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Origin and fate of copper in a small Mediterranean vineyard catchment: New insights from combined chemical extraction and δ^{65}Cu isotopic composition

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HIGHLIGHTS

- We investigated the fate of copper applied as a fungicide in a vineyard catchment.
- Soils, river sediments and suspended matter, and local bedrock were sampled.
- Copper concentrations and isotopes were measured in sequential extractions solutions.
- Based on our work fungicide application significantly enriched all samples in copper.
- Isotope data provides new information regarding Cu bonding and fractionation.

ABSTRACT

For centuries, many Mediterranean catchments were covered with vineyards in which copper was widely applied to protect grapevines against fungus. In the Mediterranean-type flow regime, brief and intense flood events increase the stream water discharge by up to 10 times and cause soil leaching and storm runoff. Because vineyards are primarily cultivated on steep slopes, high Cu fluxes are discharged by surface water runoff into the rivers. The purpose of this work was to investigate the riverine behavior and transport of anthropogenic Cu by coupling a sequential chemical extraction (SCE) procedure, used to determine Cu partitioning between residual and non-residual fractions, with δ^{65}Cu isotopic measurements in each fraction. In the Baillaury catchment, France, we sampled soils (cultivated and abandoned), river bed sediments (BS), suspended particulate matter (SPM), and river water during the flash flood event of February 2009. Copper partitioning using SCE show that most of Cu in abandoned vineyard soil was in the residual phase ($>$60%) whereas in cultivated soil, BS and SPM, Cu was mostly ($>$25%) in non-residual fractions, mainly adsorbed onto iron oxide fractions. A small fraction of Cu was associated with organic matter (5 to 10%). Calculated enrichment factors (EF) are higher than 2 and the anthropogenic contribution was estimated between 50 to 85%. Values for δ^{65}Cu in bulk samples were similar to bedrock therefore; δ^{65}Cu on SCE fractions of superficial soils and SPM allowed for discrimination between Cu origin and distribution. Copper in residual fractions was of natural mineral origin (δ^{65}Cu close to local bedrock, $+0.07$‰). Copper in water soluble fraction of SPM ($\delta^{65}\text{Cu} = +0.26$‰) was similar to dissolved river Cu ($\delta^{65}\text{Cu} = +0.31$‰). Copper from fungicide treatment ($\delta^{65}\text{Cu} = -0.35$‰) was bound to organic matter ($\delta^{65}\text{Cu} = -0.20$‰) without or with slight isotopic fractioning. A preferential adsorption of ^{65}Cu onto iron oxides ($\delta^{65}\text{Cu} = +0.5$‰) is shown.

Keywords:
Storm runoff
Soils
River sediments
Suspended matter
Non-residual fractions
Cu isotopes

1. Introduction

In the Mediterranean regions of the south of France, wine-growing is the main agricultural activity covering an extensive portion of land. The repeated spraying of Bordeaux mixture ($Ca(OH)_2 + CuSO_4$) to

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control vine downy mildew is responsible for long-term accumulation of Cu in soils reaching values commonly ranging from 100 up to 1500 mg kg^{-1} (Chaignon et al., 2003). Cu is mainly transferred from the soil to the river system as a result of physical erosion and subsequent riverine transport of particles (Rothwell et al., 2008).

Mediterranean hydrological regime, characterized by brief and intense flow events multiplying the water discharge by up to 10 times, leads to important physical erosion, soil leaching, and storm runoff (Guizien et al., 2007). Consequently, high fluxes of pollutants are exported to the outlet of the catchment during these flash flood events.

Previous studies showed that copper seemed to be predominantly transported by suspended matter in runoff water (Xue et al., 2000), which can be related to the affinity of copper for sorption onto some components like organic matter, clay minerals and hydrous metal oxides (Flemming and Trevors, 1989). Suspended particulate matter (SPM) transported during these events is deposited in the main channel during recession periods of discharge forming stream bed sediments (BS). BS are considered as representative of soils they originate from and the analysis of BS finest fraction (<63 μm) gives an integrative view of SPM transported by rivers (Gaiero et al., 2003). The total amount of Cu in soils, BS, and SPM gives little information on its availability. Copper may exist as different chemical forms that have will have different chemical binding. In natural form, Cu is derived mainly from parental rock forming minerals (Jenkins and Jones, 1980) and when bound to silicates and oxides among primary minerals forming relatively immobile species. In our case study, the bedrock (Cambrian mica schist) contained on average 20 μg g^{-1} of Cu. This rock type is mainly composed of quartz, and muscovite with rutile and magnetite as accessory minerals (Canal, 2009). Based on this bedrock type and mineralogy, the Cu in the bedrock could be bound to phyllosilicates (Wedepohl, 1972; Core et al., 2005), hydrous Cu silicates (Evans and Mrose, 1977), Apachite and Gilalite (Cesbron and Williams, 1980). In contrast, anthropogenic copper is generally more mobile, being bound to less stable fractions such as non-residual fractions. Understanding the metal fractionation between residual and non-residual fractions in soils and sediments could give a clearer understanding of copper mobility, availability and potential toxicity for living organisms (Förstner, 1993). The combination of chemical sequential extraction with isotopic approaches was applied primarily for Pb in forest soils (Probst et al., 2003) and in stream bed sediments (Bur et al., 2009). For Cu, the importance of pollution sources has not been clearly evaluated yet. Here we investigate the combined use of sequential extractions and Cu isotopes to quantification of the magnitude of contamination associated with natural and anthropogenic sources. In addition, this study could provide useful information on the potential for fractionation of Cu isotopes between residual and non-residual fractions in the samples.

In this study, we collected data during a flash flood event in the small catchment of the intermittent Baillaury River in the south central France along the Mediterranean coast. We focused on a flood event because it has been shown that pollutant concentrations in dissolved and particulate matter increases 1- to 17-fold during these flood events (Shafer et al., 1997). The studied catchment has been covered with vineyards for centuries to produce Banyuls wine. The major objectives of this study were: (1) to evaluate copper content and enrichment in soils, stream bed sediments, and suspended particulate matter in a catchment that is representative of the soils and the agricultural practices of the Mediterranean wine-growing region; (2) to estimate anthropogenic contribution to Cu concentrations using geochemical and isotopic methods; (3) to determine the distribution of Cu between solute and particulate phases, and between residual and non-residual fractions; and (4) to characterize the δ^{65}Cu isotopic value of each phase and of each fraction in order to better understand Cu origin and fate from the soil to the river system.

2. Materials and Methods

2.1. Study Site

The studied area is a small Mediterranean catchment located along the southern coast of France in the eastern part of the Pyrénées Mountains (Fig. 1). The Baillaury River, of an average discharge of 207 $L.s^{-1}$, drains a catchment of 18.2 km^2 which has been occupied almost exclusively by vineyards for centuries. Today, 38% of its surface is occupied by this culture; the rest corresponds to vineyards abandoned several decades ago that have subsequently been turned into grasslands. The landscape consists of steep slopes (25 to 50%) re-defined into small terraces cultivated with grapevines. In the catchment, acidic leptosols (according to World Reference Base) with heavy pebbles content (50 to 70%) are formed on shale colluviums with an underlying bedrock composed of Cambrian mica schist.

The climate is sub-humid Mediterranean, with a prolonged dry season and a mean annual rainfall of 697 mm. Groundwater reservoirs being limited; the creek is dried during the summer season. However, with the autumn resumption of rain, the groundwater is recharged again and maintains continuous base flow until spring. Brief but intense flash flood events between September and June are characteristic of the Mediterranean hydrological regime leading this temporary dry river to flush abruptly after strong local rainfalls. Consequently, intense surface runoff is responsible for the transport of suspended matter into the bay of Banyuls-sur-Mer at the outlet of the river (Guizien et al., 2007). This bay is located north of a marine protected area and environmental monitoring has been conducted between September 2008 and June 2011 in this catchment within the framework of the CRUMED project (Impact of Mediterranean-type flash floods on the near shore zone related to viticulture and tourism land-uses) in order to study copper impact on the marine coastal ecosystems (See the website: http://www.obs-banyuls.fr/CRUMED). As part of this project, 5 different flood events were sampled between January 2009 and April 2011. In this article, the focus

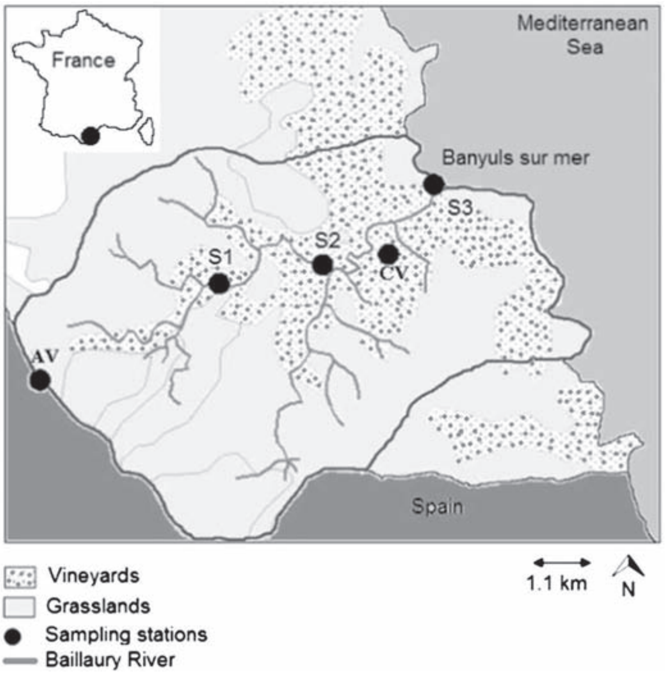

Fig. 1. Location of the study area with the main sampling points. The watershed is delimited in black. S1, S2 and S3 are river bed sediment sampling points. In S3, at the outlet, water was also sampled. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are the soil sampling points. Source: IGCS-BDSol-LR-version n°2006, INRA Montpellier SupAgro, Ministry of Agriculture and Fish.

will be on the only flash flood event of the year 2009, occurring on February 3rd. This event increased the Baillaury river discharge from 0.207 to 14 $m^3 s^{-1}$ in two days. During this event the sea was calm interfering little with the water characteristics at the outlet of the river. The pH (measured using a sensor model pH25+ (CRISON SA Instrument) with calibration at 4.01 and 9.21) varied little (7.1 to 7.8) but the suspended particulate matter (SPM separated by Continuous-Flow Ultracentrifugation at 0.22 μm) content increased from 1 to 100 mg L^{-1}. This flash-flood event with a discharge of approximately 6 months return flow period occurred before the seasonal inputs of copper fungicide that occurs during the grape growing period (April–August). Thus, this event contained erosion of residual copper contamination derived from previous years.

2.2. Sampling and Pre-treatment of the Samples

Soil samples were collected in the catchment in order to characterize likely source materials within the study area. This small catchment has the characteristic of having the same soil type in all of its area in relation with the uniform bedrock. Therefore, two sampling stations, with 3 sampling points per station, were selected according to land cover (Fig. 1): CV corresponding to a currently cultivated vineyard and AV to an upstream abandoned vineyard for more than twenty years. For each kind of agricultural parcel (AV and CV), the soils are rather homogeneous. Then, we collected in the center of each parcel, three sub-samples (replicates) at two depths (0–15 cm and 15–30 cm for AV and 0–30 cm and 30–45 cm for CV) on a circle 3 meters diameter. Each average soil sample resulting in a mixing of the 3 sub-samples, was dried at room temperature, sieved à 2 mm and quartered before to be analysed by Galys Laboratory in Toulouse (France) for CEC (Metson's method; Metson, 1956), organic carbon (Anne's method; Anne, 1945), granulometry, pH_{water} and pH_{KCl} and by SARM (Service d'Analyses des Roches et des Minéraux) laboratrory of CRPG (Centre de Recherches Pétrographiques et Géochimiques) in Nancy (France) for major and trace elements by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) after sample digestion by alkaline fusion using lithium metaborate adjunction as fusion flux as described in Carignan et al. (2001).

Soils clay content increased from the higher altitude location (350 m above sea level) (4 weight (wt) %) to the bottom valley give elevation (11 wt.%). Soil depth also increased from the 30 cm at the higher elevation location to the 45 cm at the lower elevation due to colluvium deposition. In all soil profiles, two main horizons were identified and sampled: the upper horizons (0 to 15 cm depth at the higher elevation location (AV-1) and 0 to 30 cm at the lower elevation (CV1)) and the deep horizons (respectively 15-30 cm for AV-2 and 30–45 cm for CV-2). Soil pH was 7.2 at AV-1 and 6.7 at AV-2 and 4.9 at CV-1 and 4.8 at CV-2. Cationic exchange capacity was low in all soils (<1 meq 100 g^{-1}). Organic matter content in the higher abandoned less cultivated location was higher (average 20 g kg^{-1}) than that measured in the cultivated vineyard location(10 g kg^{-1}). In each station, the three samples were mixed to prepare a representative sample of the station.

Stream bed sediments (BS) and suspended particulate matter (SPM) play a crucial role in the adsorption and dispersion of metals downstream. Subsequently, at the peak of the studied flood event, 30 liters of river water were collected manually over a bridge at the catchment outlet (S3 — Fig. 1). SPM was separated by Continuous-Flow Ultracentrifugation at 0.22 μm. One bed sediment (BS) were sampled at each of the three sites throughout the river (Stations S1, S2 and S3 — Fig. 1), immediately after the end of the flood event. They were taken in the first 10 centimeters of stream bed sediments using plastic tubes.

All BS sampling was done with plastic materials (PP) that were all washed with ultra-pure HCl (1 N) for 48 h then rinsed four times with Milli-Q water to avoid contaminations. After sampling, the samples were stored in a cold room at 4 °C.

Bed sediment, SPM and soil samples were all air-dried then carefully homogenized in an agate mortar to separate the aggregates, avoiding to crush the grains, quartered and sieved to obtain 3 separate fractions: the fine fraction (<63 μm), the coarse fraction (63 μm-2 mm) and the fraction > 2 mm.

In addition, a bedrock mica schist sample was taken in the altitudes of Banyuls at an outcrop but deep enough in the bedrock to avoid any surface contamination by anthropogenic inputs. The bedrock served as background for copper of natural mineral origin in the catchment.

Finally, a sample of the Bordeaux mixture sprayed on the vineyards of the catchment in 2008 was provided by local wine growers, even if its Cu composition could change over time.

2.3. Chemical Treatments and Analyses

2.3.1. Total Digestion

Total digestion was performed in a clean room on the fine fraction (<63 μm) of BS, SPM and soils because metals have been shown to be preferentially associated with finest fractions because the specific surface area is highest as shown by many authors and it is commonly true that the bulk of leachable trace metal contents are associated with the finest grain sizes (e.g. Gaiero et al., 2003; Zhao et al., 2011). Separation of the <63 μm fraction is done with the eventual purpose of correcting for the grain-size effect (i.e., larger grain-size fractions have a dilution effect on trace element concentrations) (Förstner and Wittman, 1979). Taking the same fraction also allows for normalizing samples to one grain size distribution.

The samples (4 replicates for each sample) were put through the following total digestion procedure: 0.1 g dry weight was digested with 1 mL of two times-distilled HNO_3 (68%) + 1 mL of concentrated HF (47 to 51%). Next, the dry residue was attacked with 1.6 mL of double-distilled HNO_3 and then the residue was digested with 0.6 mL (three times) of H_2O_2 35% to destroy the organic matter; and finally the sample underwent digestion in 2 mL of double-distilled HNO_3. At this point, most solutions were clear. If not, the residue underwent again the last step ($HNO_3 + H_2O_2$). This procedure has been successfully tested by N'Guessan et al. (2009) and Bur et al. (2009) for total digestion of fluvial sediments and soils.

During the digestion procedure, blanks and standards (SRM-1646a (estuarine sediment), SUD-1(lake sediment), WQB-1 and STSD-3 (stream sediments)) received the same treatment as the samples to evaluate potential external contamination process and valuable efficiency of the chemical procedure. Copper recovery rates of used standards (one replicate for each) were all satisfactory: 100.6% for SRM-1646a, 94.7% for SUD-1, 95.5% for WQB-1 and 93.3% for STSD-3. Thus, the total digestion can be considered reliable.

2.3.2. Sequential Chemical Extraction Procedure (SCE)

A large number of protocols for sequential chemical extractions have been proposed in the literature. In this study, the procedure applied is based on Leleyter and Probst (1999) because it has been previously developed for fluvial sediments, has been adapted for soil samples by Probst et al. (2003) and its efficiency, selectivity and repeatability have been validated. This method considers seven successive fractions extracted by specific reagents with decreasing pH: (1) soluble fraction dissolved with water; (2) exchangeable; (3) bound to carbonates; (4) bound to manganese oxides; (5) bound to amorphous iron oxides; (6) bound to crystalline iron oxides; (7) bound to organic matter and (8) residual (incorporated in the crystalline structure of the minerals). The non-residual fraction of the elements corresponds to the sum of the fractions of the first seven steps of the extraction procedure, whereas the residual fraction corresponds to the remaining part included in the mineral lattice.

The extractants, the time and the temperature of reaction for these different fractions are detailed in Leleyter and Probst, 1999. Dried samples AV-1, CV-1 and SPM sieved at to <63 μm were used to normalize the grain size distribution and to get comparable results. After each step, the residue was filtered (0.45 μm) and washed with 20 mL of distilled water. The leachates were stored in polypropylene bottles at 4 °C until chemical analyses. The residue, dried at 40 °C, then underwent the next extraction step. After the ultimate step, residual fractions were dissolved following the total dissolution procedure described above. The SCE procedure was performed in a clean room with continuous agitation to increase the interactions of surface between the reagent and the sample. All used reagents were Merck KGaA analytical grade of Ultra-pure quality. Everything was handled with Teflon or polypropylene materials in order to avoid contaminations. Blanks (composed of reagents only) were prepared in order to control the cleanness of the procedure (3 replicates for each blank).

The accuracy of SCE was validated by comparing the sum of the 8 fractions obtained by SCE with the results of total dissolution of bulk samples. The effectiveness, repeatability and selectivity of the SCE procedure used in this study was checked following the method described by Leleyter and Probst (1999) and (Probst et al., 2003). At each step of the SCE, the concentrations of major elements such as Si, Mn, Fe were analysed to check the selectivity and efficiency of the procedure. The results showed that most (>60%) of the Mn was removed in the Mn-oxide fraction, the Fe (>70%) was removed in the amorphous and crystalline Fe-oxide fraction, and little Si (<1%) was removed before the residual step.

2.3.3. Major Element and Cu Concentration Analyses

All samples were analyzed for major elements and Cu content. Major elements were measured using a Thermo IRIS INTREPID II XDL ICP-OES (Inductively coupled plasma optical emission spectroscopy). Cu and other trace element concentrations were measured by ICP-MS (Agilent 7500 CE) at the laboratory Géosciences Environnement Toulouse (GET, Toulouse, France) using five-point calibration. The concentration of these solutions are 0 (blank), 1 ppb, 30 ppb, 60 ppb and 100 ppb realized with two solutions of 10,000 ppm provided by Inorganic Ventures. ICP-MS presents lower detection limits for Cu (5 ng L^{-1}) as compared to ICP-OES (5 μg L^{-1}). Indium and rhenium were used as internal standards to correct for instrumental drift and eventual matrix effects. The Cu detection limit was 1 nM and the relative standard deviation (RSD) was lower than 5%. Quality of measurements was controlled with blanks (0.005 ± 0.002 μg kg-1) and standards (cited before). The ICP-MS internal precision is generally lower than 2% for most of the elements. Concerning the accuracy we have with respect to the reference materials [SRM-1646a (estuarine sediment), SUD-1(lake sediment), WQB-1 and STSD-3 (stream sediments)] the relative standard deviation between the certified or recommended values and our measurements expressed as $([X]_{\text{recommended or certified}} - [X]_{\text{measured}})/(([X]_{\text{recommended or certified}} + [X]_{\text{measured}})/2)*100$ were lower than 10% for the elements presented in this work. In order to compare values, P-values were calculated using STATISTICA 8.

2.3.4. Cu Stable Isotope Measurements

All the gross samples and the fractions resulting from sequential extraction of SPM, CV-1 and AV-1 were analyzed for Cu isotopes. Cu isotopic composition was measured at Toulouse (GET) using a Neptune MC-ICP-MS (ThermoFinnigan). The samples were introduced using a conventional system that consists of a tandem quartz spray chamber (cyclone + standard Scott double pass) coupled with a low flow pFA nebulizer (50 to 70 μL/min). For more detail, see Viers et al. (2007). Cu has two stable isotopes of mass 63 and 65, which have average abundances of 69.17% and 30.83%, respectively. Copper was isolated from the bulk sample using the purification procedure of Maréchal et al. (1999) on the AG-MP-1 anion exchange resin (Bio-Rad, USA). Two successive separations were performed for each sample. After the first separation procedure, Cu fraction was loaded on a new column to perform second separation for purification.

Poly-Prep chromatography columns (0.8 × 4 cm) (Bio-Rad, USA) were used for the elemental separation. After the resin was cleaned with MilliQ® deionized water (18.2 Ω) and 0.5 N HNO_3, the resin was conditioned (1.6 mL) and samples loaded (300 ng of Cu in 1 mL) with 7 N HCl. Hydrogen peroxide was added into the acid solution at a 0.001% concentration to avoid the presence of Cu in a different redox state. The matrix was eluted with 10 mL of 7 N HCl and Cu was collected in the next fraction (20 mL of 7 N HCl). Because isotopic fractionation may occur during the elemental separation on the ion-exchange resin (Maréchal and Albarède, 2002), we analyzed only the samples for which the separation procedure produced a 100% yield, taking into account the analytical uncertainties. When performing a chromatographic separation, we checked that the amount of charge (= the sample) loaded in the column was lower or close to ~10% of the maximum charge capacity of the amount of resin used in the column.

A Zn standard (JMC 3-0749 L) was added to the purified Cu fractions and a Cu (NIST 976) + Zn (JMC 3-0749 L) standard mixture was run as a bracketing standard. The concentration of Cu and Zn in the sample or standard is kept at the same concentration (300 μg L^{-1}). The mass bias correction on the $^{65}Cu/^{63}Cu$ ratio was performed using two different methods: the bracketing method and the internal correction using Zn isotopes ratio ($^{66}Zn/^{64}Zn$, $^{67}Zn/^{64}Zn$, $^{68}Zn/^{64}Zn$, and $^{68}Zn/^{66}Zn$) and an exponential law correction.

Results are given in the recommended delta notation for the $^{65}Cu/^{63}Cu$ ratio (Albarède, 2004):

$$\delta^{65}\mathrm{Cu}\ (‰) = \left(\frac{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{sample}}{\left(\frac{^{65}Cu}{^{63}Cu}\right)_{NIST976}} - 1 \right) \times 1000 \tag{1}$$

where NIST 976 is the Cu isotopic standard solution.

For most (60%) of the samples, the amount of Cu was not sufficient and we analyzed the sample only once. The sample and standard measurements consist of 2 blocks of 20 cycles of 8 s each. For a single measurement (40 cycles), the internal precision was found to be in the range 5 to 10 ppm (2σ err.) for both $^{66}Zn/^{64}Zn$ and $^{65}Cu/^{63}Cu$ ratios. Between each sample and standard, the machine was rinsed with 0.05 N HNO3 from two different vials for 1 min each. Blank measurements consisted of 1 block of 10 cycles (8 s). Blank values for Cu isotopes (^{63}Cu or ^{65}Cu) measurements with MC-ICPMS were lower than 1 millivolt.

As we were not able to duplicate samples, the error of 0.05 to 0.1‰ given is an external reproducibility obtained on the repeated analysis of the 2709a San Joaquin Soil (NIST, USA; $\delta^{65}Cu = 0.17 \pm 0.07‰$) and BEN (CRPG, France; $\delta^{65}Cu = 0.4 \pm 0.1‰$).

2.3.5. Calculation of Copper Enrichment and Anthropogenic Contribution

A geochemical approach was used considering that the total Cu (Cu_{total}) measured in each sample was equal to the sum of Cu from the natural lithogenic source and Cu resulting from anthropogenic activities (Eq. (2)).

$$Cu_{total} = Cu_{lithogenic} + Cu_{anthropogenic} \tag{2}$$

To normalize trace elements, the earth crust is often used in the literature as a reference material (Soto-Jiménez and Paez-Osuna, 2001; Pekey, 2006). However, in the case of small catchments, like the Baillaury catchment, the earth crust was shown to be non-representative of the local bedrock chemical composition (Table 1) (Reimann and De Caritat, 2005; N'Guessan et al., 2009) and thus might lead to a wrong estimation of the anthropogenic contribution. Therefore, in our case study, the local bedrock (Cambrian mica schist)

Table 1
Average major element composition (in weight percent oxide) of the samples with reference to: UCC = Upper Continental Crust by Rudnick and Gao, 2003, Ap = new median soil total concentrations determined by continental-scale geochemical surveys in Europe (GEMAS Ap), De Caritat and Reimann, 2012. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

	Bedrock	UCC	Soils				Ap	Bed sediments			SPM
%			AV-1	AV-2	CV-1	CV-2		BS S1	BS S2	BS S3	S3
Al_2O_3	13.03	15.39	14.50	13.60	13.54	15.49	10.50	15.62	14.11	15.00	14.87
Fe_2O_3	4.13	5.60	3.20	3.27	2.59	3.23	3.60	5.39	4.84	5.70	5.87
MnO	–	0.10	0.05	–	0.11	–	0.08	–	–	–	0.11
CaO	0.27	3.60	1.54	1.33	0.22	0.32	1.20	1.70	1.27	2.00	2.17
MgO	1.58	2.50	1.01	1.04	0.85	0.93	0.10	1.92	1.76	2.11	2.60
Na_2O	2.71	3.28	2.36	2.30	0.96	1.43	0.80	2.53	1.91	2.33	2.72
K_2O	2.65	2.80	2.53	2.49	1.72	2.83	1.90	2.72	2.43	2.83	2.92

was chosen as the uncontaminated reference material. Therefore, the enrichment factor (EF) was calculated by comparing to the local bedrock and by using different reference elements (X in Eq. (3)).

$$EF = \frac{\left(\frac{Cu}{X}\right)_{sample}}{\left(\frac{Cu}{X}\right)_{bedrock}} \tag{3}$$

The choice of the reference element is not universal and depends on lithological and physicochemical characteristics of the study area (Reimann and De Caritat, 2005). Elements such as Cs (Roussiez et al., 2005; N'Guessan et al., 2009), Sc (Hernandez et al., 2003; Hissler and Probst, 2006) and Fe (Schiff and Weisberg, 1999) are commonly used. In our case study, Fe, Sc and Ti were all tested. Sc and Ti are of natural origin and are supposed to be conservative during weathering processes and not readily derived from contamination (Tam and Yao, 1998). In addition, Fe, a semi-conservative element, was selected because it has been proven to have the same behavior than Cu in cultivated soils (Gavalda et al., 2005).

Anthropogenic contribution (AC) is then calculated (Eq. (4)) and expressed as the percentage of anthropogenic Cu in the total Cu of each sample.

$$AC(\%) = \frac{Cu_{sample} - X_{sample} \times \left(\frac{Cu}{X}\right)_{bedrock}}{Cu_{sample}} \times 100 \tag{4}$$

3. Results

3.1. Characteristics and Composition of the Samples: Soils, Sediments, Suspended Matters and Local Bedrock

Soils clay content increased from the higher altitude location (350 m above sea level) (4 weight (wt) %) to the bottom valley (31 m above sea level) (11 wt.%). Soil depth also increased from the 30 cm at the higher elevation location to the 45 cm at the lower elevation due to colluvium deposition. In all soil profiles, two main horizons were identified and sampled: the upper horizons (0 to 15 cm depth at the higher elevation location (AV-1) and 0 to 30 cm at the lower elevation (CV1)) and the deep horizons (respectively 15-30 cm for AV-2 and 30-45 cm for CV-2). Soil pH was 7.2 at AV-1, 6.7 at AV-2, 4.9 at CV-1 and 4.8 at CV-2. Cationic exchange capacity was low in all soils (<1 meq 100 g^{-1}). Organic matter content in the higher abandoned less cultivated location was higher (average 20 g kg^{-1}) than that measured in the cultivated vineyard location (10 g kg^{-1}).

The average major elements content in the local bedrock (mica schist, this study), in the catchment soils at different depths, in the stream BS and in SPM, are indicated in Table 1, together with the average universal continental crust composition by Rudnick and Gao (2003) and the new median European soil composition (De Caritat and Reimann, 2012) for comparison. The major element composition of the soils, BS and SPM was similar to that of the local bedrock. The ratio $R = (Fe_2O_3 + Al_2O_3)/(CaO + MgO + Na_2O + K_2O)$ is very close for AV soil (R = 0.42), BS (R = 0.38 to 0.45) and SPM (R = 0.50) and slightly lower for CV soil (R = 0.23 to 0.29).

Total copper concentrations, determined after total dissolution, are mentioned in Table 2 (in μg g^{-1}, means of triplicate analyses). The local bedrock content (19.63 ± 0.04 μg g^{-1}) was less than the universal continental crust concentration. All other samples were enriched in Cu (Table 1). The vineyard soil horizons (CV-1, CV-2) had up to two times more Cu than the abandoned cultivated soil horizons (AV-1, AV-2) and significantly more Cu than the new mean soil concentration found in European soils studied by the GEMAS project

Table 2
Copper concentrations in bulk samples (means of triplicate values) with reference to (a) UCC: Upper Continental Crust; Ap: new median soil total concentrations determined by continental-scale geochemical surveys in Europe (GEMAS Ap); this study*: average of all our measurements during different flood events between 2009 and 2012, n = 8. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

	Samples	Cu in μg g^{-1} (soil, sediment, rock) and μg L^{-1} (water)	References
Rock Cu in μg g^{-1}	Local Bedrock	19.6 ± 0.0	This study
	UCC	28	Rudnick and Gao, 2003
	Average shale	45	Turekian and Wedepohl, 1961
Soil Cu in μg g^{-1}	AV-1	60.3 ± 0.9	This study
	AV-2	57.0 ± 1.0	This study
	CV-1	112.7 ± 0.4	This study
	CV-2	102.5 ± 0.3	This study
	Ap	15	De Caritat and Reimann, 2012
	BS S1	176.3 ± 0.7	This study
Sediment Cu in μg g^{-1}	BS S2	131.0 ± 2.0	This study
	BS S3	90.4 ± 0.7	This study
	World average BS baseline	39	Callender (2004)
Suspended matter Cu in μg g^{-1}	SPM S3	146.3 ± 1.3	This study
	Average particulate Cu	191.9 ± 92.1	This study*
	World average SPM Cu	75.9	Viers et al., 2009
Water Cu in μg L^{-1}	Soluble copper	5.8 ± 0.2	This study
	Average soluble copper	7.5 ± 3.3	This study*
	World average	1.5 0.4 to 47.1	Gaillardet et al., 2003 Vance et al., 2008

(Geochemical Mapping of Agricultural Soils). Bed sediment copper content decreased from the upstream (176.3 ± 0.7 µg g^{-1}) to downstream (90.4 ± 0.7 µg g^{-1}). The SPM Cu concentration was 146.3 ± 1.3 µg g^{-1} for the 2009 event and 192 +/− 92 µg g^{-1} for other events sampled between 2009 and 2011. Based on the measured particulate content of 80 mg L^{-1}, and knowing the concentration of dissolved Cu (5.8 ± 0.2 µg L^{-1}) and of particulate Cu (146.3 ± 1.3 µg g^{-1}), we calculate a Cu partitioning coefficient Kd (dissolved/particulate) of 0.49.

The δ^{65}Cu of the local bedrock and gross BS, SPM and soils are reported in Table 3. The local bedrock (+0.07‰), BS (+0.06 to −0.10‰) and SPM (+0.09‰) presented similar isotopic compositions. Both AV and CV soils had negative δ^{65}Cu (respectively −0.06 and −0.14). The water samples (<0.2 µm after centrifugation) exhibited a higher isotopic composition (δ^{65}Cu = +0.31‰). On the contrary, the Bordeaux mixture presented the lowest isotopic signature with a δ^{65}Cu = −0.34 ± 0.08‰.

3.2. Enrichment Factors and Anthropogenic Contribution

After the sequential extractions, 69 ± 15% of Fe, 83 ± 4% of Sc and 94 ± 5% of Ti were found in the residual fraction confirming the accuracy of the choice of these normalizers (as already evidenced for Cs (98%) and Sc (75%) by N'Guessan et al., 2009).

It is generally accepted that EF smaller than 2 reflects natural variability of the mineralogical composition of the sample (Hernandez et al., 2003). Sutherland (2000) proposed a classification for all trace metals according to which a moderate enrichment is indicated by an EF ranging between 2 and 5, a significant enrichment between 5 and 20, a very high enrichment between 20 and 40, and an extreme enrichment >40. According to this classification, moderate to significant enrichments were noted for all the samples as compared to the bedrock (Fig. 2). If the local bedrock is used as a baseline enrichment threshold would be 1.5 (cf. Roussiez et al., 2005).

In AV-1, EF was smaller (2.9) than in CV-1 (5.7). The difference was also visible in the deep horizons were EF was lower for AV-2 (2.5) than for CV-2 (4.2). Bed sediment samples followed a decreasing gradient of enrichment from upstream (EF = 6.4) to downstream (EF = 3.2). Consequently, SPM at the outlet of the catchment had an intermediate EF value (5.3) which represents an average value of the different EF calculated for the finest fractions of the soils through the catchment.

Table 3
Copper isotopic ratios δ^{65}Cu (‰) of the bulk samples with an error between 0.05 and 0.1‰ and the reference ranges from the literature. Missing values result of analytical problems. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

Samples	δ^{65}Cu (‰)	References
Bordeaux mixture	−0.34	This study
Local Bedrock	0.07	
Soils		
AV-1	−0.063	
CV-1	−0.14	
River Bottom sediments		
BS S1	−0.05	
BS S2	−0.10	
BS S3	0.06	
River suspended matter	0.09	
SPM S3		
River dissolved copper	0.31	
Parent native Cu	−3.0 to +1.2	Ehrlich et al., 2004
	−13.5 to +8.3	Mathur et al., 2010
	−8.4 to +0.9	Mathur et al., 2012
Range in rocks and soils	−4.0 to +6.0	Borrok et al., 2008
Average of river soluble Cu	+0.0 to +1.45	Vance et al., 2008
	+1.4 to +1.7	Kimball et al., 2009

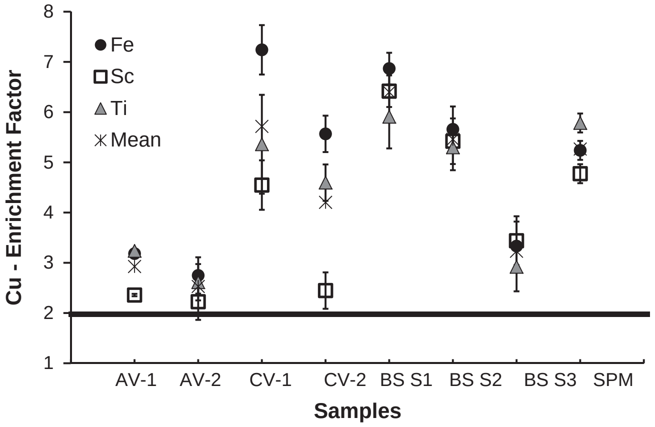

Fig. 2. Enrichment factors (EF) for copper in samples using the local bedrock as background and Fe, Sc and Ti as normalizers. The EF limit represented at 2 indicates copper exclusively provided by natural source (local bedrock). CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

The average anthropogenic contribution to the total copper concentrations in the samples was calculated using Eq. (3) and Fe, Sc and Ti as normalizers. Table 4 shows the average distribution of Cu between anthropogenic and natural sources indicating an obvious anthropogenic contamination of BS, SPM and soils. Abandoned vineyard soils showed less anthropogenic contribution (~60%) than cultivated ones (~76%). Bed sediments had a higher Cu anthropogenic contribution upstream (~84%) than downstream (~69%), SPM indicated however, the same anthropogenic contribution as BS upstream.

3.3. Sequential Extractions and Cu Isotopic Signatures of the Fractions

The concentration of Cu in each defined fraction in soil, BS and river SPM samples is presented in Table 5 whereas the percentage of each fraction as compared to the total Cu content is represented in Fig. 3. For all the samples, Cu concentration in the residual fraction was between 30 and 55 µg g^{-1}, corresponding to a range between 25 and 75% of the total Cu content of samples. Significant differences between the samples occurred in the non-residual fractions ($p\text{-value} < 0.05$ for F3, F4, F5, F6 and F7). Copper bound to carbonates (F3) increased from none detectable Cu in the abandoned soil (AV) to 13 µg g^{-1} in the suspended matter (SPM). In addition, Cu bound to amorphous iron oxides (F5) was 3 times higher in the cultivated vineyard (CV), the bed sediments (BS) and SPM as compared to AV. Cu

Table 4
Contributions of natural and anthropogenic sources to the total copper concentrations in soils, river bed sediments and suspended matters. Each value (%) is an average of the contributions calculated with the three normalizers (Fe, Sc and Ti). STD is the standard deviation for this mean value. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

	Natural Origin	Anthropogenic Contribution
	% ± STD	% ± STD
AV-1	39 ± 8	61 ± 8
AV-2	42 ± 10	58 ± 10
CV-1	21 ± 4	79 ± 4
CV-2	28 ± 8	72 ± 8
BS-S1	16 ± 1	84 ± 3
BS-S2	18 ± 1	82 ± 5
BS-S3	31 ± 3	69 ± 11
SPM-S3	19 ± 2	81 ± 2

Table 5

Copper content (μg g^{-1} of sample) and δ^{65}Cu (‰) of total fraction and in the different extraction fractions of studied samples. Represented fractions are: (F1) Dissolved with water; (F2) exchangeable; (F3) bound to carbonates; (F4) bound to manganese oxides; (F5) bound to amorphous iron oxides; (F6) bound to crystalline iron oxides; (F7) bound to organic matter and (F8) Residual. nd stands for not determined values either because of none detectable Cu contents either because of analytical problems. None filled spaces are those for which no isotopic analysis was conducted yet. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

	F1		F2		F3		F4		F5		F6		F7		F8		∑ SCE Fractions	Total digestion	
	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	δ^{65}Cu	Cu	Cu	δ^{65}Cu
AV-1	0.03 ±0.01	nd	0.05 ± 0.00	nd	0.17 ± 0.00	nd	0.07 ± 0.01	nd	10.57 ± 0.07	0.60	13.53 ± 0.05	0.32	2.28 ± 0.06	-	38.94 ± 0.91	0.00	65.63 ± 1.12	60.32 ± 0.91	−0.06
AV-2	0.02 ± 0.00	–	0.15 ± 0.00	–	0.68 ± 0.01	–	0.1 ± 0.00	–	5.84 ± 0.04	–	8.25 ± 0.04	–	1.65 ± 0.06	–	54.49 ± 0.22	–	71.19 ± 0.37	56.96 ± 0.97	–
CV-1	0.57 ± 0.02	nd	4.99 ± 0.00	nd	3.28 ± 0.09	nd	0.24 ± 0.02	nd	42.71 ± 0.71	−0.58	26.89 ± 1.34	−0.7	4.5 ± 0.16	−0.37	37.62 ± 0.42	−0.03	120.80 ± 2.77	112.74 ± 0.37	−0.14
CV-2	0.2 ± 0.02	–	6.85 ± 0.07	–	11.44 ± 0.11	–	0.33 ± 0.00	–	24.83 ± 0.13	–	19.62 ± 0.22	–	1.39 ± 0.01	–	46.01 ± 0.50	–	110.66 ± 1.05	102.54 ± 0.34	–
BS S1	0.67 ± 0.01	–	0.52 ± 0.01	–	7.98 ± 0.03	–	0.48 ± 0.02	–	90.77 ± 1.54	–	16.78 ± 0.16	–	10.55 ± 0.16	–	41.88 ± 0.64	–	169.63 ± 2.56	176.34 ± 0.72	−0.05
BS S2	0.47 ± 0.00	–	0.38 ± 0.01	–	10.47 ± 0.05	–	0.15 ± 0.02	–	66.68 ± 0.84	–	13.85 ± 0.22	–	11.01 ± 0.28	–	36.96 ± 0.68	–	139.96 ± 2.12	130.96 ± 1.97	−0.1
BS S3	0.42 ± 0.00	–	0.61 ± 0.01	–	12.67 ± 0.05	–	0.05 ± 0.17	–	33.04 ± 0.17	–	9.54 ± 0.07	–	7.6 ± 0.19	–	30.82 ± 0.79	–	94.76 ± 1.45	90.43 ± 0.73	0.06
SPM S3	3.24 ± 0.03	0.26	1.94 ± 0.01	−0.09	12.97 ± 0.12	−0.13	0.21 ± 0.01	nd	60.31 ± 0.42	0.01	14.93 ± 0.33	0.48	7.97 ± 0.11	−0.2	43.18 ± 0.77	0.07	144.76 ± 1.81	146.28 ± 1.26	0.09

bound to organic matter (F7) was 2 times higher in BS and SPM as compared to AV.

The percent Cu in the residual fraction was greater in the deep horizon (87% for AV-2 and 45% for CV-2) than in the surface horizon (60% for AV-1 and 33% for CV-1). In AV, Cu distribution differed from that found in CV, BS and SPM with most Cu measured in the residual fraction (>60%), followed by crystalline iron oxides (F6, 11 to 20%), amorphous iron oxides (F5, 8 to 16%), and organic matter (F7, ~3%). The non-residual fractions were less important in the abandoned soil horizons (AV-1, AV-2) as compared to CV horizons (CV-1, CV-2), BS and SPM. In fact, in CV, BS and SPM, residual Cu accounted for less than 40%. The sum of soluble (F1), exchangeable (F2) and acid-soluble (F3) fractions reached 7% for CV-1, 16% for CV-2, 5% for BS S1, 8% for BS S2, 14% for BS S3, and 12% for SPM S3 whereas in AV it was close to zero. Another difference is the amorphous iron oxide fraction which was 8 to 16% for AV, less than that of all other samples (20 to 53%). In all samples, Cu bound to organic matter and crystalline iron oxides was present. However, Cu seemed to have very low affinity for manganese oxides (Fraction 4) as seen in Fig. 3.

In order to validate the extraction method, the sum of Cu content in every fraction was compared to the total dissolution values. Low concentration differences were obtained in most cases between the two approaches, varying for most between −7% and +2%, except for the deep horizon AV-2 reaching −10%.

To determine the sources of Cu in the catchment, isotopic ratios (δ^{65}Cu in‰) were determined and errors ranged between 0.05 and 0.1‰ (Fig. 4). Detailed values for isotopic signatures of the fractions of the sequential extraction (applied on AV-1, CV-1 and SPM) are presented in Table 5. The residual fractions of all three samples had δ^{65}Cu values close to zero and therefore to the bedrock (+0.07‰). The non-residual fractions had δ^{65}Cu differed from the bedrock. In CV-1, non-residual fractions had negative signatures (F5 = −0.58‰, F6 = −0.7‰, F7 = −0.37‰) closer to the Bordeaux mixture signature (−0.34‰) than to the bedrock. On the contrary, in AV-1, these fractions had positive signatures (F5 = +0.60‰, F6 = +0.32‰) closer to the river dissolved Cu signature (+0.31‰). The soluble fraction (F1) of SPM exhibited a δ^{65}Cu of +0.26‰ close to the dissolved Cu. Crystalline iron oxides in AV-1 and SPM also had positive signatures (F6, respectively +0.32 and +0.48‰) close to the dissolved Cu.

4. Discussion

4.1. Cu Behavior from Soil to Suspended Sediments

Superficial Cultivated Vineyard (CV-1) Cu contents (>112 μg g^{-1}) were similar to those found by Ribolzi et al. (2002) ranging around 115 μg g^{-1} in the top soils of Mediterranean vineyard terraces. The CV soils also had higher Cu concentrations than the abandoned ones (AV >60 μg g^{-1}) but both had Cu values largely exceeding the average of European soils (15 μg g^{-1}, De Caritat and Reimann, 2012) and the baseline value of 28 μg g^{-1} for contaminated agricultural soils of the European Mediterranean region (Micó et al., 2007). Brun et al. (1998) also found higher Cu concentrations (up to 100 fold) in cultivated vineyard soils than in woodland plots in a similar Mediterranean catchment (Hérault, France). The Cu concentrations in all the soil horizons exceeded the warning and critical legislative limits (50 and 140 μg g^{-1}, respectively, Council Directive 86/278/EC, 1986) established in Europe for Cu contents in agricultural soils. In our study, the mean value for all soil samples averaged 8 μg g^{-1}. To reach these present-day concentrations, considering the surface area of the catchment (18.2 km^2), a mean depth of soil of 45 cm, and a natural Cu concentration equal to the bedrock content (19.63 ± 0.04 μg g^{-1}), at least 400 kg of Cu per hectare would have been spread

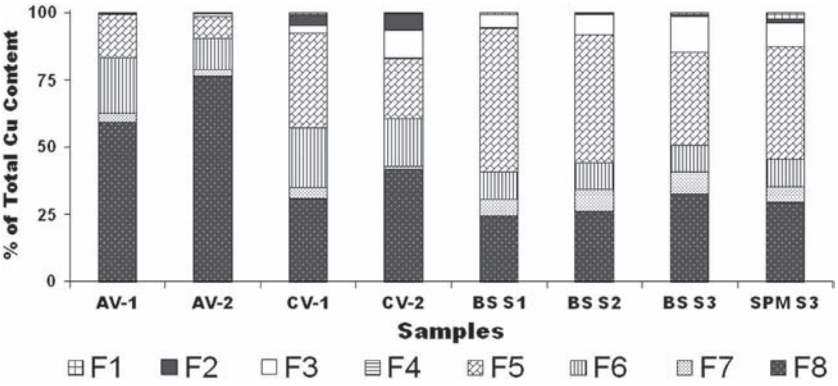

Fig. 3. Cu percentage in each fraction (expressed as a % of total Cu) extracted using SCE on the different samples during the flash flood event of February 2009. Represented fractions are: (F1) Dissolved with water; (F2) exchangeable; (F3) bound to carbonates; (F4) bound to manganese oxides; (F5) bound to amorphous iron oxides; (F6) bound to crystalline iron oxides; (F7) bound to organic matter and (F8) Residual. Fractions that are not well identified in the graph are those that contribute little to the total Cu content of the samples. CV (Cultivated Vineyard) and AV (Abandoned Vineyard) are sampled soils (from the surface 1 to depth 2). River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

on the catchment soils throughout history, and are therefore, presently stocked.

Even after being abandoned for more than twenty years, AV still contained Cu enrichments in both superficial and deep horizons (EF > 2). This shows that Cu delivered by human activities persists in soil for a long time and should be considered before changing the soil use. Surface and deep horizons of the cultivated soil (CV-1 and CV-2) were enriched in Cu relative to the local mica schist bedrock. This suggests that Cu spread on vineyard soils with the Bordeaux mixture moved from the surface to the deepest soil horizons. Nóvoa-Muñoz et al. (2007) showed identical copper contents in different layers of vineyard soils referencing it to a leveling of Cu values in the whole soil profile. Rusjan et al. (2007) also found a significant mobility of Cu content to soil depth in various soil types In the sub-Mediterranean winegrowing region of Slovenia. The removal of Cu to deeper layers would occur during heavy precipitation events and would depend on the properties of the soil.

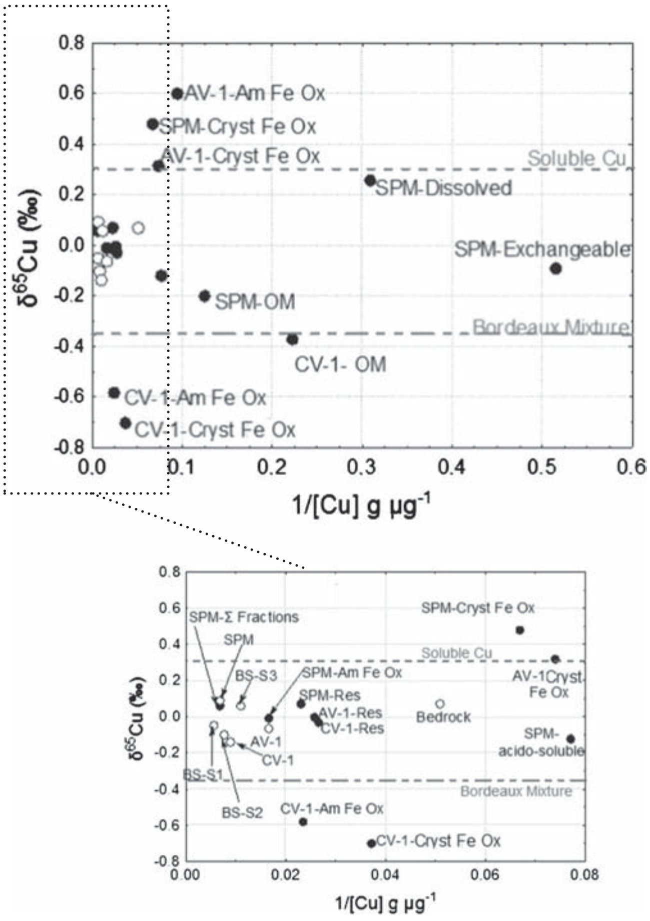

Fig. 4. Cu isotopic compositions *versus* 1/Cu: values for the bulk samples (white circles) and the different SCE fractions (black circles) of the various samples of soils, river bed sediments and suspended particulate matters (see sample references in Table 1). The figure below is a zoom of the doted part in the top figure. For the dissolved fraction and Bordeaux mixture, only the δ^{65}Cu ratio is mentioned. CV-1 (Cultivated Vineyard) and AV-1 (Abandoned Vineyard) are sampled surface soils. River Bed Sediments (BS) were collected from upstream to downstream (S1 to S3) and river Suspended Particulate Matter (SPM) was sampled at the catchment outlet (S3).

Although a component of the Cu stays in the soils, another is affected by soil leaching or by physical erosion and reaches the stream where it would be detected dissolved in water or adsorbed onto BS and SPM. Dissolved Cu concentrations (5 to 8 μg L^{-1}) in the river water were more than three-fold the worlds average (Gaillardet et al., 2003) reported for the dissolved phase (1.48 μg L^{-1}). This indicates that Cu is easily mobilized once in the environment. The SPM collected during the flood event were also highly concentrated in Cu (146.3 ± 1.3 μg g^{-1}) greater than the world average concentration of 75.9 μg g^{-1} proposed by Viers et al. (2009). The Cu content in SPM was close to that of CV-1 (110 μg g^{-1}) this indicates that (i) Cu mainly comes from vineyard soils due to erosion and (ii) Cu in SPM provides a mean integrative value of soil erosion for the whole catchment with highly Cu enriched SPM from vineyard soils being diluted by less Cu enriched SPM from abandoned soils. Despite this SPM content was slightly higher than CV-1 which might be explained by the mobilization of the finest particles with the erosion processes of the first soil centimeters. The finest particles have the highest specific surface area, and thus, are Cu enriched. Indeed, a sampling of the 0 to 2 cm surface layers of several soils in the Hérault Mediterranean vineyard basin, showed close average copper contents to SPM (~200 μg g^{-1}) (Chaignon et al., 2003). Additionally, the Cu concentration in SPM of the Baillaury River was close to that found in the Aire River (Yorkshire, England) directly receiving sewage treatment and industrial Cu enriched effluents (Dawson and Macklin, 1998). Aside from showing that fungicide treatments in vineyards can lead to significant contamination of surface waters with the suspended matter, our results reveal that agricultural practices can have the same impact as domestic and industrial activities.

If we assume a total SPM content of 1 g L^{-1} usually detected at the peak of flash flood events in the Baillaury River that corresponds to the world average concentration of suspended sediments in surface runoff (Probst and Sigha, 1989), for an average discharge of

10 $m^3\ s^{-1}$ during this storm event, 1.03 g s^{-1} of non-residual particulate Cu (concentration = 103 μg L^{-1}) would have been transported along with 0.06 g s^{-1} of dissolved Cu (concentration = 5.8 μg L^{-1}) leading to fluxes of 1.09 g s^{-1} of potentially available Cu. Flemming and Trevors (1989) determined thresholds of toxicity to most living organisms between 5 and 100 μg L^{-1}, according to the organisms. In our discharge flow conditions, these concentrations correspond respectively to fluxes between 0.05 and 1 g s^{-1}. Then the Baillaury fluxes observed in this study are within the range of these thresholds, pointing out the importance of pollutant transfer in this catchment during storm flow events.

Analyses of BS showed a decreasing Cu concentration from upstream (S1) to downstream (S3), probably due to more soil Cu erosion and leaching in upper part of the catchment where the slope are steeper than in lower part. Concentrations were higher than the world baseline of 39 μg g^{-1} (Callender, 2004) or bed sediments values (19 μg g^{-1}) from rivers draining intensively crop cultivated catchments from the Midi-Pyrenees region in the south west of France (N'Guessan et al., 2009). The highest Cu content (≈176 μg g^{-1}) was obtained for BS at S1 situated next to a cultivated parcel. Upstream the BS Cu content exceeded the surface soil layer of the cultivated soil, probably as a result of the finest concerned enriched fraction constituting BS.

4.2. Cu Partitioning Between the Different Fractions: Anthropogenic Versus Natural Sources

Based on the calculated EF, AV and BS had the lowest contamination. However, since total Cu content is an insufficient variable to characterize its behavior once in the environment, the proportions of Cu in residual and extractible fractions were identified.

The residual fraction contains the Cu incorporated into the mineral matrices. Most of the Cu in the abandoned soil samples (AV-1, AV-2) was in the residual fraction (respectively 60 and 87% of total Cu) and so can be considered as natural and unavailable. These results are in accordance with the ~60% presented by Ribolzi et al. (2002) in a nearby Mediterranean wine growing catchment. On the other hand, because of the Bordeaux mixture spreading, the cultivated vineyard (CV-1, CV-2) showed opposite distributions with less than 45% of Cu in the residual fraction, the remaining fraction having the ability to be easily mobilized from the non-residual fractions. Similar percentages were found for BS and SPM. This shows a more important contribution of cultivated soils to SPM and BS Cu content. In all cases, among the non-residual phases, the major fractions were Cu adsorbed onto amorphous and crystalline Fe oxides while the minor ones were the adsorbed onto Mn oxides, soluble, exchangeable, acid-soluble and bound to organic matter fractions. This is in agreement with the well known ability of Fe oxide coatings to scavenge trace metals from solution (Dawson and Macklin, 1998; Probst et al., 2003; Gandois et al., 2010). The strong affinity between Cu and organic matter indicated in many studies (Arias et al., 2004; Nóvoa-Muñoz et al., 2007; Komárek et al., 2008) is more evident (~10%) in sediments and suspended particulate matter than in soils (~5%) (see Fig. 3). The differences could be related to particle size distribution and content of Fe oxides and organic matter as already shown by Probst et al. (2003) for different French forested soils.

4.3. Isotopic Tracing: Constraint of Origin and Processes

4.3.1. Soils

Values of δ^{65}Cu in the residual fraction of CV-1 and AV-1 were similar to that of the local bedrock and the residual fraction of SPM, consistent with the natural origin of Cu in these fractions. Note that the Cu isotopic composition of the mica schist constituting the parental rock of the Baillaury River catchment is close to that measured by Mathur et al. (2012) in a black shale formation from Pennsylvania-USA (δ^{65}Cu = +0.03‰ ± 0.15). δ^{65}Cu in the bulk soil from CV-1 (δ^{65}Cu = −0.14‰) were close to the Bordeaux mixture (δ^{65}Cu = −0.34‰) indicating that most of Cu in this upper horizon of cultivated soil originated from the fungicide treatments. This Cu was most obviously bound to organic matter (OM) without or with slight fractionation (−0.37‰) whereas Cu associated with iron oxide in this soil sample is enriched in light Cu isotope, ^{63}Cu. This is not in accordance with the results in the literature showing that there is enrichment in heavy isotopes on the surface of oxyhydroxides (Balistrieri et al., 2008; Pokrovsky et al., 2008). In fact, these previous studies showed that aqueous Cu^{2+} ion has a coordination number of 6 with four short Cu–O bonds (1.97 Å) and two longer axial bonds (2.38 Å), whereas Cu(II) adsorption onto various Fe oxides (goethite, hematite, and lepidocrocite) indicates a coordination number of 4 with Cu–O bond distances of 1.85 to 2.05 Å. Hence, the heavier isotope should concentrate in the species to which it is bounded most strongly. Further investigations should therefore be carried out to understand why the vineyard soil showed different fractionation than laboratory experiments in literature; potential interactions with the surrounding environment and biological cycling should be suspected. In AV-1, higher δ^{65}Cu ratios were observed in the Fe oxides consistent with the literature. These isotopic ratios were close to the crystalline Fe oxides of suspended matter so Cu in this fraction of SPM might originate from the abandoned soils where an aging process, defined as the transformation of geochemically 'active' Cu to 'inactive' Cu, takes place with time and could explain the higher affinity of Cu for oxides in AV compared to CV (Pietrzak and McPhail, 2004).

4.3.2. River Bottom Sediments and Suspended Particulate Matter

Bulk BS and SPM had the same δ^{65}Cu signature as the local bedrock (δ^{65}Cu ~ 0‰) but this does not mean that isotopic signatures are not efficient indicators of Cu contamination. Indeed, by combining isotopic signatures and sequential extractions, i.e. by analyzing δ^{65}Cu not only in the bulk SPM samples but also in each residual and non-residual fraction, interesting results can be pointed out. Three SPM fractions delivered by sequential extractions had significantly different isotopic ratios than the bedrock (Cu associated to the soluble fraction ~ +0.26‰, Cu associated to crystalline Fe oxides ~ +0.5‰ and Cu associated to OM ~ −0.2‰). Organic matter linked fraction is closer to the Bordeaux mixture pole, which has a negative δ^{65}Cu (~−0.35‰).

One important consideration is whether Cu isotope fractionation occurs during the sequential extraction procedure. For example, natural processes such as sorption, complexation, or precipitation which occur during the procedure might induce some isotopic fractionation. Nevertheless, if we perform a mass balance calculation with δ^{65}Cu measured at each step of the procedure in order to check this hypothesis, we can see for SPM sample that the δ^{65}Cu value (0.06‰) resulting from the sum of δ^{65}Cu in each fraction is very close to that obtained directly on the whole SPM sample (0.09‰) after total digestion. Unfortunately, it is impossible to perform the same mass balance for the soil samples (AV1 and CV1) because δ^{65}Cu could not be determined for all fractions due to very low Cu contents.

Various studies on natural rocks (Ehrlich et al., 2004; Fernandez and Borrok, 2009) showed that the oxidative dissolution of sulfide minerals and the corresponding change from Cu(I) to Cu(II) may cause the development of isotopically higher δ^{65}Cu in the solution compared to the bedrock from which it originated. Vance et al. (2008), on the other hand, suspect that strong Cu(II)-organic complexes explain this relationship. These two processes can drive the higher isotopic δ^{65}Cu value of river water dissolved phase with respect to the local bedrock. The answer is likely somewhere in-between (or perhaps site or scale-specific). This study could not distinguish between the two, but it does appear that organic complexation may be important.

In our study, δ^{65}Cu value measured for particulate Cu was lower, -0.05‰ and $+0.09$‰ in the bulk BS and SPM, respectively, than in the dissolved Cu ($+0.31$‰). Copper associated to the soluble fraction of SPM had a δ^{65}Cu of ~$+0.26$‰ close to the signature of dissolved Cu in river water ($\delta^{65}\text{Cu} = +0.31$‰). The similarity of isotopic composition between the SPM soluble Cu and dissolved Cu may suggest that during the flash flood the dissolved phase in river water would be the main contributor of the soluble fractions contained in the SPM. The results imply that there is no fractionation during this transfer from the liquid phase to the solid phase. Note that the dissolution of the iron oxides rich in heavy isotopes during the flood event could also contribute to the dissolved flux of copper in the river. Vance et al. (2008) reported a δ^{65}Cu ranging from $+0.02$ (Missouri) to $+1.45$‰ (Changjiang) for dissolved Cu in rivers. All these rivers exhibit a clear tendency of enrichment in the dissolved phase of ^{65}Cu compared to the isotopic range of rocks ("solid Earth"). These authors proposed that this fractionation may be the result of the complexation of ^{65}Cu by dissolved organic matter. This is consistent with the experimental work of Jouvin (2009) showing that Cu-humic acids complexes favour the enrichment of ^{65}Cu. We have no data to estimate the fraction of Cu complexed by OM in the dissolved phase of the Baillaury River but the high concentration of dissolved organic carbon (DOC $=$ 3 to 8 mg L^{-1}) during the flood events may explain the high δ^{65}Cu signature of the river dissolved phase. By contrast, the low δ^{65}Cu of the Cu associated to particulate OM is not in agreement with the work of Jouvin (2009) showing the preferential association of humic substances with the heavy isotopes. The isotopic composition of Cu associated to crystalline Fe oxides is in good agreement with the work of Balistrieri et al. (2008) and Pokrovsky et al. (2008). The fact that Cu linked to crystalline Fe oxides had higher δ^{65}Cu values is consistent with previous studies showing that there is a preferential incorporation of the heavy isotope, ^{65}Cu, into the oxidized Fe and Mn species (Asael et al., 2007). Indeed, the heavier isotope adsorbs onto the oxide surface with shorter and so, stronger metal oxygen bonds. It has been recently demonstrated that ^{65}Cu will be enriched in the species where Cu is more strongly bound (Bigalke et al., 2010). This theory could explain the preferential liaison between ^{65}Cu and oxide surfaces. Cu showed greater fractionation during adsorption onto crystalline Fe oxides relative to amorphous Fe oxides (Balistrieri et al., 2008). That is why Cu in amorphous Fe had a lower δ^{65}Cu value (-0.01‰). In BS and SPM, an average of 45% of the total Cu was found to be adsorbed onto amorphous Fe oxides: this explains why the isotopic signature of the bulk BS and SPM is close to the δ^{65}Cu value of this non-residual fraction.

Nevertheless, more investigation is needed to fully understand the behavior of Cu after application of Bordeaux mixture.

5. Conclusions

Using a combination of geochemical and isotopic methods, progress was made in understanding Cu fate and transport in vineyard catchments.

Long term application of Cu-based fungicides has led to high concentrations of Cu in all the compartments of the catchment: soils (57–121 μg g^{-1}), river bed sediments (90–176 μg g^{-1}), river sus pended matters (146–191 μg g^{-1}) and dissolved fraction of river waters (5 to 8 μg L^{-1}) being greater than the legislative limit established by the EU. The most important enrichments are in the vineyard cultivated soils proving that the majority of the Cu in this catchment comes from the Bordeaux mixture treatments. The contribution of total Cu concentrations from anthropogenic sources varied from 50% in the abandoned vineyard soils to $>$75% in the cultivated soil, river bottom sediments and suspended particulate matters. Cu occurs mainly in the residual fraction in the abandoned soil however, in the cultivated topsoil layer, BS and SPM, the residual fraction accounts only for ~30%. The rest is therefore in extractible fractions potentially mobile and toxic for the ecosystems. In this extractible non-residual fraction, the minority fractions are the soluble Cu, exchangeable Cu and Cu adsorbed onto Mn oxides; the most important affinity of Cu is for amorphous and crystalline Fe oxides.

Isotopic ratios measured in bulk samples and in the different fractions (residual and non-residual) show that the signature of the total sample is not always sufficient to know the origin of the studied element and combining a chemical sequential extraction with the isotopic measurements was a powerful tool to get a clearer insight of Cu distribution and mobility in the environment. In fact, Cu in residual fractions of soils, BS and SPM is of natural origin exhibiting the same signature as the local bedrock whereas Cu in the surface horizon of the vineyard soil has an isotopic ratio close to that of the Bordeaux mixture. Copper transported in solution could be associated to the soluble fraction of SPM without the occurrence of any fractionation.

However, further analyses over a longer monitoring period including several storm events and at different moments of the storm event is needed to further determine the ranges of variation of the amounts, forms and origin of copper that were observed in this preliminary study.

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