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Charirat Kusonwiriyawong, Moritz Bigalke, Sophie Cornu, David Montagne, Zuzana Fekiacova, et al.. Response of copper concentrations and stable isotope ratios to artificial drainage in a French Retisol. Geoderma, 2017, 300, pp.44-54. 10.1016/j.geoderma.2017.04.003 . hal-01517760

HAL Id: hal-01517760

https://hal.science/hal-01517760v1

Submitted on 17 May 2018

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

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Abstract

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 $\mu g\ g^{-1}$) and increased with depth to the clay-rich Bt horizons (10.5-12 $\mu g\ g^{-1}$), because of clay eluviation and associated Cu transport. The $\delta^{65}Cu$ values significantly decreased from the surface (Ap = -0.25±0.07 ‰) to the deeper horizons, but show no significant variation among the deeper horizons (-0.41±0.28 ‰) and no correlation with the clay content, indicating that clay eluviation does not significantly affect $\delta^{65}Cu$ values. The isotopically heavier $\delta^{65}Cu$ values in the Ap horizons can probably be explained by agricultural management practises 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 to 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 $\delta^{65}Cu$ 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 $\delta^{65}Cu$ values. Cu concentrations (2.1 - 14 $\mu g\ L^{-1}$) and $\delta^{65}Cu$ (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 ($\Delta^{65}Cu_{(soil\text{-}solution)}$= -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 <2µm fraction, strongly controlled Cu concentrations, but had no discernible effect on $\delta^{65}Cu$ 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.

Keywords: Copper isotopes; Lessivation; Redox conditions; Retisol; Soil volumes; drainage; soil water.

1. Introduction

In temporal 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., 2013; 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., 2013; 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., 2013b). 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; c; 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 temporally 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 oxic weathered soils, leaching of heavy Cu because of complexation and downward transport with humic acids was also 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

93 δ^{65}Cu values. In addition, fractionations associated with plant uptake of Cu (Jouvin et al., 2012;
94 Navarrete et al., 2011; Ryan et al., 2013; Weinstein et al., 2011) might affect Cu isotope
95 distribution in the organic and surface horizons (Bigalke et al., 2011). The literature reveals that
96 the determination of Cu stable isotope ratios may be a valuable additional tool to mass budgeting
97 approaches for the identification of the processes by which Cu responds to pedogenesis (e. g., clay
98 redistribution and redox changes). To study the interaction of the latter two processes, Retisols are
99 a model soil type.

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

111 We focus on the Cu isotopic composition of soil samples collected from four soil profiles
112 located at increasing distance from a drain and the evolution of the δ^{65}Cu values of four soil
113 volumes in the E&Bt horizon as response to the drainage. We aim to answer the following
114 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 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

138 juxtaposition of four volumes differing in texture and color. The four soil volumes include white-
139 grey, pale-brown, ochre and black volumes (Montagne et al. 2008). The white-grey and the pale-
140 brown volumes are most abundant in the E&Bt-horizon, while in the underlying clay-enriched Bt
141 horizon of yellowish brown color (~55 to ~105 cm depth), the ochre soil volume is by far most
142 abundant. Soil pH increased with depth from 7.6±0.1 in the Ap horizon to 8.0±0.8 in the Bt
143 horizon. In addition to the bulk soil samples, soil monoliths (approximately 27x15x12 cm) were
144 extracted from the E&Bt horizons at all four distances to the drain. In these monoliths, the white-
145 grey, pale-brown and ochre soil volumes were manually separated from each other, while black
146 concretions and impregnations were sorted by wet sieving and the help of a magnetic separation
147 technique (Montagne et al., 2008).

148 Piezometers were installed at three positions (at 0.7, 1.5 and 4.0 m, respectively, from the
149 drain) in the E&Bt horizons and porous cups (1 x 2 cm-large) were placed in both, the ochre and
150 white-grey volumes. In addition, water was collected at the outlet of the main drain of the plot with
151 an automatic collector. Water samples were collected once a week during the years 2005 and 2006,
152 and once every two weeks during the two following years. The Eh, pH and temperature were
153 measured in the field. In the lab, all soil water samples were filtered through a 0.2-μm cellulose
154 filter, acidified with suprapur HNO_3 and stored at 4°C for Fe analysis. Soil water samples were
155 bulked to obtain a sufficient mass of Cu for isotope analysis. Bulking was done for the three
156 different water types separately (piezometer, porous cup, and drain water samples) for two
157 different time periods (2005/06 and 2007/08) resulting in seven different soil water samples. The
158 water samples were classified according to their Fe concentrations as indicator of redox conditions
159 in the soil. The Fe concentrations under oxic condition (Eh > 300 mV) were always lower than 40

160 μg L^{-1}. Therefore, 40 μg L^{-1} Fe was used as a threshold to separate between oxic and anoxic soil
161 solution samples.
162

163 ***2.2. Sample preparation and analysis***

164 Approximately, 0.25-0.40 g of soil samples were digested in a mixture of concentrated
165 HNO_3, HF and H_2O_2 (ratio 3:2:1) in PFA beakers (Savillex@ MN, USA) for 24-36 h on a hotplate
166 at 120°C. The digests were evaporated until dryness on a hot plate at 70ºC. To remove excess HF,
167 the dried residues were redigested with a mixture of concentrated HCl and HNO_3 for at least 3-4
168 hours, refluxed several times and evaporated to dryness on a hot plate. Samples were finally
169 dissolved in 7 mol L^{-1} HCl and 0.001% H_2O_2. The water samples (approximately 300 mL) were
170 evaporated yielding >300 ng of Cu for isotope analysis. The samples were refluxed in HNO_3 and
171 H_2O_2 (ratio 1:1) and finally dissolved in 7 mol L^{-1} HCl and 0.001% H_2O_2 for Cu purification.

172 All samples were purified using Poly-Prep Chromatography columns (Bio-Rad, CA, USA)
173 filled with 2 mL of pre-cleaned 100-200 mesh AG MP-1 (Bio-Rad, CA, USA) anion exchange
174 resin following an established method (Bigalke et al., 2010a). For soil samples, the column
175 purification was repeated once to gain matrix-clean Cu fractions (Bigalke et al., 2011; Petit et al.,
176 2012). After complete separation, the purified fractions were evaporated to dryness and digested
177 with concentrated HNO_3 and H_2O_2. The samples were evaporated and then dissolved in 2% HNO_3
178 for Cu isotope analysis. All samples were analyzed by ICP-MS (7700x, Agilent, CA, USA) for
179 matrix elements and Cu recovery. Column eluates, in which Cu was not completely recovered
180 (100±6%) or in which matrix elements were present, were discarded and sample purification was
181 repeated.

182 All reagents used were of suprapur quality (Merck, Darmstadt, Germany). Hydrochloric
183 and nitric acid were purified by sub-boiling distillation. Sample preparation and chemical

purification were performed in the clean chemistry laboratory at the Institute of Geology, University of Bern. Total procedural Cu blanks averaged 1.9±0.9 ng (n=3) and 3.4±1.5 ng (n=3) for the first and second runs of column purification, respectively. The quality of the method was evaluated by using USGS basalt BCR-2 (Basalt Columbia River 2, USGS, Reston, VA, USA) reference materials. The mean total Cu concentration we determined in BCR-2 was 18.6±0.3 μg g^{-1} (mean ± SD, n=11) in good agreement with the certified value of 19±2 μg g^{-1}.

2.3. Isotope analysis

Copper isotope ratios were analyzed by MC-ICP-MS (Thermo-Finnigan Neptune, Thermo Scientific, Waltham, MA, USA) at the Leibniz University Hannover, Germany. Instrument was operating in the low mass resolution mode. Samples and standards were diluted to 300 μg L^{-1} Cu with 2% HNO_3 and introduced in to the MC-ICP-MS by a glass spray chamber (double pass Scott design). Nickel (NIST 986, National Institute of Standards and Technology, Gaithersburg, MD, USA) at concentration of 1000 μg L^{-1} was used for the instrumental mass-bias correction in combination with standard-sample bracketing. Every sample was at least analyzed twice. The average Cu isotope ratio was reported in the δ^{65}Cu notation in ‰ relative to NIST 976. The accuracy of the resin purification method was validated by using spiked Cu-free matrix samples. The Cu-free matrix samples were prepared from the matrix fraction derived from the purification of the original samples and spiked with the ERM@-AE633 Cu isotope standards (Institute for Reference Materials and Measurements, Geel, Belgium), which is isotopically identical with NIST 976 (Moeller et al., 2012). The spiked matrices were treated and purified in the same manner as the original samples. The δ^{65}Cu value of the matrix samples was -0.03±0.04‰ (mean±2SD, n=5) and undistinguishable from ERM@-AE633 (-0.01±0.05‰, Moeller et al., 2012). Reproducibility

and accuracy of δ^{65}Cu measurements were monitored with the help of certified reference materials BCR-2 and NBS C 125-2 (SRM C1252, National Institute of Standards and Technology, Gaithersburg, MD, USA). The NBS C 125-2 was used as an in-house Cu standard to check the MC-ICP-MS stability yielding a δ^{65}Cu value of 0.36±0.06‰ (mean±2SD, n=10). BCR-2 yielded a $\delta^{65}Cu_{NIST976}$ = 0.15±0.08‰ (mean±2SD, n=11) comparable to the previously published data ranging from 0.14±0.05‰ to 0.22±0.06‰ (e.g., Bigalke et al., 2010a; 2013; Liu et al., 2014b; Moeller et al., 2012).

2.4. Calculations and statistics

The overall mass flux for any soil volume $m_{j;flux}$ in g cm^{-2} was then calculated for each element j using Eq. (1) proposed by Brimhall et al. (1991) and modified by Egli and Fitze (2000):

$$m_{j;flux} = \frac{1}{100} \times \frac{\rho_{ref} \times C_{j;ref} \times Th \times \tau_{j.w}}{\varepsilon_{i;w}+1} \qquad (1)$$

in which ρ is the bulk density, Cj is the concentration of j in weight percent, Th (cm) is the thickness of the considered soil horizon. The subscripts ref and w referto the soil taken as a reference and to the weathered product, respectively. We used positions 60 and 110 m as representing the weathered product (because drainage changes the soil composition at these distances) and positions 210 and 400 m as reference (because here the effect of drainage is very low, Montagne et al., 2008). This is different to the classical approach of comparing soil horizons with parent material. The $\varepsilon_{i;w}$ and $\tau_{j;w}$ values are the strain and the open-system mass-transport functions, respectively, calculated according to Eqs. 2 and 3 (Brimhall et al., 1991). The εi;w is a measure for the change of the soil volume over time using an immobile element i and τj;w; is the mass fraction of element j gained or lost from the weathered product with respect to the mass

originally present in the reference material (i.e. the soil at positions 210 and 400 m). We used quartz as an immobile compound.

$$\varepsilon_{i;w} = \frac{\rho_{ref} C_{i;ref}}{\rho_w C_{i;w}} - 1 \qquad (2)$$

$$\tau_{i;j} = \frac{\rho_w C_{i;j}}{\rho_{ref} C_{j;ref}} \left(\varepsilon_{i;w} + 1\right) - 1 \qquad (3)$$

After checking the data for homoscedasticity with the Levené test, an analysis of variance (ANOVA) followed by a Tukey's Honestly Significant Difference (HSD) post hoc test was conducted to compare the mean Cu concentrations and isotopic compositions among soil volumes. Normal distribution of residuals was checked by visual inspection. Significance was set at $p < 0.05$.

3. Results

Copper concentrations in the bulk horizons increased with depth at three of the four positions (1.1, 2.1 and 4.0 m). Copper concentrations were closely related with those of the clay fraction (Fig. 3a). The Cu concentrations in the surface (Ap) horizon and clay-rich Bt horizons varied only little along the trench. In contrast, in the E&Bt-horizon, there was a large lateral variation in the Cu concentrations, with the lowest value at position 0.6 m (Tab. 1, Fig. 4a). The δ^{65}Cu values tended to decrease from the Ap horizon to the deeper horizons (Fig. 4b), but showed no relation to Cu concentrations or the clay fraction (Fig. 3b). However, the δ^{65}Cu values at different depths in the E&Bt and Bt horizons and at the different positions along the trench were not different. We only detected a single much lower δ^{65}Cu value compared to all other samples in the 35-45 cm depth layer (E&Bt horizon) at position 0.6 m (Tab. 1, Fig. 3b, 4b).

The Cu concentrations were significantly higher in the black and ochre volumes than in the pale-brown and white-grey volumes, respectively. Copper concentrations were not related with distance to the drain in pale-brown and white-grey volumes but were lower in the black and ochre volumes at position 0.6 m than at all other positions (Fig. 5a, Tukeys HSD test, $p < 0.05$). Overall the black volumes had the significantly highest and the ochre volumes the significantly lowest δ^{65}Cu values, while the δ^{65}Cu values of the pale-brown and white-grey volumes were not significantly different from those of the ochre and black volumes (Fig. 6). The bulk δ^{65}Cu value calculated from the mass-balanced sum of the individual soil volumes (ranging from -0.36±0.04‰ to -0.41±0.04‰) showed good agreement with the δ^{65}Cu value of the bulk soil in the E&Bt horizon at the different distances from the drain (ranging from -0.38±0.03‰ to -0.41±0.02). At position 0.6 m, this is true for the lower bulk sample (45-55 cm depth), which overlaps with the depth where soil volumes were sampled (Fig. 2), while for the upper 35-45 cm depth layer of the E&Bt horizon with the low δ^{65}Cu value (-0.91±0.15‰) we did not have samples of individual soil volumes for comparison.

The dissolved Cu concentrations in the porous cup sample were highest of all analyzed soil solutions. The Cu concentrations of drain water were consistently lower than those of the piezometer sample in all three studied samples (Tab. 2). While in the hydrological year 2005/2006 the δ^{65}Cu values in the piezometer and drain waters seemed to be lower in the anoxic samples (Fe > 40 µg L^{-1}); compared to the oxic samples, the δ^{65}Cu values of the anoxic samples were similar to those in the oxic samples from the Piezometer in the following hydrological year 2007/08. Consequently, the variations in δ^{65}Cu values among the various solution types and sampling dates could neither be clearly assigned to redox conditions nor to the way of sampling. There was no clear difference in Cu concentrations in waters taken under anoxic conditions (Fe > 40µg L^{-1})

compared with oxic conditions (Fe < 40µg L^{-1}). There were no clear differences in δ^{65}Cu values among the water samples from the piezometers and the drain in 2005/2006, but small variations in 2007/08. The single porous cup sample showed the lowest δ^{65}Cu value. Overall, the water samples showed higher δ^{65}Cu values than the solid soil samples, with $\Delta^{65}Cu_{(soil\text{-}solution)}$= -0.61±0.41.

4. Discussion

4.1. Depth distribution of Cu concentrations and δ^{65}Cu values

The vertical distribution of Cu in the study soil is influenced by (1) the amendment of limed sludge from 1998 to 2001 resulting in a Cu input of approx. 0.9 g m^{-2} (Montagne et al., 2007), (2) regular fertilization e.g., with mineral fertilizer (no manure application) and (3) pedogenetic processes including lessivation and hydromorphy (Montagne et al., 2008). The Cu input with sludge and fertilizer has increased Cu concentrations in the Ap horizons and also might have changed the δ^{65}Cu value. In the deeper horizons, clay eluviated from the Ap horizons which accumulated in the Bt horizons likely explains the increase in Cu concentrations because the clay fraction usually contains higher Cu concentrations than the coarser particle sizes (Minkina et al., 2011). The latter is also confirmed by the close correlation between the clay and the Cu concentrations ($r = 0.80$; $p < 0.001$). This correlation even became closer, when Ap horizons (with anthropogenic Cu input) were removed (Fig. 3a). No δ^{65}Cu values for agriculturally used sludge or mineral fertilizers have up to now been reported. However, in case that these additions carry a heavier δ^{65}Cu value than the soilthey might be responsible for the higher δ^{65}Cu values in the Ap horizons. The different soil depths in E&Bt and Bt horizons show no significant δ^{65}Cu changes, despite the significant changes in Cu concentrations linked to the clay eluviation. We explain this finding by the fact that Cu bound to clay controls the concentration and the δ^{65}Cu value of total soil Cu. Our findings suggests

that lessivation does not change δ^{65}Cu values of the bulk soils, because the eluviated and illuviated horizons have the same Cu isotopic composition. The lacking influence of clay concentrations on δ^{65}Cu values is reflected by the absence of a correlation between these two variables ($r < 0.001$, $p = 0.95$). Furthermore, soil volumes with different clay concentrations (Montagne et al, 2008) did not show a significant difference in δ^{65}Cu values, again indicating that other soil processes than the clay concentration (e.g. sludge application, weathering; Fig. 7) controlled Cu isotope ratios.

4.2. Response of Cu concentrations and δ^{65}Cu values to drainage

The low Cu concentration in the E&Bt at position 0.6 m, suggests that the drainage induced Cu leaching (Table 1, Fig. 4a). Mass flux calculations indicated that Cu mass flux ($m_{Cu\ flux}$) at position 0.6 m was, on average, three times higher than at positions 2.1 and 4.0 m (43.8 and 15.3 mg cm^{-2}, respectively). This loss of Cu from the E&Bt horizon at position 0.6 m is linked with substantial loss of Fe and clay at positions 0.6 m and 1.1 m, (6.5 and 2.3 kg m^{-2} Fe and 75.8 and 25.6 kg m^{-2} clay, respectively; Montagne and Cornu, 2010). The loss has been explained by strongly enhanced eluviation caused by drainage-induced higher water fluxes, and is most pronounced in the upper part of the E&Bt horizon at position 0.6 m (Montagne and Cornu, 2010). These findings agree with the close correlation between the clay and the Cu concentrations (Fig. 3a), which furthermore suggests that clay is the dominant Cu pool in this soil. In contrast, the observed eluviation had no significant effect on the δ^{65}Cu value of the drained soil, as illustrated by the lack of a correlation between δ^{65}Cu values and clay concentrations (Fig. 3b).

At 0.6 m distance, the E&Bt horizon showed a strong negative δ^{65}Cu value in its upper part (35-45cm), while its lower part (45-55cm) with similar properties (clay and Cu concentrations) did not show differences in δ^{65}Cu values from the soil at other distances (Fig. 3b). This strongly

negative value was ascertained by three replicate analyses including separate digestion, purification and analysis of each replicate. We suggest that the light δ^{65}Cu value in the upper part of the E&Bt horizon at position 0.6 m might be attributable to the change in redox conditions following drainage. Redox changes can cause a comparatively large fractionation of δ^{65}Cu values with the reduced Cu(I) enriched in the light isotopes (Fig. 1; Zhu et al., 2002). Under anoxic conditions, the reduced Cu fraction may account for a major part of total soil Cu and may carry a heavy isotope signal to balance that of a Cu-isotopically light residual fraction (Kusonwiriyawong et al., 2015). This Cu-isotopically heavy reduced fraction might be lost by oxidation (Fulda et al., 2013b) attributable to drainage, leaving the residual Cu isotopically lighter. The reason for the absence of this isotope effect in the deeper E&Bt Horizon (45-55cm), might be its closer proximity to the soil water table and thus less pronounced episodic oxidation. Fekiacova et al. (2015) reported a similar negative value (-0.89 ‰) for a Retisol at approximately the same depth, which they interpreted as light Cu enrichment linked to Fe oxide precipitation and sorption of light Cu leached from the surface horizons. However, Fekiacova et al. (2015) observed an increase in Cu concentrations in contrast to our study soil where the low δ^{65}Cu value was related with a decrease in Cu concentrations. Consequently, the low δ^{65}Cu values in the study of Fekiacova et al. (2015) and ours must have different reasons.

Additionally to analyzing the bulk soil samples, we partitioned the soil in the E&Bt horizon into four different soil volumes. The differentiation starts from the ochre volume, developing successive pale-brown and white-grey soil volumes by increasing eluviation and redox-induced bleaching (Montagne et al., 2008). Within the ochre volume, the black volume forms because of the precipitation of Mn oxides. With increasing proximity to the drain the ochre volumes decreased and the black, pale-brown and white-grey volumes increased (Montagne et al., 2008). The black

volumes always had the highest Cu concentrations, probably because of precipitation with and sorption of Cu on Mn oxides (Negra et al., 2005). The ochre volume always showed higher Cu concentrations than the pale-brown and white grey volumes because of eluviation and reductive leaching of clay minerals and (oxyhydr)oxides in the latter two volumes (Fig. 5a, Montagne et al., 2008). Because of the drainage, Cu concentrations in the black and ochre volumes decreased by approx. 50% in the direct vicinity (position 0.6 m) of the drain, which is consistent with the decrease in the bulk soil. The decrease in the Cu concentrations of the ochre and black volumes at position 0.6 m is driven by the strong clay loss by eluviation. In contrast, the more oxidizing conditions near the drain caused an increase in the abundance of the ochre and black volumes, attributable to the precipitation of Mn and Fe oxi(hydr)oxides. Because ochre and black volumes formed in a soil, which was already depleted in Cu, they showed lower Cu concentrations.. Independent of the distance to the drain, the contributions of the Cu stocks in the black, pale-brown and white-grey volumes to the total Cu stock of the bulk E&Bt horizon did not change, while the contribution of the Cu stock in the ochre volume to the total Cu stock of the bulk horizon decreased (Fig. 5b).

There were no clear variations in the δ^{65}Cu values of the individual volumes with distance to the drain ($p < 0.05$) indicating that the drainage-induced morphological changes at position 0.6 m did not cause a Cu isotope fractionation among the soil volumes. At position 0.6 m, the soil volumes were taken from the lower depth layer (45-55 cm), which had a similar δ^{65}Cu value as all other bulk soil samples (Fig. 2). The black volumes showed always significantly higher δ^{65}Cu values than the ochre volumes they develop from. This might be attributable to variable redox at the small spatial scale at which the differentiation into the four soil volumes occurred and related Cu isotope fractionation or by the sorption on Fe and Mn oxy(hydr)oxides in the black volumes.

As redox variation usually causes a strong isotope fractionation (Fig. 1) we consider more likely that the limited changes observed in the δ^{65}Cu values of the different soil volumes depended on the adsorption to Fe and Mn (oxyhydr)oxides (which preferentially adsorb heavy isotopes, Fig. 1b, Pokrovsky et al., 2008; Balistrieri et al., 2008).

The overall lack of a correlation between the clay concentration and δ^{65}Cu values, the differences in δ^{65}Cu values between the 35-45 and 45-55cm depth layers despite a similar degree of eluviation and the absence of significant variations between the ochre and the white-grey soil volumes (Fig. 5, the white grey volume is clay-depleted) imply limited importance of clay eluviation for the δ^{65}Cu values of the soil, despite the marked effect of lessivation on Cu concentrations in bulk horizons (Fig. 3).

4.3. Cu in soil water

The Cu concentrations in our soil water samples were similar to the previously published range of Cu concentrations in soil pore water during weathering of black shale of 1-16 μg L^{-1} (Mathur et al., 2012), dissolved Cu in river of 0-3 μg L^{-1} (Vance et al., 2008) and dissolved Cu in wetlands 1-12 μg L^{-1} (Babcsányi et al., 2014). The low concentrations in the drain water may be caused by co-precipitation with or sorption to Mn and/or Fe (oxyhydr)oxides precipitating near the drain pipe where the reduced Mn and Fe comes into contact with oxygen. Samples with low (<40 μg L^{-1}) and high (>40 μg L^{-1}) Fe concentrations (indicative for oxic and reducing conditions, respectively) did not show systematically different Cu concentrations, indicating that the redox potential was not sufficiently low to reduce Cu.

The δ^{65}Cu values in our water samples are well within the range reported for soil, river, and wetland water ranging from 0.02-1.45‰ (Vance et al., 2008; Mathur et al., 2012; Babcsányi

et al., 2014). The δ^{65}Cu values during anoxic conditions in 2005/06 overlapped with those during oxic conditions in 2007/08, showing no clear relationship with the redox potential in the piezometer. In the drain water, the δ^{65}Cu values seemed to be lower under anoxic conditions, but were similar to the oxic sample from the piezometer in 2007/08. The uniform Cu concentrations and δ^{65}Cu values indicate that there was no redox-induced change in Cu mobility, agreeing well with the findings from the bulk soils, where we also did not observe an indication for redox mobilization of Cu. The δ^{65}Cu value of dissolved Cu was heavier than that of the bulk solid soil ($\Delta^{65}Cu_{(soil\text{-}solution)}$= -0.61±0.41), but fractionation was less pronounced than reported for redox-induced fractionations in field and laboratory experiments (Fig. 1). The pattern of Cu isotopically light solid soils and heavy dissolved Cu fits well into the findings of a weathering experiments with basalts at pH 5 (Li et al. 2016) and results of the analysis of soil solutions from oxic weathering of black shales, which both always showed an enrichment of the isotopoically heavy Cu in the dissolved phase (Mathur et al., 2012).

Independent of the redox conditions, the δ^{65}Cu values of the dissolved fraction in rivers, wetlands and soils always showed a heavy δ^{65}Cu value, while the particulate and colloidal fraction showed light δ^{65}Cu values and a strong response to redox changes (Babcsányi et al, 2014; Vance et al., 2008). The lack of a relationship of the δ^{65}Cu values of dissolved Cu with the redox potential might be explained by the fact that the Cu isotope ratio of dissolved Cu in soils and rivers is more strongly controlled by complexation with strong dissolved ligands (Vance et al., 2008, Vance et al., 2016) than by redox changes. The responsible ligands were identified by cathode-stripping voltametry and are subdivided in the ligand classes L1 and L2 (Muller et al., 2001). Both ligand classes have high stability constants up to 10^{16} and often occur in excess compared to Cu

concentrations in solution (Vance et al., 2008). Therefore, it can be assumed that almost all dissolved Cu occurs in complexed form in environmental solutions (Muller et al., 2001).

5. Conclusions

1) The slightly decreasing δ^{65}Cu values with increasing depth in the bulk soils might be caused by addition of heavy Cu (e.g., fertilizer and sewage sludge) to the surface soil.
2) Drainage did not change δ^{65}Cu values in bulk soil and soil volumes, despite Cu redistribution by enhanced clay eluviation, with the exception of one point. A low δ^{65}Cu value and Cu concentration in the upper E&Bt horizon near to the drain may indicate oxidative weathering and leaching of heavy Cu isotopes formerly stored in the reduced Cu pool and is the only δ^{65}Cu value which we could link to redox changes. The drainage caused changes in the Cu distribution among the soil volumes indicative of locally changed pedogenetic processes. The δ^{65}Cu values showed significant differences among the soil volumes but did not change with distance to the drain, indicating that the Cu isotope signals are dominated by sorption processes but little by redox changes.
3) The Cu concentrations and δ^{65}Cu values in the solution samples did not respond to changes in soil redox conditions, indicating that short-term changes in redox conditions in the soil have a small or no effect on the isotope signals of dissolved Cu. The overall δ^{65}Cu value of dissolved Cu was heavier than that of bulk solid soil ($\Delta^{65}Cu_{(soil\text{-}solution)}$= -0.61±0.41), which we attribute to weathering and sorption of dissolved Cu to strong ligands in solution in line with several reports of soils solutions and river waters in the literature.

A conceptual model of the effect of the different processes on Cu distribution and δ^{65}Cu values in the soil is displayed in Fig. 7. In summary, the two dominant pedogenetic processes in the study soils (lessivation and hydromorphy) seem to have limited influence on the Cu stable isotope ratios although lessivation strongly controls Cu concentrations. The effect of drainage on δ^{65}Cu is visible only at one position close to the drain, which probably showed the strongest change in redox conditions. Our results illustrate that redox induced Cu leaching is only visible where the soil is most oxidized. Instead, in the Retisol clay eluviation and leaching of organically complexed Cu, drive Cu mobility. In general the δ^{65}Cu approach on bulk soils is helpful to investigate the influence of redox and sorption processes on Cu mobility in the soil system, but does not help for clay eluviation were two pools (e.g. clay and soil) are isotopically not discernible. The application of δ^{65}Cu values to investigate into redox controlled Cu mobility might be of high importance as reductive Cu mobilisation is driving the mobilisation of a number highly relevant pollutant elements (Ag, Cd, Hg, Pb; Abgottspon et al., 2015; Hofacker et al., 2013b; Weber et al., 2009b).

Acknowledgments

We thank the group of Isotope Geology of the University of Berne, Klaus Mezger, Thomas Nägler, Igor Villa and Gabriela Balzer for access to the clean room and support. The authors are grateful to L. Prud'Homme, B. Renault, G. Giot, N. Chigot from URSol (INRA, Orléans, France) for field sampling and monitoring. We thank the AE Edward Nater, and Ryan Mathur as well as two anonymous reviewers for their constructive comments, which significantly improved the manuscript. We thank the Agricultural Research Development Agency (Public Organization), ARDA, Thailand, for funding Charirat Kusonwiriyawong.

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Table 1

Copper concentrations and $\delta^{65}Cu$ values of the different soil horizons as a function of distance to the drain.

Horizon	Depth (cm)	Cu ($\mu g\ g^{-1}$)	SD	$\delta^{65}Cu$ (‰)	2SD	n[a]
	position 0.6 m					
Ap	10-20	7.3	0.1	-0.25	0.01	1
E&Bt	35-45	5.7	0.1	-0.91	0.15	3
	45-55	5.6	0.1	-0.40	0.02	1
Bt	55-65	9.1	0.2	-0.39	0.06	2
	65-75	10.8	0.4	-0.40	0.09	2
	position 1.1 m					
Ap	10-20	8.1	0.6	-0.28	0.01	1
E&Bt	40-55	8.2	0.7	-0.39	0.03	1
Bt	55-65	10.7	0.2	-0.40	0.06	2
	65-80	10.5	0.3	-0.31	0.03	1
	position 2.1 m					
Ap	10-20	6.5	0.1	-0.27	0.01	1
E&Bt	40-50	10.6	0.9	-0.41	0.02	2
	50-60	10.8	0.7	-0.39	0.01	2
Bt	70-83	11.4	0.3	-0.37	0.04	2
	position 4.0 m					
Ap	10-20	8.5	0.2	-0.20	0.01	2
E&Bt	35-45	8.4	0.2	-0.38	0.03	1
	45-55	10.2	0.6	-0.39	0.03	1
Bt	55-65	11.7	0.8	-0.33	0.02	3
	65-75	12.0	1.1	-0.35	0.01	3

[a] n is the number of independent digestions and purifications for isotope analysis

Table 2

Copper concentration and $\delta^{65}Cu$ values of piezometer, drain water and porous cup samples in the hydrological years 2005/06 and 2007/08.

Sample name	2005/06						2007/08		
	Fe < 40 µg L^{-1}			Fe > 40 µg L^{-1}			Fe < 40 µg L^{-1}		
	Cu µg L^{-1}	$\delta^{65}Cu$ (‰)	2SD	Cu µg L^{-1}	$\delta^{65}Cu$ (‰)	2SD	Cu µg L^{-1}	$\delta^{65}Cu$ (‰)	2SD
Piezometer	5.5	0.40	0.08	5.3	0.10	0.09	6.5	0.11	0.03
Drain water	2.5	0.42	0.18	2.9	0.17	0.01	2.1	0.36	0.02
Porous cup	14.1	0.04	0.05						

Figure captions

Fig. 1 Compilation of a) δ^{65}Cu values found in soils, soil and river waters and b) Δ^{65}Cu values reported for different processes, which might be of relevance in the Retisol. [1]Bigalke et al. (2011), [2]Bigalke et al. (2010a), [3]Bigalke et al. (2010c), [4] Vance et al. (2016), [5]Bigalke et al. (2013), [6]Fekiacova et al. (2015), [7] Mathur et al. (2012), [8] Ilina et al. (2013), [9]Petit et al. 2013), [10]Vance et al. (2008), [11]Balistrieri et al. (2008), [12]Clayton et al. (2005), [13]Pokrovsky et al. (2008), [14]Li et al. (2015), [15]Bigalke et al. 2010b), [16]Ryan et al. 2014), [17]Ehrlich et al. (2004), [18]Zhu et al. (2002), [19]Asael (2006), [20]Mathur et al. (2005), [21]Mathur and Fantle (2015), [22]Mathur et al. (2012).

Fig. 2 Schematic diagram of the study design showing the drain, the disturbed zoned caused by subsurface drainage installation, the soil sampling depth at positions 0.6, 1.1, 2.1 and 4.0 m, respectively, the sampling area of individual soil volumes and the sampling position of water samples extracted from positions 0.7, 1.5 and 4.0 m, respectively and the variation of the soil water table as registered in a piezometer.

Fig. 3. Relationship between a) the ‚clay and Cu concentrations among all soil samples (solid line, upper equation). If the Ap horizons (which received anthropogenic Cu) were removed, the relationship would become stronger (dotted line, lower equation). In b), the relationship between clay and Cu concentrations (black diamonds) and clay concentrations and δ^{65}Cu values (open triangles) of the E&Bt horizons are displayed separately because these horizons should initially have a homogeneous Cu isotope signal, which is then affected by the drainage. While clay and Cu concentrations show a strong linear correlation (solid line, equation), there was correlation between the clay concentrations and the δ^{65}Cu values. The red arrow illustrates the shift between the δ^{65}Cu

values of the uppermost sample at position 60 and the other Bt horizon samples which show identical δ^{65}Cu values.

Fig. 4. Vertical distribution of a) Cu concentrations, b) δ^{65}Cu values of the different bulk soil horizons as a function of the distance to the drain. Horizontal bars indicate sampling depth. Vertical bars indicate a) SD of concentrations and b) 2SD of Cu isotope ratios. Vertical error bars indicate the depth interval the sample was taken from. The letters at the right site of the figure are pedogenetic horizon designations.

Fig. 5. Copper concentrations in the soil volumes at different distances from the drain (a) and Cu stock of a given soil volume (b). Horizontal error bars indicate a) SD of concentration analysis and b) error propagation based on the standard deviation of concentrations, volumes and bulk densities.

Fig. 6. Mean δ^{65}Cu values of the four soil volumes indicative of the dominating pedogenetic processes combined from all four distances from the drain. Error bars indicate 2SD between the four positions. Different superscript letters indicate significant differences in δ^{65}Cu values among soil volumes according to ANOVA with Tukey's HSD taking the four distances from the drain as replicates.

Fig. 7. Mechanistic model of the fate of Cu in the drained Retisol. The size of the arrows indicate the dimension of Cu mass fluxes and the ‰ values refer to $\Delta^{65}Cu_{process\text{-}bulk\ soil}$ values caused by the various processes.

Figure 1

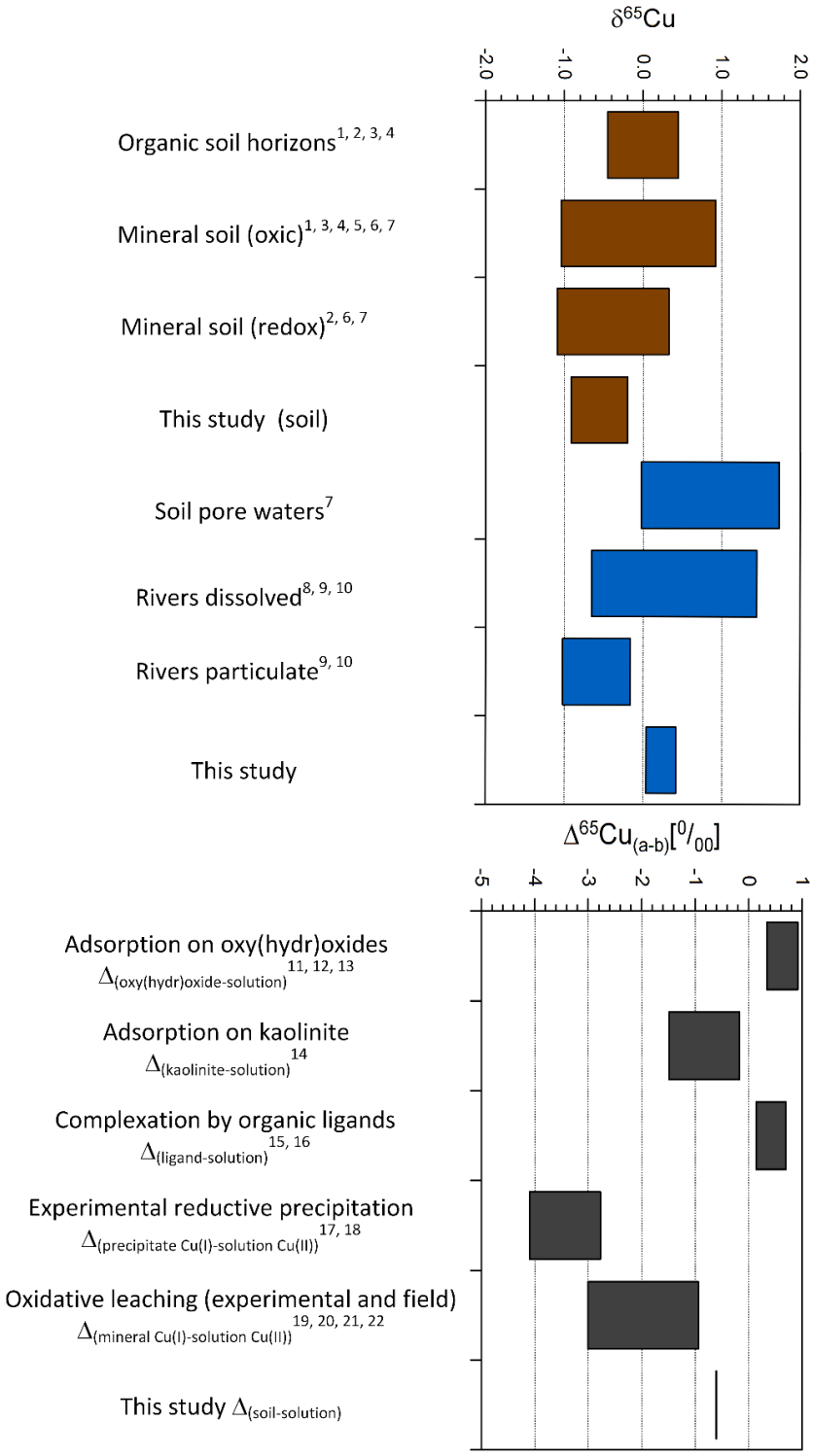

δ65Cu
-2.0
-1.0
0.0
1.0
2.0
Organic soil horizons1, 2, 3, 4
Mineral soil (oxic)1, 3, 4, 5, 6, 7
Mineral soil (redox)2, 6, 7
This study (soil)
Soil pore waters7
Rivers dissolved8, 9, 10
Rivers particulate9, 10
This study
Δ65Cu(a-b)[0/00]
-5
-4
-3
-2
-1
0
1
Adsorption on oxy(hydr)oxides
Δ(oxy(hydr)oxide-solution)11, 12, 13
Adsorption on kaolinite
Δ(kaolinite-solution)14
Complexation by organic ligands
Δ(ligand-solution)15, 16
Experimental reductive precipitation
Δ(precipitate Cu(I)-solution Cu(II))17, 18
Oxidative leaching (experimental and field)
Δ(mineral Cu(I)-solution Cu(II))19, 20, 21, 22
This study Δ(soil-solution)

Figure 2

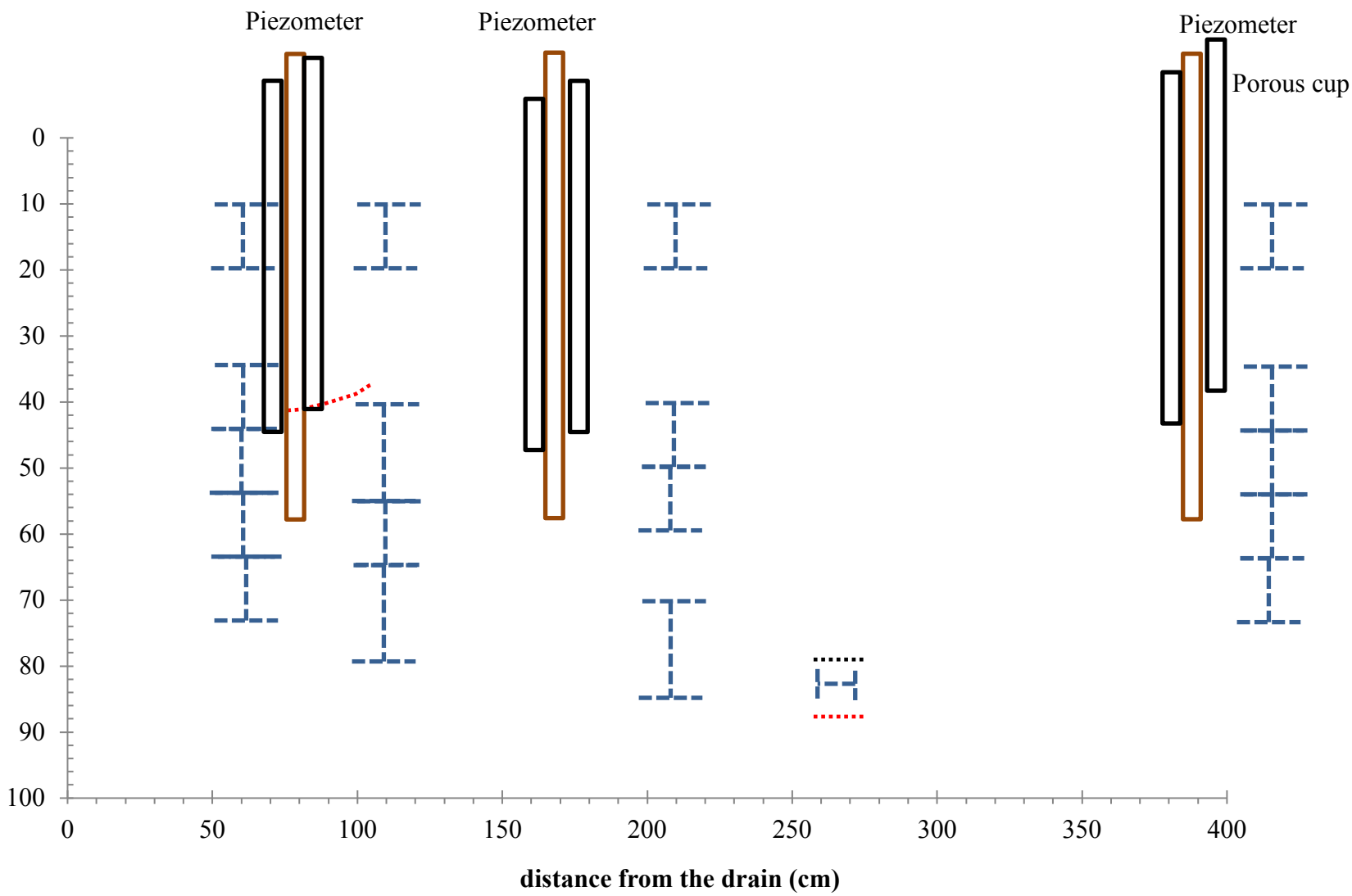

Piezometer
Piezometer
Piezometer
Porous cup
0
10
20
30
40
50
60
70
80
90
100
0
50
100
150
200
250
300
350
400
distance from the drain (cm)

Figure 3

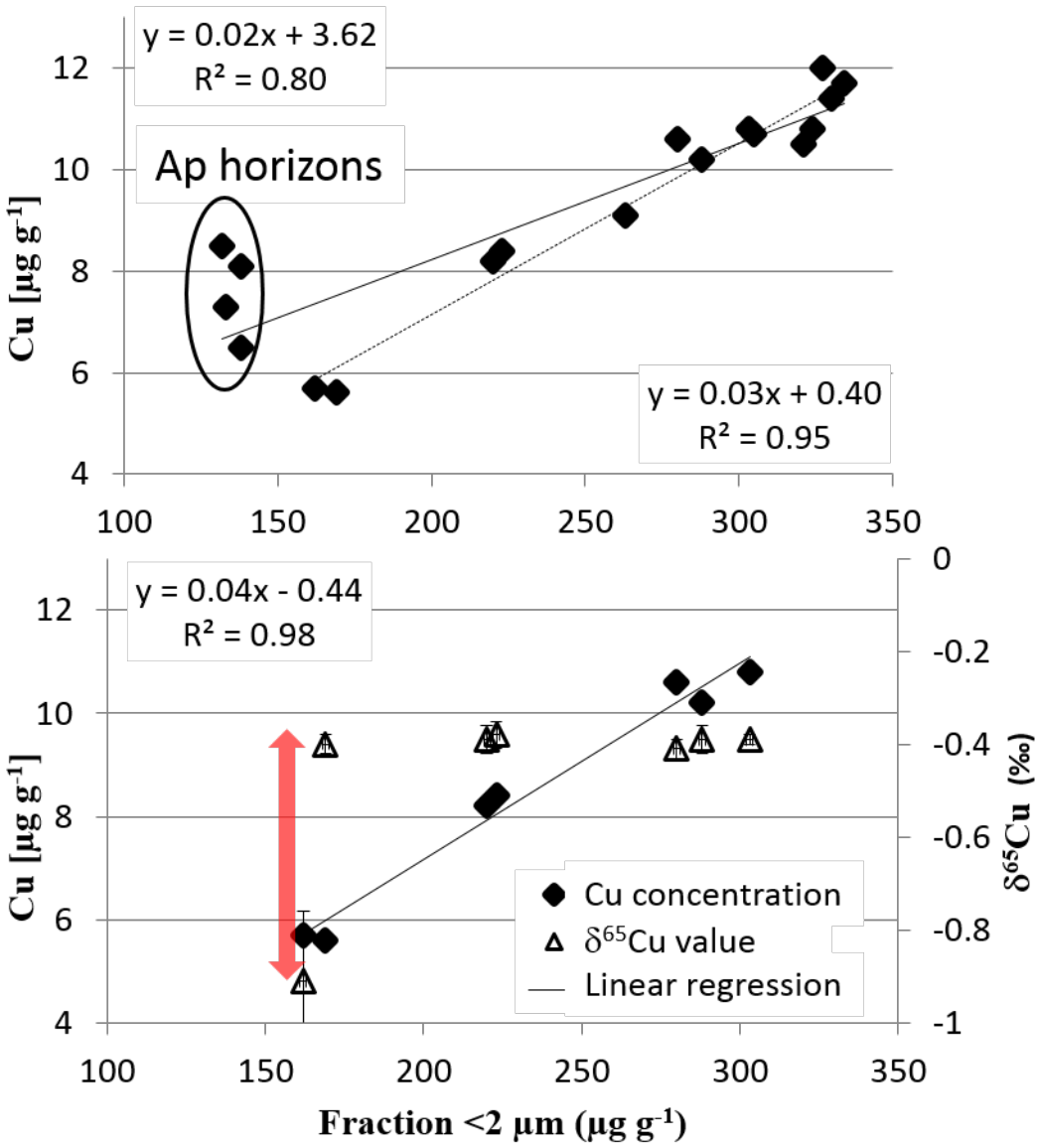

y = 0.02x + 3.62
R² = 0.80
Ap horizons
y = 0.03x + 0.40
R² = 0.95
Cu [µg g-1]
y = 0.04x - 0.44
R² = 0.98
Cu concentration
δ65Cu value
Linear regression
δ65Cu (‰)
Fraction <2 µm (µg g-1)

Figure 4

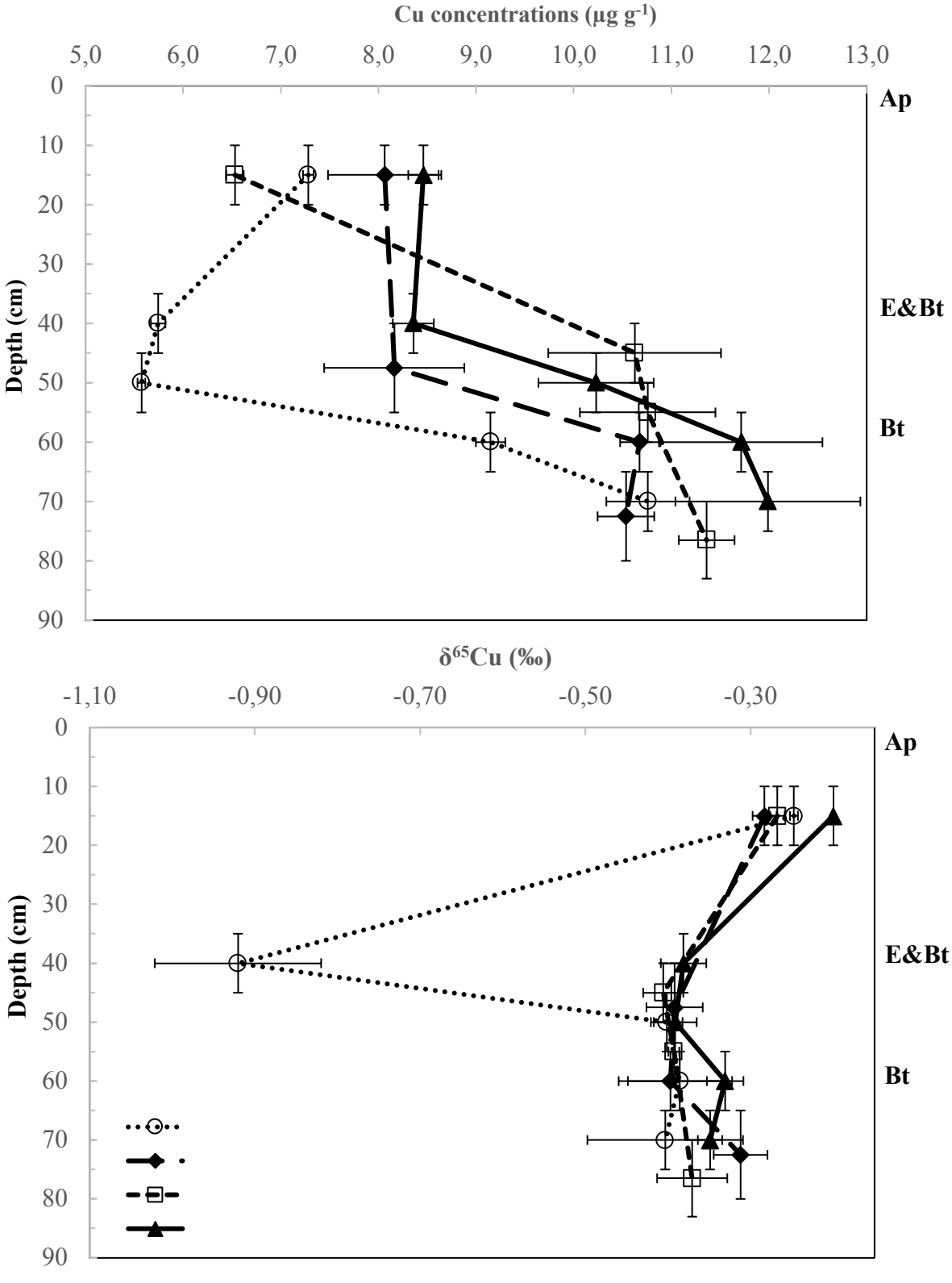

Cu concentrations (µg g-1)
5,0
6,0
7,0
8,0
9,0
10,0
11,0
12,0
13,0
Depth (cm)
0
10
20
30
40
50
60
70
80
90
Ap
E&Bt
Bt
δ65Cu (‰)
-1,10
-0,90
-0,70
-0,50
-0,30
Depth (cm)
0
10
20
30
40
50
60
70
80
90
Ap
E&Bt
Bt

Figure 5

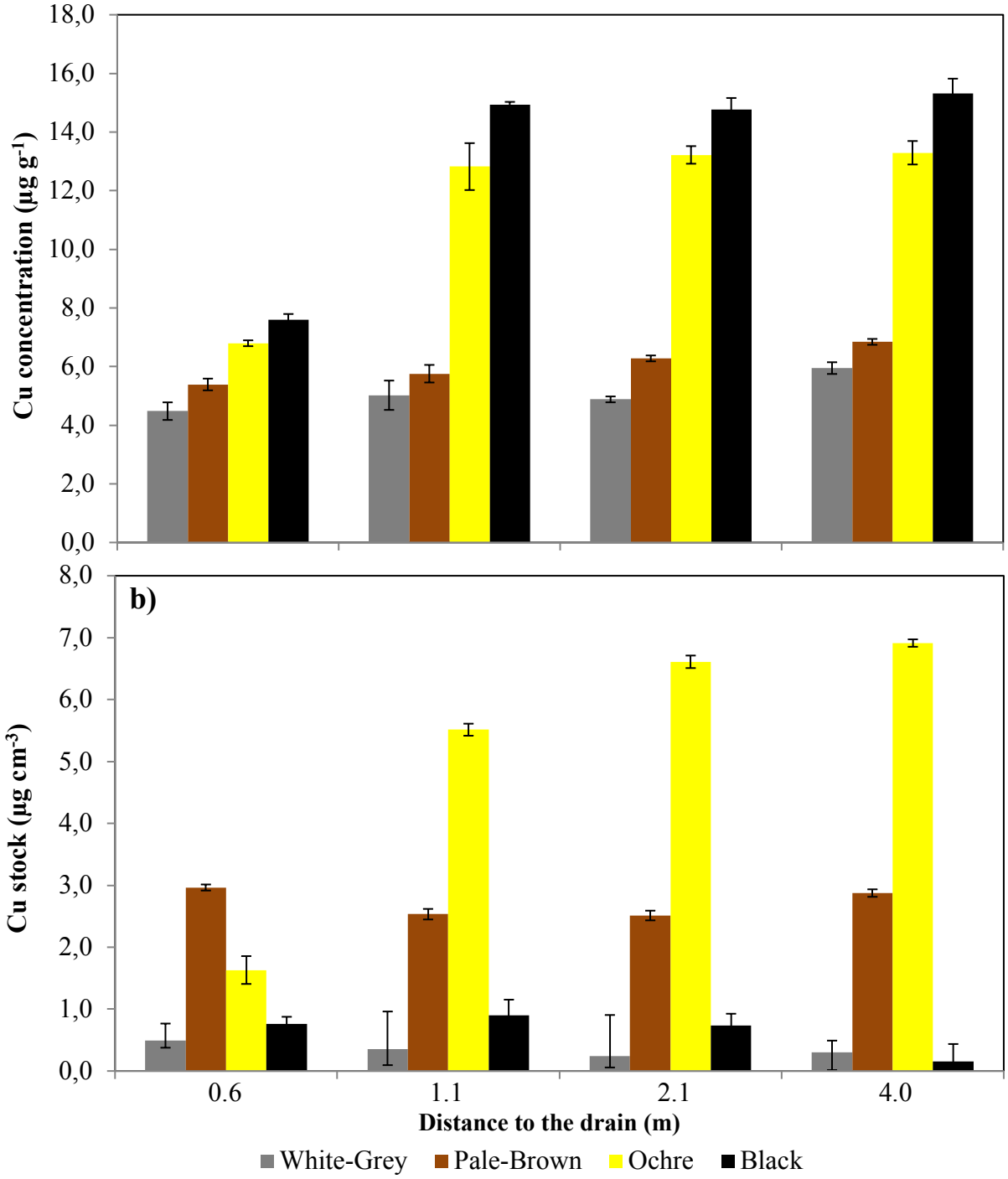

18,0
16,0
14,0
12,0
10,0
8,0
6,0
4,0
2,0
0,0
Cu concentration (µg g-1)
8,0
7,0
6,0
5,0
4,0
3,0
2,0
1,0
0,0
b)
Cu stock (µg cm-3)
0.6
1.1
2.1
4.0
Distance to the drain (m)
White-Grey
Pale-Brown
Ochre
Black

Figure 6

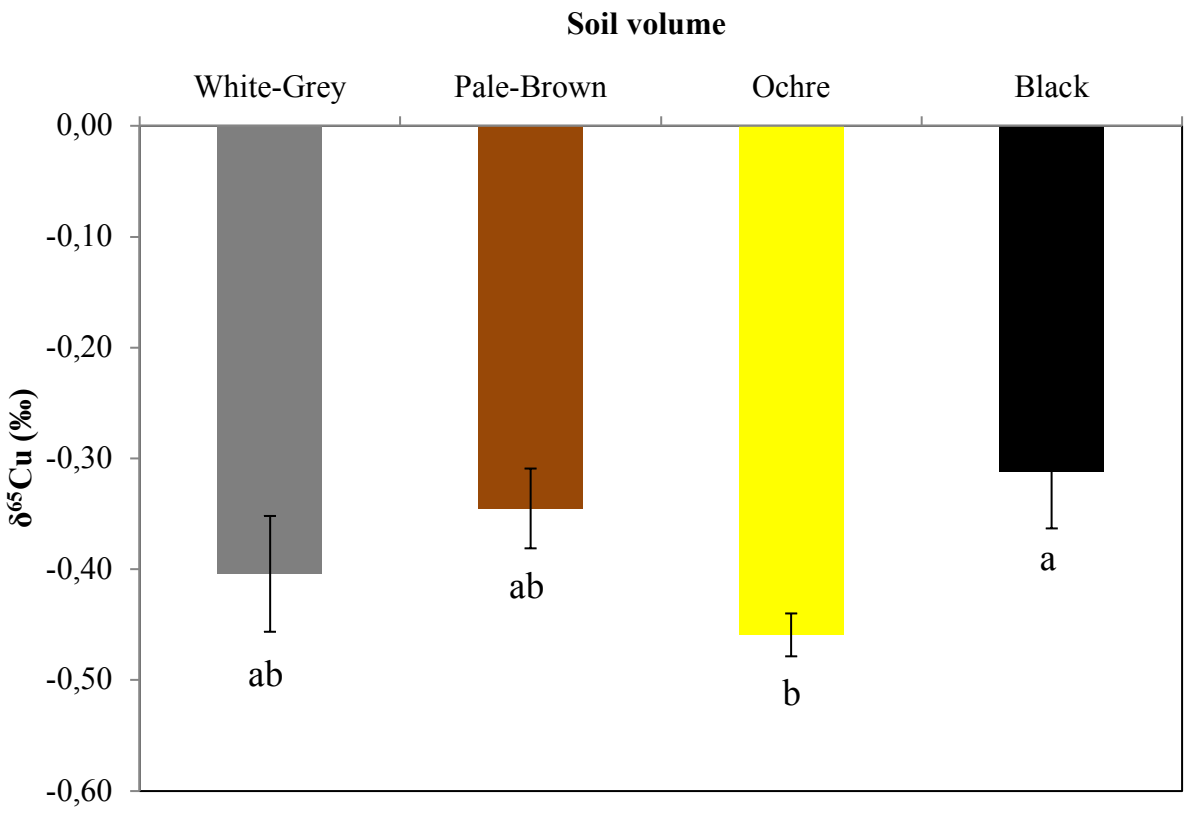
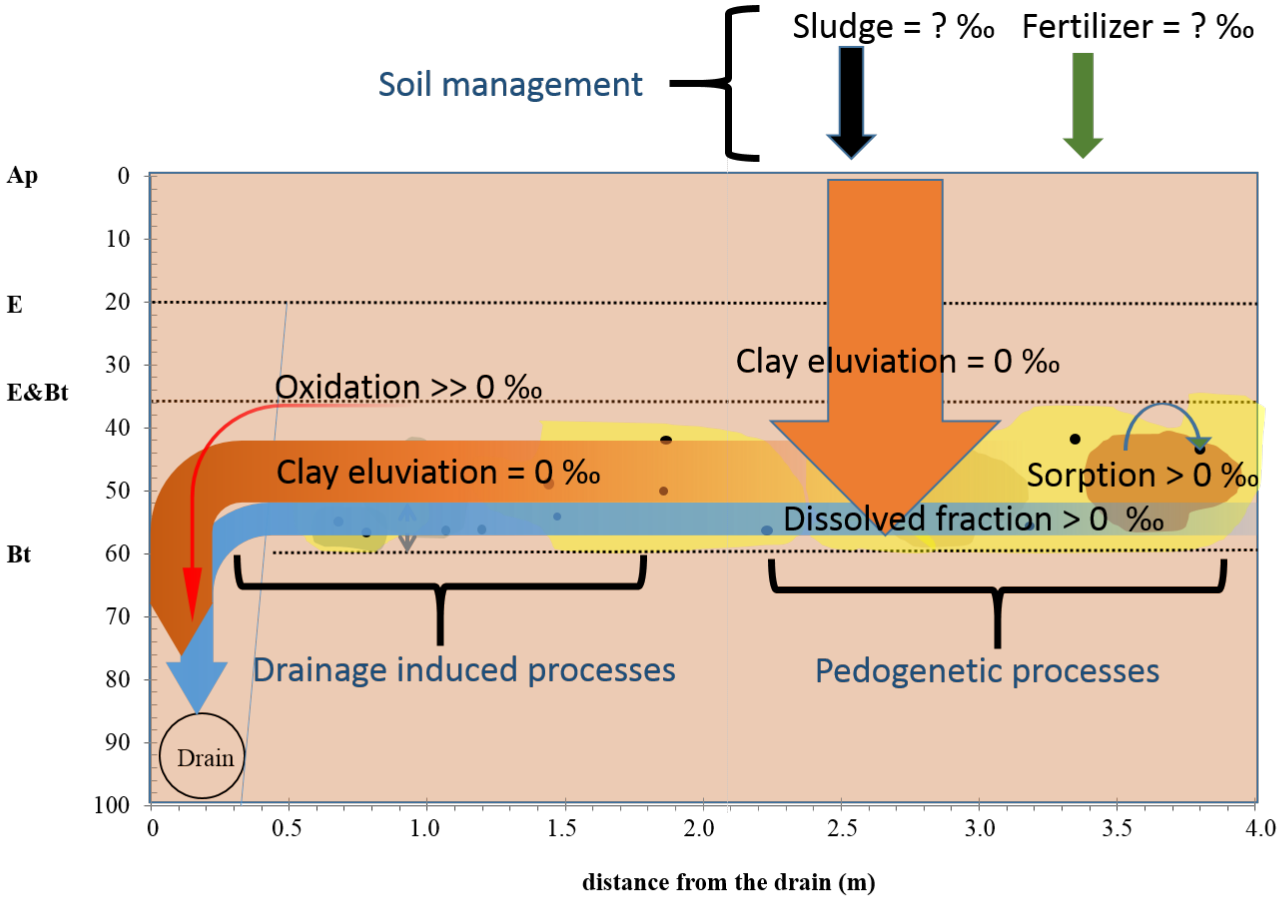

Soil volume
White-Grey
Pale-Brown
Ochre
Black
0,00
-0,10
-0,20
-0,30
-0,40
-0,50
-0,60
δ65Cu (‰)
ab
ab
b
a

Figure 7


Sludge = ? ‰
Fertilizer = ? ‰
Soil management
Ap
E
E&Bt
Bt
Oxidation >> 0 ‰
Clay eluviation = 0 ‰
Clay eluviation = 0 ‰
Sorption > 0 ‰
Dissolved fraction > 0 ‰
Drainage induced processes
Pedogenetic processes
Drain
0
10
20
30
40
50
60
70
80
90
100
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
distance from the drain (m)