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

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16 **Keywords:** Soil metal bioavailability, metal distribution, pollution, copper stable isotopes

17 **Abstract**

18 Soils in the Lower Swansea Valley, UK, contain elevated level of metals, enough to cause direct or indirect
19 effects on human health. This study assesses the severity of soil pollution and bioavailability of Cu and
20 other metals (Zn, Cr, Co, Ni, and Pb) from soils with various distances from the Ni refinery in Clydach,
21 Lower Swansea Valley. We compare Cu concentrations in operationally-defined soil fractions
22 (bioavailable, bound to Fe/Mn oxide and incorporated in organic matter) with other metals (Ni, Zn, Pb, Co,
23 Cr) usually occurring in ores used in metallurgic processes, and report the pollution and the
24 geoaccumulation indices (PI and I_{geo}). Further, we use Cu stable isotope ratios ($\delta^{65}\text{Cu}$) to trace the fate and
25 mobility of Cu in soils.

26 Our data suggest a point source of contamination for some of the heavy metals including Ni ($I_{geo} = 1.9$), Zn
27 ($I_{geo} = 0.28$) and Cu ($I_{geo} = 3.6$) near the Clydach Ni refinery. However, Co ($I_{geo} = 0.15$) and Pb ($I_{geo} = 3.3$)
28 contaminations is likely to be linked to different sources. No elevated Cr levels ($I_{geo} = -0.07$) occur in any
29 of the studied soils. The Cu isotope data show that Cu in soil organic matter is enriched in ^{65}Cu while the
30 lighter isotopes (^{63}Cu) remain in the dissolved bioavailable Cu fraction ($\Delta^{65}\text{Cu}_{\text{organic-bioavailable}}$ is $+0.12 \pm$
31 0.13%). This suggests the preferential complexation of ^{65}Cu with soil organic matter after dissolution of
32 Cu deposited to the soil. Thus, Cu isotope data can effectively indicate pathways of metal migration in
33 polluted soils.

34 **Keywords:** Heavy metals, soil, spatial distribution, bioavailability, copper isotopes, pollution

35 **Introduction**

36 In the EU, about 45% of the soils are estimated to be contaminated (van Liedekerke et al., 2014). Heavy
37 metals are with 35% the major contaminants in soils. Anthropogenic activity, including mining, smelting,
38 and refining significantly redistributes heavy metals in the environment. Despite the biological role of some
39 heavy metals, most are toxic at high concentrations (Hodson and Donner, 2013). This means if heavy metals
40 are bioavailable they cause large ecological damage (Hutchinson and Whitby, 1974, Kabata-Pendias, 2010,
41 Kim et al., 2015) and bear a significant health risk for humans (Hodson and Donner, 2013, Entwistle et al.,
42 2019).

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

55 Specifically, soils in regions with long history of metallurgical industry are often contaminated with heavy
56 metals. The Lower Swansea Valley has been affected by metal smelting and refining since the 18th century
57 up to the present day (Perkins, 2011). During the 18th century two thirds of copper in the UK was processed
58 in smelters at this region (Marchant et al., 2011, Perkins, 2011). Nickel refining began in the early 20th
59 century. Despite a decline of the metal industry in the Lower Swansea Valley during the 1920s and 1930s,

60 with the closing of many of the metalworks (Alban, 1984), the nickel refinery for instance in the Clydach
61 Village is still operational.

62 From all metals, specifically Cu tends to accumulate in topsoils in areas with intensive mining and/or
63 metallurgic activity (Hutchinson and Whitby, 1974, Temple and Bisessar, 1981, Ettler et al., 2011). Copper
64 is normally found in unpolluted soils at concentrations below 30 $\mu\text{g g}^{-1}$ (Artiola, 2005) but becomes
65 detrimental to wildlife above 60 $\mu\text{g Cu g}^{-1}$ (Kabata-Pendias et al., 1981, Alloway, 1995, Kabata-Pendias,
66 2010). With an estimated soil residence time between 1000 and 3000 years for temperate climates (Bowen,
67 1979), Cu soil pollution becomes a long-term ecological issue.

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

81 The objectives of this study are (i) to characterize the spatial distribution of metals in soils in the vicinity
82 of a refinery (ii) to assess the environmental risk factors by quantifying metal fractions associated with
83 different soil constituents and (iii) to unravel the fate of soil Cu using Cu isotope composition ($\delta^{65}\text{Cu}$) of

84 operationally-defined Cu soil pools. The results of this study help identify potential sources of heavy metals
85 as by-products of the metallurgic processes in the Lower Swansea Valley relative to the natural background
86 signal, and to trace pathways of metal migration. Additionally, our results provide a way to evaluate the
87 environmental quality and environmental health of the Lower Swansea Valley, an area with a long history
88 of metal refining.

89 **2. Materials and Method**

90 **2.1 Study site and soil sampling**

91 The study site is located in South Wales in the Lower Swansea Valley, approximately 10 km northeast of
92 Swansea city (Figure 1). Soil samples were collected from various locations within the vicinity of the Ni
93 refinery in the village Clydach (Figure 1, Table S1). Soils in the Swansea Valley are primarily formed from
94 the product of glacial erosion of Carboniferous sedimentary rocks generating sandy clay loam soils. A
95 control sample was selected from an uncontaminated location about 30 km ‘downwind’ of the Ni refinery,
96 an area of Devonian rocks (Old Red Sandstone). For sample collection, vegetation was removed from the
97 soil surface and soil was collected from the upper 5 cm. We assume that topsoils reflect mainly metals
98 originating from long-term metallurgical industry and are less likely derived from bedrock geochemistry.
99 The collected soils were then dried for 48 hours at 40°C. Mortar and pestle were used to disaggregate
100 material and create a homogeneous texture. The dried soils were stored in clear plastic bags prior further
101 analysis.

102 **2.2 Sequential extraction (SEP)**

103 To determine the heavy metal speciation in soils, we used the well-established BCR extraction technique
104 (Tessier et al., 1979; Davidson et al., 1998; Rauret et al., 1999). One gram of air-dried soil was weighed
105 into a 50 ml metal-free centrifuge tube (VWR). Then, for the first extraction step (= exchangeable and
106 bioavailable fraction) 30 ml of 0.1M acetic acid was added and shaken on a rotary shaker at room
107 temperature overnight. Afterwards the sample was centrifuged at 3000 rpm (Eppendorf Centrifuge 5810R)
108 for 20 min, the supernatant was decanted and soil residual was washed with 20 ml of double-deionized

109 water. Subsequently, 30 ml of 0.5 M hydroxylamine hydroxide was added to the soil to extract the reducible
110 fraction, namely metals associated with Fe/Mn (hydr)oxides. For the third step, 5 ml of 8.8M hydrogen
111 peroxide (Romil Ltd.) was added to the soil and left at room temperature for one hour. The samples were
112 then placed on a hotplate at 85°C to reduce the sample volume to less than 3 ml. The hydrogen peroxide
113 step was repeated twice before adding 20 ml of 1M ammonium acetate (adjust to pH 4) and shaken
114 overnight at 40 rpm. The supernatants from all extraction steps were filtered through 0.45 µm membrane
115 filters. Procedural blanks were prepared to estimate the metal content in reagents used for each SEP step.

116 For reproducibility check and validation of the BCR method, triplicate extractions (n =5) were performed
117 using the reference material NIST 2711a, a moderately contaminated Montana soil. We selected certified
118 reference soil NIST 2711a because the BCR extraction method has previously been performed and assessed
119 for several metals (Sutherland and Tack 2002; Kubova et al., 2004; Larner et al. 2006). The triplicate
120 extractions of the three-steps show a good reproducibility (Table S2) with relative standard deviation (RSD)
121 for the three fractions (bioavailable and exchangeable, Fe/Mn oxide-bound and organically-bound metals)
122 of less than <10%. Further, the metal values for the three individual fractions are in good agreement with
123 previously reported data for NIST 2711a (Sutherland and Tack 2002; Kubova et al., 2004; Larner et al.
124 2006).

125 **2.3 Concentration analysis**

126 The concentrations of Cu, Ni, Zn, Co, Pb, and Cr in sequentially extracted pools were measured using a
127 PerkinElmer NexION 350D Inductively Coupled Plasma-Mass Spectrometer (ICPMS) equipped with an
128 Elemental Scientific (Omaha, USA) prepFASTM5 autosampler and autodiluter. A calibration curve was
129 calculated using premade calibration solutions with varying concentrations of each metal. After every 11
130 samples, standard quality control and calibration blanks were analyzed to evaluate potential memory effects
131 and cross contamination. Quality control procedures confirmed the reproducibility of measurements.
132 Procedural blanks show very low or below detection levels of the analyzed metals (<6% relative to control
133 sample with lowest metal concentrations), confirming that the reagents and procedure don't contribute

134 significantly to the final metal concentration. Uncertainties are ~2% (1SD) for the majority of
135 measurements.

136 **2.4 Cu isotope analysis**

137 Subsamples of the sequentially extracted pools (exchangeable/bioavailable, bound to Fe/Mn oxide and
138 incorporated in organic matter) were analyzed for Cu isotopes. The samples were purified using ion
139 exchange chromatography to separate Cu from the sample matrix prior isotope analysis. Briefly, Cu
140 separation was performed with AG MP1 resin (100-200 mesh, BioRad) using 250-300 μL resin volume.
141 The columns were first cleaned with 10 ml of 0.1M HNO_3 and double-deionized water, conditioned with
142 8M HCl + 0.001% H_2O_2 and equilibrated with 4 x 2ml 8M HCl + 0.001% H_2O_2 . The sample re-dissolved
143 in 1 ml 8M HCl + 0.001% H_2O_2 was loaded on the column and subsequently rinsed with 3 ml of 8M HCl
144 + 0.001% H_2O_2 . In the last step, 9 ml of 8M HCl + 0.001% H_2O_2 were added to elute Cu from the column.
145 Each sample was put through the column twice in order to produce an eluate Cu fraction that is pure enough
146 to yield accurate stable isotope measurements. The procedural blank for Cu was $\leq 1.9\%$ of total Cu. The
147 Cu isotope ratio ($^{65}\text{Cu}/^{63}\text{Cu}$) was measured with a Nu Plasma HR MC-ICP-MS and a DSN at low mass
148 resolution. Cu isotope measurement for each sample was normalized using sample-standard bracketing. All
149 Cu isotope values were expressed in the delta notation as $\delta^{65}\text{Cu}$ (‰) relative to the NIST 976:

$$150 \quad \delta^{65}\text{Cu} = \left(\frac{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{sample}}}{(^{65}\text{Cu}/^{63}\text{Cu})_{\text{NIST976}}} \right) \times 1000 \quad (\text{Eq. 1})$$

151 The uncertainty on $\delta^{65}\text{Cu}$ was estimated using twice root mean square (RMS) for samples prepared and
152 analyzed in duplicate. The RMS yields in $\pm 0.12\text{‰}$ ($n = 6$). The reproducibility of $\delta^{65}\text{Cu}$ for duplicate SEP
153 of NIST-2711a is $\pm 0.08\text{‰}$ for Fe/Mn oxide-bound Cu ($n = 2$) and $\pm 0.08\text{‰}$ for organically-bound Cu ($n =$
154 4).

155 **2.5 Spatial distribution and health risk assessment of metals**

156 The total soil content (sum of all sequentially extracted soil fractions) and the bioavailable soil metal
157 fractions were used as input data to produce distribution maps using QGIS version 3.11. We determined

158 the pollution index (PI) and the geoaccumulation index (I_{geo}) for the bioavailable metal soil fraction and the
159 total soil metal concentration.

160 The pollution index (PI) is defined as:

$$161 \text{ PI} = \text{Soil}_{\text{metal}} / C_{\text{metal}} \quad (\text{Eq. 1})$$

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

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

$$166 I_{\text{geo}} = \log_2 \frac{\text{Soil}_{\text{metal}}}{1.5 \times C_{\text{metal}}} \quad (\text{Eq. 2})$$

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

169 **3 Results**

170 **3.1 Soil metal concentrations and distribution**

171 The median total soil concentration of metals follows the pattern of $\text{Cu} > \text{Pb} > \text{Zn} > \text{Ni} > \text{Cr} > \text{Co}$. The
172 bioavailable and exchangeable soil fraction show that the concentration decreases in the order of $\text{Zn} > \text{Ni} >$
173 $\text{Cu} > \text{Co} > \text{Pb} > \text{Cr}$. A detailed description of concentration distribution and bioavailability for each metal is
174 given in the following section.

175 **3.2.1 Copper**

176 The spatial distribution map shows the highest soil Cu concentrations closest to the refinery and in the
177 village of Clydach (Figure 2). The total Cu soil concentrations range between 64.5 and 365.8 $\mu\text{g g}^{-1}$ (median
178 $\text{Cu} = 202 \mu\text{g g}^{-1}$) and decreases systematically with distance from the refinery (Figure 4A). The background
179 Cu content measured in soils from the control site is 11.6 $\mu\text{g g}^{-1}$ which is almost twenty times lower than
180 the median Cu soil content observed at the study site. Bioavailable Cu and Cu bound on Fe/Mn (hydr)oxides

181 account for 4.6% and 0.5% of total Cu in the topsoils. The bioavailable (exchangeable) Cu shows a strong
182 negative correlation with pH (Figure 5A). The largest Cu soil fraction is associated with organic matter
183 (>95%, Table S2) with a strong positive correlation with soil C_{org} ($r^2 = 0.80$) (Figure 5B). The mean *PI* and
184 *I*_{geo} indicate extreme soil contamination with Cu (Figure 6). The Cu concentrations correlate with Ni ($r^2 =$
185 0.70) soil concentrations and show similar spatial distribution pattern.

186 **3.2.2 Nickel**

187 The highest Ni soil concentration of 230.7 $\mu\text{g Ni g}^{-1}$ occurs northeast of the refinery (Figure 2). Total Ni
188 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
189 increasing distance to the refinery (Figure 4B). The median Ni soil concentration around the refinery is
190 nearly four times higher than the average Ni value of 20 $\mu\text{g g}^{-1}$ reported for English and Welsh soils
191 (McGrath and Loveland, 1992; UKSHS Report, 2007). Nickel in the topsoils around the refinery are up to
192 twenty times higher compared to the control soil. Interestingly, the median Ni soil concentration is about
193 three times lower than the median Cu soil concentration. The largest Ni soil fraction is associated with soil
194 organic matter (>72%; Figure S1). On average, bioavailable Ni accounts for 23% of the Ni soil content and
195 Ni bound on Fe/Mn (hydr)oxides accounts for 5.3%. Median *I*_{geo} and *PI* indices for total Ni soil content
196 describe moderately to very strong Ni contamination (Figure 6).

197 **3.2.3 Zinc**

198 The highest Zn concentration in the topsoils occurs northeast of the refinery (2457 $\mu\text{g g}^{-1}$) (Figure 2). Zinc
199 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
200 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
201 $\mu\text{g g}^{-1}$ for Welsh soils (UKSHS Report, 2007). On average, 37% of total soil Zn is present as bioavailable
202 and exchangeable Zn. Organically-bound Zn fraction accounts for about 52% of the total Zn, while Zn
203 associated with Fe/Mn (hydr)oxides is about 10% (Figure S1). Mean *PI* and *I*_{geo} show that the soils around
204 the refinery are not contaminated with Zn (Figure 6). Only the sampling location northeast of the refinery
205 can be classified as extremely Zn contaminated.

206 **3.2.4 Cobalt**

207 The spatial distribution map shows the highest soil Co concentrations southwest of the refinery (37.4 $\mu\text{g g}^{-1}$;
208 1 ; Figure 2). Total Co soil concentrations range between 3.9 and 37.4 $\mu\text{g g}^{-1}$ (median Zn = 10 $\mu\text{g g}^{-1}$). The
209 median Co soil concentration is about 1.5 times higher than in the topsoil at the control site (6.6 $\mu\text{g g}^{-1}$).
210 Cobalt content in all soils are above the global Co soil concentration of 7.9 $\mu\text{g g}^{-1}$ (Kabata-Pendias, 2010).
211 The largest Co soil fraction is associated with organic matter (50%; Figure S1). Bioavailable Co and Co
212 bound on Fe/Mn (hydr)oxides account in average for 35% and 16% of the total Co soil content. The average
213 PI and I_{geo} for the soils in vicinity of the refinery belong to uncontaminated to moderately contaminated
214 category (Figure 6). Despite a strong correlation between Co and total Ni ($r^2 = 0.73$) and a moderate
215 correlation between Co and total Cu contents ($r^2 = 0.65$), the spatial distribution pattern of Co concentrations
216 does not match that of Ni or Cu. Similar to Ni, organically-bound Co correlates strongly with the soil C_{org}
217 ($r^2 = 0.75$).

218 **3.2.5 Lead**

219 The highest Pb soil concentration (595 $\mu\text{g g}^{-1}$) occurs southwest of the refinery at the Clydach village
220 (Figure 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
221 median Pb soil concentration is more than an order of magnitude greater than for the soil at the control site
222 (8.3 $\mu\text{g g}^{-1}$) and exceeds the average value of Welsh soils of 59.2 $\mu\text{g g}^{-1}$ (UKSHS Report, 2007). On average,
223 95% of Pb is associated with soil organic matter. Bioavailable Pb and Pb bound on Fe/Mn (hydr)oxides are
224 with 1.6% and 4.3% very low (Figure S1). The PI and I_{geo} indices for Pb classify the soils as heavily to
225 extremely contaminated (Figure 6). Total Pb soil concentration shows no correlation with Ni, Cu, Cr, Zn
226 and Co.

227 **3.2.6 Chromium**

228 The median Cr content in the soil around the refinery is with 11.6 $\mu\text{g g}^{-1}$ almost similar to the Cr soil content
229 at the control site (9.1 $\mu\text{g g}^{-1}$). Chromium content in all soils are below the average value of Welsh soils of
230 25.5 $\mu\text{g g}^{-1}$ (UKSHS Report, 2007). The spatial distribution map of Cr shows the maximum soil Cr content

231 northeast of the refinery (Figure 2). Chromium is with more than 98% predominantly associated with soil
232 organic matter (Figure S1). The bioavailable and Fe/Mn (hydr)oxides bound Cr account for less than 2%
233 of the total soil Cr. The average PI and I_{geo} for Cr can be classified as uncontaminated (Figure 6).

234 **3.2. $\delta^{65}\text{Cu}$ for different soil fractions**

235 The Cu isotopic composition of the three sequentially extracted soil fractions are reported in Table 1. The
236 $\delta^{65}\text{Cu}$ values for organically-bound Cu vary between -0.19 and +0.10‰. The $\delta^{65}\text{Cu}$ values of bioavailable
237 Cu range between -0.43 and +0.22‰ and $\delta^{65}\text{Cu}$ of the Fe/Mn (hydr)oxides -bound fraction ($n = 3$) vary
238 between -0.43 and +0.07‰. When pooled together, $\delta^{65}\text{Cu}$ for the various soil fractions show a clear trend
239 (Figure 7A). In each sample, the bioavailable Cu is isotopically lighter than the organically-bound Cu
240 (Figure 7A). Further, there is a strong positive correlation for $\delta^{65}\text{Cu}$ of bioavailable and organically-bound
241 Cu ($r^2 = 0.76$; Figure 7B).

242 **4 Discussion**

243 **4.1. Assessment of metal pollution in the soils**

244 Most soil metal concentrations (except Cr) reach potentially harmful levels at multiple sampling locations.
245 Nickel, Zn, Cu, and Cr show the highest soil concentrations in samples northeast of the refinery while the
246 highest concentrations of Co and Pb are found southwest of the refinery. The I_{geo} values for Ni, Zn, Cu, Pb
247 and Co indicate soil pollution of different magnitude. While the median Cu and Pb soil concentrations can
248 be classified as heavily contaminated ($I_{geo} < 3$), Ni shows on average moderate contamination levels ($I_{geo} =$
249 2.1). Cobalt and Zn reflect rather disperse patterns of contamination ranging from uncontaminated to
250 heavily contaminated levels depending on the sampling location. This shows that a clear risk assessment of
251 soil contamination levels for Co and Zn is difficult in the Lower Swansea Valley.

252 **4.2 Metal source tracing**

253 The spatial distribution patterns delineate two possible well-defined sources (Figure 3). The strong positive
254 correlations between the metals Ni, Cu, Cr and Zn suggest an identical point source of pollution. A previous

255 study has shown that in particular the elevated soil content of Cu and Ni is linked to historic activities of
256 smelting and refining at the Lower Swansea Valley (Davies, 1997). The Ni refinery at Clydach is over 100
257 years in operation and processes Ni-Cu-sulfides from Sudbury, Canada. Sudbury sulfide ores contain large
258 amount of Ni and Cu with minor constituents of Zn, Cr and Pb (Hawley, 1962; Adamo et al., 2001).
259 Previous studies have demonstrated elevated levels of metals in soils associated with the Ni and Cu smelting
260 in Sudbury, Canada (Hutchinson and Whitby 1974; Freedman and Hutchinson, 1980; Adamo et al., 2001);
261 and it is plausible that similar ore processing activities over time have led to elevated soil metal
262 concentrations at our study site.

263 The decreasing concentrations of Cu, Ni, Cr and Zn in the soils with increasing distance from the refinery
264 are consistent with a wind driven mode of transport. Accordingly, the highest Cu and Ni concentrations in
265 the soil occur closest to the refinery, with a logarithmic dependence between soil concentrations with
266 distance to the point source (Figure 4). We hypothesize that the spatial distribution pattern of Ni, Cu, Cr
267 and Zn concentrations is caused by the predominantly SW prevailing wind. It is known that fine particulates
268 ($< 2.5\mu\text{m}$) originating from smelting and refining can be transported over long distances (Entwistle et al.,
269 2019). Our data of the spatial distribution of these metals in topsoils around the refinery are in good
270 agreement with the modelled Ni emission from the refinery by Hayman (2009). Hayman (2009) has shown
271 that the metal deposition center is about 1100 m ENE of the refinery chimney. Furthermore, the wind driven
272 transport has also been proposed by previous studies tracing the source of airborne metals emitted by the
273 Clydach Ni refinery from the metal accumulation in plant biomass (Goodman and Roberts, 1971; Goodman
274 et al., 1975).

275 The highest soil Pb and Co concentrations southwest of the refinery indicate a different source than for Ni,
276 Cu, Cr and Zn. As a clear evidence is missing causing such high Pb and Co concentrations in the village of
277 Clydach we can only speculate about potential sources. The high Co soil concentration might be linked to
278 traffic emissions and burning of fossil fuels (Smith and Carson, 1981) based on the vicinity to an urban

279 area. The source for high Pb could be related to historic Pb processing refineries lower down the valley
280 (Davies, 1997).

281 **4.4 Metal soil status**

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

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

300 Organically-bound metals are the largest soil fraction (> 50%). Biogeochemical soil processes (e.g., redox
301 reactions, assimilation, adsorption and complexation) transform inorganic metal forms originated from
302 anthropogenic sources to metal-organic complexes (Pandey et al., 2000; Nierop et al., 2002, Kabata-

303 Pendias, 2010). The sequence of Cr>Pb>Cu>Ni>Zn>Co for the organically-bound soil fraction describes
304 the stability of metal-organic complex based on the metal ion radii, redox stability and pH. Metals with
305 large ion radius such as Pb are more retained by organic matter than those with small ion radius such as Co
306 (Rieuwerts et al, 1998). Although Cr has a small ion radius, its highest stability with soil organic matter
307 results from redox changes of Cr(VI) to Cr(III) by organic matter (Wittbrodt and Palmer, 1996, Gustafsson
308 et al., 2014). A substantial part of soil organic matter is comprised of fulvic and humic acid which have a
309 high capacity of binding heavy metals. More specifically, Zn, Pb, Ni and Cu (<95%) bind predominantly
310 on fulvic acid (Donisa et al., 2003, Boruvka and Drabek, 2004, Lalas et al., 2018). The binding preference
311 of Cr on humic acid or fulvic acid depends on the Cr concentrations (Donisa et al., 2003). Therefore, we
312 can surmise that a larger fraction of organically-bound metals is associated with fulvic rather than humic
313 acid. Nevertheless, the stability of metal–organic complexes depends on the soil pH and is generally low
314 for Ni, Zn, and Co and high for Cu, Pb and Cr at pH between 5 and 7.1 for the studied soils (Kim et al.,
315 2015).

316 **4.5 Biogeochemical soil cycling based on Cu isotope signature**

317 The $\delta^{65}\text{Cu}$ values of three extracted soil fractions (bioavailable, Fe/Mn (hydr)oxides bound and organically-
318 bound Cu) provide a more comprehensive framework for soil biogeochemical processes. Copper
319 concentrations in the extracted soil fractions alone are not sufficient to determine the processes of Cu
320 cycling in the soils. During the refining process especially during the early years of operation, aeolian
321 particles were emitted and deposited in the soils (Perkins, 2011). Copper associated with aeolian particles
322 accumulated in the topsoils in vicinity to the Ni refinery. Slow dissolution of the deposited aeolian particles
323 releases Cu into the bioavailable soil fraction (Figure 5A). As metallurgic processes do not isotopically
324 fractionate Cu (Gale et al., 1999; Mattielli et al., 2006), any soil Cu originated from refining processes
325 should be isotopically similar to the ore material. Sudbury sulfide ores used as feeding material in the Ni
326 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
327 bioavailable soil fraction ($\delta^{65}\text{Cu}_{\text{mean}} = -0.16\text{‰} \pm 0.25\text{‰}$, $n = 6$).

328 Once released in a soluble form, most of the bioavailable Cu is scavenged by soil organic matter. This idea
329 is supported by our observation that more than 95% of Cu is present in the organically-bound soil fraction.
330 Aqueous Cu binds to the hydroxyl functional groups of dissolved organic matter and forms stable chelate-
331 complexes, which decrease the bioavailability of Cu (Davis, 1984, Pandey et al., 2000; Nierop et al., 2002).
332 Even without redox changes, the coordination of ligand complexes causes Cu isotope fractionation
333 (Wiederhold, 2015). The stronger bonding environments between Cu and dissolved organic matter favor
334 the heavy ^{65}Cu isotope (Vance et al., 2008; Bigalke et al., 2010; Ryan et al., 2014). The strong positive
335 correlation between $\delta^{65}\text{Cu}$ of the bioavailable and $\delta^{65}\text{Cu}$ of the organically-bound Cu fraction (Figure 7B)
336 confirms that complexation of Cu in organic matter leads to the enrichment of heavy ^{65}Cu . For the studied
337 soils, the magnitude of Cu isotopic fractionation, expressed as $\Delta^{65}\text{Cu}_{\text{organic-bioavailable}}$, of $+0.12 \pm 0.13\text{‰}$
338 corresponds to experimentally determined Cu isotope fractionation for Cu complexation by different types
339 of organic ligands ($\Delta^{65}\text{Cu}$ +0.14 to +0.84‰; Ryan et al., 2014).

340 **Conclusion**

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

349 The difference in $\delta^{65}\text{Cu}$ between bioavailable and organically bound Cu is attributed to the complexation
350 of Cu with organic matter after the dissolution of the deposited aeolian particles originating from refining
351 practices. Thus, isotope systematics of Cu help explain biogeochemical process of Cu related to a long-
352 term pollution in topsoils.

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

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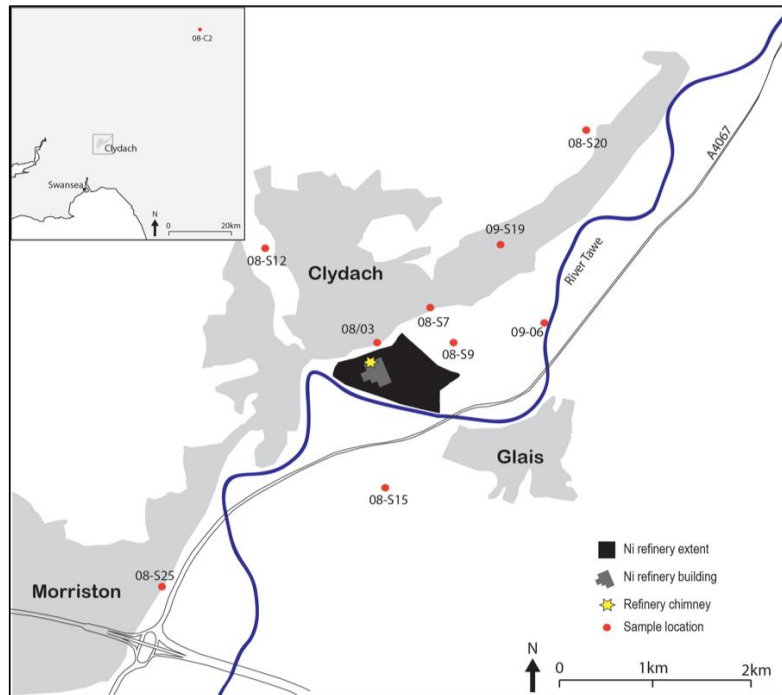


Figure 1: Sampling location map adapted from Perkins (2011).

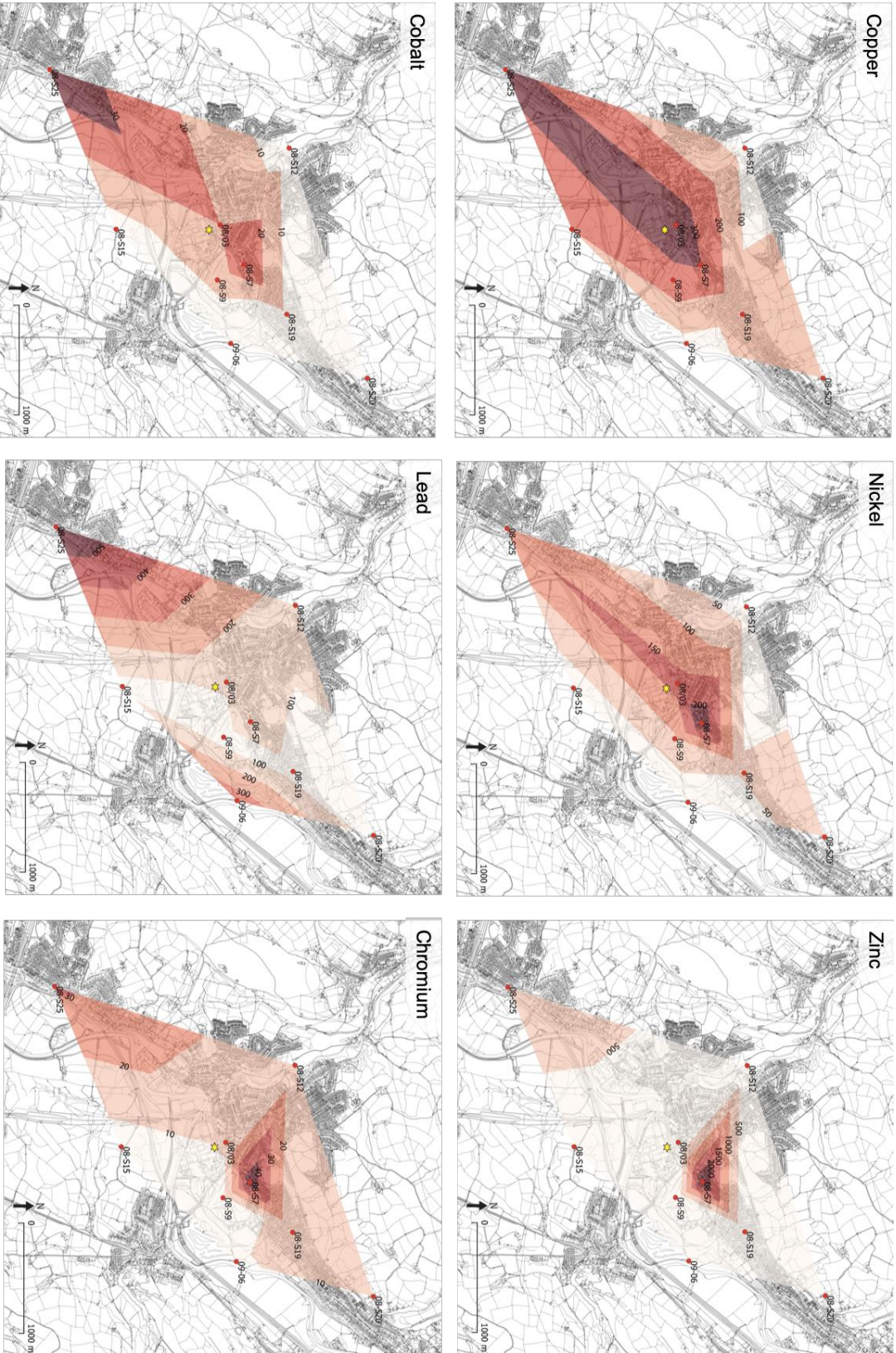


Figure 2: Spatial distribution map of total content of copper, nickel, zinc, cobalt, lead and chromium in topsoils. Yellow star represents the location of the smelter; red dots = sampling location.

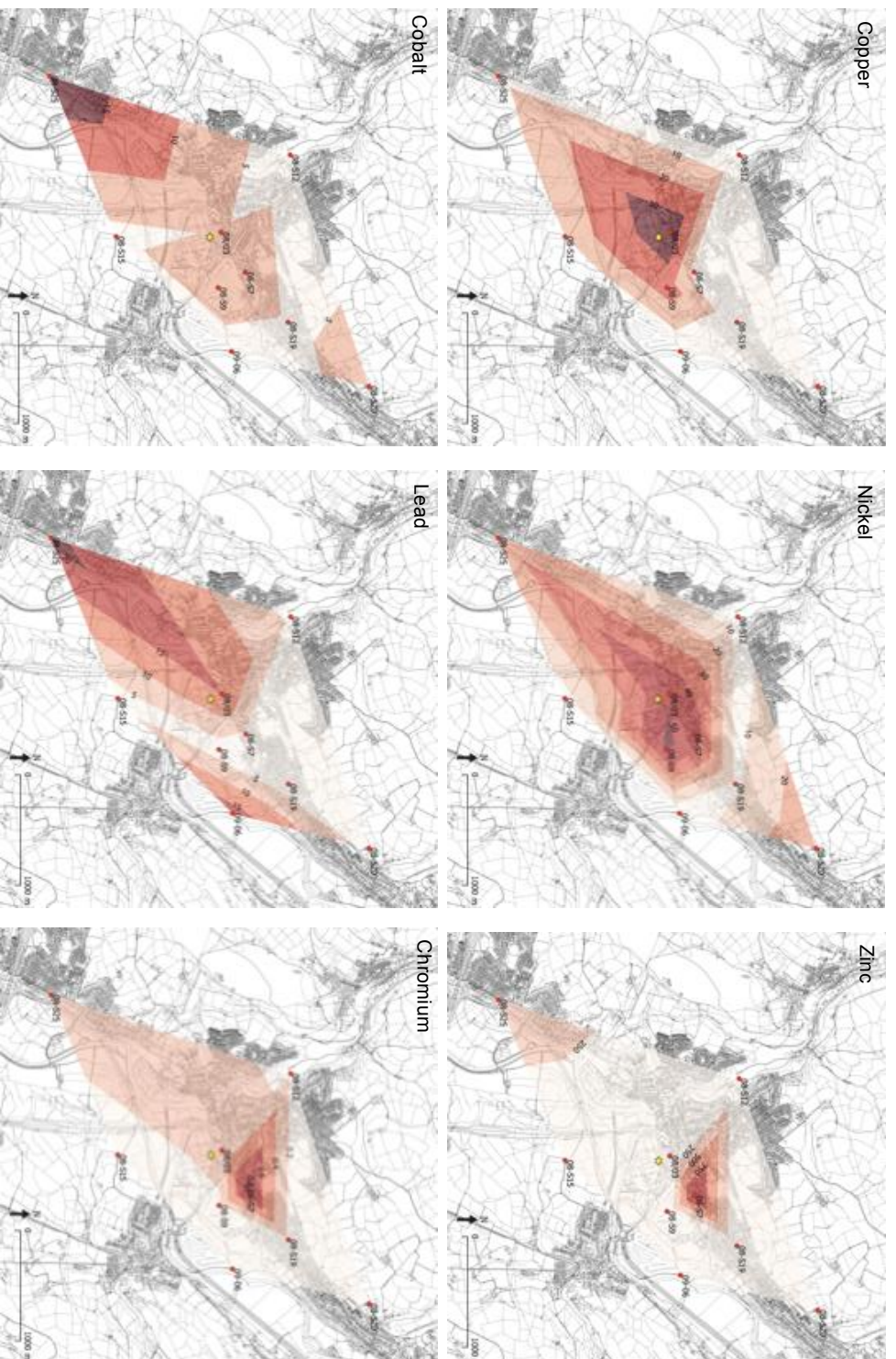


Figure 3: Spatial distribution map of bioavailable fraction of copper, nickel, zinc, cobalt, lead and chromium in topsoils. Yellow star represents the location of the smelter; red dots= sampling location.

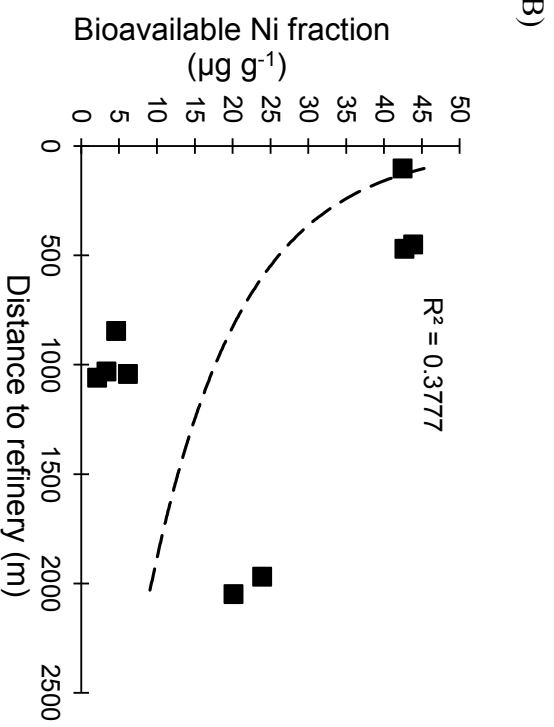
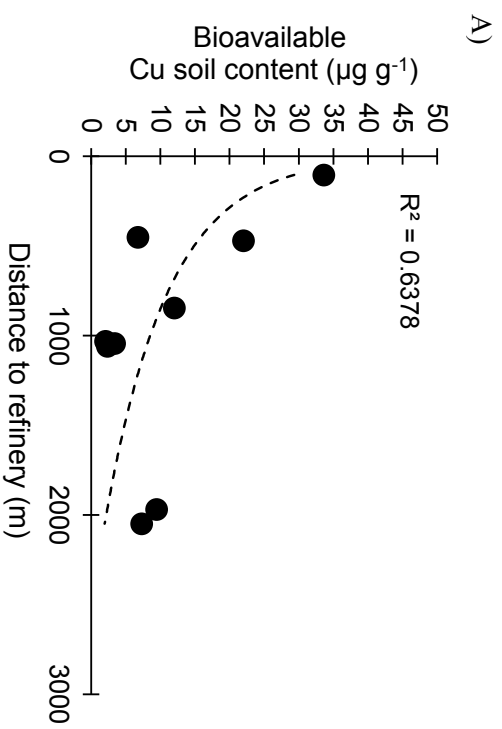


Figure 4. Concentration of bioavailable soil fraction of A) copper and B) nickel as a function of distance (in m) to the Ni refinery in Clydach. Dashed lines are the best fitted curve described as $y = ax^{-b}$ and the correlation coefficient (R^2)

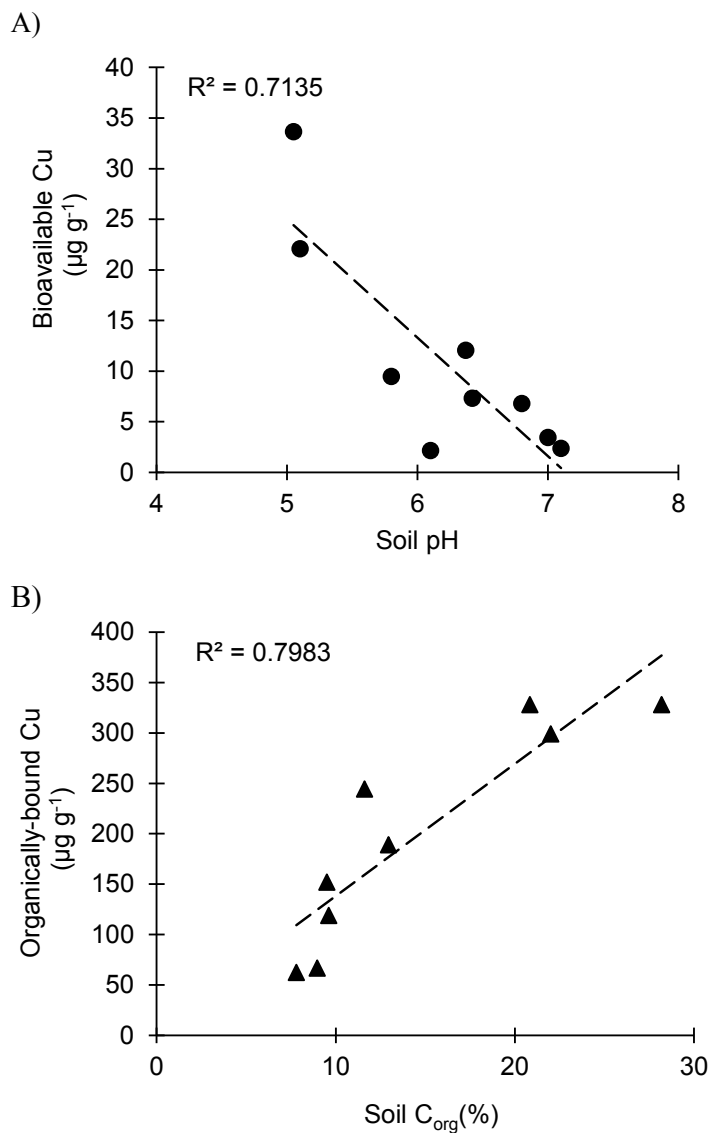


Figure 5. Relationship between A) soil pH and bioavailable Cu soil fractions and B) soil organic carbon and organically-bound Cu soil fraction. The dashed lines describe the best fit of a linear regression.

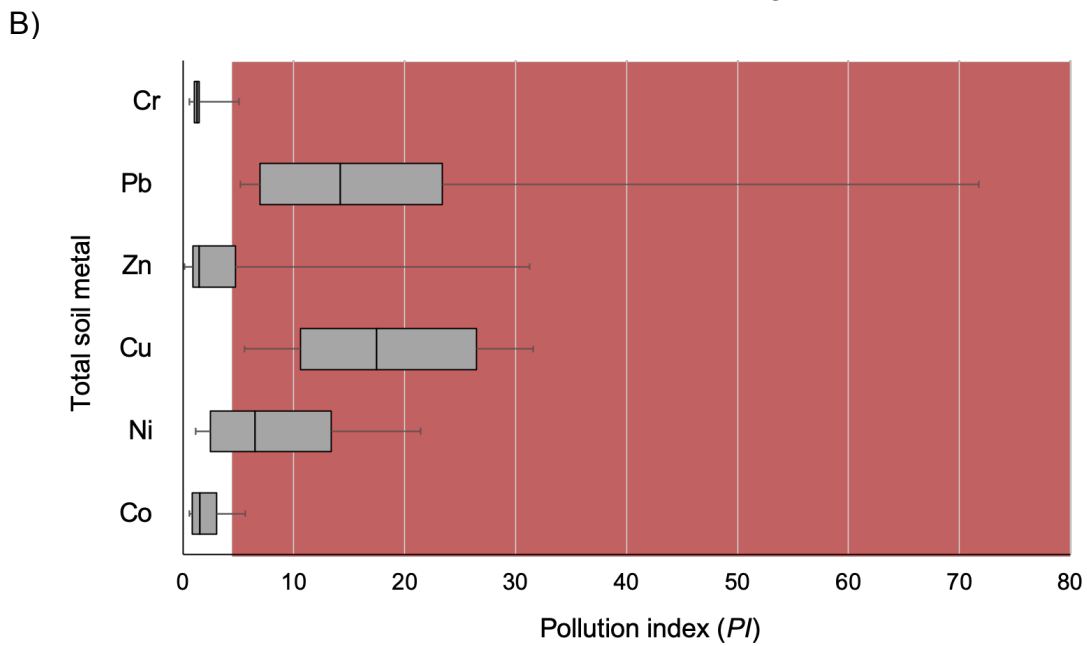
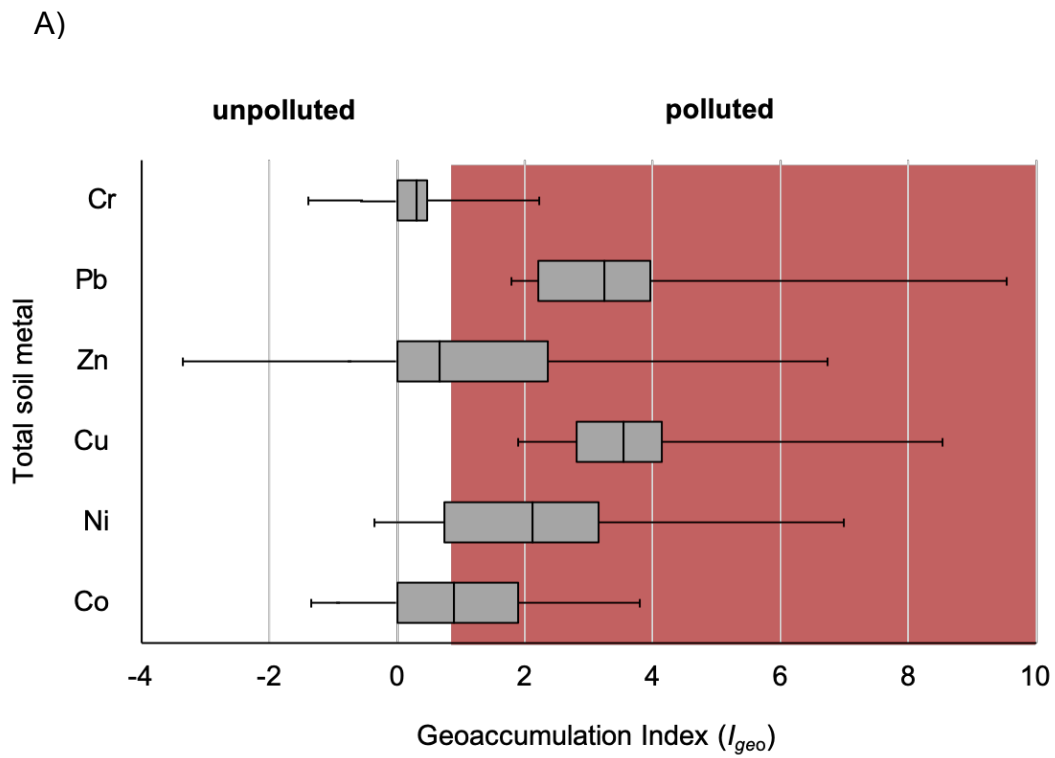


Figure 6: A) Index of geoaccumulation I_{geo} and B) pollution index (PI) of the total metal soil content (Cr, Pb, Zn, Cu, Ni and Co)

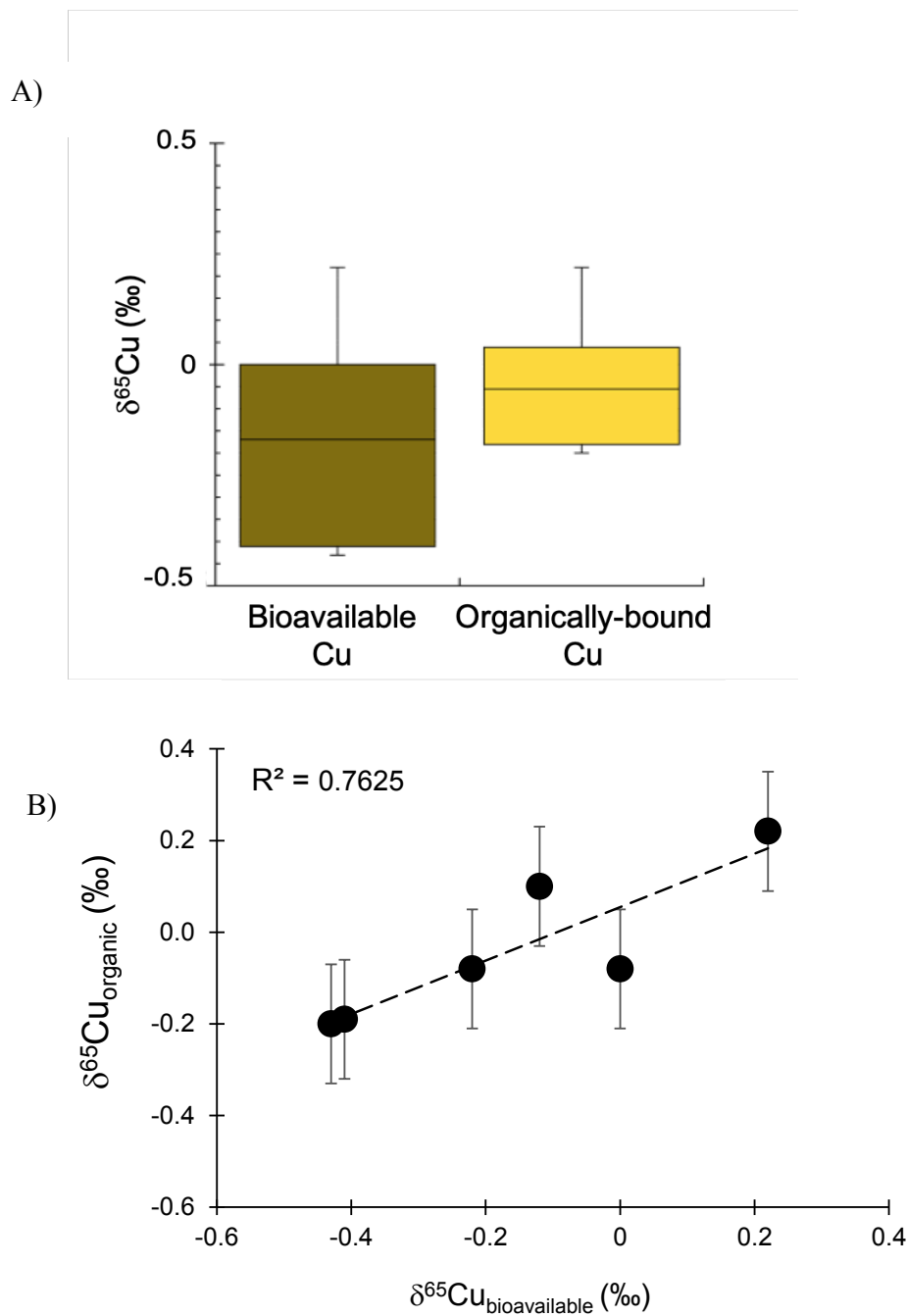


Figure 7. A) Whisker-box plot of $\delta^{65}\text{Cu}$ of the bioavailable (beige) and the organically-bound (yellow) soils fraction. For the whiskers plot the central line marks the median value. The lower quartile (25th percentile) and upper quartile (75th percentile) of the dataset and the whiskers present the most extreme data points. **B)** Relationship between $\delta^{65}\text{Cu}$ of the bioavailable soil fraction to the $\delta^{65}\text{Cu}$ of the organically-bound soils fraction. The dashed line represents the linear fit.

Table 1: Cu concentrations ($\mu\text{g g}^{-1}$) and $\delta^{65}\text{Cu}$ (‰) for operationally-defined 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)	29474	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

Supporting Information

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

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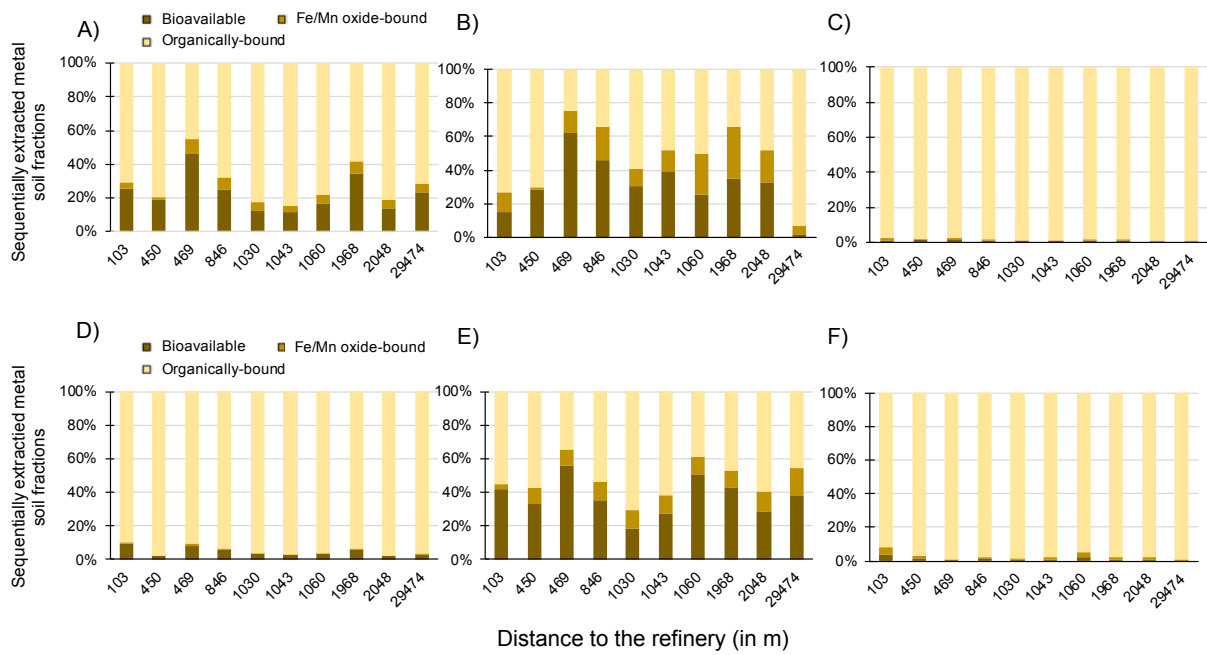


Figure S1: Sequentially extracted soil fractions (%) of A) nickel B) cobalt C) chromium D) copper E) zinc and F) lead with distance to the refinery. The extracted soil fractions include bioavailable, oxide bound and organically bound metals.

Table S1: Selected soil properties and sampling location

Sample ID	Land use/Soil description	Distance to refinery (in m)	pH	C_{org} (%)
08-C2	nd	29474	nd	10.18
08-09	Rough vegetation	469	5.1	11.6
08-S25	Road verge on the old A 4067	2048	6.42	20.83
09-06	golf course	1060	7.1	8.96
08-19	Garden soil	1043	7	9.6
08-12	Agricultural soil	1030	6.1	7.8
08-S15	Agricultural soil	846	6.37	12.94
08-20	Agricultural soil	1968	5.8	9.5
08/03	Graveyard soil	103	5.05	28.19
08-07	Agricultural soil	450	6.8	22

nd = not determined

Table S2: Metal concentration of the reference soil NIST 2711A (Montana soil) from replicate sequential extractions (n = 5).

Soil metal content soil ($\mu\text{g/g}$)						
	Cr	Co	Ni	Cu	Zn	Pb
<i>Exchangeable and bioavailable bound fraction</i>						
NIST 2711a_1	0.09	0.64	1.00	3.44	34.31	94.65
NIST 2711a_2	0.11	0.77	1.18	3.99	37.77	92.50
NIST 2711a_3	0.11	0.83	1.25	4.11	39.27	97.52
NIST 2711a_4	0.11	0.79	1.21	4.00	38.62	93.49
NIST 2711a_5	0.11	0.89	1.43	4.35	41.78	101.82
Mean	0.11	0.79	1.21	3.98	38.35	96.00
RSD	0.01	0.09	0.15	0.34	2.71	3.76
<i>Reducible fraction (bound to Fe and Mn (hydr)oxides)</i>						
NIST 2711a_1	0.01	0.95	0.38	0.51	13.87	60.83
NIST 2711a_2	0.01	1.01	0.41	0.63	14.83	79.65
NIST 2711a_3	0.01	0.99	0.43	0.64	14.77	81.24
NIST 2711a_4	0.01	1.00	0.42	0.65	15.03	81.35
NIST 2711a_5	0.01	1.00	0.41	0.63	13.41	77.61
Mean	0.01	0.99	0.41	0.61	14.38	76.13
RSD	0.00	0.02	0.02	0.06	0.70	8.69
<i>Oxidizable fraction (bound to organic matter)</i>						
NIST 2711a_1	2.26	1.52	4.08	44.52	92.78	1204.16
NIST 2711a_2	2.23	1.37	3.73	40.72	74.69	1096.89
NIST 2711a_4	2.36	1.40	3.92	47.59	56.36	1037.99
NIST 2711a_5	2.30	1.34	4.03	49.83	53.00	1099.98
Mean	2.29	1.41	3.94	45.67	69.21	1109.75
RSD	0.06	0.08	0.15	3.95	18.38	69.10

Table S3: Metal content (Cr, Co, Ni, Cu, Zn and Pb) for the operationally-defined soil fractions (i) water soluble, exchangeable and carbonate-bound (ii) bound to Fe and Mn (hydr)oxides, and (iii) bound to organic matter and sulfides with distance to the Ni refinery in Clydach, Swansea (United Kingdom).

		Soil metal concentration ($\mu\text{g g}^{-1}$)					
	Distance to refinery (m)	Cr	Co	Ni	Cu	Zn	Pb
<i>Bioavailable, exchangeable and carbonate-bound fraction</i>							
Control	29474	0.07	0.11	2.47	0.35	30.03	0.02
08-09	469	0.12	7.69	42.69	22.07	17.22	0.24
08-S25	2048	0.25	12.26	20.13	7.33	286.19	7.07
09-06	1060	0.14	1.01	2.12	2.38	188.32	9.26
08-19	1043	0.13	3.29	6.17	3.45	30.88	0.65
08-12	1030	0.14	1.66	3.36	2.14	13.99	1.29
08-S15	846	0.06	2.43	4.60	12.05	25.43	0.83
08-20	1968	0.15	3.51	23.92	9.48	52.60	0.56
08/03	103	0.15	2.99	42.43	33.66	4.86	4.63
08-07	450	0.71	8.25	43.87	6.80	811.97	3.06
<i>Reducible fraction (bound to Fe and Mn (hydr)oxides)</i>							
Control	29474	0.01	0.36	0.58	0.03	12.64	0.02
08-09	469	0.06	1.65	8.60	2.70	3.04	0.24
08-S25	2048	0.07	7.05	6.96	0.56	117.61	7.07
09-06	1060	0.02	0.95	0.62	0.16	37.82	9.26
08-19	1043	0.04	0.99	1.98	0.27	12.77	0.65
08-12	1030	0.04	0.53	1.26	0.13	8.10	1.29
08-S15	846	0.02	1.03	1.43	1.29	8.02	0.83
08-20	1968	0.04	3.07	5.55	0.91	12.86	0.56
08/03	103	0.11	2.46	7.15	4.01	0.37	4.63
08-07	450	0.15	0.48	3.34	0.54	230.49	3.06
<i>Oxidizable fraction (bound to organic matter and sulfides)</i>							
Control	29474	9.06	6.17	7.73	11.20	35.97	8.09
08-09	469	7.29	3.06	42.07	244.22	10.68	40.56
08-S25	2048	31.25	18.05	117.18	328.14	595.80	574.19
09-06	1060	9.30	1.99	9.91	66.75	145.62	348.04
08-19	1043	11.48	4.00	45.33	118.75	71.09	55.70
08-12	1030	12.97	3.19	22.39	62.19	53.53	135.96
08-S15	846	5.16	1.82	12.70	188.90	38.82	62.37
08-20	1968	12.31	3.37	40.89	151.80	57.80	52.42
08/03	103	10.66	14.55	119.41	328.14	6.36	102.99
08-07	450	45.14	20.59	183.51	298.98	1414.96	189.81

Table S4: Pollution indices [Pollution index (*PI*); Geoaccumulation index (*I_{geo}*)] for the total metal soil content and the bioavailable and exchangeable metal soil content for each metal (Co, Ni, Cu, Zn, Pb and Cr).

Pollution Index (<i>PI</i>)						
Total metal soil content						
Sample ID	Co	Ni	Cu	Zn	Pb	Cr
08-09	1.87	8.66	23.22	0.39	5.17	0.82
08-S25	5.63	13.38	29.00	12.71	71.74	3.45
09-06	0.59	1.17	5.98	4.73	44.05	1.03
08-19	1.25	4.96	10.57	1.46	6.93	1.27
08-12	0.81	2.51	5.56	0.96	16.88	1.44
08-S15	0.79	1.74	17.45	0.92	7.85	0.57
08-20	1.50	6.53	14.00	1.57	6.70	1.37
08/03	3.01	15.68	31.57	0.15	14.22	1.20
08-07	4.42	21.41	26.44	31.25	23.41	5.03
Bioavailable, exchangeable and carbonate bound fraction						
08-09	72.31	17.31	62.49	0.57	10.32	1.56
08-S25	115.19	8.16	20.75	9.53	309.36	3.41
09-06	9.49	0.86	6.73	6.27	405.38	1.86
08-19	30.92	2.50	9.77	1.03	28.61	1.77
08-12	15.65	1.36	6.06	0.47	56.65	1.82
08-S15	22.86	1.86	34.13	0.85	36.12	0.87
08-20	33.03	9.70	26.85	1.75	24.41	2.08
08/03	28.06	17.21	95.30	0.16	202.86	2.04
08-07	77.51	17.79	19.26	27.04	133.84	9.60
Class	Value of <i>PI</i>				Soil pollution*	
1	PI < 1				absent	
2	1 < PI < 2				low	
3	2 < PI < 3				moderate	
4	3 < PI < 5				strong	
5	PI > 5				very strong	

Geoaccumulation Index (<i>I_{geo}</i>)						
Total metal soil content						
Sample ID	Co	Ni	Cu	Zn	Pb	Cr
08-09	0.32	2.53	3.95	-1.93	1.79	-0.88
08-S25	1.91	3.16	4.27	3.08	5.58	1.20
09-06	-1.34	-0.35	2.00	1.66	4.88	-0.54
08-19	-0.27	1.73	2.82	-0.04	2.21	-0.24
08-12	-0.89	0.74	1.89	-0.64	3.49	-0.06
08-S15	-0.92	0.21	3.54	-0.71	2.39	-1.39
08-20	0.00	2.12	3.22	0.06	2.16	-0.13
08/03	1.01	3.39	4.40	-3.35	3.24	-0.33
08-07	1.56	3.83	4.14	4.38	3.96	1.75
Bioavailable, exchangeable fraction						
08-09	5.59	3.53	5.38	-1.39	2.78	0.06
08-S25	6.26	2.44	3.79	2.67	7.69	1.18
09-06	2.66	-0.80	2.17	2.06	8.08	0.31
08-19	4.37	0.74	2.70	-0.54	4.25	0.24
08-12	3.38	-0.14	2.02	-1.69	5.24	0.28

08-S15	3.93	0.31	4.51	-0.83	4.59	-0.79
08-20	4.46	2.69	4.16	0.22	4.02	0.47
08/03	4.23	3.52	5.99	-3.21	7.08	0.44
08-07	5.69	3.57	3.68	4.17	6.48	2.68
Class	Value of I_{geo}				Soil pollution[#]	
1	$I_{geo} > 0$				uncontaminated	
2	$0 < I_{geo} < 1$				uncontaminated to moderately contaminated	
3	$1 < I_{geo} < 2$				moderately contaminated	
4	$2 < I_{geo} < 3$				moderately to heavily contaminated	
5	$3 < I_{geo} < 4$				heavily contaminated	
6	$4 < I_{geo} < 5$				heavily to extremely contaminated	
7	$I_{geo} < 5$				extremely contaminated	

* after Kowalska et al. (2018)

after Müller (1969)