Response of copper concentrations and stable isotope ratios to artificial drainage in a French Retisol

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A R T I C L E   I N F O

A B S T R A C T

Copper is a redox-sensitive trace element, which can be both, an essential micronutrient and a pollutant. We therefore analyzed Cu concentrations and stable isotope ratios (δ^{65}Cu values) in a drained Retisol to trace the response of Cu to a changing hydrological regime and enhanced clay eluviation. The study soil was artificially drained 16 years before sampling resulting in macroscopically visible pedogenetic changes and is thus a suitable site to investigate the influence of pedogenetic processes on the fate of Cu. Samples were collected from all horizons along a trench at four distances from the drain: 0.6 m, 1.1 m, 2.1 m and 4.0 m. In the E & Bt horizon, four different soil volumes (ochre, pale brown, white-grey and black) were sampled at all four distances from the drain. Furthermore, we analyzed soil solutions sampled with piezometer, porous cups, and at the drain outlet. The Cu concentrations were lowest in the surface (Ap) horizons (6.5–8.5 µg g^{-1}) and increased with depth to the clay-rich Bt horizons (10.5–12 µg g^{-1}), because of clay eluviation and associated Cu transport. The δ^{65}Cu values significantly decreased from the surface (Ap = − 0.25 ± 0.07‰) to the deeper horizons, but showed no significant variation among the deeper horizons (− 0.41 ± 0.28‰) and no correlation with the clay content, indicating that clay eluviation did not significantly affect δ^{65}Cu values. The isotopically heavier δ^{65}Cu values in the Ap horizons can probably be explained by agricultural management practices like sludge application and fertilization. Close to the drain (position 0.6 m), Cu concentrations were depleted and the lighter Cu isotope was enriched (− 0.91 ± 0.15‰) in the uppermost part of the E & Bt horizon. We attribute this to the changing redox conditions, caused by the lowering of the water level close to the drain. Copper concentrations in black and ochre volumes were significantly higher than in pale-brown and white-grey volumes. The black volume had significantly higher δ^{65}Cu values than the ochre volume indicating preferential sorption/occlusion of the heavy Cu isotope by Fe oxides. Enhanced clay eluviation in bulk soil close to the drain and in specific soil volumes did not affect δ^{65}Cu values. Cu concentrations (2.1–14 µg L^{-1}) and δ^{65}Cu (0.04–0.42‰) values in water samples showed no clear relation with redox changes along the trench perpendicular to the drain. The enrichment of the heavy Cu isotope in the solution samples (Δ^{65}Cu$_{(soil\text{-}solution)}$ = − 0.61 ± 0.41) indicates that reductive Cu mobilization is not the main driver of Cu leaching, because this would preferentially mobilize isotopically light Cu. We conclude that the eluviation of the < 2 µm fraction, strongly controlled Cu concentrations, but had no discernible effect on δ^{65}Cu values. The changing redox conditions did not seem to control Cu concentrations and the stable isotope distribution in most of the bulk soil, soil volumes and soil water. Instead, weathering, complexation of leached Cu, Cu application with fertilizers and sorption processes within the soil controlled its δ^{65}Cu values.

1. Introduction

In temporary or permanently water-saturated soils, episodic anoxic redox conditions couple back to many soil chemical properties and may cause mobilization and redistribution of redox-sensitive elements like Cu. Copper is of interest because of its nutritional importance as well as pollution risk. Furthermore, the redox behavior of Cu is assumed to play an important role in colloidal mobilization of a number of toxic elements like Ag, Cd, Hg and Pb (Abgottspon et al., 2015; Hofacker et al., 2013a, 2013b; Weber et al., 2009a). Thus, information about Cu behavior in temporarily water-saturated soils and the response of Cu to changes in the soil water regime might help to understand the release mechanisms of redox-sensitive trace elements.

When soils get waterlogged, the redox potential drops and Fe and Mn (oxyhydr)oxides are dissolved releasing associated trace elements (e.g., As, Ba, Co, Cr, V; Abgottspon et al., 2015; Du Laing et al., 2009; Sipos et al., 2011). Changes to anoxic conditions may cause microbial formation of reduced metal (Cu^+ and Cu[0]) colloids (Weber et al., 2009b). When the redox potential drops sufficiently, microbial sulfate reduction is initialized and the mobility of Cu can be limited by the formation of or co-precipitation with sulfides (Weber et al., 2009b; Borch et al., 2010). However, sulfate reduction may also favor the release of Cu-sulfide colloids into soil solution, resulting in enhanced mobility during several days after flooding (Abgottspon et al., 2015; Hofacker et al., 2013a, 2013b; Weber et al., 2009a). When the conditions in the soil change to oxic, Cu(0) is rapidly oxidized to Cu^{2+}, while Cu^+-S_{org} or Cu_xS is only slowly oxidized limiting Cu solubility in soil (Fulda et al., 2013). Balint et al. (2014) confirmed that Cu leaching decreased over four redox cycles, which they attributed to the redistribution of Cu from labile to more recalcitrant chemical fractions in soil.

Several soil processes result in fractionation of Cu isotopes (Fig. 1, Bigalke et al., 2010a, 2010c, 2011, 2013). Sorption of Cu to Al and Fe (oxyhydr)oxides caused an enrichment of heavy Cu on the surface of the Fe (oxyhydr)oxides (Balistrieri et al., 2008; Pokrovsky et al., 2008). Sorption to organic ligands shows different fractionation factors depending on the type of organic ligand and pH (Bigalke et al., 2010b; Ryan et al., 2014). Lighter Cu isotopes are preferentially adsorbed on clay mineral surfaces (Li et al., 2015). Redox reactions cause pronounced fractionation, leaving the reduced Cu species enriched in lighter Cu isotopes (Ehrlich et al., 2004; Zhu et al., 2002). Babcsányi et al. (2014) and Bigalke et al. (2010a, 2011, 2013) found temporary water-saturated soil horizons and wetlands to be enriched in heavy Cu isotopes, which they attributed to the loss of light Cu by leaching of reduced colloidal Cu forms. Liu et al. (2014a) studied weathering and soil formation under different climatic conditions and attributed variations in the isotopic composition to sorption of Cu to organic carbon in soils and leaching of heavy Cu, while also different redox conditions in the soils may have caused significant fractionation. In an oxic weathered podzol, leaching of heavy Cu because of complexation and downward transport with humic acids from the E to the Bhs horizon was described by Bigalke et al. (2011). Fekiacova et al. (2015) recently compiled data from contaminated and uncontaminated soils and found that contaminated soils tended to show heavier δ^{65}Cu values. In addition, fractionations associated with plant uptake of Cu (Jouvin et al., 2012; Navarrete et al., 2011; Ryan et al., 2013; Weinstein et al., 2011) might affect Cu isotope distribution in the organic and surface horizons (Bigalke et al., 2011). The literature reveals that the determination of Cu stable isotope ratios may be a valuable additional tool to mass budgeting approaches for the identification of the processes by which Cu responds to pedogenesis. To study the interaction of two pedogenetic processes (clay redistribution and redox changes), Retisols are considered as a model soil type.

Retisols are characterized by the eluviation of clay from the surface horizons (E horizon) and transport and accumulation of the clay in deeper horizons (Bt horizon). The subsoil clay accumulation impedes drainage and leads to temporary water saturation in winter. In such soils, the combination of eluviation and redox processes is responsible for the morphological degradation of the soil and the formation of the E & Bt-horizon, characterized by the juxtaposition of four soil volumes differing in texture and color. To improve agricultural suitability, many Retisols have been drained (FAO, 2001; IUSS Working Group WRB, 2014). Artificial drainage was demonstrated to induce i) an increasing intensity of the eluviation process in the immediate vicinity of the drains and ii) the transport of dissolved Fe and Mn towards the drain lines where more oxidative conditions favored the precipitation of Fe and Mn oxides in various forms of black concretions and impregnations (Montagne et al., 2008).

We focus on the Cu isotopic composition of soil samples collected from four soil profiles located at increasing distance from a drain and the evolution of the δ^{65}Cu values of four soil volumes in the E & Bt horizon as response to the drainage. We aim to answer the following questions:

1) What is the effect of clay eluviation and accumulation in the Bt horizons on Cu concentrations and δ^{65}Cu values?
2) What is the effect of drainage and associated changes in soil chemistry on Cu concentrations and δ^{65}Cu values?
3) How do redox and eluviation processes effect Cu concentrations and δ^{65}Cu values of soil solutions?

2. Materials and methods

2.1. Site description and soil sampling

The study site is located on the crest of the Yonne plateau in France where Retisols developed on quaternary loamy deposits overlying an Eocene clay layer. The deposit contains 70–90% of silt and 5–20% of clay. The soil was extensively cultivated for at least 200 years. Since 1988, an artificial subsurface drainage was installed at 1 m depth. The drain spacing was 15 m between parallel drainage pipes. The soil water regime fluctuates seasonally with saturation from December or January to February or March depending on the year. The temporary water table possibly reaches to the A horizon and is lowered close to the drain (Fig. 2; Montagne et al., 2008).

Details of the soil sampling procedure are available in Montagne et al. (2008). Briefly, in 2004, i.e. 16 yr after installation of the drainage, soil profiles were sampled from a trench perpendicular to one drain at four different positions with increasing distance to the drain (0.6, 1.1, 2.1 and 4.0 m, respectively). At each position, bulk soil samples were collected from three soil horizons (Ap/E & Bt/Bt). The Ap horizon (0 to ~30–35 cm depth) has a silty texture and is enriched with organic matter (7.3 ± 0.3 g kg^{-1} organic C; Montagne et al., 2008). The E & Bt horizon (~35 to 60 cm depth) shows pronounced eluviation and redoximorphic features resulting in the juxtaposition of four volumes differing in texture and color. The four soil volumes include white-grey, pale-brown, ochre and black volumes (Montagne et al., 2008). The white-grey and the pale-brown volumes are most abundant in the E & Bt-horizon, while in the underlying clay-enriched Bt horizon of yellowish brown color (~55 to ~105 cm depth), the ochre soil volume is by far most abundant. Soil pH increased with depth from 7.6 ± 0.1 in the Ap horizon to 8.0 ± 0.8 in the Bt horizon. In addition to the bulk soil samples, soil monoliths (approximately 27 × 15 × 12 cm) were extracted from the E & Bt horizons at all four distances to the drain. In these monoliths, the white-grey, pale-brown and ochre soil volumes were manually separated from each other, while black concretions and impregnations were sorted by wet sieving and the help of a magnetic separation technique (Montagne et al., 2008).

Piezometers were installed at three positions (at 0.7, 1.5 and 4.0 m, respectively, from the drain) in the E & Bt horizons and porous cups (1 × 2 cm-large) were placed in both, the ochre and white-grey volumes. In addition, water was collected at the outlet of the main