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Response of Cu partitioning to flooding: A δ^{65}Cu approach in a carbonatic alluvial soil

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ABSTRACT

The mobility and bioavailability of Cu in soils depend on the chemical Cu forms and are strongly influenced by water-induced changes in soil redox conditions. We chose an experimental approach by flooding a carbonatic floodplain soil and incubating it in a glovebox for 35 days. We used a five-step sequential chemical extraction to characterize the changes in chemical partitioning (F1–F5; NH_4NO_3-extractable, NaOAc-extractable, NH_4Ox-extractable, hot H_2O_2/NH_4OAc-extractable and residual fractions, respectively) of Cu and δ^{65}Cu values in the soil during the 35 days. After flooding, Cu concentrations decreased in F1–F3 and increased in F4–F5. Overall, 73% of the total Cu was redistributed among the five studied fractions. Before flooding (Day 0), δ^{65}Cu values in F1–F4 followed the estimated bonding strengths of Cu in the respective fractions, indicating equilibrium distribution of Cu at the beginning of the experiment. The total variation in δ^{65}Cu values among F1–F5 changed strongly from 0.83 ± 0.18‰ on Day 0 to a maximum of 2.18 ± 0.17‰ on Day 7. This change indicates the reduction of Cu^{2+} to Cu^{+} or Cu^{0} after flooding. The strongest variations in δ^{65}Cu values occurred in F3 (0.09 ± 0.07‰ to 1.43 ± 0.13‰) and F4 (−0.24 ± 0.07‰ to 0.55 ± 0.07‰), while flooding had no or small effects on the δ^{65}Cu values of F1, F2 and F5. Our results suggest a direct transfer of Cu from F3 to F4 because both concentration changes and changes in δ^{65}Cu values were balanced between the two fractions. The responses of Cu partitioning and δ^{65}Cu values to flooding are in line with the formation of Cu_xS or other reduced Cu species and reduction of Cu associated to Fe (oxyhydr)oxides. Our results emphasize the strong influence of redox conditions on Cu partitioning in soils and indicate a reduction in Cu availability under anoxic redox conditions.

1. Introduction

Beneficial or negative effects of Cu to organisms needing small amounts of Cu as essential nutrient but responding negatively to high Cu concentrations depend on the availability and mobility of Cu in soil. These parameters can be assessed with the help of operationally defined sequential extraction methods enabling to study the Cu partitioning in the soil (Svendsen et al., 2011; Balint et al., 2014). The partitioning among various chemical Cu fractions depends on soil composition, physico-chemical properties such as pH and redox conditions, and on sources and residence time of Cu in the soil (Bacon and Davidson, 2008; Shaheen and Rinklebe, 2014). Sequential chemical extraction (SCE) methods have been widely used to study partitioning of metals in soils (Tessier et al., 1979; Gleyzes et al., 2002; Dold, 2003). The results were used to draw conclusions on bioavailability, mobility and redistribution or sources of metals (Bacon and Davidson, 2008). Soil metal pools are mostly separated into 3–7 different operationally defined fractions, which are supposed to represent different metal pools. The operationally defined fractions commonly addressed include exchangeable forms, metals associated with carbonates, metals associated with (oxyhydr)oxides which might be further differentiated into Fe or Mn (oxyhydr)oxides and amorphous or crystalline forms, metals complexed by natural organic matter (NOM), metals in the reduced fraction (mainly metal sulfides), and the residual fraction (Gleyzes et al., 2002; Shaheen and Rinklebe, 2014). However, because of the limited ability of sequential extraction methods to target defined chemical phases, SCE usually only delivers operationally defined fractions usually consisting of a mixture of different chemical species. By now, a considerable number of sequential extraction methods has been developed for various applications (Gleyzes et al., 2002; Rao et al., 2008) and a number of weaknesses of these methods have been reported (e.g., Wallmann et al., 1993; Peltier et al., 2005; Sulkowski and Hirner, 2006). However, SCE has still a great potential to gain insights into metal partitioning and how the partitioning responds to environmental changes, especially when combined with stable isotope approaches (Bacon et al., 2006; Bacon and Davidson, 2008).

Partitioning and speciation of Cu in soil strongly depend on soil redox conditions (Kersten and Förstner, 1986; Larner et al., 2008; Fulda et al., 2013a; Abgottspon et al., 2015), driving also the mobility

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and bioavailability of Cu in redox-dynamic ecosystems like floodplain soils (Du Laing et al., 2009). Flooding of soil and the associated decrease in redox potential strongly influence soil physico-chemical conditions by increasing pH in acid soils, reducing available sulfate and dissolving Fe and Mn (oxyhydr)oxides. Increasing pH may cause a release of organic matter, a change in surface charge of (oxyhydr)oxides and organic matter, and a changing solubility of salts, which may cause precipitation or dissolution of components (Grybos et al., 2009; Borch et al., 2010). Soil Cu tends to repartition from mobile fractions into the more stable fractions e.g. by complexation with the reduced S group of humic acids (Fulda et al., 2013a 2013b; Maurer et al., 2013). Sulfate reduction to sulfide may result in the precipitation of Cu sulfides (Weber et al., 2009a). If Cu concentrations in soil solution exceed those of sulfate, Cu is reduced to solid Cu^0 phases (Fulda et al., 2013a). Reductive dissolution of Fe and Mn (oxyhydr)oxides reduces the sorption capacity of soil and releases occluded metals. Furthermore high dissolved Fe and Mn concentrations in soil solution increase ionic strength and result in the subsequent release of adsorbed metals (Du Laing et al., 2009; Borch et al., 2010). When water saturation of soil ends and conditions become oxic, physico-chemical properties change back and reduced Cu forms (Cu^0 and Cu$^+$ compounds) oxidize causing another repartitioning of Cu in soils. However, Cu$_x$S phases have been reported to be stable in soils under oxidizing conditions even after several weeks (Fulda et al., 2013a).

Copper stable isotope ratios (δ^{65}Cu values) have been reported to be fractionated in the soil–plant system by adsorption to organic substances, bacteria, (oxyhydr)oxides and clay minerals, uptake in microorganisms, uptake and transport in plants, and redox processes (Fig. 1). The δ^{65}Cu values have been used to improve our understanding of weathering and soil formation processes (Bigalke et al., 2011; Mathur et al., 2012; Liu et al., 2014a), to identify Cu sources, and to quantify Cu transport in contaminated soil (Bigalke et al., 2010b; El Azzi et al., 2013; Fekiacova et al., 2015). Furthermore, δ^{65}Cu values helped in assessing Cu leaching from and retention in temporally water-saturated soils and wetlands (Bigalke et al., 2010c, 2013; Babcsányi et al., 2014). Up to now, most authors used δ^{65}Cu values of bulk soil samples, which allow one to study the transport of Cu between different horizons or soil depth layers, but not the Cu partitioning among different soil pools in the same horizon. The combination of sequential extraction with stable isotope analysis is an established method for Fe (Wiederhold et al., 2007a; Percak-Dennett et al., 2013) and has also been successfully applied for Se (Schilling et al., 2014), Zn (Thapalia et al., 2010), Mo (Siebert et al., 2015), Hg (Wiederhold et al., 2015, 2013) and Ca (Hindshaw et al., 2011). The previous studies revealed considerable isotopic variation among different fractions and mainly aimed to study soil weathering, contaminant sources and transformations. By now, only two studies reported δ^{65}Cu values in the fractions of an SCE. El Azzi et al. (2013) investigated the fate of fungicide-derived Cu in French vineyard soil and sediments of nearby rivers and found a total variation of ca. 0.6‰ among the SCE fractions. El Azzi et al. (2013) related δ^{65}Cu values of the different pools directly with the sources of Cu and found that the residual fraction was dominated by native Cu while the organic fraction mainly contained fungicide-derived Cu. Thapalia et al. (2010) used a three-step SCE procedure to assess Cu partitioning in a sediment core of a lake. However, because of methodical problems they only reported δ^{65}Cu values of one of the pools (the organically bound Cu). This pool showed a total variation around 1‰ with depth, being lighter in some sediment layers and heavier in others. When using SCE, it must be borne in mind that there may be methodological problems because of incomplete dissolution of target pools and/or secondary precipitation and sorption which might both artificially change the partitioning of Cu and the δ^{65}Cu values of the various chemical fractions (Wiederhold et al., 2007b; Bacon and Davidson, 2008).

In this study, we conducted a 35-day anoxic incubation experiment to simulate soil flooding. We partitioned Cu into five different fractions with SCE, which were analyzed for Cu concentrations and δ^{65}Cu values.

We hypothesized that:

1. Cu partitioning in oxygenated soil is driven by equilibrium fractionation among the various reactive Cu fractions (F1–F4);
2. changes of Cu partitioning among the first four fractions (F1–F4, representing the reactive Cu pool in soil) in water saturated soils will be linked with changes in δ^{65}Cu values, while the fifth fraction (the little reactive residuum) will show no change in δ^{65}Cu values;
3. the response of δ^{65}Cu values to our experimental flooding allows for drawing conclusions about the processes causing redistribution of Cu among the different pools.

To limit the risk of artificial changes in partitioning and δ^{65}Cu values of chemical fractions by the SCE, we sampled the same soil – which was homogenized before the start of the experiment – at different times after experimental flooding of the soil and realized independent

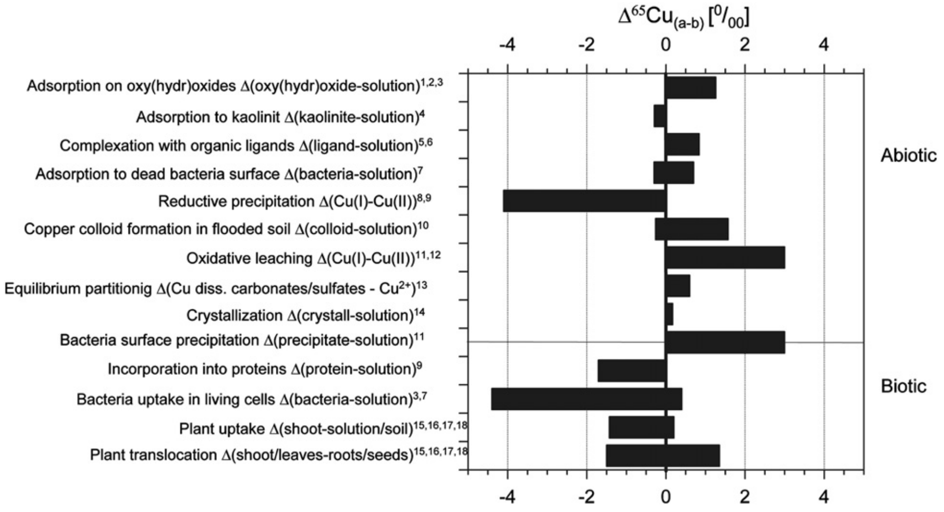

Fig. 1. Fractionation of Cu isotopes by environmental processes. Gray bars show the minimum fractionation observed, black areas show the interval of observed fractionations. Data from: 1) Balistrieri et al. (2008); 2) Clayton et al. (2005); 3) Pokrovsky et al. (2008); 4) Li et al. (2015); 5) Bigalke et al. (2010a); 6) Ryan et al. (2014); 7) Navarrete et al. (2011a); 8) Ehrlich et al. (2004); 9) Zhu et al. (2002); 10) Kusonwiriyawong (2015); 11) Mathur et al. (2005); 12) Asael et al. (2007); 13) Fujii et al. (2013); 14) Li et al. (2009); 15) Jouvin et al. (2012), 16) Weinstein et al. (2011); 17) Navarrete et al. (2011b); and 18) Ryan et al. (2013).