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## Tracing contamination sources in soils with Cu and Zn isotopic ratios

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### Abstract

Copper (Cu) and zinc (Zn) are naturally present and ubiquitous in soils and are important micronutrients. Human activities contribute to the input of these metals to soils in different chemical forms, which can sometimes reach a toxic level for soil organisms and plants. Isotopic signatures could be used to trace sources of anthropogenic Cu and Zn pollution. The aim of this paper is to determine whether it is possible to identify (i) Cu and Zn contamination in soils and their sources, on the basis of their isotopic signatures, and (ii) situations that are *a priori* favorable or not for tracing Cu and Zn pollution using the isotopic approach. Therefore, we compiled data from the literature on Cu and Zn isotopes in soils, rocks and pollutants and added to this database the results of our own research. As only a few studies have dealt with agricultural contamination, we also studied a soil toposequence from Brittany, France, that experienced spreading of pig slurry for tens of years. In the surface horizons of the natural soils, the  $\delta^{65}\text{Cu}$  values vary from -0.15 to 0.44 ‰ and the  $\delta^{66}\text{Zn}$  from -0.03 to 0.43 ‰. Furthermore, vertical variations along soil profiles range from -0.95 to 0.44 ‰ for  $\delta^{65}\text{Cu}$  and from -0.53 to 0.64 ‰ for  $\delta^{66}\text{Zn}$  values. We concluded that pedogenetic processes can produce isotopic fractionation, yet, it is not always discernible and can be overprinted by an exogenous isotopic signature. Furthermore, some contaminants are enriched in heavy Cu or in light

Zn compared to the rock or soil, but no generalization can be made. The anthropogenic inputs can be identified based on stable Cu and Zn isotope ratios if the isotope ratios of the sources are different from those of the soil, which needs to be tested for each individual case.

**Keywords:**

Cu and Zn isotopic compositions, pollution, pig slurry, parent material, pedogenesis

**Highlights**

- Pedogenetic processes produce some Cu and Zn isotope fractionation.
- Pollution with distinct isotopic signatures can be traced using Cu and Zn isotopes.
- Tracing of the metal redistribution and sources in soils cannot yet be generalized.

## 1. INTRODUCTION

Copper (Cu) and zinc (Zn) are naturally present and ubiquitous in soils and are important micronutrients. Natural concentrations or pedogeochemical backgrounds are generally low. In unpolluted soils over the world, the most commonly observed values range from 2 to 109 mg kg<sup>-1</sup> for Cu and from 10 to 100 mg kg<sup>-1</sup> for Zn (Baize, 1997; Kabatas-Pendias, 2011). Higher values are either due to natural anomalies, generally encountered in ore areas, or due to contamination. Indeed, human activity contributes significantly to the increase of Cu and Zn concentrations in soils. When they are present in excess, these metals become toxic for living organisms.

External anthropogenic inputs are spatially and quantitatively variable, and a large number of possible pollution sources exist. Major contamination sources are industrial activities (mining and refinery, fossil fuel combustion, chemical industries), urban activity (waste incineration, traffic) or agriculture (fertilizers, soil amendments). In the case of point source pollution, the source of the pollution is often known and the impact area is restricted. In the case of diffuse pollution the contamination history may be more complicated and could involve multiple sources and long-range transport of the pollutants. In addition, Cu and Zn may be deposited or inherited in soils in a number of different forms that are more or less mobile or potentially mobilizable (Vacha et al., 2002), and their fate in the environment differs depending on their origin. Thus, it is necessary not only to assess the total concentration of these metals in soils but also to determine their sources.

Discrimination of the anthropogenic input from the natural metal contribution is not always straightforward. Ratios between surface and deep horizons are often used to determine surface contamination. The deep horizon can be either the 30-50 cm layer (e.g., Colbourn and Thorton, 1978; Saby et al., 2009) or the deepest horizon available (Bourenane et al., 2010), and the approach is based on the calculation of an enrichment factor. When applied to the

study of soil metal contamination in a highly populated and industrialized region of Northern France, the Nord-Pas-de Calais, enrichment factors and geostatistical analyses showed that the contamination originated from various industries, agriculture or urban sources (Bourenne et al., 2010). Another approach consists of identifying the relationship of Cu and Zn with Fe or fine particles ( $<2 \mu\text{m}$ ) in a given pedogeochemical region (Baize 1997). Any sample in a region presenting a Cu or Zn concentration deviating from this relationship can be considered contaminated (Baize 1997). All these methods allow for recognition of the contamination of a soil but are generally inadequate to identify the source(s) of metal contamination (e.g., Reimann and de Caritat, 2005).

Isotopic signatures of radiogenic Pb have been used to trace the source of anthropogenic Pb pollution (e.g., Chow et al., 1970; Erel et al., 1997; Hou et al. 2006; Véron et al., 1999;). Thanks to the recent development of high-resolution mass spectrometry, which allows high-precision analysis and resolution of small isotopic variations, other isotopes such as Cu and Zn may now also be studied (e.g., Maréchal et al., 1999; Pichat et al., 2003). These isotopes have been used to research anthropogenic pollution in airborne particles (e.g., Cloquet et al., 2008; Matielli et al., 2009), rivers and lakes (e.g., Sivry et al., 2008; Thapalia et al., 2010), metal industry processes (Shiel et al., 2010; Sonke et al. 2008), and soils surrounding heavily contaminated sites (Bigalke et al., 2010a; Juillot et al., 2011). In some cases of a major source of pollution (e.g., Juillot et al., 2011; Mattielli et al., 2009; Sonke et al., 2008), Cu and Zn isotopic compositions reflect the source metal because the isotopic signatures of the pollution were clearly different from that of the soil parent material. In other cases, the isotopic signatures of the anthropogenic metal were too similar to that of the natural metal to be distinguished (Bigalke et al., 2010a). Thus, in order to trace Cu and Zn contamination in soils, the differences in isotopic signatures between the anthropogenic and the geogenic sources must be systematically verified.

Few publications exist on the effects of different pedogenetic processes on the metal isotopic signature in soils. Results from batch and chromatographic experiments showed that redox processes and adsorption/desorption induce Cu isotope fractionation (e.g., Balistrieri et al., 2008; Pokrovsky et al., 2008; Zhu et al., 2002). In field studies, Bigalke et al. (2011) showed that podzolization produces significant isotopic fractionation, particularly during the translocation of Cu between E and B horizons. In contrast, Bigalke et al. (2010b, 2011) observed only slight trends in depth distributions of  $\delta^{65}\text{Cu}$  values in oxic weathered and hydro-morphic soils, and they did not obtain definite conclusions on the systematics of Cu isotopic fractionation during oxic weathering or in water-influenced soils.

The aim of this paper is to determine (i) whether it is possible to identify Cu and Zn contamination in soils and their sources on the basis of isotopic signatures and (ii) whether it is possible to identify situations that are *a priori* favorable or not for tracing Cu and Zn pollution using the isotopic approach. We first assessed the variability of the isotopic signature in unpolluted soils and attempted to answer the following questions: Does the isotopic signature vary with the nature of the parent material? How does the isotopic signature of the parent material evolve along pedogenesis? Then, we examined the signatures of different sources of pollution to determine whether different pollution sources can be discriminated from each other and from the pedogeochemical isotopic signature.

To do so, we compiled data from the literature on Cu and Zn isotopes in soils, rocks and pollutants, and we added the results of our research to this database. In addition, as only a few studies dealt with agricultural contamination, we examined a soil toposequence from Brittany, France, that experienced spreading of pig slurry for tens of years.

## 2. MATERIAL AND METHODS

### *2.1 Isotopic database*

We have compiled the published Cu and Zn isotopic data on unpolluted and polluted soils and expanded this data set with new analyses of 11 soils (Table 1). The database includes six studies and includes eight groups of soils developed on different parental materials. The published polluted soils represent mainly industrial (smelting and metal processing) or mining-related (ore extraction) pollution. Studied soil profiles collected from the literature are located in Europe (Germany, Slovakia, France) and Africa (Cameroon). Our samples represent different geochemical backgrounds of France. We have selected soils (i) within the range of “normal” concentrations according to thresholds published by Baize (1997), (ii) unpolluted soils with anomalous metal concentrations (Baize 1997) and (iii) soils polluted by various types of contaminants (agriculture or industrial). We considered sites to be unpolluted when no pollution was explicitly recognized, as opposed to sites where pollution was described. Soils affected by diffuse contamination were considered to be unpolluted because their metal concentrations did not exceed the “normal” concentrations.

### *2.2 Selection of eight soils from the French soil quality monitoring network*

The French soil quality monitoring network (RMQS) consists of 2,200 sites located at the center points of a 16-km<sup>2</sup> grid that covers the whole French territory. At each site, the 0-30 cm soil layer was sampled by mixing 25 individual samples collected with an auger and using a randomly stratified sampling design covering 400 m<sup>2</sup>. These samples were analyzed for pedological characteristics and trace metal concentrations. Saby et al. (2009) demonstrated that background and peak concentrations of metals could be identified on the basis of this database. Eight soils were selected from the RMQS archives in order to represent the range of possible multi-metallic signatures in France. For this, we used the results of the multivariate

analysis of Saby et al. (2009) by selecting the RMQS sites that showed high scores on the first four axes of the PCA. Thus, we selected soil samples with trace element concentrations but with different multivariate signatures. The main characteristics of the selected samples are reported in Table 1.

### *2.3 Sampling of a toposequence contaminated by pig slurry spreading in Brittany, France*

Brittany (Western France) exhibits anomalous Cu and Zn concentrations because of pig slurry spreading on the soils (e.g., Saby et al., 2009). We sampled a toposequence composed of Cambisol, Albeluvisol, and Gleysol located in the Kervidy-Naizin catchment, Brittany. The area belongs to the Environmental Research Observatory ERO AgrHyS. Details describing the sampling area, climate and soil were published previously (Fekiacova et al., 2013). The three soil types were sampled with auger up to a 1 m depth. Two pig slurry samples from the area were also analyzed in order to ascertain the Cu and Zn isotopic compositions of this type of organic pollutant. The slurry was homogenized with a propeller mixer for several minutes, and the samples were extracted using a beaker immersed in the middle of the slurry container. Agitation was maintained during sampling in order to avoid sedimentation and minimize heterogeneity.

### *2.4 Sample preparation and analysis*

Soil samples were dried at 40°C and sieved to < 2 mm. An aliquot of each sample was ground using an agate mortar. Total Cu and Zn concentrations of bulk soils were determined at the INRA Soil Analysis Laboratory (Arras, France) on 0.25 g aliquots dissolved in a mixture of HF and HClO<sub>4</sub> and after calcination of organic matter (450 °C).

Sample preparation and analyses of the isotopic compositions were conducted at the Laboratoire de Géologie de Lyon. One hundred to 300 mg of ground sample was dissolved using a mixture of concentrated HF-HNO<sub>3</sub>-HCl acids, at ~130°C, after a 30% H<sub>2</sub>O<sub>2</sub> treatment to eliminate organic matter. Copper and Zn were separated by anion-exchange chromatography (AG MP1, 100-200 mesh, chloride form). Samples were loaded on the resin in 7 N HCl-0.001 % H<sub>2</sub>O<sub>2</sub>; Cu was eluted with 7 N HCl-0.001 % H<sub>2</sub>O<sub>2</sub>, and Zn was eluted with 0.5 N HNO<sub>3</sub> (Maréchal et al., 1999). Copper was further purified using the same procedure (Maréchal et al., 1999), while Zn was purified by anion-exchange chromatography (0.2 ml AG1X8 column, 100-200 mesh) following Moynier et al. (2009). Yields were found to be better than 95%. Blanks for the entire procedure (dissolution and separation) did not exceed 50 ng.

The Cu and Zn isotopic ratios were measured on a MC-ICP-MS (Nu Plasma 500, Nu Instruments) operated in wet plasma mode at the Laboratoire de Géologie de Lyon. Samples were introduced by free aspiration in 0.05 N sub-boiled distilled HNO<sub>3</sub> using a glass micro-concentric nebulizer (uptake rate: 100 µl/min). We used the standard-sample bracketing method and addition of an internal standard in the samples to correct for instrumental mass fractionation. The Zn samples were doped with a Cu standard solution (NIST 976), and the Cu samples were doped with a Zn standard solution (the “Lyon” JMC 3-0749 L). Sample measurement solutions were diluted to match the concentration of the standard within 15%, i.e., 300 to 500 ppb, depending on the measurement session. Accuracy was further improved by bracketing each sample analysis with the measurement of a reference mixed Zn-Cu standard solution. It has been shown that this combined approach provides the best results with regard to long-term precision and accuracy (less than 0.05‰ amu<sup>-1</sup>) (e.g., Cloquet et al., 2008; Marechal et al., 1999; Pichat et al., 2003). The results were expressed in ‰ using the conventional  $\delta$  notations:  $\delta^{65}\text{Cu} = (\delta^{65}\text{Cu}_{\text{sample}} / \delta^{65}\text{Cu}_{\text{standard}} - 1) \times 1000$  and  $\delta^{66}\text{Zn} =$

$(\delta^{66}\text{Zn}_{\text{sample}}/\delta^{66}\text{Zn}_{\text{standard}} - 1) \times 1000$ . The precision of the isotopic compositions (external reproducibility,  $2\sigma$ ) calculated on the basis of repeated measurement of the standards was 0.09 ‰ (N=81) for  $\delta^{65}\text{Cu}$  and 0.08 ‰ (N=31) for  $\delta^{66}\text{Zn}$ .

### 3. RESULTS AND DISCUSSION

#### *3.1 Variability of copper and zinc isotopic compositions in soils*

Isotopic compositions of 73 and 33 unpolluted horizons and 23 and 25 polluted horizons are compiled in Table 1 for Cu and Zn, respectively. The overall variation of  $\delta^{65}\text{Cu}$  ranges from -0.89 to 0.44 ‰. The sample distribution is centered on 0 ‰ for the unpolluted soils and on 0.2 ‰ for the polluted soils (Figure 1a) indicating that, in general, the polluted soils have isotopic signatures significantly enriched in heavy isotopes (ANOVA using the Fischer test at 95 % confidence level). The overall range of the Zn isotopic compositions in soils is -0.53 to 0.63 ‰. The unpolluted soils have compositions significantly enriched in heavy isotopes (ANOVA using the Fischer test at 95 % confidence level), with the distribution centered at 0.2 ‰ (Figure 1b). The range of the observed  $\delta^{66}\text{Zn}$  values in polluted soils is large, yet, the sample distribution is centered on -0.2 ‰ (Figure 1b). We hypothesize that isotopic variations observed in the polluted soils may reflect the input of contaminants with Cu and Zn isotopic signatures distinct from that of the unpolluted soils. We discuss this hypothesis later in the text.

According to published studies, Cu is preferentially linked to organic matter and oxides (e.g., Domergue and Vedy, 1992; Singh and Gilles, 1992) while Zn is associated with oxides and clay minerals (Singh and Gilles, 1992). Therefore, we examined the correlations between the Cu and Zn concentrations and isotopic compositions and the organic matter and clay fraction (< 2  $\mu\text{m}$ ) abundances in mineral horizons of unpolluted soils. The organic O horizons were excluded from this analysis because an amount of < 2  $\mu\text{m}$  particles is negligible. The  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  values are significantly correlated with the  $C_{\text{org}}$  concentrations, and the Cu and Zn concentrations are significantly correlated with the < 2  $\mu\text{m}$  fractions (ANOVA using the Fischer test at 95 % confidence level). In the case of Cu, the isotopic composition was independent from its concentration, though were significantly anti-correlated in the case

of Zn. Because the concentration and isotopic compositions are either independent or anti-correlated and isotopic compositions are correlated with organic matter, the isotopic composition is likely to be a more sensitive indicator than the concentration. Thus, changes in the soil chemistry could be detected using the isotopic signature before the concentrations start to vary.

This analysis shows that (i) the soil isotopic signature range is rather large for both Cu and Zn, which is most likely due to the high variability of parent materials and different types of soil evolution; (ii) the polluted soils have an isotopic signature different from that of the non-polluted soils, but its value depends on the source of pollution; and (iii) pedological processes may fractionate the isotopic composition of these two elements. Thus, in the following section, we examined (i) the variability of the isotopic signature of the different soil parent materials; (ii) the impact of the pedogenetic processes on these signatures; (iii) the variability of the isotopic signature of different sources of pollution and (iv) the feasibility of tracing agricultural pollution along a contaminated toposequence using Zn and Cu isotopes.

### *3.2 Copper and zinc isotopic signature in soil parent material (rocks and C horizons)*

The average Cu and Zn concentrations in the upper continental crust are 28  $\mu\text{g.g}^{-1}$  and 67  $\mu\text{g.g}^{-1}$ , respectively (e.g., Rudnick and Gao, 2003). Collected isotopic data on terrestrial rocks include 54  $\delta^{65}\text{Cu}$  and 121  $\delta^{66}\text{Zn}$  values from five types of rocks and C horizons (Figure 2).

The Cu isotopic composition of volcanic extrusive rocks, i.e., basalts and tuffites, ranges from -0.12 to 0.18 ‰ (N=5). For igneous acidic rocks, i.e., granites and granodiorites (N=33), it ranges from -0.15 to 0.2 ‰, with some extreme values of up to 1.51 ‰ (Li et al., 2009). The  $\delta^{65}\text{Cu}$  value of sedimentary rocks, i.e., loess, sandstones and fluvic material (N=13), ranges from -0.39 to 0.13 ‰ and that in metamorphic rock (N=3) ranges from 0.32 to

-0.07 ‰ (Figure 2a). We have also collected data on continental Cu mineralization (N=79), which represents a natural, yet anomalous, pool as they have extremely high metal concentrations. Most of their  $\delta^{65}\text{Cu}$  values (67 % of the observations) vary from -0.5 to 0.5 ‰, with 50 % of the values between -0.19 and 0.40 ‰. This data compilation shows that the overall range of  $\delta^{65}\text{Cu}$  values of terrestrial bedrocks is large but that most of the observed values cluster at approximately 0 ‰, with no observed significant differences among rock types (ANOVA using the Fischer test at 95 % confidence level).

The compilation of published  $\delta^{66}\text{Zn}$  values contains 171 data on five types of rocks and Zn ores. The  $\delta^{66}\text{Zn}$  value in basalts and tuffites, i.e., basic extrusive rocks, varies from -0.08 to 0.5 ‰ (N=97) and that in acidic rocks (granites, granodiorites, andesites, dacite, and rhyolite) varies from 0.27 to 0.47 ‰ (N=12). The  $\delta^{66}\text{Zn}$  value in sedimentary rocks ranges from 0.17 to 0.34 ‰ in loess, shales and dust, but the variation is large in carbonates and limestones, ranging from 0.32 to 1.34 ‰ (Figure 2b). No significant differences among rock types were observed, with the exception of carbonates that have significantly heavier  $\delta^{66}\text{Zn}$  values (ANOVA using the Fischer test at 95 % confidence level).

The range of the Cu and Zn isotopic compositions in both unpolluted and polluted soils partly overlaps with the isotopic values of terrestrial rocks. However, unpolluted soils have significantly lighter  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  values than rocks (ANOVA using the Fischer test at 95 % confidence level), indicating that the initial weathering of the rocks that contributes to the soil formation induces observable isotopic fractionation.

### *3.3 Copper and zinc isotopic fractionation during pedogenesis*

Pedogenetic processes contribute to a redistribution of the metals originating from the parental material into different soil horizons. This redistribution may generate isotopic fractionation producing a distinct isotopic signature for each soil horizon. Figure 3 shows an

overview of the Cu and Zn isotopic data in the O, A, B and C horizons of both polluted and unpolluted soils. While the Cu isotopic signature has a bimodal distribution in the C horizons, with a light  $\delta^{65}\text{Cu}$  mode centered on  $-0.4\text{‰}$  and a second mode centered on  $0\text{‰}$ , the distribution of the isotopic signatures in the B horizons is centered on  $0\text{‰}$ , indicating that the lighter values of the C horizons were shifted towards  $0\text{‰}$  in the B horizons (Figure 3c and d). As a result, the B horizons have significantly heavier  $\delta^{65}\text{Cu}$  values than the C horizons (ANOVA using the Fischer test at 95 % confidence level, Table 2). The distribution of the isotopic signatures do not change much from the B horizons up to the A horizons but shifts towards lower values in the O horizons of unpolluted soils (ANOVA using the Fischer test at 95 % confidence level, Table 2). The Cu isotopic compositions of the mineral A and B horizons may be influenced by plant uptake, which could explain the observed tendency towards heavier  $\delta^{65}\text{Cu}$  values. Indeed, most published data indicate preferential incorporation of light Cu in plant roots during uptake from soil (e.g., Navarrete et al., 2011; Weinstein et al., 2011). In contrast, polluted soils have O horizons enriched in heavy Cu with a positive  $\delta^{65}\text{Cu}$  (ANOVA using the Fischer test at 95 % confidence level, Table 2). These values suggest that the exogenous metal, which is likely to be incorporated in the organic O horizons, can overprint the natural signature.

The Zn isotopic compositions of the C horizons exhibit a bimodal distribution with a heavy mode centered on  $0.6\text{‰}$  and the second mode on  $0\text{‰}$ . From the C to the B horizons, there is a significant shift towards lighter values (ANOVA using the Fischer test at 95 % confidence level, Table 2), and the distribution in the B horizon is centered on  $0.1\text{‰}$  (Figures 3 g and h). This distribution becomes narrower in the A horizons and more centered on  $0.2\text{‰}$  with no apparent change in the O horizons (two samples only). During plant uptake, heavy Zn isotopes are preferentially adsorbed in the roots (e.g., Aucour et al., 2011; Houben et al., 2014; Tang et al., 2014; Weiss et al., 2005). In contrast, during Zn translocation within the

plant, light Zn is preferentially mobilized towards the shoots. Thus, plant uptake and dead plant biomass recycling should yield an isotopically light signature. However, only one study, available in the literature (Viers et al., 2007), provided two  $\delta^{66}\text{Zn}$  values for O horizons. Thus, no generalized conclusion can be made based on such limited data. Furthermore, while the plant-induced fractionation is an important source of isotopic variations in the biogeochemical cycling of Zn, it appears negligible compared to the industrial process-induced fractionation (e.g., Weiss et al., 2005). In the O horizons of polluted soils, we observed a large shift towards lighter  $\delta^{66}\text{Zn}$  (ANOVA using the Fischer test at 95 % confidence level, Table 2). This distinct  $\delta^{66}\text{Zn}$  is likely to be a fingerprint of the external source (e.g., the industrial process-induced fractionation).

### *3.4 Copper and zinc isotopic signature of the different anthropogenic metal sources*

Only limited data (N=5) are available on the Cu isotopic compositions of potential industrial soil contaminants (Figure 2a). Both the industrial wastes and pig slurry have Cu isotopic compositions enriched in heavy isotopes.

The  $\delta^{65}\text{Cu}$  values of industrial wastes could either reflect the isotopic signature of the processed ores or a process induced-fractionation. It has been shown that there is no smelting-derived fractionation due to the high boiling point of Cu (e.g., Gale et al., 1999; Mattielli et al., 2006). However, the metal refining process could still result in variable  $\delta^{65}\text{Cu}$  values in the wastes, depending on the type of the waste. Indeed, metal industry waste products analyzed by Bigalke et al. (2010a) ranged from 0.05 to 1.81 ‰. While the volatile and solid products (ash, slag, solid waste) have isotopic compositions close to the parental rock signatures, heavy  $\delta^{65}\text{Cu}$  values (0.81 and 1.81 ‰) were recorded in the smelter sludge. These heavy values were explained to be a result of chemical reduction during electrolytic refining (Bigalke et al., 2010a).

The industrial wastes produced by smelting or metal processing have highly variable Zn isotopic compositions depending on the type of waste. The  $\delta^{66}\text{Zn}$  of smelter sludge varies from -0.44 to +0.43 ‰ (Bigalke et al., 2010a), that of solid wastes (slags, tailings, coal ash) from -0.09 to 1.49 (Bigalke et al., 2010a; Juillot et al., 2011; Mattielli et al., 2009; Sivry et al., 2008) and that of volatile products (fly ash, emissions, smelter dust) from -0.67 to 0.21 ‰ (Bigalke et al., 2010a; Mattielli et al., 2009; Sonke et al., 2008). Nevertheless, volatile contaminants (dust, ash, emissions) and solid waste tend to have a light and heavy isotopic signature, respectively (Figure 2b).

The pig slurry samples yield  $\delta^{65}\text{Cu}$  values of 0.12 and 0.52 ‰ (Figure 2a), revealing the isotopic variability of this material. We hypothesize that the heavy enrichment observed in the pig slurry results from its speciation. In the pig slurry, the Cu is present mainly in sulfide form ( $\text{Cu}_2\text{S}$ ) and the Cu(I) oxidation state. These species might have formed either by precipitation under reducing condition or by complexation with thiol (-SH) functional groups of the organic matter (e.g., Legros et al., 1999). Both of these processes could lead to the heavy Cu enrichment in the pig slurry. In contrast to the observed variability of the Cu isotopic composition in the two pig slurry samples, the  $\delta^{66}\text{Zn}$  values are similar, 0.21 and 0.24 ‰.

The range of isotopic composition in natural rocks and soils is large. However, some waste products show extreme values and clear enrichment in heavy Cu or in light Zn compared to the general rock and soil range. Indeed, in the case of smelter dust and emissions, Zn isotopes can always be used for tracing pollution. Furthermore, Cu and Zn isotopes are likely to be used for tracing the pollution related to smelter sludge and smelter solid waste, respectively, with the exception of calcareous soils for Zn. In other cases, determination of the Cu and Zn isotopic signatures of both the pollutant and the parent material of the soil remain to be a prerequisite for tracing the pollution.

### *3.5 Copper and zinc isotopic fractionation in a soil sequence contaminated by pig slurry*

Published studies on the effect of a long-term pig slurry application on soil showed that some metals (e.g., Cd, Mn) are leached from the slurry and washed away (e.g., Herreux et al., 1997) while others (e.g., Cu, Zn) accumulate in different soil horizons (e.g., Jaffrezic, 1997; Legros et al., 2013; Martinez and Peu, 2000). However, the metal trajectories and residence time in the soil are not clearly understood. We used the isotopic approach to monitor the spreading of Cu and Zn introduced by pig slurry in a soil sequence comprising Cambisol, Albeuvisol and Gleysol. The soils are differentiated by two main factors, parental material and water regime (Fekiacova et al., 2013). The relative distributions of silt and sand fractions in these soils form three distinct patterns (Figure 4). All Cambisol horizons have patterns characterized by high silt and low sand content. The ratio of 2-20  $\mu\text{m}$  to 20-50  $\mu\text{m}$  fractions in the Cambisol profile is close to one indicating that this soil developed from a material of eolian origin (Walter and Curmi, 1998), likely similar to the loess of northern and/or western Brittany (Haase et al., 2007; Le Calvez, 1979). The Gleysol also exhibits a sole particle-size distribution pattern characterized by a 2-20  $\mu\text{m}$  to 20-50  $\mu\text{m}$  ratio close to two, indicating that this soil developed from the schist bedrock (Walter and Curmi, 1998). The Albeuvisol is characterized by two distinct particle size distribution patterns (Figure 4). The two deepest horizons have patterns similar to that recorded for the Gleysol and thus most likely developed from the schist. The upper horizons (A and upper B<sub>t</sub>) are intermediate between those of the loess and of the schist, with the 2-20  $\mu\text{m}$  to 20-50  $\mu\text{m}$  ratios ranging between 1 and 2, suggesting that these horizons result from mixing between the two parental materials. A mass balance calculation showed that these Albeuvisol patterns could be produced by mixing of 40 to 45 % of loess into the schist material. The Cambisol received two spreadings of pig slurry per year over the last 10 years. Jaffrezic (1997) estimated that  $\sim 48$  g/ha of Zn and  $\sim 40$  g/ha

of Cu are introduced to the soil with each slurry spreading and that these metals accumulate in the surface plowed horizons of the field (Cambisol) and in the subsurface horizons of the Albeluvisol.

The Cu concentration varies only slightly down the Cambisol profile (Figure 5a). We observed a minor but statistically significant increase in Cu concentration in the upper A horizons and in the 40-50 cm B horizon (ANOVA with a Fischer test at a 95 % level of confidence, Table 3). The Cu concentrations of the B horizon of the Cambisol are within the range of the published average values of European loess (e.g., Gallet et al., 1998; Ujvari et al., 2008). Thus, the increase that we observe in the surface and in the 40-50 cm horizon of the Cambisol can either be a result of contamination by the pig slurry or of a vertical variability in the composition of loess. A mass balance calculation shows that the Cu and Zn input would, if it was all retained in the uppermost 10 cm of the soil, result in an increase of Cu and Zn concentrations of approximately 1 ‰, which is within the range of analytical uncertainty estimated to be 5 %. Thus, the observed variations in Cu and Zn concentrations along the Cambisol profile are most likely due to the natural background variability of the loess. In addition, in the Cambisol, the  $\delta^{65}\text{Cu}$  range is -0.03 to +0.13 ‰ (Figure 5b), which is at the limit of the resolution. Despite the clearly different Cu isotopic signatures of the pig slurry, the total Cu input is too low to be detected in the upper soil isotopic signature.

We observed significant variations in the Cu concentration in the Albeluvisol and Gleysol profiles. Gleysol horizons developed from the schist parental material. The Cu concentrations decrease upwards, with the exception of the surface horizon, which can be interpreted as Cu removal due to weathering. However, this decreasing trend is interrupted in the surface horizons. We suggest that the loss of Cu due to weathering is partially counterbalanced by an input of the exogenous metal originating from the pig slurry. In the Albeluvisol, the two deepest horizons have a Cu concentration comparable to that observed in the Gleysol.

The Cu concentration in the upper B horizons (25 and 35 cm depth) could be explained by a mix of schist and loess, while the surface A horizon is strongly depleted in Cu. This depletion could be interpreted in terms of both clay loss and redox processes.

Deep Gleysol horizons correspond to the weathered schist material and have low average  $\delta^{65}\text{Cu}$  values of -0.24 ‰ (Figure 5b). No change is observed in the upper B horizon, indicating that weathering in soil does not impact the Cu isotopic signature of the bulk soil. However, there is a large shift towards positive  $\delta^{65}\text{Cu}$  in the surface horizons, suggesting an input of Cu with a positive isotopic signature, such as in the pig slurry. The deepest Albeluvisol horizons also developed from the schist; thus, we would expect similar isotopic compositions than those observed in the Gleysol. However, the deep part of the Albeluvisol profile has significantly higher  $\delta^{65}\text{Cu}$  (Table 3), suggesting that Cu with positive  $\delta^{65}\text{Cu}$  was incorporated into the soil.

We hypothesize that the slurry related-Cu could have been transported through the soil in a complexed form. While the isotopic effect of organo-complexation on Cu is not known, it has been shown that the complexed forms of Fe and Zn are enriched in heavy isotopes (Dideriksen et al., 2008; Jouvin et al., 2009). Thus, similar fractionation could affect the slurry related-Cu.

The uppermost B horizon of the Albeluvisol at a 25 cm depth shows an extremely low  $\delta^{65}\text{Cu}$  of -0.89 ‰. We interpret this negative peak either as due to the leaching of heavy Cu with organic complexes or as enrichment in light Cu originating from the upper horizon. No decrease in Cu concentration is observed in the uppermost B horizon, which would support the leaching hypothesis. Instead, the Cu concentration starts increasing; thus, the negative peak most likely indicates enrichment in light Cu isotopes. This horizon is characterized by the maximum content of Fe oxides (Fekiacova et al., 2013), possibly due to the precipitation of Fe released from the surface horizon. The light Cu most likely also released from the sur-

face horizons is associated with the Fe oxides, which would explain the observed light signature.

The Zn concentration and isotopic compositions in the Cambisol are consistent with the depth, and no evidence for contamination or weathering can be detected (Figure 6). In contrast, large variations are observed in the Albeluvisol and Gleysol profiles, with a particularly sharp decrease of the Zn concentration in the surface horizon of the Gleysol. It corresponds to Zn removal due to Fe-oxide dissolution (Fekiacova et al., 2013) as shown by the correlation between the Zn concentration and the Fe-oxide content (Figure 7). Such an association was previously described in the literature (e.g., Smith and Gilles, 1992). The surface horizons have significantly higher  $\delta^{66}\text{Zn}$  compared to the deep horizons. In the deep horizons, a progressive dissolution of Fe-oxides associated with Zn removal does not impact the  $\delta^{66}\text{Zn}$ , which remains stable (Figure 6b). Therefore, the high  $\delta^{66}\text{Zn}$  values observed in the surface horizon cannot be explained by Zn removal. Rather, this increase could be indicative of the exogenous input of Zn with a positive isotopic signature, such as that observed in the slurry. A similar observation can be made for the Albeluvisol.

To conclude, these hydromorphic soils most likely bear traces of contamination by slurry-related metals. While the slurry spreading occurs on the Cambisol, metals do not accumulate significantly there. When this organic contaminant decomposes after the spreading, the metals are released and are transported laterally down the profile. However, the magnitude of the contamination is so low and the variability of the parental material so complex that firm conclusions are difficult to draw.

#### 4. CONCLUSION

The overview of existing data on worldwide soils and known contaminants shows that tracing metal redistribution and identifying metal sources in soils is not straightforward. The

isotopic signatures encountered in terrestrial rocks cover a large range of  $\delta^{65}\text{Cu}$  and  $\delta^{66}\text{Zn}$  values. While pedogenetic processes may produce isotopic fractionation, the range of variation of the resulting isotopic signatures is often too small to be distinguished from that of the original parental material. In addition, we are far from a comprehensive overview of all the effects of pedogenetic processes on the metal isotopic compositions in soils. While the direction of fractionation by a given pedogenetic process should be consistent, the observed stable isotope ratio varies depending on the initial value of the Cu and Zn sources. Therefore, no particular isotopic fractionation could be assigned to a given pedogenetic process in this work, and more studies on specific pedological processes are needed. The contaminated O horizons show some degree of isotopic differentiation, which might allow for tracing the source of contaminant in the soil. We showed that the contaminants have a large range of isotopic signatures partially overlapping those of the parent rocks. Thus, no general rule can be formulated on the possibility of tracing soil Cu and Zn pollution using their isotopes. In some cases, as for smelter dust and emissions, Zn isotopes can always be used for tracing pollution. In the case of smelter sludge and smelter solid waste, Cu and Zn isotopes, respectively, are likely to be used for tracing the pollution, except in calcareous soils for Zn. In other cases, determination of the Cu and Zn isotopic signatures of both the pollutant and the parent material of the soil remains to be a prerequisite for tracing pollution. In this last case, the presence of a diffuse type of contamination can possibly be recognized in soils when a complete study including the geogenic source is performed and if this contamination is sufficiently concentrated in soil and has a clear, differentiated isotopic signature.

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### Table captions

Table 1: Cu and Zn concentrations and isotopic composition of the soil compiled from the literature or analyzed in this study. The organic carbon and 0-2- $\mu\text{m}$  fraction content are also provided.

Table 2: Summary of all pairwise comparisons for different soil horizons of the unpolluted and polluted soils (ANOVA using the Fischer test at 95 % confidence level). Data represent mean values of each type of horizons. a, b, c: letters indicate groups with significantly different means ( $a < b < c$ ).

Table 3: Summary of the pairwise comparisons for soil horizons of the Naizin soils (ANOVA using the Fischer test at 95% confidence level). Data represent the mean values. a, b, c: letters indicate groups with significantly different means ( $a < b < c$ ).

### Figure captions

Figure 1: Isotopic composition distribution of both the unpolluted and polluted soils of our database: a-Cu; b-Zn.

Figure 2: Isotopic composition range of different horizons of unpolluted and polluted soils, different types of parent materials and contaminants. a-Cu; b-Zn. Numbers in the legend refer to the origin of the plotted data with 1: Maréchal et al. (2000); 2: Ben Othman et al. (2003); 3: Bigalke et al. (2011); 4: Bigalke et al. (2010a); 5: Weinstein et al. (2011); 6: Li et al. (2009); 7: Mathur et al. (2012); 8: Bigalke et al. (2010b); 9: this work; 10: Zhu et al. (2000); 11: Sonke et al. (2008); 12: Larson et al. (2003); 13: Cloquet et al. (2006); 14: Chen et al. (2013); 15: Viers et al. (2007); 16: Albarède (2004); 17: Pichat et al. (2003); 18: Mattielli et al. (2009); 19: Sivry et al. (2008). a, b, c: letters indicate groups with significantly different means (ANOVA using the Fischer test at 95% confidence level).

Figure 3: Isotopic composition range of different horizons of the unpolluted and polluted soils. a, b, c, d: Cu; e, f, g, h: Zn; a and e: O horizons; b and f: A horizons; c and g: B horizons; d and h: C horizons.

Figure 4: Relative distribution of fine silt (FSi), coarse silt (CSi), fine sand (FSa) and coarse sand (CSa) in the different horizons of the Cambisol developed on loess (in green), of the Albeluvisol developed in schist for the two lowest horizons (in red) and in a mixture of loess and schist (in brown) and of the Gleysol developed in schist (in blue).

Figure 5: Depth evolution of Cu concentration (a) and isotopic composition (b) in the Cambisol (blue), the Albeluvisol (red) and the Gleysol (green). The regression line (black dash line) corresponds to the decreasing trend in Cu concentration observed in the deep (B) horizon of the Gleysol. The grey field represents the range of the pig slurry Cu isotopic composition analyzed in this work.

Figure 6: Depth evolution of Zn concentration (a) and isotopic composition (b) in the Cambisol (blue), the Albeluvisol (red) and the Gleysol (green). The grey field represents the range of the pig slurry Zn isotopic composition analyzed in this work.

Figure 7: Correlation between the Zn and Fe-oxide concentrations in the Albeluvisol (in red) and the Gleysol (in green).

	Soil order <sup>a</sup>	Parent material	Contamination	C <sub>org</sub> , g.kg <sup>-1</sup>	Clay, g.kg <sup>-1</sup>	δ <sup>65</sup> Cu, ‰	[Cu], μg.g <sup>-1</sup>	δ <sup>66</sup> Zn, ‰	[Zn], μg.g <sup>-1</sup>	<sup>b</sup> N	Reference
Poorly-evolved soils	Arenosol	sable		1.48	11	-0.15	0.01	0.22	0.01	1	<i>this work</i>
	Cambisol	sandstone with muscovite, mudstone		4 to 66	243 to 290	-0.34 to 0.08	7.8 to 19.8			7	<i>Bigalke et al., 2010b</i>
	Cambisol	slate		1 to 123	8 to 78	-0.32 to -0.02	7.4 to 12.9			7	<i>Bigalke et al., 2011</i>
	Cambisol	sandstone		11 to 39	65 to 205	-0.29 to 0.08	4.3 to 27.6			7	<i>Bigalke et al., 2011</i>
	Cambisol	basalte		58.7	365	0.09	42.40	0.43	152.00	1	<i>this work</i>
	Cambisol	eolian deposits		5.47 to 27.2	143 to 169	0.01 to 0.13	13.6 to 18.0	0.05 to 0.22	31.1 to 36.6	6	<i>this work</i>
	Cambisol	granite		21.3	133	0.01	5.81	0.34	47.30	1	<i>this work</i>
	Cambisol	tuffite	Cu production	8.9 to 47.9	na	-0.12 to 0.33	12 to 8087	-0.48 to -0.08	97 to 2084	6	<i>Bigalke et al., 2010a</i>
	Cambisol	tuffite	Cu production	14.2 to 31.9	na	-0.05 to 0.34	16 to 4605	-0.47 to 0.00	52 to 1889	6	<i>Bigalke et al., 2010a</i>
	Cambisol	tuffite	Cu production	6 to 29.3	na	0.00 to 0.36	17 to 2164	-0.53 to -0.06	57 to 1071	6	<i>Bigalke et al., 2010a</i>
	Cambisol	calcaire	metal processing	79.7	525	-0.20	16.20	0.19	220.00	1	<i>this work</i>
Cambisol	sables	steel industry	35.6	114	-0.07	6.14	-0.01	23.70	1	<i>this work</i>	
Fluvisol	Sediments	different activities (e.g., wastewater discharges, metallic Zn from smelters)	na		-0.02 to 0.16	199 to 320	0.22 to 0.30	1199 to 2084	16	<i>Bigalke et al. 2013</i>	
Leptosol	serpentine	pig farming	19.6	250	-0.48	16.70	0.25	118.00	1	<i>this work</i>	
Clay translocation	Luvisol	Tertiary glauconite-rich Ostricourt Sands	Pb/Zn processing plant	na	na			0.22 to 0.49	48 to 571	6	<i>Juillot et al., 2011</i>
	Luvisol	Tertiary glauconite-rich Ostricourt Sands	Pb/Zn processing plant	na	na			0.31 to 0.76	45 to 1379	5	<i>Juillot et al., 2011</i>
	Luvisol	slate		25 to 52	46 to 120	-0.17 to 0.16	12.1 to 20.2			8	<i>Bigalke et al., 2010b</i>
	Albeluvisol	sedimentary Brioverian schist (older than 530 Ma)		2.71 to 19.6	192 to 268	-0.95 to 0.04	6.7 to 22.6	-0.18 to 0.12	17.7 to 37.5	6	<i>this work</i>
Redox	Gleysol	fluvic material		2 to 78	120 to 250	-0.08 to 0.13	9 to 34.2			6	<i>Bigalke et al., 2010b</i>
	Gleysol	granite and sandstone		3 to 99	105 to 252	-0.26 to 0.33	5.4 to 11.7			6	<i>Bigalke et al., 2010b</i>
	Gleysol	sedimentary Brioverian schist (older than 530 Ma)		3.66 to 24.10	203 to 296	-0.54 to 0.07	7.1 to 22.3	0.06 to 0.19	45.8 to 129.2	7	<i>this work</i>
	Stagnosol	clay with buhrstone	orchard	22.66	156	-0.11	94.07	0.20	37.24	1	<i>this work</i>
Podzolization	Podzol	sandstone		2 to 83	2 to 122	-0.57 to 0.44	1.4 to 8.50			10	<i>Bigalke et al., 2011</i>
	Podzol	granodiorite		42 to 67	92 to 170	-0.23 to -0.04	1.9 to 22.50			6	<i>Bigalke et al., 2011</i>
	Podzol	sable		6.44	26.0	-0.14	2.15	0.19	0.01	1	<i>this work</i>
Highly weathered soils	Ferralsol	granodiorite		na	na			0.04 to 0.50	29 to 59	5	<i>Viers et al., 2007</i>
	Ferralsol	granodiorite		na	na			-0.05 to 0.64	35 to 59	4	<i>Viers et al., 2007</i>
	Ferralsol	granite		na	na			0.42 to 0.55	14 to 26	3	<i>Viers et al., 2007</i>

<sup>a</sup>Soil type as translated to WRB using the information available.

<sup>b</sup>N is the number of data points in each profile

Table 1

Horizon	Unpolluted soils				Polluted soils			
	N	$\delta^{65}\text{Cu}$	N	$\delta^{66}\text{Zn}$	N	$\delta^{65}\text{Cu}$	N	$\delta^{66}\text{Zn}$
O	18	-0.15 <sup>ab</sup>	2	0.19 <sup>ab</sup>	9	0.24 <sup>b</sup>	9	-0.35 <sup>a</sup>
A	20	0.00 <sup>c</sup>	15	0.18 <sup>ab</sup>	8	-0.06 <sup>a</sup>	10	0.14 <sup>b</sup>
B	26	-0.04 <sup>bc</sup>	11	0.06 <sup>a</sup>	4	0.03 <sup>a</sup>	3	-0.08 <sup>b</sup>
C	10	-0.28 <sup>a</sup>	10	0.24 <sup>b</sup>	2	-0.03 <sup>a</sup>	2	-0.04 <sup>b</sup>

N effectives for each horizon

a, b, c different letters between horizons indicate groups with significantly different means obtained by ANOVA (Fischer test) at a 95 % level of confidence: a<b<c

Table 2

Soil type	Horizon designation	N	Cu, $\mu\text{g.g}^{-1}$	$\delta^{65}\text{Cu}$	Zn, $\mu\text{g.g}^{-1}$	$\delta^{66}\text{Zn}$
Cambisol	Ap (0-20 cm)	2	20.95 <sup>a</sup>	0.03 <sup>a</sup>	66.6 <sup>b</sup>	0.11 <sup>a</sup>
	B (20-60 cm)	4	17.95 <sup>ab</sup>	0.09 <sup>a</sup>	64.0 <sup>b</sup>	0.12 <sup>a</sup>
Albeluvisol	Ap (0-20 cm)	2	8.61 <sup>c</sup>	-0.10 <sup>ab</sup>	33.0 <sup>c</sup>	0.11 <sup>a</sup>
	Bt (20-40 cm)	2	19.65 <sup>a</sup>	-0.52 <sup>c</sup>	70.8 <sup>b</sup>	-0.13 <sup>c</sup>
	Bt II (40-60 cm)	2	25.80 <sup>a</sup>	0.06 <sup>a</sup>	64.9 <sup>b</sup>	-0.08 <sup>bc</sup>
Gleysol	Ap (0-30 cm)	2	9.34 <sup>bc</sup>	0.02 <sup>a</sup>	59.5 <sup>b</sup>	0.18 <sup>a</sup>
	B/C (30-80 cm)	4	24.02 <sup>a</sup>	-0.34 <sup>bc</sup>	137.6 <sup>a</sup>	-0.02 <sup>b</sup>

N        effectives for each horizon

a, b, c    different letters between horizons indicate groups with significantly different means obtained by ANOVA (Fischer test) at a 95 % level of confidence: a<b<c

Table 3

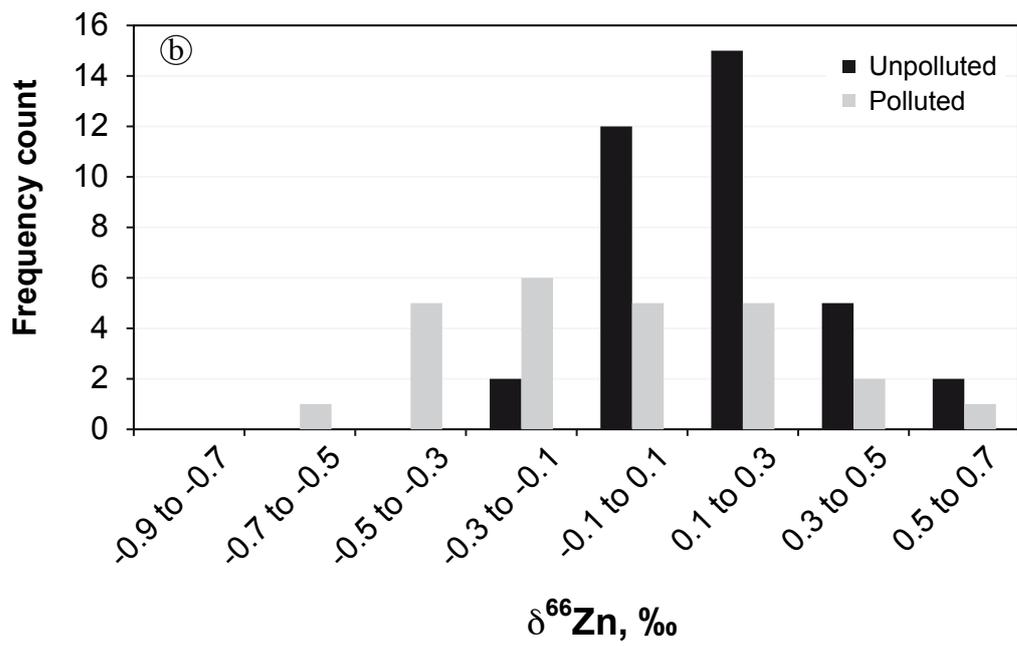
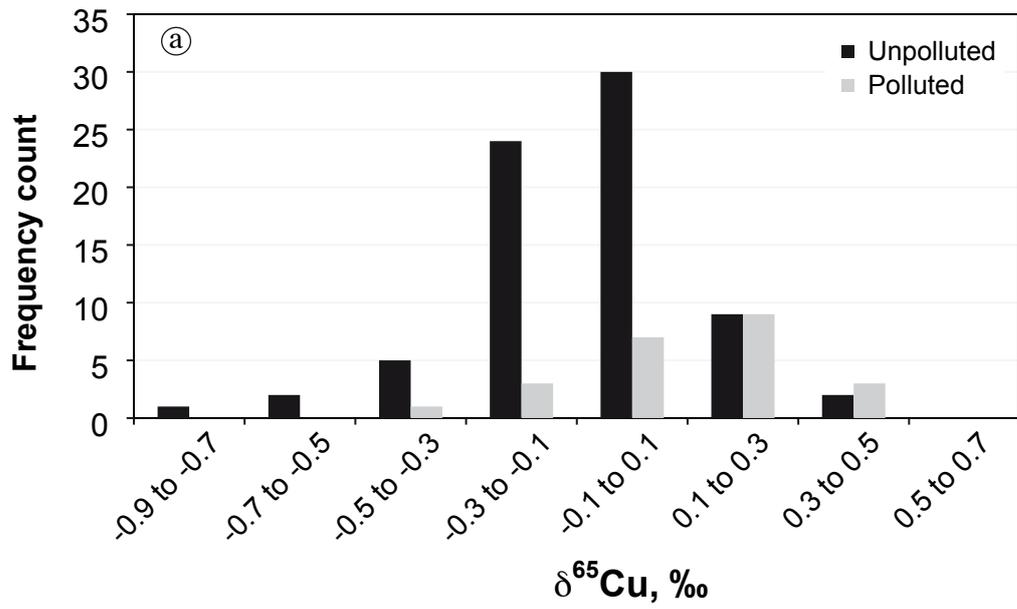


Figure 1

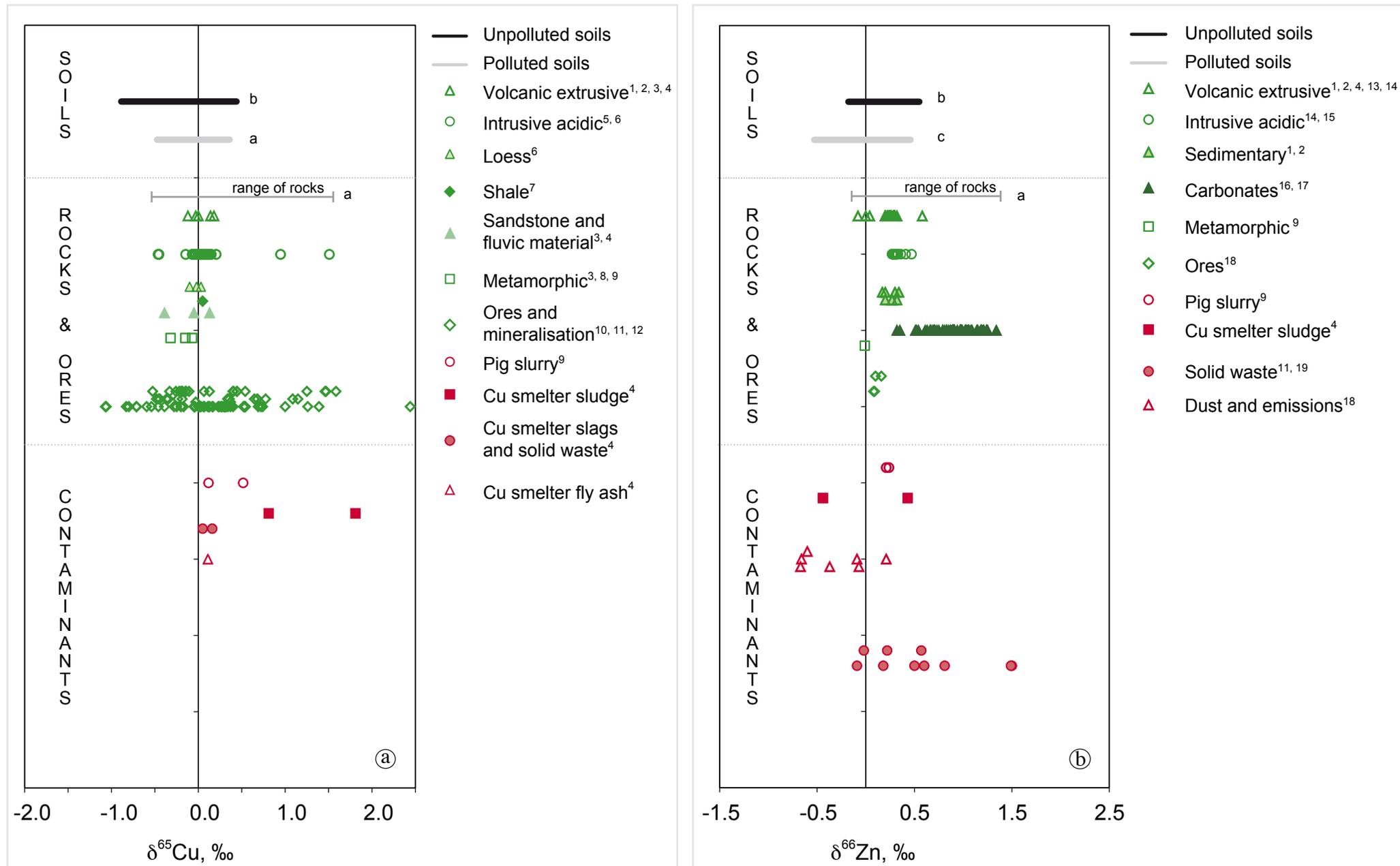


Figure 2

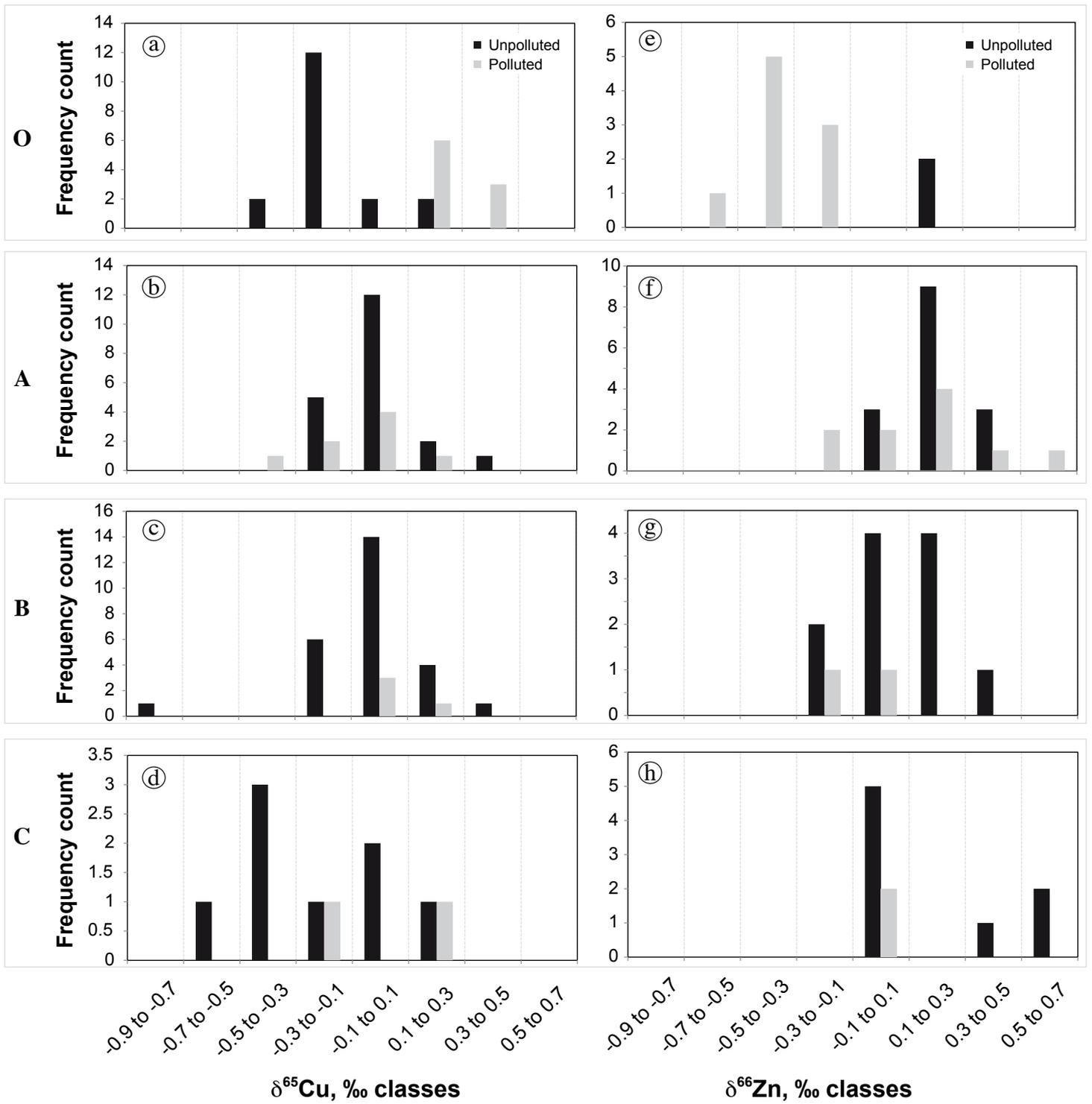


Figure 3

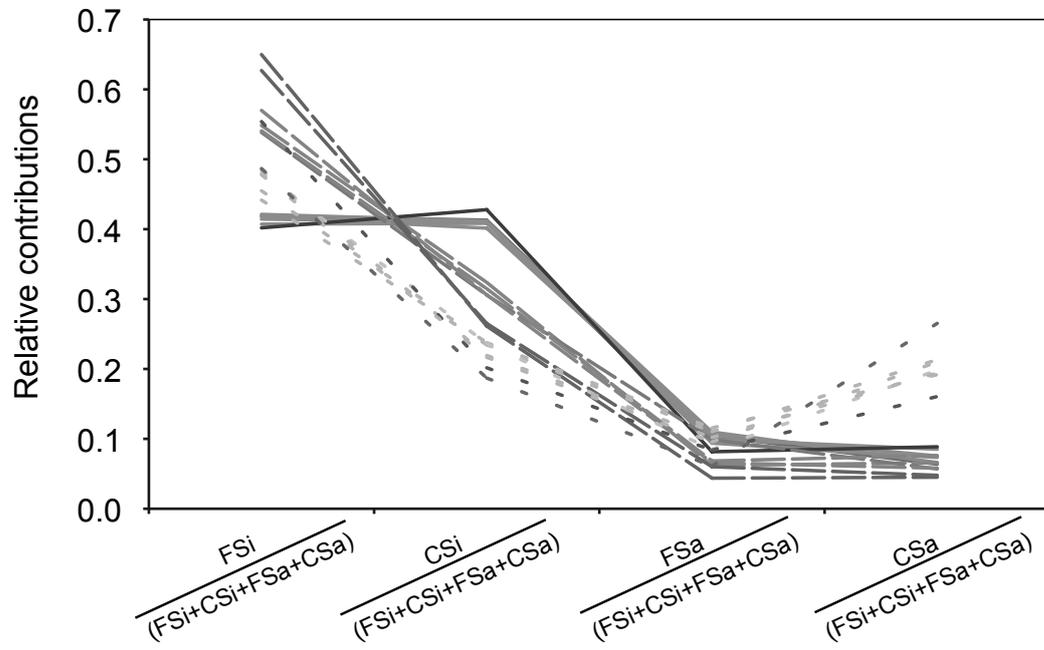


Figure 4

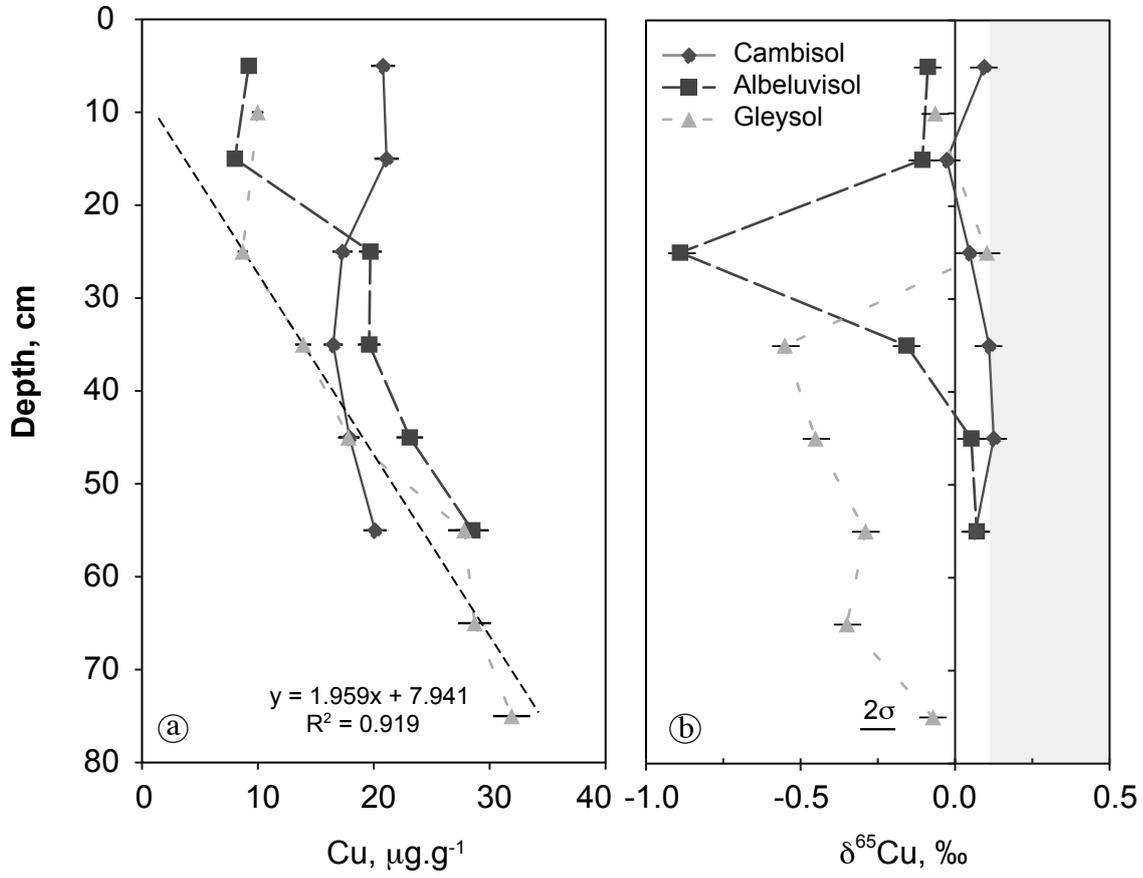


Figure 5

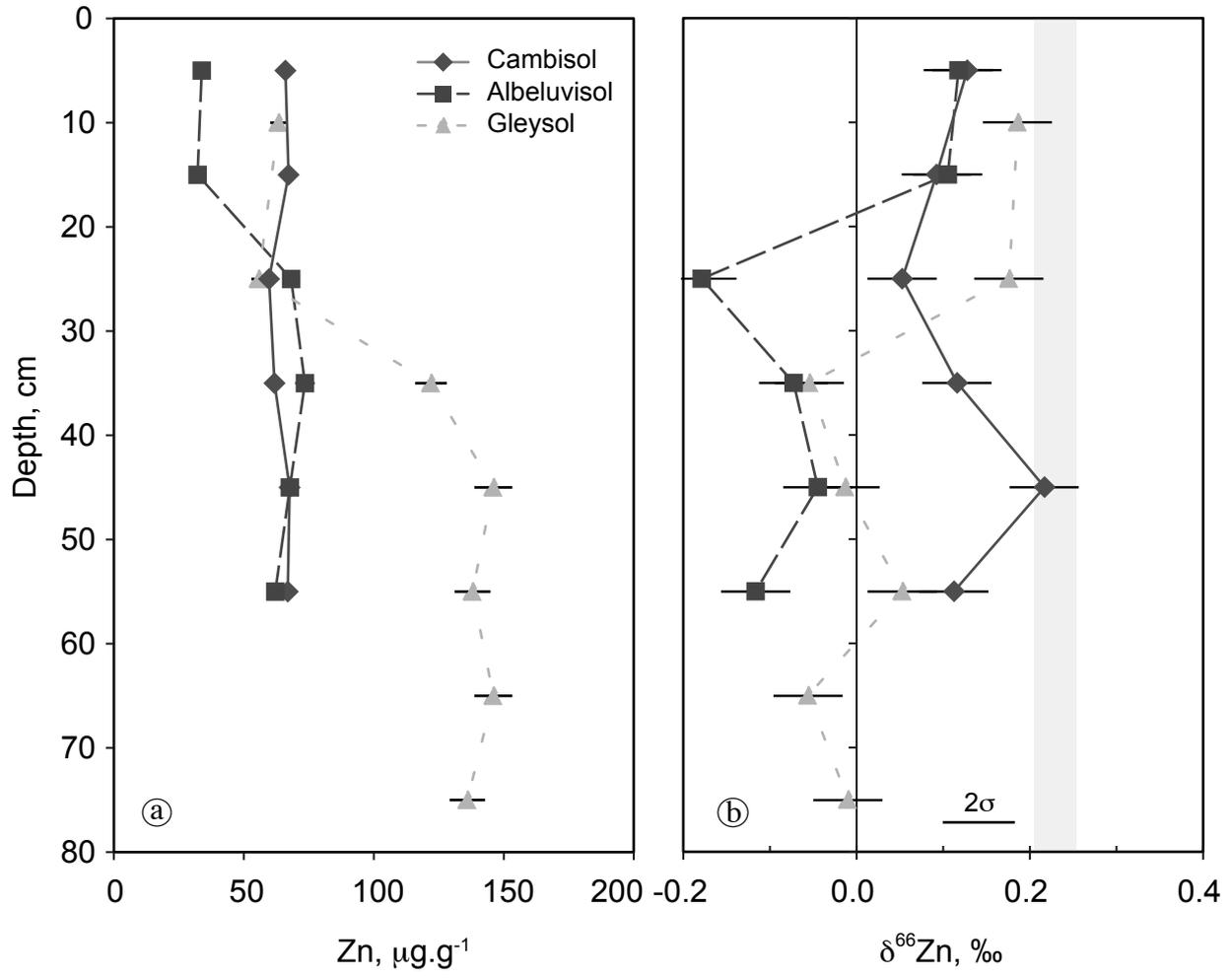


Figure 6

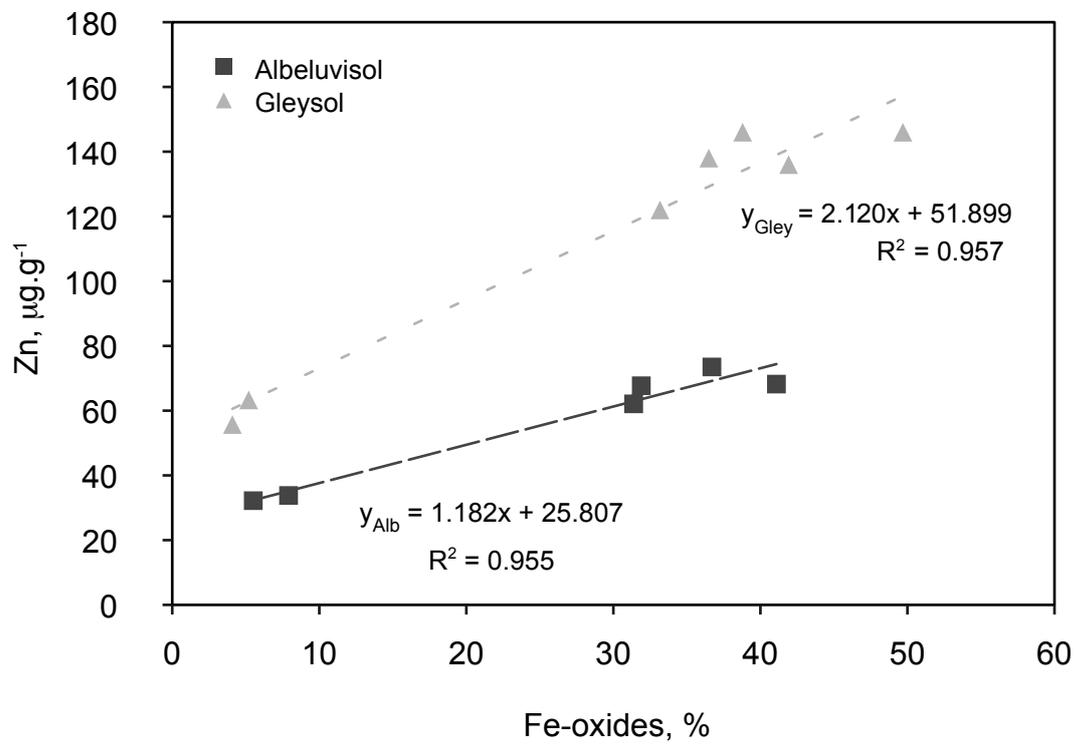


Figure 7