



Metal distribution, bioavailability and isotope variations in polluted soils from Lower Swansea Valley, UK

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Received: 16 July 2020 / Accepted: 8 December 2020

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Abstract Soils in the Lower Swansea Valley, (United Kingdom) contain elevated level of metals, enough to cause direct or indirect effects on human health. This study assesses the severity of soil pollution and bioavailability of Cu and other metals (Ni, Zn, Co, Pb and Cr) in soils with various distances from a Ni refinery. We compare Cu concentrations in operationally defined soil fractions (bioavailable, bound to Fe/Mn oxide and incorporated in organic matter) with other metals (Ni, Zn, Pb, Co, Cr) usually occurring in ores used in metallurgic processes and report their

pollution and geoaccumulation indices (PI and I_{geo}). Further, we use Cu stable isotope ratios ($\delta^{65}\text{Cu}$) to trace the fate and mobility of Cu in soils. Our data suggest a point source of contamination for some of the heavy metals including Ni ($I_{geo} = 1.9$), Zn ($I_{geo} = 0.28$) and Cu ($I_{geo} = 3.6$) near the Ni refinery. However, Co ($I_{geo} = 0.15$) and Pb ($I_{geo} = 3.3$) contaminations are likely to be linked to different sources. No elevated Cr levels ($I_{geo} = -0.07$) occur in any of the studied soils. All soil metals are predominantly associated with organic matter (>50%) which reduces their bioavailability and thus their risk for ecological and human health. The Cu isotope data show that Cu in soil organic matter is enriched in ^{65}Cu , while the lighter isotopes (^{63}Cu) remain in the dissolved bioavailable Cu fraction ($\Delta^{65}\text{Cu}_{\text{organic-bioavailable}}$ is $+0.12 \pm 0.13\text{‰}$). This suggests the preferential complexation of ^{65}Cu with soil organic matter after dissolution of Cu deposited to the soil. Thus, Cu isotope data can effectively indicate pathways of metal migration in polluted soils.

Supplementary Information The online version of this article (<https://doi.org/10.1007/s10653-020-00794-x>) contains supplementary material, which is available to authorized users.

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Keywords Heavy metals · Soil · Spatial distribution · Bioavailability · Copper isotopes · Pollution

Introduction

In the EU, about 45% of the soils are estimated to be contaminated (van Liedekerke et al. 2014). Heavy

metals are with 35% the major contaminants in soils. Anthropogenic activity including mining, smelting and refining significantly redistributes heavy metals in the environment. Despite the biological role of some heavy metals, most are toxic at high concentrations (Hodson and Donner 2013). This means if heavy metals are bioavailable, they cause large ecological damage (Hutchinson and Whitby 1974; Kabata-Pendias 2010; Kim et al. 2015) and bear a significant health risk for humans (Hodson and Donner 2013; Entwistle et al. 2019).

Human health risk from heavy metals in soils might even increase due to a changing climate. Changing climate can alter the physicochemical soil properties and soil processes resulting in an increase of dissolved and bioavailable heavy metals (Rieuwerts et al. 1998; Gonzalez-Alcaraz and van Gestel 2015; Grobelak and Kowalska 2020; Jarsjö et al. 2020). In particular, soil metals from anthropogenic sources are more bioavailable than those of pedogenic origin (Kaasalainen and Yli-Halla 2003; Kabata-Pendias 2010). To predict potential changes in the bioavailability of highly toxic metals in a changing climate, it is crucial to assess the current metal status in soils including the spatial metal distribution, speciation and phase association, and mechanisms controlling the spatial metal distribution. As threshold values of metal contaminants for most national and international guidelines [*e.g.*, Soil Guideline Values (SGVs)] are based on total soil metal content, these guidelines provide only limited information about the metal bioavailability. Additionally, soils are compositionally heterogeneous, and thus changes in metal bioavailability largely depend on the metal speciation and phase association.

Specifically, soils in regions with long history of metallurgical industry are often contaminated with heavy metals. The Lower Swansea Valley has been affected by metal smelting and refining since the eighteenth century up to the present day (Perkins 2011). During the eighteenth century, two-thirds of copper in the UK was processed in smelters at this region (Marchant et al. 2011; Perkins 2011). Nickel refining began in the early twentieth century. Despite a decline of the metal industry in the Lower Swansea Valley during the 1920s and 1930s, with the closing of many of the metalworks (Alban 1984), the nickel refinery for instance in the village Clydach is still operational.

From all metals, specifically Cu tends to accumulate in topsoils in areas with intensive mining and/or

metallurgic activity (Hutchinson and Whitby 1974, Temple and Bisessar 1981, Ettler et al. 2011). Copper is normally found in unpolluted soils at concentrations below $30 \mu\text{g g}^{-1}$ (Artiola 2005) but becomes detrimental to wildlife above $60 \mu\text{g Cu g}^{-1}$ (Kabata-Pendias et al. 1981, Alloway 2012, Kabata-Pendias 2010). With an estimated soil residence time between 1000 and 3000 years for temperate climates (Bowen 1979), Cu soil pollution becomes a long-term ecological issue.

Previous studies have demonstrated that Cu isotope signature is an excellent environmental tracer to identify Cu sources and understand the Cu cycling in human-impacted areas (Mathur et al. 2009; Bigalke et al. 2010a; Thapalia et al. 2010; Fekiacova et al. 2015; Kribek et al. 2018; Mihaljevic et al. 2018). Fractionation of Cu isotopes can change the isotopic signature through a variety of low-temperature processes both biological and abiotic. Abiotic isotope fractionation is caused by adsorption onto mineral surfaces (Balistrieri et al. 2008; Pokrovsky et al. 2008) or incorporation of Cu into organic matter (Bigalke et al. 2010b; Ryan et al. 2014). Biological processes include the isotopic fractionation of Cu by plants, which have a systematic preference of taking up the light isotope (^{63}Cu), leaving a soil enriched in ^{65}Cu (Weinstein et al. 2011). Furthermore, sequential extraction combined with Cu stable isotope analysis has been successfully applied to determine Cu release in a soil flooding event (Kusonwiriawong et al. 2016) and to monitor the mobilization of Cu from mine tailing sediments (Roebbert et al. 2018). Thus, Cu isotope analysis can provide a better understanding of the biogeochemical soil cycling of Cu (Bigalke et al. 2010a, Babcsanyi et al. 2016; Vance et al. 2008).

The objectives of this study are (1) to characterize the spatial distribution of metals in soils in the vicinity of a refinery (2) to assess the environmental risk factors by quantifying metal fractions associated with different soil constituents and (3) to unravel the fate of soil Cu using Cu isotope composition ($\delta^{65}\text{Cu}$) of operationally defined Cu soil pools. The results of this study help identify potential sources of heavy metals as by-products of the metallurgic processes in the Lower Swansea Valley relative to the natural background signal, and to trace pathways of metal migration. Additionally, our results provide a way to evaluate the environmental quality and environmental

health of the Lower Swansea Valley, an area with a long history of metal refining.

Materials and methods

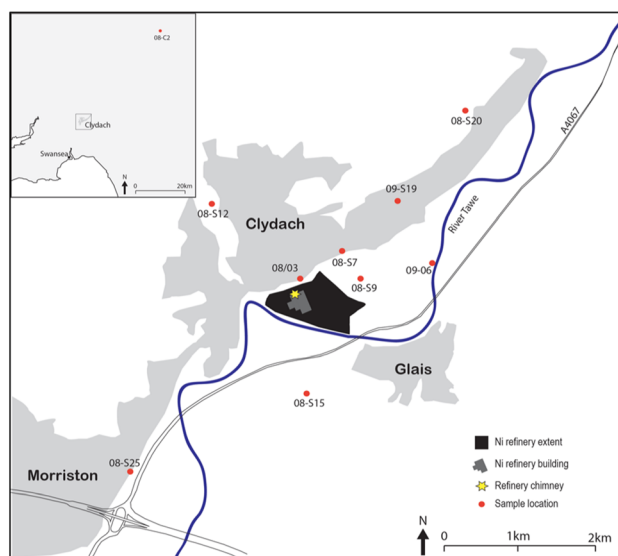
Study site and soil sampling

The study site is located in South Wales in the Lower Swansea Valley, approximately 10 km northeast of Swansea city (Fig. 1). Soil samples were collected from various locations within the vicinity of the Ni refinery in the village Clydach (Fig. 1, Table S1). Soils in the Swansea Valley are primarily formed from the product of glacial erosion of Carboniferous sedimentary rocks generating sandy clay loam soils. A control sample was selected from an uncontaminated location about 30 km 'downwind' of the Ni refinery, an area of Devonian rocks (Old Red Sandstone). For sample collection, vegetation was removed from the soil surface and soil was collected from the upper 5 cm. We assume that topsoils are mainly impacted by metals originated from long-term metallurgical industry and are derived to a smaller extent from the bedrock. The collected soils were dried for 48 h at 40 °C. Mortar and pestle were used to disaggregate the soil and create a homogeneous texture. The dried soils were stored in clear plastic bags prior to further analysis.

Sequential extraction procedure (SEP)

To examine the heavy metal speciation and phase association, we used the well-established BCR extraction technique (Tessier 1979; Davidson et al. 1998; Rauret et al. 1999). One gram of air-dried soil was weighed into a 50-ml metal-free centrifuge tube (VWR). Then, for the first extraction step (= exchangeable and bioavailable fraction), 30 ml of 0.1 M acetic acid was added and shaken on a rotary shaker at room temperature overnight. Afterward, the sample was centrifuged at 3000 rpm (Eppendorf Centrifuge 5810R) for 20 min, the supernatant was decanted and the soil residual was washed with 20 ml of double-deionized water. Subsequently, 30 ml of 0.5 M hydroxylamine hydroxide was added to the soil residual to extract the reducible fraction, namely metals associated with Fe/Mn (hydr)oxides. Similar to the first extraction step, the samples were shaken overnight, centrifuged, the supernatant was decanted and the soil residual was washed with double-deionized water. For the third step, 5 ml of 8.8 M hydrogen peroxide (Romil Ltd, Cambridge, UK) was added to the soil and left at room temperature for 1 h. The samples were then placed on a hot plate at 85 °C to reduce the sample volume to less than 3 ml. The hydrogen peroxide step was repeated twice before adding 20 ml of 1 M ammonium acetate (adjusted to pH 4) and shaken overnight at 40 rpm. Afterward, the sample was centrifuged at 3000 rpm (Eppendorf

Fig. 1 Sampling location map adapted from Perkins (2011)



Centrifuge 5810R) for 20 min, the supernatant was decanted and the soil residual was washed with 20 ml of double-deionized water. The supernatants from all extraction steps were filtered through 0.45 µm syringe membrane filters. Procedural blanks were prepared to estimate the metal content in the reagents used for each SEP step.

For reproducibility check and validation of the BCR method, triplicate extractions ($n = 5$) were performed using the reference material NIST 2711a, a moderately contaminated Montana soil. We selected the certified reference soil NIST 2711a because the BCR extraction method has been performed and assessed previously for several metals (Sutherland and Tack 2002; Kubova et al. 2004; Larner et al. 2006). The triplicate extractions of the three SEP steps show a good reproducibility (Table S2) with relative standard deviation (RSD) for the three fractions (bioavailable and exchangeable, Fe/Mn oxide-bound and organically bound metals) of less than < 10%. Further, the metal concentrations for the three individual fractions are in good agreement with previously reported data for NIST 2711a (Sutherland and Tack 2002; Kubova et al. 2004; Larner et al. 2006).

Concentration analysis

The concentrations of Cu, Ni, Zn, Co, Pb and Cr in the sequentially extracted soil fractions were measured using a PerkinElmer NexION 350D inductively coupled plasma-mass spectrometer (ICP-MS) equipped with an Elemental Scientific (Omaha, USA) prepFASTM5 autosampler and autodiluter. A calibration curve was calculated using premade calibration solutions with varying concentrations of each metal. After every 11 samples, standard quality control and calibration blanks were analyzed to evaluate potential memory effects and cross contamination. Procedural blanks are very low or below detection levels of the analyzed metals (< 6% relative to control sample with lowest metal concentrations), and confirm that the reagents and extraction procedure do not contribute significantly to the final metal concentration in the sample. Uncertainties are ~ 2% (1SD) for the majority of measurements.

Cu isotope analysis

Subsamples of the sequentially extracted soil fractions (exchangeable/bioavailable, bound to Fe/Mn oxide and incorporated in organic matter) were analyzed for Cu isotopes. The samples were purified using ion-exchange chromatography to separate Cu from the sample matrix prior isotope analysis. Briefly, Cu separation was performed with AG MP-1 resin (100–200 mesh, BioRad) using 250–300 µL resin volume. The columns were first cleaned with 10 ml of 0.1 M HNO₃ and 10 ml of double-deionized water, conditioned with 8 M HCl + 0.001% H₂O₂ and equilibrated with 4 × 2 ml 8 M HCl + 0.001% H₂O₂. The sample re-dissolved in 1 ml 8 M HCl + 0.001% H₂O₂ was loaded on the column and subsequently rinsed with 3 ml of 8 M HCl + 0.001% H₂O₂. In the last step, 9 ml of 8 M HCl + 0.001% H₂O₂ was added to elute Cu from the resin. Each sample was put through the column twice in order to produce an eluate Cu fraction that is pure enough to yield accurate Cu isotope measurements. The procedural blank for Cu was ≤ 1.9% of total Cu. The Cu isotope ratio (⁶⁵Cu/⁶³Cu) was measured with a Nu Plasma HR MC-ICP-MS (Nu Instruments, Wrexham, UK) and a DSN desolvating sample introduction system. Copper isotope measurement of each sample was performed at low mass resolution and normalized using sample-standard bracketing. The Cu isotope values were expressed in the delta notation as δ⁶⁵Cu (‰) relative to the NIST 976:

$$\delta^{65}\text{Cu} = \left(\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST976}}} \right) \times 1000 \quad (1)$$

The precision of δ⁶⁵Cu measurement is ± 0.12‰, estimated using twice the root-mean-square for samples prepared and analyzed in replicates ($n = 6$). The reproducibility of δ⁶⁵Cu for replicate SEP of NIST 2711a is ± 0.08‰ for Fe/Mn oxide-bound Cu ($n = 2$) and ± 0.08‰ for organically bound Cu fraction ($n = 4$).

Spatial distribution and health risk assessment of metals

The total metal soil content (sum of all sequentially extracted soil fractions) and the bioavailable soil metal fraction were used as input data to produce distribution

maps using QGIS version 3.11. Further, we determined the pollution index (PI) and the geoaccumulation index (I_{geo}) for the total soil metal content.

The pollution index (PI) was defined as:

$$\text{PI} = \text{Soil}_{\text{metal}} / C_{\text{metal}} \quad (2)$$

where $\text{Soil}_{\text{metal}}$ is the concentration of each metal in the topsoil collected around the refinery and C_{metal} is the metal concentration in the control soil (= background value of each metal), which is located ~ 30 km ‘downwind’ from the refinery. The level of pollution is classified on a scale from 1 to 5 and specified in Table S3.

The geoaccumulation index I_{geo} was determined as described by Müller (1969):

$$I_{\text{geo}} = \log_2 \frac{\text{Soil}_{\text{metal}}}{1.5 \times C_{\text{metal}}} \quad (3)$$

where $\text{Soil}_{\text{metal}}$ is the concentration of each metal in the topsoil and C_{metal} is the metal concentration in the control soil (= background value).

Results

Soil metal concentrations and distribution

The spatial distribution for the total soil concentration of each metal and their bioavailable fraction are shown in Fig. 2 and Fig. 3. The median total soil concentration of metals follows the pattern of $\text{Cu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cr} > \text{Co}$. The bioavailable soil fraction shows that the concentration decreases in the order of $\text{Zn} > \text{Ni} > \text{Cu} > \text{Co} > \text{Pb} > \text{Cr}$. A detailed description of concentration, distribution, and bioavailability for each metal is given in the following section.

Copper

The spatial distribution map shows the highest soil Cu concentrations closest to the refinery and in the village of Clydach (Fig. 2). The total Cu soil concentrations range between 64.5 and 365.8 $\mu\text{g g}^{-1}$ (median Cu = 202 $\mu\text{g g}^{-1}$) and decreases systematically with distance from the refinery (Fig. 4a). The background Cu content measured in soils from the control site is 11.6 $\mu\text{g g}^{-1}$ which is almost 20 times lower than the median Cu soil content observed at the study site. Bioavailable Cu and Cu bound on Fe/Mn (hydr)oxides

account for 4.6% and 0.5% of total Cu in the topsoils. Bioavailable Cu has with 33.7 $\mu\text{g Cu g}^{-1}$ soil the highest concentration northeast of the refinery (Fig. 3). The bioavailable (exchangeable) Cu shows a strong negative correlation with pH (Fig. 5a). The largest Cu soil fraction is associated with organic matter (> 95%, Table S2) with a strong positive correlation with soil C_{org} ($r^2 = 0.80$) (Fig. 5b). The mean PI and I_{geo} indicate extreme soil contamination with Cu (Fig. 5). The Cu concentrations correlate with Ni ($r^2 = 0.70$) soil concentrations and show similar spatial distribution pattern.

Nickel

The highest Ni soil concentration of 230.7 $\mu\text{g Ni g}^{-1}$ occurs northeast of the refinery (Fig. 2). Total Ni soil concentrations range between 12.6 and 230.7 $\mu\text{g g}^{-1}$ (median Ni = 70 $\mu\text{g g}^{-1}$) and decrease with increasing distance to the refinery (Fig. 4b). The median Ni soil concentration around the refinery is nearly four times higher than the average Ni value of 20 $\mu\text{g g}^{-1}$ reported for English and Welsh soils (McGrath and Loveland 1992; UK Soil and Heritage Pollutant Survey (UKSHS) 2007). Nickel in the topsoils around the refinery is up to 20 times higher compared to the control soil. The median Ni soil concentration is about three times lower than the median Cu soil concentration. The largest Ni soil fraction is associated with organic matter (> 72%; Figure S1). Bioavailable Ni accounts on average for 23% of the total Ni soil content and reaches the highest concentration of 42.7 $\mu\text{g Ni g}^{-1}$ northeast of the refinery (Fig. 3). Nickel bound on Fe/Mn (hydr)oxides accounts for 5.3% of the total Ni soil content. Median I_{geo} and PI indices for total Ni soil content describe moderate to very strong Ni contamination (Fig. 6).

Zinc

The highest Zn concentration in the topsoils occurs northeast of the refinery (2457 $\mu\text{g g}^{-1}$) (Fig. 2). Zinc soil concentrations range between 11.6 and 2457 $\mu\text{g g}^{-1}$ (median Zn = 115 $\mu\text{g g}^{-1}$). The median soil content of Zn is approximately 1.5 times higher than that at the control site (79 $\mu\text{g g}^{-1}$) and the average value of 88 $\mu\text{g g}^{-1}$ for Welsh soils (UKSHS Survey 2007). On average, 37% of total soil Zn is present as bioavailable Zn with the highest

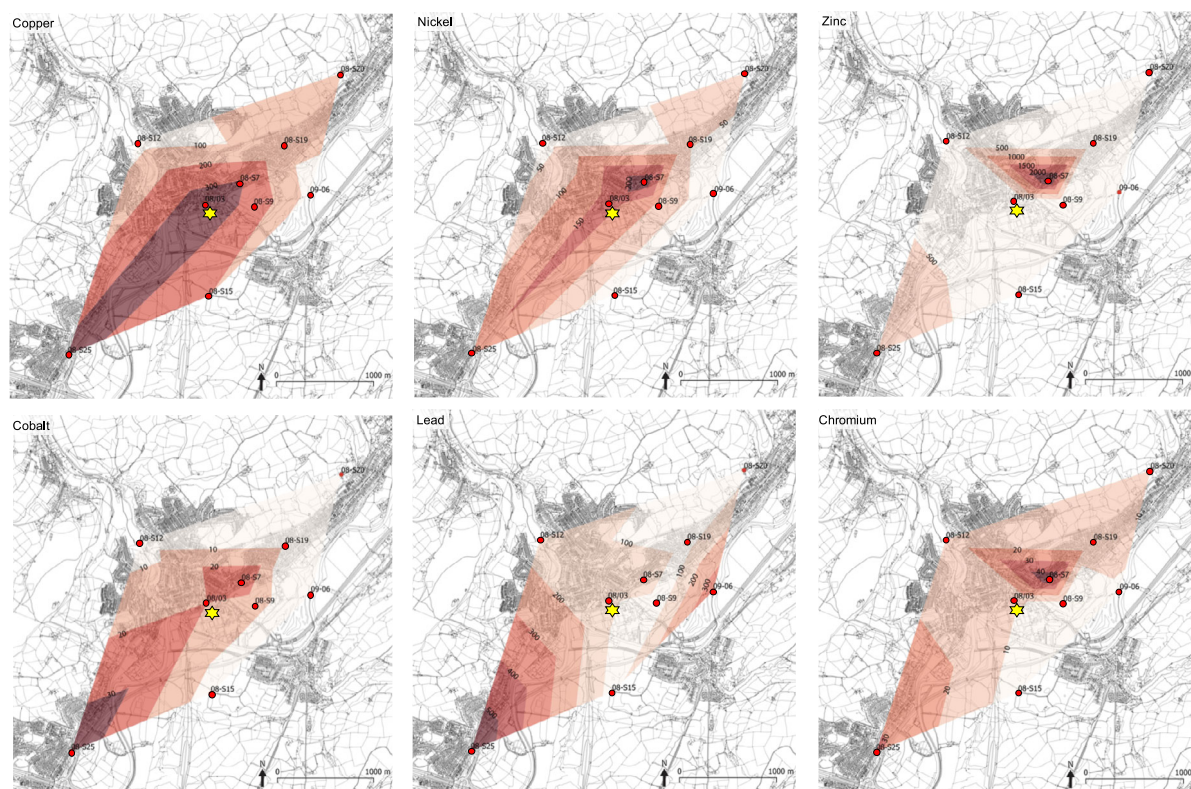


Fig. 2 Spatial distribution maps for total copper, nickel, zinc, cobalt, lead and chromium in topsoils. Dark color indicates highest soil metal content and bright color indicates the lowest

soil metal content. Yellow star represents the location of the smelter; red dots show the individual sampling locations

concentration of $812 \mu\text{g Zn g}^{-1}$ northeast of the refinery (Fig. 3). Organically bound Zn fraction accounts for about 52% of the total Zn, while Zn associated with Fe/Mn (hydr)oxides is about 10% (Figure S1). Mean PI and I_{geo} show that the soils around the refinery are not contaminated with Zn (Fig. 6). Only the sampling location northeast of the refinery can be classified as extremely Zn contaminated.

Cobalt

The spatial distribution map shows the highest soil Co concentrations southwest of the refinery ($37.4 \mu\text{g g}^{-1}$; Fig. 2). Total soil Co ranges between 3.9 and $37.4 \mu\text{g g}^{-1}$ (median Zn = $10 \mu\text{g g}^{-1}$). The median Co soil concentration is about 1.5 times higher than in the topsoil at the control site ($6.6 \mu\text{g g}^{-1}$). Cobalt at all sampling locations is above the global Co soil concentration of $7.9 \mu\text{g g}^{-1}$ (Kabata-Pendias 2010).

The largest Co soil fraction is associated with organic matter (50%; Figure S1). Bioavailable Co and Co bound on Fe/Mn (hydr)oxides account in average for 35% and 16% of the total Co soil content. The spatial distribution reveals the highest bioavailable Co soil concentration of $12.3 \mu\text{g Co g}^{-1}$ in the village Clydach (Fig. 3). The average PI and I_{geo} for the soils in vicinity of the refinery belong to uncontaminated to moderately contaminated category (Fig. 6). Despite a strong correlation between Co and total Ni ($r^2 = 0.73$) and a moderate correlation between Co and total Cu ($r^2 = 0.65$), the spatial distribution pattern of Co concentrations does not match that of Ni or Cu. Similar to Ni, organically bound Co correlates strongly with the soil C_{org} ($r^2 = 0.75$).

Lead

The highest Pb soil concentration ($595 \mu\text{g g}^{-1}$) occurs southwest of the refinery at the Clydach village

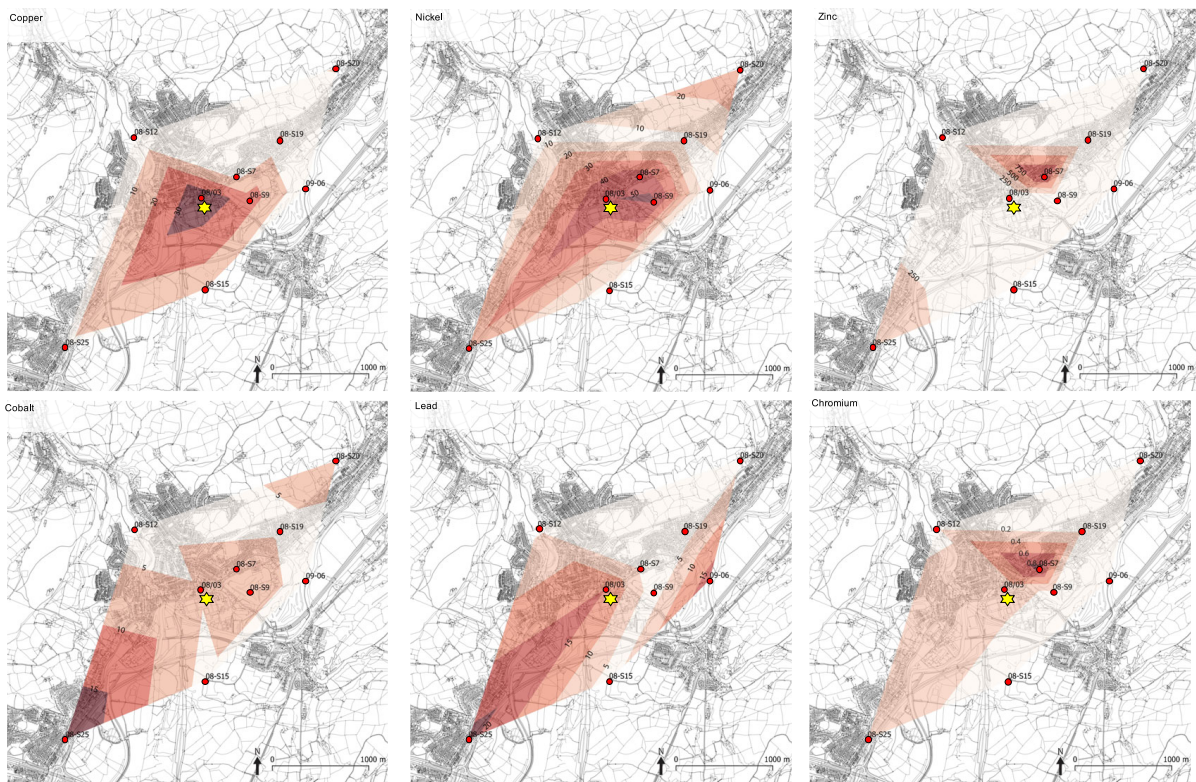


Fig. 3 Spatial distribution maps for bioavailable fraction of copper, nickel, zinc, cobalt, lead and chromium in topsoils. Dark color indicates highest soil metal content and bright color

indicates the lowest soil metal content. Yellow star represents the location of the smelter; red dots = sampling location

(Fig. 2). Total Pb soil concentrations range between 42.9 and 595 $\mu\text{g g}^{-1}$ (median Pb = 118 $\mu\text{g g}^{-1}$). The median Pb soil concentration is more than an order of magnitude greater than for the soil at the control site (8.3 $\mu\text{g g}^{-1}$) and exceeds the average value of Welsh soils of 59.2 $\mu\text{g g}^{-1}$ (UKSHS Survey 2007). On average, 95% of Pb is associated with soil organic matter. Bioavailable Pb and Pb bound on Fe/Mn (hydr)oxides are with 1.6% and 4.3% very low (Figure S1). The spatial distribution shows the highest bioavailable Pb soil concentration of 9.3 $\mu\text{g Pb g}^{-1}$ in the village Clydach. The PI and I_{geo} indices for Pb classify the soils as heavily to extremely contaminated (Fig. 6). Total Pb soil concentration shows no correlation with Ni, Cu, Cr, Zn and Co.

Chromium

The median Cr concentration in the soil around the refinery is with 11.6 $\mu\text{g g}^{-1}$ almost similar to the total Cr at the control site (9.1 $\mu\text{g g}^{-1}$). Total Cr in all

soils is below the average value of Welsh soils of 25.5 $\mu\text{g g}^{-1}$ (UKSHS Survey 2007). The spatial distribution map of Cr shows the maximum soil Cr content northeast of the refinery (Fig. 2). Chromium is with more than 98% predominantly associated with soil organic matter (Figure S1). The bioavailable and Fe/Mn (hydr)oxides bound on Cr account for less than 2% of the total soil Cr. The spatial distribution map for the bioavailable Cr fraction shows the highest concentration of 0.7 $\mu\text{g Cr g}^{-1}$ northeast of the refinery (Fig. 3). The average PI and I_{geo} for Cr can be classified as uncontaminated (Fig. 6).

$\delta^{65}\text{Cu}$ for different soil fractions

The Cu isotopic composition of the three sequentially extracted soil fractions is reported in Table 1. The $\delta^{65}\text{Cu}$ values for organically bound Cu vary between -0.19 and +0.10‰. The $\delta^{65}\text{Cu}$ values of bioavailable Cu range between -0.43 and +0.22‰, and $\delta^{65}\text{Cu}$ values of the Fe/Mn (hydr)oxides-bound fraction vary

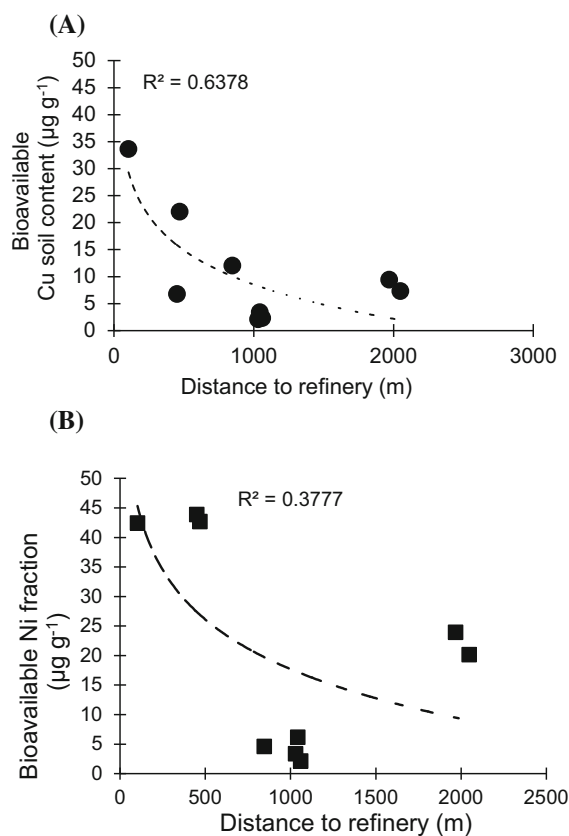


Fig. 4 Concentration of bioavailable soil fraction of A) copper and B) nickel as a function of distance (in m) to the Ni refinery in Clydach. Dashed lines are the best fitted curve described as $y = ax^{-b}$ and the correlation coefficient (R^2)

between -0.43 and $+0.07\%$. When pooled together, $\delta^{65}\text{Cu}$ values for the various soil fractions show a clear trend (Fig. 7a). In each sample, the bioavailable Cu is isotopically lighter than the organically bound Cu (Fig. 7a). Further, there is a strong positive correlation between $\delta^{65}\text{Cu}$ of bioavailable and organically bound Cu ($r^2 = 0.76$; Fig. 7b).

Discussion

Assessment of metal pollution in the soils

Most soil metal concentrations (except Cr) reach potentially harmful levels at multiple sampling locations. Nickel, Zn and Cu show the highest soil concentrations in samples northeast of the refinery, while the highest concentrations of Co and Pb are

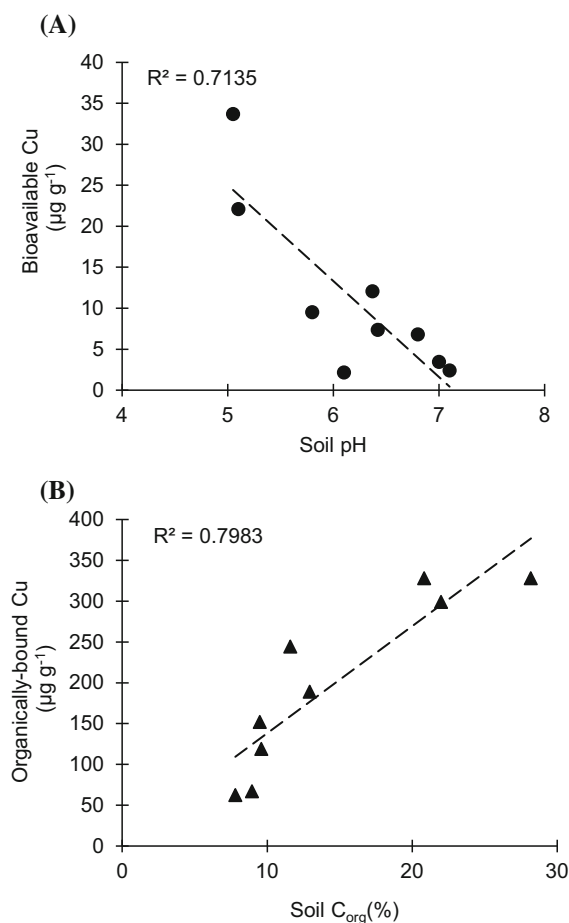


Fig. 5 Relationship between **a** soil pH and bioavailable Cu soil fractions and **b** soil organic carbon and organically bound Cu soil fraction. The dashed lines describe the best fit of a linear regression and the correlation coefficient (R^2)

found southwest of the refinery. The I_{geo} values for Ni, Zn, Cu, Pb and Co indicate soil pollution of different magnitude. While the median Cu and Pb soil concentrations can be classified as heavily contaminated ($I_{\text{geo}} < 3$), Ni shows on average moderate contamination levels ($I_{\text{geo}} = 2.1$). Cobalt and Zn reflect rather disperse patterns of contamination ranging from uncontaminated to heavily contaminated levels depending on the sampling location. This shows that a clear risk assessment of soil contamination levels for Co and Zn is difficult in the Lower Swansea Valley.

Metal source tracing

The spatial distribution patterns delineate two well-defined sources (Figs. 2 and 3). The spatial distribution

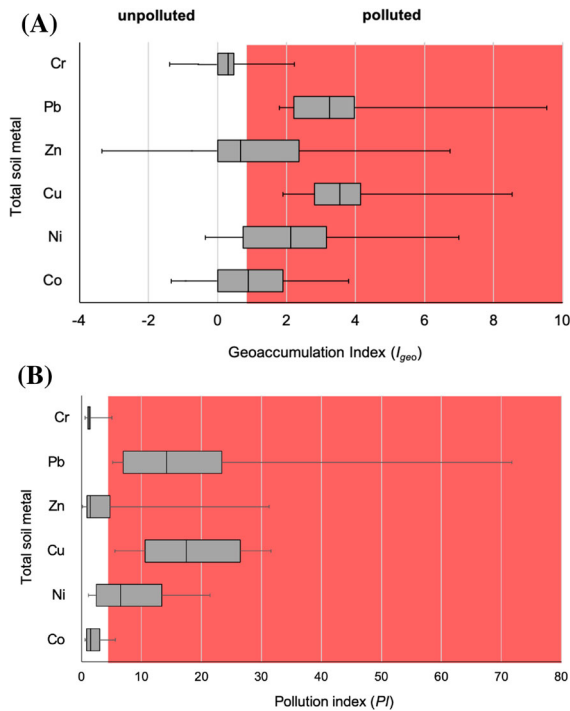


Fig. 6 **a** Index of geoaccumulation I_{geo} and **b** pollution index (PI) of the total soil metal content (Cr, Pb, Zn, Cu, Ni and Co)

pattern of Ni, Cu, Cr and Zn suggest an identical point source of pollution near the refinery. A previous study has shown that in particular the elevated soil content of

Cu and Ni is linked to historic activities of smelting and refining at the Lower Swansea Valley (Davies 1997). The Ni refinery at Clydach is over 100 years in operation and processes Ni–Cu–sulfides from Sudbury, Canada. Sudbury sulfide ores contain large amount of Ni and Cu with minor constituents of Zn, Cr and Pb (Hawley 1962; Adamo et al. 2002). Previous studies have demonstrated elevated levels of metals in soils associated with the Ni and Cu smelting in Sudbury, Canada (Hutchinson and Whitby 1974; Freedman and Hutchinson 1980; Adamo et al. 2002), and it is plausible that similar ore processing activities over time have led to elevated soil metal concentrations at our study site.

The decreasing concentrations of Cu, Ni, Cr and Zn in the soils with increasing distance from the refinery are consistent with a wind driven mode of transport. Accordingly, the highest Cu and Ni concentrations in the soil occur close to the refinery, with a logarithmic dependence of soil concentrations with distance to the point source (Fig. 4). We hypothesize that the spatial distribution pattern of Ni, Cu, Cr and Zn is caused by the predominantly SW prevailing wind. It is known that fine particulates ($< 2.5 \mu\text{m}$) originating from smelting and refining can be transported over long distances (Entwistle et al. 2019). Our data of the spatial distribution of these metals in topsoils around the refinery are in good agreement with the modeled

Table 1 Cu concentrations ($\mu\text{g g}^{-1}$) and $\delta^{65}\text{Cu}$ (‰) for operationally defined soil fractions (exchangeable/bioavailable, Fe/Mn-bound and organically bound Cu)

| Sample ID | Distance to refinery (in m) | Exchangeable and bioavailable fraction | | Reducible fraction (bound to Fe and Mn (hydr)oxides) | | Oxidizable fraction (bound to organic matter) | |
|-----------------|-----------------------------|--|---|--|---|---|---|
| | | $\delta^{65}\text{Cu}$ (‰) | Cu concentration ($\mu\text{g g}^{-1}$) | $\delta^{65}\text{Cu}$ (‰) | Cu concentration ($\mu\text{g g}^{-1}$) | $\delta^{65}\text{Cu}$ (‰) | Cu concentration ($\mu\text{g g}^{-1}$) |
| Control (08-C2) | 29,474 | nd | 0.4 | nd | 0.03 | – 0.03 | 11.2 |
| 08-09 | 469 | – 0.41 | 22.1 | nd | 2.70 | – 0.19 | 244.2 |
| 08-S25 | 2048 | nd | 7.3 | nd | 0.56 | – 0.18 | 328.1 |
| 09-06 | 1060 | nd | 2.4 | nd | 0.16 | 0.04 | 66.8 |
| 08-19 | 1043 | – 0.43 | 3.5 | nd | 0.27 | – 0.2 | 118.7 |
| 08-12 | 1030 | 0 | 2.1 | nd | 0.13 | – 0.08 | 62.2 |
| 08-S15 | 846 | 0.22 | 12.1 | 0 | 1.29 | 0.22 | 188.9 |
| 08-20 | 1968 | – 0.22 | 9.5 | 0.07 | 0.91 | – 0.08 | 151.8 |
| 08/03 | 103 | – 0.12 | 33.7 | – 0.43 | 4.01 | 0.1 | 328.1 |
| 08-07 | 450 | nd | 6.8 | nd | 0.54 | – 0.03 | 299.0 |

nd = not determined

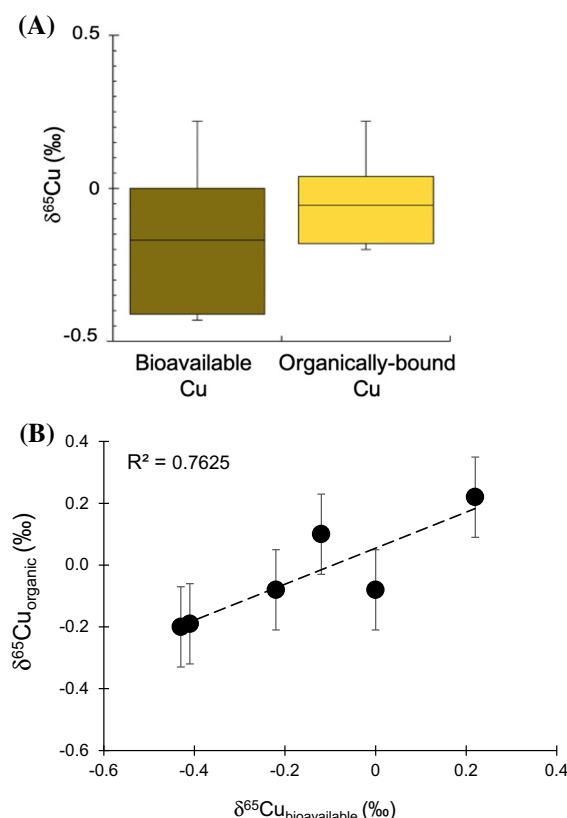


Fig. 7 **a** Whisker-box plot of $\delta^{65}\text{Cu}$ of the bioavailable (beige) and the organically bound (yellow) soils fraction. For the whiskers plot, the central line marks the median value. The lower quartile (25th percentile) and upper quartile (75th percentile) of the dataset and the whiskers present the most extreme data points. **b** Relationship between $\delta^{65}\text{Cu}$ of the bioavailable soil fraction and the $\delta^{65}\text{Cu}$ of the organically bound soils fraction. The dashed line describes the linear fit. The error bars represent the root-mean-square of 0.12‰ for replicate sample analysis

Ni emission from the refinery by Hayman (2009). Hayman (2009) has shown that the metal deposition center is about 1100 m ENE of the refinery chimney. Furthermore, the wind-driven transport has also been proposed by previous studies tracing the source of airborne metals emitted by the Clydach Ni refinery from the metal accumulation in plant biomass (Goodman and Roberts 1971; Goodman et al. 1975).

The highest soil Pb and Co concentrations southwest of the refinery indicate a different source than that for Ni, Cu, Cr and Zn. As a clear evidence is missing causing such high Pb and Co concentrations in the village of Clydach, we can only speculate about potential sources. The high Co soil concentration in

vicinity to an urban area might be linked to traffic emissions and burning of fossil fuels (Smith and Carson 1981). The source for high Pb could be related to historic Pb processing refineries lower down the valley (Davies 1997).

Metal soil status

Although soil concentration of most metals in vicinity of the Ni refinery can be classified as moderately to extremely contaminated, the majority of the metals are not bioavailable. Mobility and bioavailability of metals decrease in order of the extraction sequence (Tessier 1979) where the exchangeable fraction indicates the metals most available for plant uptake, while metals bound to Fe/Mn (hydr)oxides and incorporated into organic matter are less mobile and thus less bioavailable.

The bioavailable metal fraction can be grouped into metals with low and high bioavailability relative to their total soil content. Zinc, Co and Ni are with 23–37% of the total metal soil content highly bioavailable, whereas only 1.3–4.5% of Cu, Cr and Pb are bioavailable. Low or high, each bioavailable metal fraction correlates with its total soil content. This correlation is attributed not only to specific soil processes (e.g., adsorption, reduction, complexation) but also to the critical soil metal load from anthropogenic or natural sources (Rieuwerts et al. 1998, Kaasalainen and Yli-Halla 2003, Kabata-Pendias 2010, Kim et al. 2015). It has been observed that metals from anthropogenic sources tend to be more bioavailable than those of pedogenic origin (Kaasalainen and Yli-Halla 2003, Kabata-Pendias 2010). Thus, the high bioavailability of Ni and Zn can clearly be explained by the anthropogenic input of these metals to the soil from the long-term operation of the Ni refinery at Clydach. Although the bioavailability of Cu and Cr is extremely low, the spatial distribution patterns (Fig. 2) show that both metals probably originated also from refining operations in this region. The low bioavailability of Cr, Pb and Cu is mainly related to their high affinity to adsorb on soil oxide minerals and the formation of strong metal–organic complexes (Rieuwerts et al. 1998; Kim et al. 2015).

Organically bound metals are the largest soil fraction (> 50%). Biogeochemical soil processes (e.g., redox reactions, assimilation, adsorption and complexation) transform inorganic metal forms

originated from anthropogenic sources to metal–organic complexes (Pandey et al. 2000; Nierop et al. 2002; Kabata-Pendias 2010). The sequence of $\text{Cr} > \text{Pb} > \text{Cu} > \text{Ni} > \text{Zn} > \text{Co}$ for the organically bound soil fraction describes the stability of metal–organic complexes based on the metal ion radii, redox stability and pH. Metals with large ion radius such as Pb are more retained by organic matter than those with small ion radius such as Co (Rieuwerts et al. 1998). Although Cr has a small ion radius, its high stability with soil organic matter results from redox changes of Cr(VI) to Cr(III) by organic matter (Wittbrodt and Palmer 1996; Gustafsson et al. 2014). A substantial part of soil organic matter is comprised of fulvic and humic acids which have high metal binding capacity. More specifically, Zn, Pb, Ni and Cu (< 95%) bind predominantly on fulvic acid (Donisa et al. 2003; Boruvka and Drábek 2004; Lalas et al. 2018). The binding preference of Cr on humic acid or fulvic acid depends on the Cr concentrations (Donisa et al. 2003). Therefore, we can surmise that a larger fraction of organically bound metals are associated with fulvic rather than humic acid. Nevertheless, the stability of metal–organic complexes depends on the soil pH and is generally low for Ni, Zn, and Co and high for Cu, Pb and Cr at pH between 5 and 7.1 (Kim et al. 2015).

Biogeochemical soil cycling based on Cu isotope signature

The $\delta^{65}\text{Cu}$ values of three extracted soil fractions (bioavailable, Fe/Mn (hydr)oxides bound and organically bound Cu) provide a more comprehensive framework for soil biogeochemical processes. Copper concentrations in the extracted soil fractions alone are not sufficient to determine the processes of Cu cycling in the soils. During the refining process especially during the early years of operation, aeolian particles were emitted and deposited in the soils (Perkins 2011). Slow dissolution of the deposited aeolian particles releases Cu into the bioavailable soil fraction (Fig. 4a). As metallurgic processes do not isotopically fractionate Cu (Gale et al. 1999; Mattielli et al. 2006), any soil Cu originated from refining processes should be isotopically similar to the ore material. Sudbury sulfide ores used as feeding material in the Ni refinery have an average $\delta^{65}\text{Cu}$ of $-0.32 \pm 0.54\text{‰}$ (Christoffersen 2017) which matches $\delta^{65}\text{Cu}$ of the bioavailable

soil fraction ($\delta^{65}\text{Cu}_{\text{mean}} = -0.16\text{‰} \pm 0.25\text{‰}$, $n = 6$).

Once released in a soluble form, most of the bioavailable Cu is scavenged by soil organic matter. This is supported by our observation that more than 95% of Cu is present in the organically bound soil fraction. Aqueous Cu binds to the hydroxyl functional groups of dissolved organic matter and forms stable chelate complexes, which decrease the bioavailability of Cu (Davis 1984; Pandey et al. 2000; Nierop et al. 2002). Even without redox changes, the coordination of ligand complexes causes Cu isotope fractionation. The stronger bonding environments between Cu and dissolved organic matter favor the heavy ^{65}Cu (Vance et al. 2008; Bigalke et al. 2010a, b; Ryan et al. 2014). The strong positive correlation between $\delta^{65}\text{Cu}$ of the bioavailable and $\delta^{65}\text{Cu}$ of the organically bound Cu fraction (Fig. 7b) confirms that complexation of Cu in organic matter leads to the enrichment of heavy ^{65}Cu . For the studied soils, the magnitude of Cu isotopic fractionation, expressed as $\Delta^{65}\text{Cu}_{\text{organic-bioavailable}}$, of $+0.12 \pm 0.13\text{‰}$ corresponds to experimentally determined Cu isotope fractionation for Cu complexation by different types of organic ligands ($\Delta^{65}\text{Cu} +0.14$ to $+0.84\text{‰}$; Ryan et al. 2014).

Conclusion

Our integral approach of sequential extraction method, spatial metal distribution maps and Cu isotope analysis clearly elucidates the source, bioavailability, and flux of metals in polluted top soils. The results show that after more than 100 years of metallurgical industry in the Lower Swansea Valley, the intensity of soil pollution is high for Cu, Ni and Pb and often exceeds guideline values for total metal soil concentrations. The spatial distribution of the metals in these top soils indicates two sources with the primary point source being the long-term metallurgical industry in this area. Significant proportion of soil metals (> 50% of total metal soil concentration) is associated with soil organic matter which is less bioavailable and thus potentially minimizes the ecological risk and health risk for human.

The difference in $\delta^{65}\text{Cu}$ between bioavailable and organically bound Cu is attributed to the complexation of Cu with organic matter after the dissolution of the

deposited aeolian particles originating from refining practices. Thus, isotope systematics of Cu help explain biogeochemical process of Cu related to a long-term pollution in topsoils.

In future studies, systematic monitoring and more intensive sampling are required to evaluate any prospective alteration of the metal distribution, bioavailability and metal flux in these soils. This would also include sampling of soil profiles to assess the vertical impact of the metal pollution.

Acknowledgements The project was supported by the Department of Earth Sciences, Oxford University. We thank Phil Holdship for assisting with the ICP-MS analysis. We also thank two anonymous reviewers for their constructive feedback.

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