu isotope analysis

For Cu isotope analysis, 100 mg of soil powder was weighed in PFA vials. Depending on the initial Cu concentrations, different volumes of water samples (runoff and the solution following particle size separation) were evaporated to reach 200 ng Cu. The SPM and fine clays were digested on filter membranes. All samples were dissolved in successive acid baths of HF-HNO₃ (v:v 4:1) at 70 °C, HClO₄ at 150 °C and HCl-H₃BO₃ (v:v 4:1) at 110 °C.

A protocol for double Cu purification was adapted from Maréchal et al. (1999) for each sample matrix (Babcsányi et al., 2014). The total procedural blank (sample digestion and purification) for Cu was ≤2 ng (*n* = 3) for water samples (≤1% of Cu in water samples) and 6.3 ± 4.4 ng ($\bar{x} \pm 2\sigma$, *n* = 5) for soil and SPM samples, including the Cu on the filter membranes (2.5 ng) (≤1% of the Cu in the soil and SPM samples).

Cu isotope ratios were measured in both wet and dry plasma modes with a Finnigan-Neptune MC-ICP-MS (Thermo Scientific, Waltham, MA, USA) using a nickel standard (NIST SRM 986) and a Cu standard (NIST 976) for correction of instrumental mass biases as previously described (Li et al., 2009). The total uncertainty that incorporates both accuracy and reproducibility for the mean δ⁶⁵Cu-values for the entire procedure (digestion, purification and isotope analysis) was ≤0.08%. The uncertainty was determined by using the soil reference material CRM-7003 (0.18 ± 0.08‰, including 3 separately digested samples and 15 isotope measurements), and confirmed by the δ⁶⁵Cu values of 0.07‰ (2σ) for three distinct catchment topsoil samples collected on 6th April, 11th May and 8th June 2011. The Cu isotope ratios were expressed as δ⁶⁵Cu values [‰] relative to the NIST 976 reference material.

2.6. Data analysis

An enrichment factor (EF) was used to compare changes of the Cu concentrations in the soil profiles at site 1 and 2 with the reference soil at 70 cm depth (Eq. 1):

$$EF_{Cu} = \frac{\left(\frac{Cu_{sample}}{Fe_{sample}}\right)}{\left(\frac{Cu_{reference}}{Fe_{reference}}\right)} \quad (1)$$

where Cu and Fe are, respectively, the concentrations of Cu and Fe (mg kg⁻¹ d.w.) in the vineyard soil sample and the reference soil (Fig.

1). Fe was selected as the reference element to limit EF variations due to local heterogeneities as its variation coefficient over the soil profiles was low (Reimann and de Caritat, 2005).

A seasonal export coefficient was calculated as the ratio of the total Cu load exported from the vineyard catchment by runoff over the total Cu mass applied during the study period (11th May to 20th July 2011) (Eq. 2).

The mean δ⁶⁵Cu value of the applied Cu fungicides was calculated by isotopic mass balance accounting for each individual Cu fungicide:

$$\delta^{65}Cu_{mean} = f_{CuSO_4} \times \delta^{65}Cu_{CuSO_4} + f_{3Cu(OH)_2CuCl_2} \times \delta^{65}Cu_{3Cu(OH)_2CuCl_2} + f_{Cu(OH)_2} \times \delta^{65}Cu_{Cu(OH)_2} + f_{Cu_2O} \times \delta^{65}Cu_{Cu_2O} \quad (2)$$

where *f* is the mass fraction of the Cu fungicides used and δ⁶⁵Cu value is the Cu isotope composition of the fungicides.

Hydro-climatic data and chemical compositions of soils and runoff were compared using the paired non-parametric Spearman rank correlation test using *R* (www.r-project.org), with *p*-values set at 0.05.

3. Results

3.1. Cu fungicides

From 5th May (first Cu application) until 1st August (last Cu application) 2011, 1.24 kg ha⁻¹ of elemental Cu was applied on the catchment (i.e. 26.07 kg for the entire vine-growing season). 16.50 kg of elemental Cu was applied during the study period (11th May to 20th July), which represented ~1% of the initial Cu stock in the top 5 cm of the vineyard soils (~1670 kg) (Table 1). The seven Cu fungicides used by local farmers had δ⁶⁵Cu values ranging from -0.21 to 0.91‰. The δ⁶⁵Cu values of the four Cu fungicides used in 2011 (Bordeaux mixture (CuSO₄ + Ca(OH)₂), Nordox (Cu₂O), Syphal (3Cu(OH)₂·CuCl₂), Cuprofix (CuSO₄)) varied from -0.21 to 0.11‰ (Table S.3). Kocide (Cu(OH)₂), Champ flo (Cu(OH)₂) and Cursor (3Cu(OH)₂CuCl₂) were not used in 2011.

3.2. Cu accumulation and variations of δ⁶⁵Cu values in the vineyard soils

The Cu concentration of grass-covered topsoils (0–18 cm) of both sampling sites was lower than that of the weeded topsoils (0–21 cm) (Table S.1). However, the δ⁶⁵Cu values of bulk grass-covered (0–18 cm) and weeded (0–10 to 21 cm) topsoils were similar. This suggests that grass cover did not affect Cu isotope fractionation in the bulk soil. Estimated Cu in the grass biomass (~5.2 kg) accounted for ~0.3% of the total Cu stock in the first 5 cm of the vineyard soils, indicating low Cu uptake in the grass (Table 1).

At site 2, concentrations in the top 20 cm (231 mg kg⁻¹) were higher than in the top 10 cm at site 1 (74 mg kg⁻¹) (Table S.1), and decreased with depth down to 11.5 mg kg⁻¹ at 100 cm depth. Correspondingly, enrichment factors (EF) were significantly higher at site 2 (4.0 to 27.6) compared to site 1 (1.4 to 9.6) (Fig. 2), which reflects the longer use of Cu fungicide (i.e., the vines were planted 11 years earlier at site 2 than at site 1). The estimated Cu accumulation rate in the first 5 cm of the vineyard soils of the catchment during the 50 years of vine-growing (~1.20 kg ha⁻¹ year⁻¹) corresponds to that of current Cu application rates (1.24 kg ha⁻¹ year⁻¹) (Table 1). The δ⁶⁵Cu values in the soil profile ranged from -0.12 to 0.24‰ at site 1, and did not significantly vary at site 2 (-0.05 to 0.04‰) (Fig. 2). The δ⁶⁵Cu value of the background Cu in the reference soil (0.08‰ at 67–77 cm depth) was slightly higher than that in the deepest soil horizon at site 1 (-0.12‰) (Fig. 2).

3.3. Cu distribution and δ⁶⁵Cu values in the soil particle-size fractions

The particle-size separation yielded qualitatively distinct soil fractions (Table S.2). The fine clays and the clay fractions represented 26

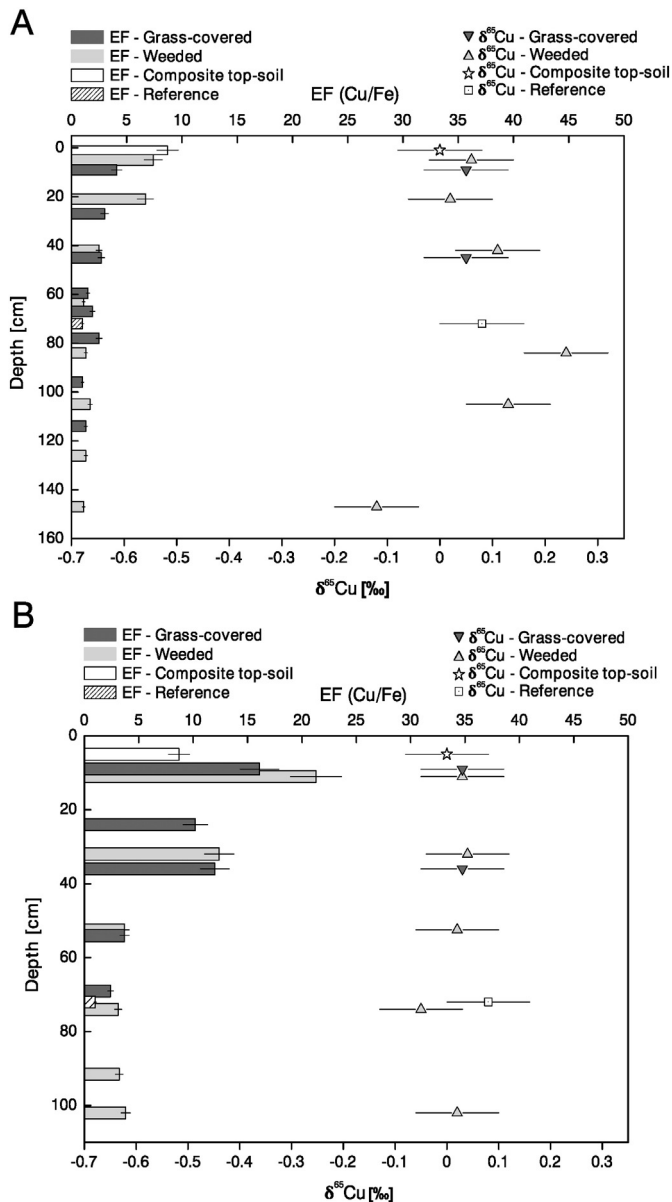


Fig. 2. Cu enrichment factors (EF) and $\delta^{65}\text{Cu}$ values in the soil depth profiles at site 1 (A) and site 2 (B) of the vineyard catchment (Rouffach, France). The deepest soil horizon (67–77 cm) of the reference site and the composite top-soil samples (0–5 cm) are also displayed. Error bars correspond to the analytical uncertainty of the Cu isotope measurements ($\pm 0.08\text{‰}$).

to 31% (total weight) of the bulk vineyard soils. Cu concentrations were twice as high in the fine clay and the clay fractions (111 to 467 mg kg^{-1}) than in the bulk soils (Tables S.1 and S.4). Cu concentrations were significantly higher in the fine clay fraction (76 to 408 mg kg^{-1} Cu, accounting for 2.6 to 4.8%) than in the silt fraction (62 to 154 mg kg^{-1}), except at site 1 ($p < 0.05$). At site 1, proportion of Cu in the silt fraction (55%) was higher than that in the clay fraction (40%), the fine clay fraction (3%) and the soil solution (2%) (Table S.4). Topsoils at site 2 (0–21 cm) were coarser with less clay and larger sand fractions compared to site 1 (0–10 cm) (Table S.4). At site 2, 51% of Cu accumulated mainly in the clay fractions (47% was in the clay and 4% in the fine clay), and in lower proportions in the silt (27%) and the sand (~20%). Cu concentrations in the aqueous solution obtained from the clay separations varied from 5 to 32 $\mu\text{g L}^{-1}$. The reference soil was composed of sand (30.0%), silt (39.5%), clay (23.5%) and fine clay (0.1%) fractions, with geogenic Cu concentrations of 11.7, 9.4, 16.6, 3.6 (i.e., 30.6%, 23.3%, 33.9%,

<0.1%), respectively, and 3 $\mu\text{g L}^{-1}$ (i.e., 3.1%) in the aqueous solution (Table S.4).

Significant differences of Cu concentrations and $\delta^{65}\text{Cu}$ values in the soil fractions indicated Cu isotope fractionation in the vineyard soils (Table S.4). The fine clay fraction was the most depleted in ^{65}Cu ($\delta^{65}\text{Cu}$ values from -0.42 to -0.32‰ , $\bar{x} \pm 2\sigma$: $-0.37 \pm 0.10\text{‰}$), followed by the clay fraction (-0.15 to -0.06‰ ; $\bar{x} \pm 2\sigma$: $-0.08 \pm 0.09\text{‰}$). In contrast, the silt fraction was enriched in ^{65}Cu (0.19 to 0.24‰; $\bar{x} \pm 2\sigma$: $0.23 \pm 0.07\text{‰}$) (Figs. 3 & 4, Table S.4). Cu in the solution was also isotopically heavier (0.04 to 0.44‰). $\delta^{65}\text{Cu}$ values of the particle-size fractions of the reference soil (-0.09‰ in the silt, 0.18‰ in the clay and 1.28‰ in the solution) differed from those of the vineyard soils. The $\delta^{65}\text{Cu}$ value of the fine clay fraction in the reference soil could not be analyzed due to insufficient amounts of Cu.

3.4. Cu export and $\delta^{65}\text{Cu}$ values in SPM-bound and dissolved runoff phases

A total of 43 rainfall events occurred during the study period that generated 27 runoff events. At least 1 rainfall-runoff event occurred weekly (weekly hydrological data are summarized in Table S.5). For the 43 rainfall events, rainfall depth ranged from 0.2 to 23.9 mm with mean intensities from 0.3 to 14.0 mm h^{-1} . The runoff volumes per event ranged from 2.5 to 195.4 m^3 , amounting to a total volume of 1247.8 m^3 for the investigation period. SPM concentrations in runoff ranged from 110 to 2866 mg L^{-1} (Table S.5). SPM-bound Cu concentrations in runoff ranged from 90 to 366 mg kg^{-1} ($\bar{x} \pm 2\sigma$: $164 \pm 177 \text{ mg kg}^{-1}$) and from 40.1 to 395.2 $\mu\text{g L}^{-1}$ ($\bar{x} \pm 2\sigma$: $118 \pm 219.7 \mu\text{g L}^{-1}$) on a volumetric basis. Dissolved Cu (<0.45 μm particle-size fraction) concentrations in runoff ranged from 7.7 to 32.0 $\mu\text{g L}^{-1}$ ($\bar{x} \pm 2\sigma$: $21.6 \pm 16.0 \mu\text{g L}^{-1}$) (Table S.6), which was 7 to 27 fold higher than average dissolved Cu concentrations in earth's rivers (1.19 $\mu\text{g L}^{-1}$) (Vance et al., 2008). The $\delta^{65}\text{Cu}$ values of the dissolved Cu in runoff ranged from 0.52 to 1.35‰ and from -0.02 to -0.34‰ in the SPM-bound Cu fraction (Fig. 4). $\delta^{65}\text{Cu}$ values of SPM-bound Cu were similar to those of the clay and the fine clay fractions of the vineyard topsoils (0–10/21 cm). This suggests a preferential mobilization of fine soil particles during rainfall-runoff (Fig. 4), in agreement with previous observations (Wang et al., 2014; Fernández-Calviño et al., 2008a).

Altogether, 144 g of Cu was exported in runoff from the catchment, representing 0.9% of the Cu mass applied during the investigation period (Table 1). Cu export in runoff was mainly associated with SPM (56 to 93% depending on the rainfall-runoff events), which indicated that physical erosion drove Cu mobilization from the vineyards during rainfall-runoff events. Intense rainfall events resulted in higher concentrations of dissolved Cu in the runoff ($\rho = 0.96$, $p = 0.003$, $n = 7$, without the June 8 sample) that may be due to the higher contribution of runoff generated on the vineyard soils. Estimates of Cu deposition onto non-target areas such as road surfaces prone to runoff ranged between 0.05 and 0.4% of the applied Cu amount during the investigation period. This estimation assumes the same application mode and device as for the fungicide kresoxim methyl applied in the same catchment (Lefrancq et al., 2013), but with a spray volumetric rate of 160 L ha^{-1} . This indicates that Cu was mainly exported in surface runoff from the vineyard plots and not from the non-target areas.

The annual Cu export from the catchment was estimated to 388 g, based on the detailed Cu mass balance in the stormwater wetland located at the catchment's outlet that accumulated over 2.5 years 92% for the SPM-bound and 68% for the dissolved Cu (Babcsányi et al., 2014). This suggests that about 37% (144 g) of the Cu export occurred during the investigation period (11th May to 20th July). Hence, freshly applied Cu may contribute to the Cu export to a larger extent than older Cu applied in the previous years as also suggested by the larger weekly dissolved loads of Cu in runoff following Cu fungicide use (Figure S.2). However, no correlation could be found between the $\delta^{65}\text{Cu}$ values of Cu fungicides and those of runoff-associated Cu (Fig. 4).

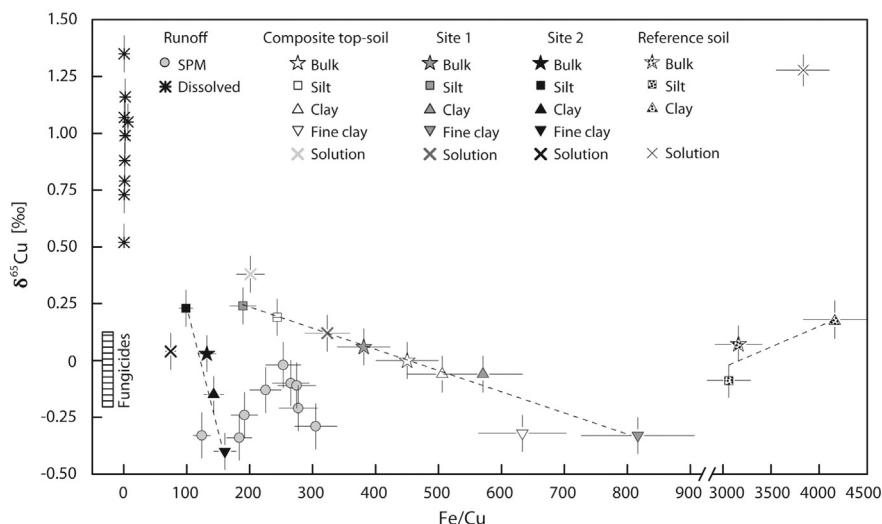


Fig. 3. $\delta^{65}\text{Cu}$ values of the SPM-bound and dissolved Cu in runoff at the outlet of the catchment (Rouffach, France). The soil fractions of a composite top-soil (0–5 cm), the surface soils under weeded inter-rows at site 1 (0–10 cm) and 2 (0–21 cm) as well as the reference soil are displayed as a function of the Fe/Cu molar ratios and linked with dashed lines. The vertical bars (horizontal hatching) represent the range of $\delta^{65}\text{Cu}$ values of Cu fungicides. Cu concentrations of the soils differed at site 1 and 2 (Fe concentrations are similar). Error bars correspond to the analytical uncertainty of the Cu isotope measurements ($\pm 0.08\%$).

4. Discussion

4.1. Cu retention and distribution in the vineyard soils.

In the vineyard, $\delta^{65}\text{Cu}$ values for the grass-covered (0–18 cm) were similar to those of weeded topsoils (0–21 cm). Cu translocation from the soil to the grass was low ($\sim 0.3\%$) (Table 1). This supports the idea that vegetation did not affect the Cu isotope pattern in the vineyard soils. Indeed, plant uptake of Cu is expected to enrich in ^{63}Cu the plants, yielding a $\Delta^{65}\text{Cu}_{\text{plant-nutrient}}$ of -0.1 to -1% (Jouvin et al., 2012; Ryan et al., 2013). In addition, $\delta^{65}\text{Cu}$ values did not vary significantly with depth at site 2, which suggests that Cu uptake by vines is limited in calcareous vineyards (Chopin et al., 2008).

The depletion in ^{65}Cu with soil depth associated with lower Cu enrichments ($\text{EF} \leq 2$) below 70 cm at site 1 concurs with the Cu isotope distribution patterns of geogenic Cu observed in oxic weathered soils (Bigalke et al., 2011). The variation in the $\delta^{65}\text{Cu}$ values below 70 cm at

site 1 suggest that Cu isotope fractionation occurred during weathering of the bedrock and transport of geogenic Cu into the soil or loess deposits of different origins from which the soil layering developed (Bigalke et al., 2011). In addition, the vertical transport of isotopically lighter colloidal or solid-bound Cu during the rainwater infiltration may also contribute to the vertical distribution of Cu isotopes.

The bulk soils at site 1 and 2, regardless of the level of Cu enrichment, had similar $\delta^{65}\text{Cu}$ values since the mean $\delta^{65}\text{Cu}$ value of Cu fungicides (0‰) encompassed that of geogenic Cu in the soil. The $\delta^{65}\text{Cu}$ values of the bulk vineyard soils thus cannot indicate sorption or accumulation of anthropogenic Cu. This supports the idea that pedogenetic processes produce Cu isotope fractionation that cannot always be discerned in bulk soil, or can even be overprinted by an exogenous isotopic signature (Fekiacova et al., 2015). However, the $\delta^{65}\text{Cu}$ and the Fe/Cu molar ratios for the particle-size fractions of vineyard soils negatively correlated, whereas no correlation was found in the case of the reference soil (Fig. 3). Fe is distributed not only in the Fe oxy(hydr)oxides, such as goethite

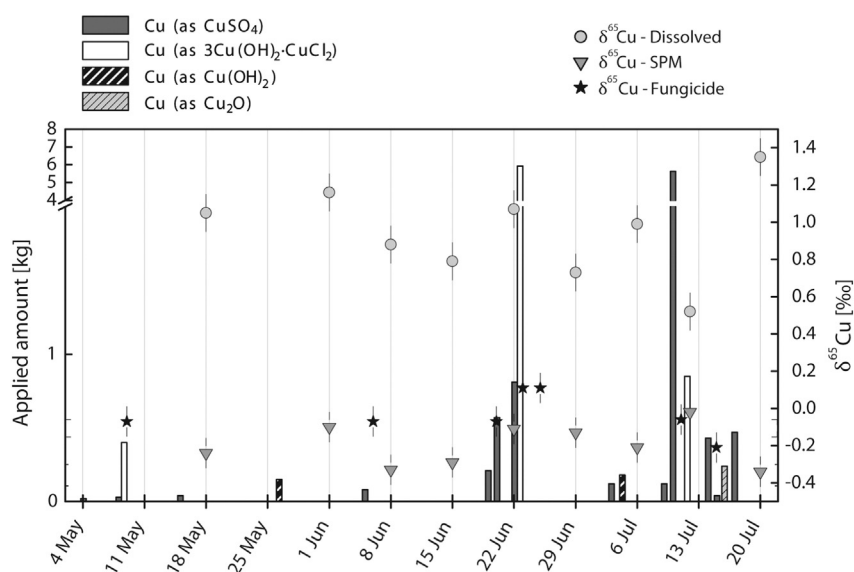


Fig. 4. Amounts and $\delta^{65}\text{Cu}$ of the Cu fungicides applied on the vineyard catchment (Rouffach, France) and $\delta^{65}\text{Cu}$ of runoff-associated Cu in the dissolved and the SPM-bound phases from May 11 to July 20. Error bars correspond to the analytical uncertainty of the Cu isotope measurements ($\pm 0.08\%$).

(as detected by XRD analysis in the clay fractions), but also in the clay minerals, such as chlorite (Table S.2). The relationship between the $\delta^{65}\text{Cu}$ values and the Fe/Cu molar ratios indicates that Cu isotope fractionation was associated with Cu distribution processes in the soil. Cu distribution processes in the calcareous vineyard soils include Cu precipitation as carbonates and sorption of Cu to SOM and mineral phases.

Precipitation of Cu as carbonates or hydroxides was previously noted as the prevailing process of Cu retention in calcareous soils (El Azzi et al., 2013; Komárek et al., 2009; Ma et al., 2006b; Ponizovsky et al., 2007). The precipitation of malachite is expected to enrich the precipitates in ^{63}Cu ($\Delta^{65}\text{Cu}_{\text{Cu(II)aq-malachite}} = 0.17$ to 0.38%) (Maréchal and Sheppard, 2002). Hence, the relative enrichment in ^{63}Cu observed in the clay fractions as compared to the $\delta^{65}\text{Cu}$ values in the reference soil may indicate Cu carbonate precipitation. In this case, Cu carbonate precipitation would enrich in ^{65}Cu the silt and the sand fractions of the vineyard soils. However, XRD data showed that carbonate phases (calcite, dolomite) prevailed in the silt fraction that was enriched in ^{65}Cu , whereas only traces of calcite in the clay and no carbonates were found in the fine clay fractions that were enriched in ^{63}Cu (Table S.2). Cu precipitation as carbonate thus cannot explain the enrichment in ^{65}Cu in the silt fraction nor that in ^{63}Cu in the clay fractions. Cu retention processes involving SOM and the mineral phases, should therefore be considered.

The formation of SOM-Cu complexes (Strawn and Baker, 2009) (e.g. Fernández-Calviño, 2008a, 2008b; El Azzi et al., 2013), Fe oxide (de Santiago-Martín et al., 2013; Sayen et al., 2009) as well as clay minerals and organo-clay complexes (Besnard et al., 2001; Sipos et al., 2008) control the Cu sorption and accumulation in soils. Cu sorption to SOM ($\Delta^{65}\text{Cu}_{\text{SOM-Cu(II)aq}} = 0.15$ to 0.37%) (Bigalke et al., 2010b), Fe oxy (hydr)oxides ($\Delta^{65}\text{Cu}_{\text{Fe oxy(hydr)oxides-Cu(II)aq}} = 0.24$ to 0.98%) (Balistrieri et al., 2008; Pokrovsky et al., 2008) is expected to enrich bound Cu in ^{65}Cu . In contrast, preferential sorption of ^{63}Cu onto clay minerals has been recently evidenced ($\Delta^{65}\text{Cu}_{\text{kaolinite-Cu(II)aq}} = -0.29$ to -1.46%) (Li et al., 2015). Given that the mean $\delta^{65}\text{Cu}$ values of Cu fungicides were $\sim 0\%$, the enrichment in ^{63}Cu in the clay fractions may indicate preferential Cu sorption onto clay minerals (Table S.2). Indeed, Cu sorption to Fe oxides or SOM is expected to enrich the clay fractions in ^{65}Cu . However, efficient Cu complexation with SOM in the calcareous vineyard soils at pH values above is expected (Komárek et al., 2010; Ryan et al., 2014), and should be primarily considered to explain the trends of $\delta^{65}\text{Cu}$ values variations in the grain-size fractions (Fig. 4). In particular, Cu complexation to different SOM quality may explain the Cu isotope fractionation in the soil fractions. The SOM quality may vary among the soil fractions and affect the stability constant of the Cu-SOM complexes ($\Delta^{65}\text{Cu}_{\text{complex-free}}$ from 0.14 to 0.84%; Bigalke et al., 2010b; Ryan et al., 2014). For instance, less degraded SOM, such as plant fragments and polysaccharides, is more common in the coarser fractions (silt), while more altered (oxidized) SOM is more common in the clay fractions (Besnard et al., 2001; Parat et al., 2002; Quenea et al., 2009). Hence, labile N-containing and aromatic compounds and highly altered organic matter (e.g., fulvic acid) may accumulate and stabilize in the clay fractions in the form of organo-mineral complexes (Mertz et al., 2005; Poirier et al., 2005).

Preferential Cu sorption to SOM likely caused the enrichment in ^{65}Cu in the silt fraction. The silt fraction contains essentially primary minerals to which Cu has lower affinity compared to the secondary mineral phases in the clay fractions (Table S.2) (Komárek et al., 2010). The higher SOM/Al and SOM/Fe ratios in the silt fraction than in the clay fractions also underscore that Cu-SOM interactions prevailed in the silt fraction. In organic matter, Cu(II) is typically bonded to carboxyl and carbonyl O and amino N ligands (Karlsson et al., 2006). Cu binding to N atoms is suggested to form less stable Cu-SOM complexes compared to Cu-O bonds. The lower stability of the Cu-SOM complexes may enrich in ^{63}Cu the SOM-complexed Cu (Ryan et al., 2014). Hence, N-groups and Cu-N interactions may prevail in the clay fractions (Mertz et al., 2005), thereby leading to an enrichment in ^{63}Cu . In contrast, larger

amounts of polysaccharides and Cu binding may prevail in the silt fractions, resulting in an enrichment in ^{65}Cu .

Overall, Cu distribution processes in the vineyard soils involve preferential Cu sorption in the clay fractions with concomitant enrichment in ^{63}Cu , as well as sorption to SOM and enrichment in ^{65}Cu in the silt fraction. This pattern is also reflected in runoff from the vineyard catchment.

4.2. Cu distribution in runoff and export from the vineyard catchment

Previous studies have shown that the dissolved phase of Cu in rivers was enriched in ^{65}Cu compared to the suspended solids due to the equilibrium partitioning of Cu isotopes between the organically complexed Cu and the Cu sorbed to the SPM phase (El Azzi et al., 2013; Vance et al., 2008). In our study, speciation modelling using Minteq with Nica-Donnan and Stockholm Humic (SH) models (data not shown) indicates Cu complexation with DOM in the dissolved phase of runoff occurring at pH values above 7 (Thompson and Ellwood, 2014; Vance et al., 2008). $\delta^{65}\text{Cu}$ values of the silt and clay fractions are congruent with those in the dissolved phase of runoff provided that Cu sorption to the soil occurred through primary sorption to the clay fractions and secondary sorption of the residual Cu to the silt fraction. In this case, Cu mobilized by the rainwater and dissolved in runoff consisted of Cu-DOM complexes, mainly released from the silt fraction and enriched in ^{65}Cu , although the correlation between DOM and Cu concentrations in runoff was low ($\rho = 0.18$, $p = 0.63$, $n = 9$) (Table S.6). In addition, Cu(I) oxide fungicides (Nordox, $\delta^{65}\text{Cu}$: -0.21%) may be oxidized in the soil, which is expected to release isotopically heavier Cu(II) in solution as found in the case of Cu (I) sulfide re-oxidation (Mathur et al., 2014). It can also be hypothesized that kinetic isotope fractionation during Cu ageing in the vineyard soil results in higher $\delta^{65}\text{Cu}$ values in the runoff. Correspondingly, Cu diffusion into the microstructure of organo-clay complexes during Cu ageing may cause sequential depletion in ^{63}Cu in the clay fractions, while reducing Cu mobility and availability in the soil (Ma et al., 2006a). Cu ageing has been observed in calcareous (Sayen et al., 2009) and acidic soils (Arias-Estévez et al., 2007). However, the extent and the direction of Cu isotope fractionation during Cu ageing in soils are currently unknown.

The elemental composition and the $\delta^{65}\text{Cu}$ values of the SPM provided complementary information on SPM and Cu-bound SPM in runoff. The Al/Ca ratios can be used to evaluate the relative contribution of the particle-size fractions for each SPM sample, as silt contain higher Ca (due to carbonates) and clay minerals are enriched in Al (Chen et al., 2014). Al/Ca ratios of SPM in runoff ranged between the silt (0.5) and the clay (>2) end-members, and revealed the larger contribution of silt with increasing rainfall intensities (Fig. 5). In addition, Cu/Ca ratios show that the greater contribution of the silt fractions to the Cu export during intense rainfall events decreased the concentration of SPM-bound Cu in runoff. However, the greater contribution of the silt fraction increased the exported mass of SPM-bound Cu, but in a lower extent than if an equivalent mass of the clay fractions was exported (Figure S.3). In contrast, the $\delta^{65}\text{Cu}$ values of the SPM-bound Cu in runoff almost all ranged between those of the clay and the fine clay (Fig. 4). Although the relationship between $\delta^{65}\text{Cu}$ values and the Fe/Cu ratios in the SPM also indicates a mixing between the clay fractions and the silt fractions of the topsoil (0–5 cm) as end-members (Fig. 3), the $\delta^{65}\text{Cu}$ values is sensitive to processes affecting the clay fractions that contributed to a minor extent to the SPM-bound Cu exported by runoff. In this case, the $\delta^{65}\text{Cu}$ values may specifically reflect pedogenetic processes controlling the mobility in soil and export of the fine clay fraction during rainfall-runoff events.

5. Conclusions

We investigated the distribution of Cu-fungicides in the grain-size fraction of vineyard soils and runoff transport at the catchment scale

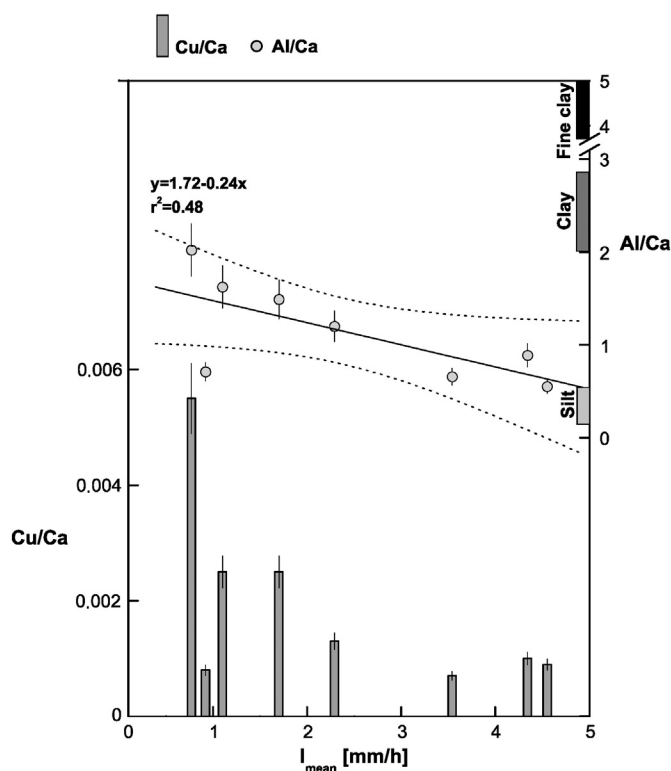


Fig. 5. Impact of the rainfall intensity on the SPM chemical composition in runoff (Ca normalized Cu concentrations and Al to Ca molar ratios) at the outlet of the vineyard catchment (Rouffach, France). The error given for the elemental ratios was calculated via error propagation based on the analytical uncertainty of the elemental analysis ($\pm 5\%$).

using Cu stable isotopes, mineralogical, hydrological and hydrochemical analyses. As the $\delta^{65}\text{Cu}$ values in the bulk soils were in the same range as those of Cu fungicides and geogenic Cu, the anthropogenic inputs could not be identified based on the $\delta^{65}\text{Cu}$ values of the bulk soils. In our case, $\delta^{65}\text{Cu}$ values of the sources did not clearly differ from those of the bulk soil. However, the $\delta^{65}\text{Cu}$ values differed between the particle-size soil fractions. Together with the soil mineralogy, the $\delta^{65}\text{Cu}$ values in the soil fractions reflect the contribution of the clay fractions in the Cu isotope distribution in the vineyard soils, and as the main vector of Cu in surface runoff. Isotopically heavier dissolved Cu and lighter SPM-bound Cu in runoff stemmed from Cu distribution between the vineyard soil constituents and Cu mobilization by rainfall. The negative $\delta^{65}\text{Cu}$ values and Al/Ca ratios of the SPM-bound Cu in runoff indicated that Cu was mainly bound to the clay and fine clay fractions, although coarser particles can also contribute to Cu export during more intense rainfall events. Cu export by runoff from the catchment accounted for 1% of the applied Cu mass on a seasonal basis, 84% of which was Cu bound to SPM. Overall, the results show that Cu distribution processes occurring in soils of agricultural catchment may be relevant to interpret the resulting $\delta^{65}\text{Cu}$ values in runoff and predict the Cu load transported downstream to vulnerable aquatic ecosystems. The isotope fractionation upon individual processes influencing Cu distribution in soils, especially those driving the Cu transformation over time, may help in the future to better understand the fate of anthropogenic Cu in contaminated soils.

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Appendix A. Supplementary data

Additional information as noted in the text contains the summary of physico-chemical properties of the soil profiles, XRD and isotopic data obtained for the different particle-size fractions, as well as the description of the particle-size separation method, chemical composition of SPM, hydrological and rainfall patterns. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2016.03.037>.

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