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5 **Assessing Comparative Terrestrial Ecotoxicity of Cd, Co, Cu, Ni, Pb, and Zn: The Influence**  
6 **of Aging and Emission Source**

7  
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21  
22 **Abstract**

23 Metal exposure to terrestrial organisms is influenced by the reactivity of the solid-phase metal pool.  
24 This reactivity is thought to depend on the type of emission source, on aging mechanisms that are  
25 active in the soil, and on ambient conditions. Our work shows, that when controlling for soil pH or  
26 soil organic carbon, emission source occasionally has an effect on reactivity of Cd, Co, Cu, Ni, Pb  
27 and Zn emitted from various anthropogenic sources followed by aging in the soil from a few years  
28 to two centuries. The uncertainties in estimating the age prevent definitive conclusions about the  
29 influence of aging time on the reactivity of metals from anthropogenic sources in soils. Thus, for  
30 calculating comparative toxicity potentials of man-made metal contaminations in soils, we  
31 recommend using time-horizon independent accessibility factors derived from source-specific  
32 reactive fractions.

33  
34 **Capsule abstract**

35 Improving current life cycle inventory (LCI) and life cycle impact assessment (LCIA) practice in  
36 terrestrial ecotoxicity assessment of metals.

37

## 38 **1. Introduction**

39 Life cycle assessment (LCA) is used to quantify the potential environmental impacts of goods and  
40 services (ISO, 2006). The life cycle inventory (LCI) phase of the LCA quantifies the flows of  
41 resource consumptions and emissions that are associated with the good or service (e.g., the  
42 generation of 1 kWh of electricity to the grid from a pulverized coal power plant), when considering  
43 all the processes that are involved in the whole underlying life cycle. In the life cycle impact  
44 assessment (LCIA) phase these input and output flows are translated into potential environmental  
45 impacts using substance-specific characterization factors (CF) (Hauschild, 2005). CFs are also  
46 referred to as comparative toxicity potentials (CTP) for those impacts that are related to chemical  
47 pollution. CTPs should be seen as relative performance indicators and must ensure a fair  
48 comparison between substances in terms of their potential impact on an ecosystem (Hauschild and  
49 Huijbregts, 2015). In this paper, we address two limitations of the current LCI and LCIA practice of  
50 terrestrial ecotoxicity assessment of metals, namely: (i) the reporting of anthropogenic metal  
51 emissions based on their elemental content and oxidation stage, ignoring potentially relevant  
52 information about the emission sources (e.g., deposition to soil of an airborne emission of a metal in  
53 fly ash vs. direct emission to soil of a metal in a coal slag); and (ii) the disregarding aging of the  
54 contamination in the calculation of the CTP values.

55 The CTP of a substance in soil is calculated as the product of three factors: (i) a fate factor, FF  
56 (which expresses the resident mass of the substance in soil per unit of emission flow); (ii) an  
57 exposure factor, XF (which represents the bioavailability of the substance to organisms in soil), and  
58 (iii) an effect factor, EF (which describes the ecotoxicological impacts on the soil ecosystem)  
59 (Henderson et al., 2011). In soils, apart from immediate bioavailability of a metal as influenced by  
60 the metal speciation pattern in soil pore water, the potential for metal exposure also depends on the  
61 metal's potential to undergo environmental processes (such as dissolution) from the solid phase  
62 disposing it for uptake by biota and leaching to deep soil layers or runoff to surface water  
63 (Owsianiak et al., 2013). This potential is referred to as accessibility and defined as "the mass  
64 quantity of a chemical that is or can become available within a given time span and under given  
65 conditions" (Reichenberg and Mayer, 2006). To take into account the influence of the accessible  
66 metal pool in the soil, the XF of metals in soils has recently been defined as the product of an  
67 accessibility factor, ACF (representing the accessible fraction of the total metal in the soil) and a  
68 bioavailability factor, BF (that represents the fraction of the accessible metal in the soil that is  
69 present in directly bioavailable, toxic forms) (Owsianiak et al., 2013).

70 The accessible metal pool is often approximated by “available” metal measured with diffusive  
71 gradient in thin films ) or by “reactive” metal (also called “labile” or “exchangeable”) measured  
72 with single or sequential extraction procedures (SEP) or isotope-based methods (Hamon et al.,  
73 2008, 2002; Harper et al., 1998; Rodrigues et al., 2010; Zhang et al., 2004). Recently, Hamels et al.  
74 (2014) showed that the isotopically exchangeable fraction of the total soil metal in field-  
75 contaminated soils explained lower toxicity of metals as compared with spiked soils. The term  
76 “reactive” is based on the operational definition presented in Degryse et al. (2009) as metal in the  
77 solid phase that “equilibrates with the solution phase within a few days”. The reactive metal  
78 typically includes outer-sphere and weakly bound inner-sphere complexes on mineral surfaces or  
79 organic matter and should not be confused with the “chemically labile” metal (Sarret et al., 2004).  
80 The latter may include strongly sorbed inner-sphere complexes which are chemically reactive, but  
81 not necessarily available for solid-liquid partitioning within a time scale of days (Hamon et al.,  
82 2008). Reversible transformations between chemically labile (but often non-reactive) and reactive  
83 metal pools can occur, implying that the size of the reactive fraction in soil can change with the  
84 aging time. The reactivity of a metal in soil can vary depending on the anthropogenic source from  
85 which it is emitted (Degryse et al., 2004; Roberts et al., 2002; Vespa et al., 2010) and furthermore it  
86 can increase with time due to weathering (resulting in destruction of chemical bonds, most often  
87 those between metal and oxygen) (Casey et al., 1993) or it can decrease with time due to fixation in  
88 the soil through short- and long-term reactions with soil constituents (Buekers et al., 2008b; Crout  
89 et al., 2006; Ma et al., 2013, 2006; Wendling et al., 2009).

90 To accommodate these potentially important influences on the metal ecotoxicity in LCA, some  
91 modifications and further developments of the methodology are needed: (i) in the LCI phase, metal  
92 emissions should be reported together with sufficient information to allow capturing the differences  
93 that exist in reactivity between the various chemical forms that are present in the emissions from  
94 different sources; (ii) in the LCIA phase, CTPs for the metal of interest have to be available that  
95 match the information from the emission inventory and represent the ecotoxicity potential of the  
96 different metal forms; and (iii) in the LCIA phase, such a set of CTPs for the metal of interest has to  
97 consider metal aging in the soil, as influenced both by soil properties and by the aging pattern  
98 exhibited by the different metal forms reported in the LCI phase.

99 The aim of our study is to present the methodology needed to improve current LCI and LCIA  
100 practice in terrestrial ecotoxicity assessment of metals in soil, and to make it operational for the  
101 metals Cd, Co, Cu, Ni, Pb, and Zn. We first present a conceptual aging model for metals in soils  
102 and propose a framework for inclusion of aging in calculation of CTPs of metals in soils. In the  
103 second part of the study, we determine the important factors for the reactivity of the six metals

104 (such as metal emission source, soil properties, aging time in the soil, and the rate of water  
 105 exchange on metal ions) based on empirical data from an extensive literature review, and show how  
 106 reactivity affects CTP of the studied metals. The empirical data represent particle-bound metal in  
 107 fly ashes, metal occluded in biosolids and other organic matrices, and metal released from mining  
 108 activities or industrial waste, which together constitute the major sources of anthropogenic metals in  
 109 soils (Nicholson et al., 2003). The age of the man-made metal contamination in many cases had to  
 110 be assumed and is therefore uncertain. Furthermore, the availability of measured data for some  
 111 potentially important soil properties, is limited. Therefore, insights into aging mechanisms had to be  
 112 gained by comparison with metal reactivity measured in soils spiked with soluble metal ion salts  
 113 and soils contaminated with geogenic metal, and by comparison with predictions of existing kinetic  
 114 aging models and empirical regression models.

115

## 116 **2. Methods**

### 117 *2.1. Definitions and Presentation of a Conceptual Aging Model for Metals in Soil*

118 Aging of a Metal in Soil is defined as “change in solid-phase reactivity of a metal in soil over time”.  
 119 This includes fixation that reduces metal reactivity (up to now referred to just as “aging” for soils  
 120 spiked with soluble salts), and weathering that potentially increases metal reactivity in soils.

121

122 Time-Dependent Reactive Fraction of a Metal in Soil ( $f_{\text{reactive}}$ ,  $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) represents the  
 123 fraction of total metal in soil at that is available for solid-liquid partitioning within a time scale of  
 124 days as it varies with the aging time  $t$  (in years) of the metal in the soil (eq 1).

$$125 \quad f_{\text{reactive}}(t) = \frac{C_{\text{reactive}}(t)}{C_{\text{total}}(t)} = \frac{s_{\text{reactive solid}}(t) + L/S \cdot c_{\text{total dissolved}}(t)}{s_{\text{total solid}}(t) + L/S \cdot c_{\text{total dissolved}}(t)} \quad \text{eq 1}$$

126 where  $C_{\text{reactive}}(t)$  ( $\text{kg}_{\text{reactive}}/\text{kg}_{\text{soil}}$ ) and  $C_{\text{total}}(t)$  ( $\text{kg}_{\text{total}}/\text{kg}_{\text{soil}}$ ) are the concentrations of reactive metal  
 127 and total metal in soil at time  $t$  (year), respectively;  $s_{\text{reactive solid}}(t)$  ( $\text{kg}_{\text{reactive solid}}/\text{kg}_{\text{solid}}$ ) and  $s_{\text{total solid}}(t)$   
 128 ( $\text{kg}_{\text{total solid}}/\text{kg}_{\text{solid}}$ ) are the concentrations of reactive metal and total metal in the solid phase at time  
 129  $t$ , respectively;  $c_{\text{total dissolved}}(t)$  ( $\text{kg}_{\text{total dissolved}}/L_{\text{pore water}}$ ) is the concentration of total dissolved metal  
 130 (assumed reactive) in soil pore water at time  $t$ ; and  $L/S$  ( $L_{\text{pore water}}/\text{kg}_{\text{soil}}$ ) is the ratio of pore water  
 131 volume to soil mass.

132

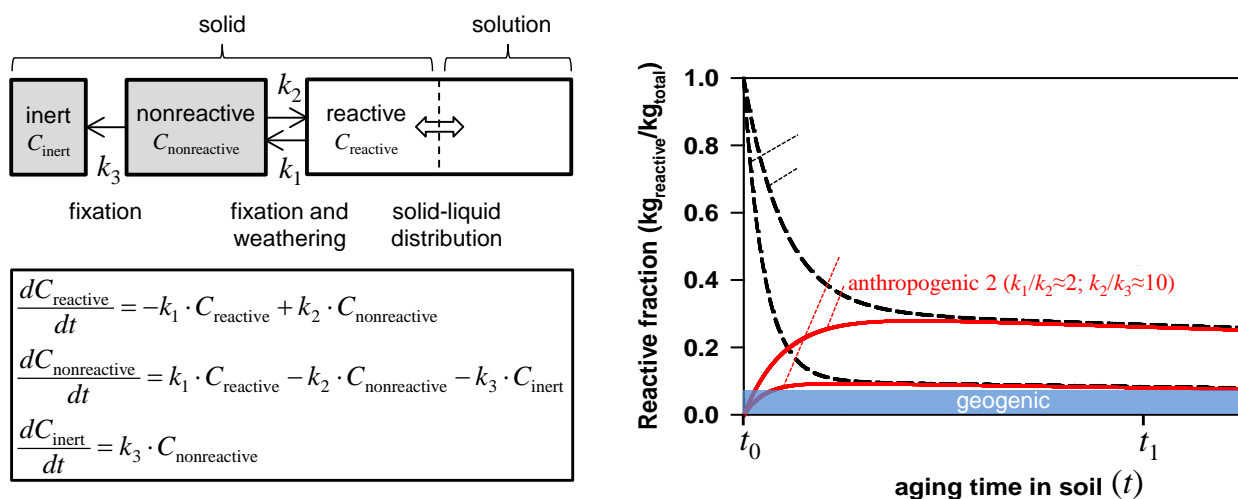
133 Conceptual Aging Model for Metals in Soil. Figure 1 illustrates the temporal evolution of the  
 134 reactive fraction of a metal in a soil that is either spiked with readily soluble salt of the metal or is  
 135 contaminated with an anthropogenic non-reactive form of the metal. The evolution is predicted

136 using a three-compartment conceptual aging model, developed from a two-compartment model  
137 presented by Crout et al. (2006). The model takes into account reversible, exchange between  
138 reactive and nonreactive (but chemically labile) compartments, obeying first-order kinetics. In  
139 addition, to capture long-term aging mechanisms, an additional irreversible first order exchange  
140 between nonreactive (but chemically labile) and inert (chemically not labile) metal pools had been  
141 incorporated (Amacher, 1991; Davis et al., 1994).

142 The model is conceptual as it does not take into account various processes that may alter the  
143 shape of reactivity curves, such as the possibility of biphasic exchange kinetics, the presence of  
144 several metal pools with pool-specific exchange rate constants, very slow release of a metal from  
145 the inert metal pool, or mobilization of strongly bound metal phases in plant rhizosphere in the  
146 events of nutrient deficiency (Hinsinger, 2001). Yet, it allows us to illustrate how temporal  
147 developments of the reactive fraction may depend on the form in which the metal is emitted and on  
148 rate constants for the fixation and weathering reactions. The reactive fraction of a readily soluble  
149 salt of the metal is initially (at time  $t_0$ ) equal to 1, but it can be reduced due to fixation into soil  
150 constituents ( $t_0$  to  $t_1$ ). This fixation mechanism occurs readily in spiked soils (Buekers et al., 2007;  
151 Crout et al., 2006). In contrast, the reactive fraction of an anthropogenic emission of the metal is  
152 expected to be lower initially (equal to 0 in the extreme case, as was assumed here), but can  
153 increase due to weathering ( $t_0$  to  $t_1$ ) and then decrease due to fixation (after  $t_1$ ). For example,  
154 weathering of metal sulfides (CdS, CuS, or PbS) in mine tailings through oxidation and dissolution  
155 of the primary sulfide increases reactive fraction initially; metals will form reactive outer-sphere  
156 and weakly bound inner-sphere complexes on mineral surfaces or organic matter (Ribeta et al.,  
157 1995). If soil is limed to neutralize its acidity, however, metals will precipitate because of formation  
158 of poorly-ordered (amorphous) oxides and/or carbonates that are not reactive. These poorly-ordered  
159 minerals will over time change to well-ordered (crystalline) minerals that can be inert; time ranges  
160 required to attain equilibrium for crystallization reactions in soils are in range of years to millennia  
161 (Amacher, 1991; Sparks, 2000). The fixation of the non-reactive metal pool into the inert pool is  
162 expected to further contribute to reduce the reactive fraction of anthropogenic metal at longer-time  
163 scales (after  $t_1$ ). On the other hand, if the soil is not limed, the reactive fraction is expected to  
164 remain at a higher level as compared to limed soils (Ahnstrom and Parker, 2001; Li et al., 2014;  
165 Nakhone and Young, 1993). If metal is occluded in solid particles (as e.g. ZnO in car tire debris),  
166 the solid phase matrix in which the metal is emitted may influence weathering kinetics by slowing  
167 down metal release from the matrix (Rhodes et al., 2012; Smolders and Degryse, 2002)

168 We hypothesize that after a certain time  $t_1$  long-term aging mechanisms will eventually lead to  
169 formation of the same chemical forms in the soils, regardless of the initial emission source, and it

170 will no longer be possible to distinguish between metals from spiked and anthropogenic sources.  
 171 This time may be several hundreds or thousands of years, depending on the dominant aging  
 172 mechanisms and their rates. If metal forms in the soil at  $t_1$  are the same regardless the initial  
 173 emission form of the metal, aging mechanisms that occur after  $t_1$  will be the same. We also  
 174 hypothesize that as aging time goes toward infinite time, metal reactivity may become equal to the  
 175 reactivity of the metal constituting the geogenic background. This is because metal forms derived  
 176 from either initial form of the metal may over very long (sufficient) time end as the same as in the  
 177 background and it will no longer be possible to distinguish whether the metal is geogenic or from an  
 178 anthropogenic emission. In practice, this situation may never be reached, as processes that influence  
 179 the ultimate fate of the soil such as erosion by surface water or glacial events, will also determine  
 180 the ultimate fate of metal present in the soil. However, Vespa et al. (2010) showed that Zn  
 181 phyllosilicate species formed from smelter-related ZnS and ZnO were analogous to the native  
 182 phyllosilicate species which formed over time during pedogenesis.



183  
 184 Fig. 1. Left panel shows a three-compartment conceptual aging model for metals in soil; right panel  
 185 shows predicted evolution of the reactive fraction ( $f_{\text{reactive}}$ , in  $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) of a metal in soil  
 186 spiked with readily soluble metal salt assumed to be 100% reactive initially (black dashed lines),  
 187 and in soil contaminated with metal from an anthropogenic source (red lines) assumed to be 100%  
 188 nonreactive initially, shown against the background reactivity of geogenic metal. Predictions are  
 189 shown for two sets of first order exchange rate constants for the fixation and weathering reactions  
 190 ( $k_1$ ,  $k_2$  and  $k_3$ , in  $\text{day}^{-1}$ ).

191  
 192 2.2. Framework for Inclusion of Aging in Calculation of Comparative Toxicity Potentials of Metals  
 193 in Soils



194 Time-Horizon Dependent Accessibility Factor of a Metal in Soil ( $ACF^T$ ,  $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) represents  
 195 the reactive fraction  $f_{\text{reactive}}$  integrated over the metal's aging time  $t$  (in years) in the soil, from  $t=0$  to  
 196  $t=T$  (where  $T$  is the chosen time-horizon, in years) divided by the  $T$  (eq 2). This definition of the  
 197 ACF builds on that proposed earlier in Owsianiak et al. (2013) where ACF was assumed equal to  
 198 (time-independent)  $f_{\text{reactive}}$  and no time-horizon dependency of the ACF was considered.

$$199 \quad ACF^T = \frac{\int_0^T f_{\text{reactive}}(t) dt}{T} \quad \text{eq 2}$$

201 Time-Dependent Distribution Coefficient between Total Solid Phase and Solution Phase

202 ( $K_{\text{d,total}}(t)$ , in  $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$ ) is calculated from the time-dependent solid-phase reactivity of the  
 203 metal and its time-independent distribution coefficient between reactive solid phase and solution  
 204 phase ( $K_{\text{d,reactive}}$ , in  $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$ ) (eq 3). Because the amount of metal in solution ( $L/S \cdot c_{\text{pore water}}$  in  
 205 eq 1) is usually very small in soils compared with the total metal concentration (Buekers et al.,  
 206 2008a) this solid-phase reactivity can be approximated by  $f_{\text{reactive}}$ .

$$207 \quad K_{\text{d,total}}(t) = K_{\text{d,reactive}} \cdot \frac{s_{\text{total}}(t)}{s_{\text{reactive}}(t)} \approx \frac{K_{\text{d,reactive}}}{f_{\text{reactive}}(t)} \quad \text{eq 3}$$

209 Time-Horizon Dependent Distribution Coefficient between Total Solid Phase and Solution Phase (

210  $K_{\text{d,total}}^T$ , in  $\text{L}_{\text{pore water}}/\text{kg}_{\text{solid}}$ ; eq 4) can be applied for calculating time-horizon dependent fate factors  
 211 (FF) to compensate for the fact that time-dependent partitioning is not considered in existing  
 212 multimedia fate models.

$$213 \quad K_{\text{d,total}}^T \approx \frac{K_{\text{d,reactive}}}{ACF^T} \quad \text{eq 4}$$

214 Time-Horizon Dependent Comparative Toxicity Potential ( $CTP_c^T$ , in  $\text{m}^3/\text{kg}_{\text{total emitted}} \cdot \text{day}$ ; eq 5) of a

215 metal in soil after a unit emission to compartment  $c$  for the time horizon  $T$ , is calculated as  
 216 (Owsianiak et al., 2013):

$$217 \quad CTP_c^T = FF_c^T \cdot ACF^T \cdot BF \cdot EF \quad \text{eq 5}$$

218 where  $FF_c^T$  (in days) is the time-horizon dependent fate factor in soil calculated for total metal  
 219 emitted to compartment  $c$  calculated using  $K_{d,total}^T$  values;  $ACF^T$  ( $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) is the time-  
 220 horizon dependent accessibility factor;  $BF$  ( $\text{kg}_{\text{free}}/\text{kg}_{\text{reactive}}$ ) is the time-horizon independent  
 221 bioavailability factor defined as the free ion fraction of the reactive metal in soil, and  $EF$  ( $\text{m}^3/\text{kg}_{\text{free}}$ )  
 222 is the time-horizon independent terrestrial ecotoxicity effect factor defined as potentially affected  
 223 fraction (PAF) of species for the free ion form of the metal.<sup>43</sup>

224 Metal aging will influence CTP of a metal through its control of both fate and accessibility. A  
 225 reduction in reactive fraction increases  $K_{d,total}^T$  and thereby the FF, because metal's residence time in  
 226 soil increases with an increase in  $K_{d,total}^T$  (Owsianiak et al., 2013). This leads to increasing the CTP.  
 227 On the other hand, a reduction in reactive fraction reduces the ACF, which leads to decreasing the  
 228 CTP. These two effects only partly compensate each other, because metal fate in soil also depends  
 229 on the loss of the soil to surface water through soil erosion. The influence of metal aging on CTP is  
 230 expected to be higher for those metals, for which  $K_{d,reactive}$  is high. To illustrate this, we compared  
 231 CTPs calculated for the infinite time horizon assuming reactive fraction equal to  $1 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ,  
 232 with the CTPs calculated for the ACFs derived from reactive fractions as determined in the current  
 233 study (which were always below  $1 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ). The FFs were calculated employing USEtox  
 234 using  $K_{d,total}$  values estimated from  $K_{d,reactive}$  and the corresponding ACFs (eq 4), assuming default  
 235 values of 0.03 mm/yr for the soil erosion rate and 0.1 m for soil depth (Rosenbaum et al., 2008).  
 236 Details of the calculations are presented in Appendix 1, Section A5.

$$237 \frac{CTP_{ACF=f(f_{\text{reactive}})}}{CTP_{ACF=1}} = \frac{FF_{ACF=f(f_{\text{reactive}})} \cdot ACF_{ACF=f(f_{\text{reactive}})} \cdot BF \cdot EF}{FF_{ACF=1} \cdot 1 \cdot BF \cdot EF} = ACF_{ACF=f(f_{\text{reactive}})} \cdot \frac{FF_{ACF=f(f_{\text{reactive}})}}{FF_{ACF=1}} \quad \text{eq 6}$$

238

### 239 2.3. Data Collection and Treatment

240 Metals were included if data on reactive fraction for at least two different emission sources could be  
 241 found. We thus included Cd, Co, Cu, Ni, Pb and Zn, and excluded Ag, Al and Fe (Collins and  
 242 Waite, 2009; Gabler et al., 1999; Settimo et al., 2014). Data for the three latter were, however, used  
 243 to see if our findings about factors controlling metal reactivity in soils apply also to other metals.  
 244 Data were retrieved from peer-reviewed studies available until April 2013 identified through  
 245 searching the ISI Web of Knowledge, version 5.7 (Thomson Reuters, New York, NY), using a  
 246 combination of keywords: (i) isotop\*; and either (ii) exchang\*, or dilute\*; and either (iii) labil\*, or  
 247 soil\*; and either (iv) Cd, Co, Cu, Ni, Pb, Zn, cadm\*, cobalt\*, copp\*, nick\*, lead, or zinc\*. A  
 248 complementary search was conducted in ISI to retrieve publications citing references retrieved in

249 the previous step, and those which were cited in the collected publications, but were not found  
250 through the initial search in ISI. The two latter steps were iterated until no new data were found. A  
251 study of Degryse et al. (2004) containing data on reactivity of various anthropogenic forms of Cd  
252 and Zn is excluded and was used to compare our results with their findings, as is a recent study of  
253 Marzouk et al. (2013) containing data on reactivity of anthropogenic forms of Cd, Pb and Zn that  
254 was published after the searching had been done. Data were included if the following criteria were  
255 met: (i) emission source was reported; (ii) reactive fraction or reactive concentration were measured  
256 in soils; and (iii) reactive fraction or reactive concentration were measured using isotope dilution  
257 methods. The last criterion was applied to minimize uncertainties associated with the determination  
258 of the concentration of reactive metal in soil; others showed the lack of correspondence between  
259 metal fractions extracted using sequential extraction procedures and the size of reactive metal pool  
260 measured using isotope-based methods (Ahnstrom and Parker, 2001). We combined methods that  
261 measure either isotopically exchangeable (comprising reactive metal in the solid-phase only) or  
262 isotopically available (comprising reactive metal both in the solid phase and in the soil solution)  
263 pools to increase the number of data. This can introduce an error of >10% if soil sorption capacity is  
264 low (Hamon et al., 2002). Details of harmonization of soil properties and descriptive statistics are  
265 presented in Appendix A, Section A1.

266  
267 Classification of Emission Sources. Data were first classified into three major categories: (i)  
268 “spiked” for soils spiked with soluble salts; (ii) “anthropogenic” for soils contaminated with  
269 primarily solid-phase metal of anthropogenic origin, excluding nanoparticles and massive products  
270 such as Cu ingots which are outside the scope of this study; and (iii) “geogenic” for soils  
271 contaminated with primarily solid-phase metal forms of geogenic origin.

272 Anthropogenic emissions that originate from similar processes or are similar with regard to the  
273 composition of the matrix surrounding the metal in the emission are expected to have similar  
274 chemical composition. For example, metal oxides are typically created during combustion processes  
275 in power plants, smelters or incinerators, mining-related metal emissions can contain a large  
276 proportion of metal sulfides, while metals found in biosolids or those found in wastewater are likely  
277 to be found in association with organic carbon. It is thus hypothesized that statistically significant  
278 differences in reactive fraction between these emissions source classes can be found. Therefore,  
279 the “anthropogenic” category was further classified into four subcategories: (i) “airborne” including  
280 emissions from smelters, metal refineries, factories, combustion of petrol, and unspecified  
281 atmospheric deposition; (ii) “organic-related” including direct application of biosolids, manure,  
282 compost, or wastewater irrigation; (iii) “mining and industrial waste” including emissions from

283 mine spoils, mining-affected sediment, material containing metal ores, alluvial deposition,  
284 unspecified industrial waste, and technosols; and (iv) “other anthropogenic” including emissions  
285 from ZnO (isolated or in tire debris), mixed anthropogenic sources, unspecified anthropogenic  
286 sources, and dissolved metal forms of anthropogenic origin (such as Cd present as a co-contaminant  
287 in phosphate fertilizer or Cu sulfate applied as a fungicide, or aqueous Zn dissolving from  
288 galvanized power lines). It was assumed that if one emission source was given in the respective  
289 publication, that source was the sole metal source in the soil. Mixed anthropogenic sources were  
290 classified as other anthropogenic because no information could be retrieved about the dominant  
291 metal source in the included soils. Note, that in contrast to many studies for readily soluble salts,  
292 metal reactivity in anthropogenically contaminated soils cannot be attributed exclusively to  
293 anthropogenic sources because reactivity of geogenic metal prior to anthropogenic input is not  
294 known.

295

296 Estimation of Aging Time in Soil. A metal's aging time in soil (ideally) represents the time that the  
297 metal has been in soil prior to the measurement of its reactivity. To get more insight into the  
298 influence of contamination age on metal reactivity for anthropogenic sources, we often had to make  
299 assumptions about the age by setting it equal to the time from the emission peak to the publication  
300 year, or equal to half of the time interval between start and termination of the emission (if emission  
301 peak was not reported). If an emission was reported to have occurred for more than or less than a  
302 certain time period, contamination age was assumed equal to the starting date plus double or half  
303 the length of that time period, respectively. If only a century of emission start was reported, time  
304 from the middle of that century to publication year was assumed as the age. If the emission source  
305 could be unambiguously identified, and information on contamination age could be retrieved from  
306 sources reporting emission data this information was used as the contamination age for that source.  
307 Acknowledging the uncertainty in estimating the age, the anthropogenic contaminations were  
308 classified into 5 age groups: (1) from 0 to 20 years; (2) from 20 to 50 years; (3) from 50 to 100  
309 years; (4) from 100 to 150 years; and (5) from 150 to 220 years. Spiked soils, where aging time is  
310 certain, were classified into 2 age groups: (I) from 0 to 0.5 years; and (II) from 0.5 to 2.5 years.

311

#### 312 *2.4. Analysis of Covariance (ANCOVA) and Wilcox Procedures*

313 To increase the opportunity to find statistical significance of the effects of metal emission source on  
314 reactive fraction while controlling for the effect of given soil property, we used one-way analysis of  
315 covariance (ANCOVA), as explained in Appendix A, section A2. ANCOVA models were  
316 expressed as ordinary least squares (OLS) regression models with the metal source term coded

317 employing the effect coding system and a given soil property being a covariate. If non-constant  
318 variance related to the source term was identified, weighted least squares (WLS) regression was  
319 employed with weights being based on the metal source. Models were developed for each soil  
320 property separately. Logit-transformation of  $f_{\text{reactive}}$  was done when it improved normality of  
321 distribution of the independent variable (in practice for all metals except of Cd), consistently with  
322 the ANCOVA assumption, and was chosen among other transformation types as it an appropriate  
323 transformation option for proportions. To identify where significant differences in (logit-  
324 transformed, apart from Cd)  $f_{\text{reactive}}$  between metal emission sources occur, ANCOVA was followed  
325 by post-hoc multiple comparison tests based on the Tukey HDS method (employing the `glht`  
326 function available in the R package `multcomp`) controlling for the soil property explaining the  
327 largest part of the variance in the (logit-transformed, apart from Cd)  $f_{\text{reactive}}$ . In cases where  
328 regression slopes were not homogeneous, the Wilcox modification of the Johnson-Neyman (J-N)  
329 procedure was performed for pairwise comparisons as it allows identifying ranges of a soil property  
330 where significant differences in metal reactivity between emission sources occur. Similarly, to test  
331 for the effect of aging, pairwise comparisons between age groups for each anthropogenic source.  
332 Comparisons were also made between anthropogenic sources and the two age groups for spiked  
333 soils. OLS and WLS regression models were developed by R version 3.1.2 (R Core Team, Vienna,  
334 Austria). The Wilcox procedure was executed using the program `WILCOX.exe` written by  
335 Constable. Details of the analyses are presented in the Appendix A, Section A2.

336

### 337 **3. Results and discussion**

338 Below, we show how reactive fraction depends on emission source and aging time in the soil. We  
339 also show how it relates to a metal-specific property, the metal's water exchange rate constant.  
340 Implications of our findings for reporting and impact assessment of anthropogenic metal emissions,  
341 are then discussed.

342

#### 343 *3.1. Does Emission Source Matter?*

344 Figure 2 (left panel) shows the variability in the reactive fraction of the metals as influenced by  
345 metal source. One-way ANCOVA and WILCOX procedures revealed statistically significant  
346 differences between geogenic and various anthropogenic forms of Cd, Co, Cu and Zn (Table 1)  
347 when the covarying effects of soil pH or soil organic carbon are taken into account. Across these  
348 metals, anthropogenic sources generally have higher reactive fraction as compared to geogenic  
349 metals forms, apart from Cd where the opposite is the case. No differences were found between

350 geogenic and various anthropogenic sources for Ni and Pb. Between anthropogenic forms of Cd,  
351 Co, Cu and Zn, statistically significant differences in the reactive fraction were found occasionally.  
352 Again, no differences were found between anthropogenic sources for Ni and Pb.

353 A significant effect of anthropogenic metal source on reactive fraction of the studied metals  
354 was not unexpected, particularly for Zn where the differences in reactive fraction were the most  
355 apparent. Molina et al. (2013) showed that reactivity of Zn in pure-phase minerals and mine waste  
356 varied between chemical forms of Zn. Also Degryse et al. (2011) showed that Zn layered double  
357 hydroxide (Zn-LDH) and Zn in hydroxy-interlayered minerals (Zn-HIM), which are common forms  
358 of Zn in soils, had relatively low reactivity compared to other common forms of Zn, such as zinc  
359 carbonate ( $\text{ZnCO}_3$ ) and hydrozincite ( $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ ). The differences in reactive fraction of  
360 different forms of Zn can be explained by their differences in resistance to proton-promoted  
361 dissolution. This is supported by the fact that we found a small negative effect of soil pH on  
362 reactivity of Zn, and may suggest that the soils included contained forms of a metal that are not  
363 resistant to proton-promoted dissolution, such as Zn-LDH or carbonates, with relatively small  
364 contribution of forms more resistant to proton-promoted dissolution, such as Zn-HIM (Degryse et  
365 al., 2011; Khaokaew et al., 2012). Jacquat et al. (2009) showed that Zn in primary smelter minerals  
366 accounted for only 5% of total Zn in the bulk soil.

367 In many cases we found no consistent effect of emission source on reactivity of other sources  
368 and metals. This could be partly by explained by low number of data points for individual emission  
369 sources, combined with limited information on potentially relevant soil parameters, such as content  
370 of Al or Mn (hydr)oxides that were not available for all data points collected. Differences in  
371 reactive fraction between metal sources due to differences in resistance to proton-promoted  
372 dissolution of metal forms could be expected for other metals as well (Peltier et al., 2010; Voegelin  
373 and Kretzschmar, 2005), and we did find a small negative effect of soil pH on the reactivity of Cd,  
374 Cu, and Pb. Yet, for Ni and Pb we did not find any differences between anthropogenic and geogenic  
375 sources at all. This might be because metal forms in the emitted material either transform to forms  
376 for which reactivity is close to the reactivity of the geogenic background, or transform to forms  
377 constituting the geogenic background. Ettler et al. (2012) showed that dissolution of primary Pb  
378 minerals (caracolite and K-Pb chloride) in a smelter fly ash led to formation of secondary anglesite,  
379 minor Pb sulfate, and trace cerussite in soils, whereas about half of total Pb originating from mine  
380 tailings and smelters was included in Fe- and Mn-(oxyhydr)oxides (Morin et al., 1999) which are  
381 common geogenic forms of Pb (Teutsch et al., 1999). Published regression models developed for  
382 soils contaminated with anthropogenic and/or geogenic metal generally predict reactive metal  
383 concentrations within one order of magnitude around the measured values (see Appendix 1, Section

384 A4). Thus, the published models do not allow distinguishing between various anthropogenic  
385 contamination forms as the error of prediction of the reactive fraction for the six studied metals  
386 using any regression model is similar to the variability in the reactive fraction that is also within one  
387 order of magnitude (see Appendix 1, Section A4). This supports our findings about some  
388 difficulties to capture influence of contamination form on reactivity of anthropogenic metals in  
389 soils.

390 Reactive fraction of Cd, Cu, Pb and Zn generally decreases with soil pH. Reactivity of Co and  
391 Ni increases with an increase in organic carbon content of the soil but for Cd regression slopes are  
392 not homogeneous; reactivity of organic-related Cd is significantly different from that measured for  
393 both airborne and geogenic sources of Cd in acidic soils (pH<6.2) only (Table 1). These findings  
394 are in agreement with Marzouk et al. (2013) who also found a negative effect of soil pH on  
395 reactivity of Cd, Pb and Zn for a large set of 246 mining-impacted soils, and also in agreement with  
396 Degryse et al. (2004) who found weak correlations between pH and reactive Zn in soils for a set of  
397 74 soils contaminated with metals from various sources. By contrast, Degryse et al. (2004) did not  
398 find any pH effect for Cd. We also found a small positive effect of soil organic carbon on reactivity  
399 of Co and Ni. Differences in number of soils included for the different metals, combined with the  
400 associated differences in property ranges between the soils in our data set may also explain why we  
401 are not able to see any influence of organic carbon for Cd, Cu, Pb and Zn. Metals bound to organic  
402 carbon are generally reactive in soils (Sarret et al., 2004), but soils spanning a rather wide range of  
403 soil organic carbon content are needed to capture the relationship (Marzouk et al., 2013).

404

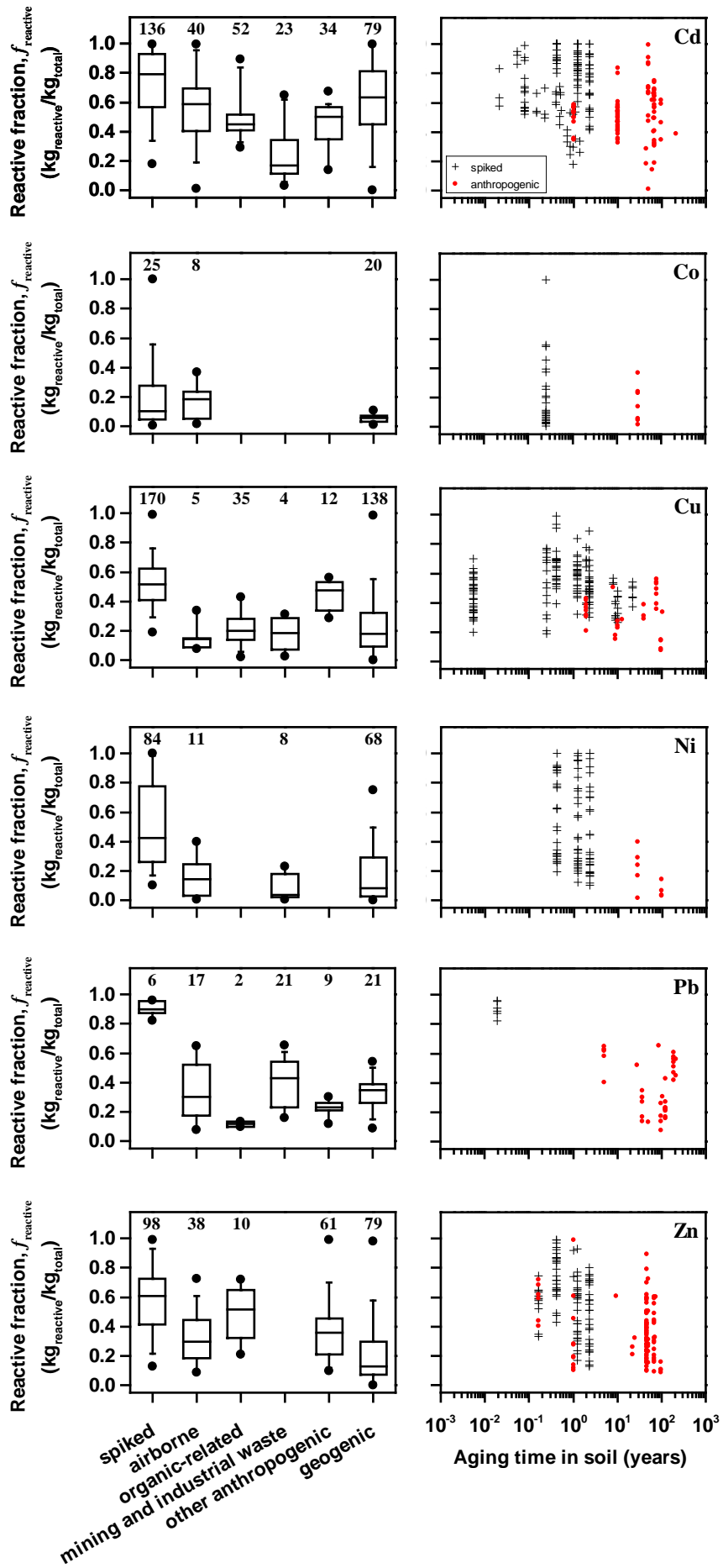
### 405 3.2. Does Aging Matter?

406 Figure 2 (right panel) shows the variability in the reactive fraction of the studied metals as  
407 influenced by contamination age for the anthropogenic emission forms. There was no consistent  
408 effect of aging in reactive fraction. There is a statistically significant difference between Pb aged for  
409 100-150 years and Pb aged for 150-220 years (with the latter being more reactive), but there is no  
410 statistically significant difference between airborne Cd aged for 20-50 years and airborne Cd aged  
411 for 50-100 years. The difference between airborne Cd aged for 20-50 years and that aged for 50-100  
412 years depends on soil pH, however, and there is no difference in the pH range 4.1 – 6.9. Due to  
413 missing information about aging time for many data points for anthropogenic sources, statistical  
414 comparison for other metals and sources was not possible.

415 Reactive fractions in spiked soils aged for up to 0.5 year were significantly higher than those  
416 measured for geogenic and various anthropogenic sources, irrespective of the anthropogenic source  
417 and its age (see Table 2 and Appendix A, Section A3). The difference in reactive fraction between

418 spiked soils aged for more than 0.5-2.5 years and anthropogenic sources was smaller, but remained  
419 statistically significant for organic-related Cu and airborne Zn. This is probably because such short-  
420 term (< 2.5 years) experiments in spiked soils do not allow for occurrence of long-term aging  
421 mechanisms, such as precipitation of salts or formation of non-reactive minerals of lower reactivity  
422 (Amacher, 1991). This is in agreement with Ma et al. (2013), who showed how a kinetic aging  
423 model overestimates reactivity of Ni in field-contaminated, agricultural and serpentine soils. By  
424 contrast, the difference in reactive fraction between spiked soils aged for 0.5-2.5 years and  
425 anthropogenic sources was not statistically significant for airborne Cd, other anthropogenic forms  
426 of Cu, and organic-related Zn (see Table Ax and Figure Ay). For Cd, this reflects a rather high  
427 reactivity of Cd in soils and can mainly be explained by the fact that Cd is mostly present in soil  
428 solutions in dissolved forms as free ions or labile complexes which bind to soil constituents through  
429 weak electrostatic forces (Rodrigues et al., 2010). Chrastny et al. (2012) and Nowack et al. (2010)  
430 also reported higher amounts of weakly bound, reactive Cd in organic-rich soils contaminated with  
431 Cd originating from a smelter. The other anthropogenic forms of Cu (being wood impregnate and a  
432 fungicide) contained readily soluble Cu sulphate that had aged for several decades in field  
433 condition, while some of soils spiked with Cu were leached. This may explain the lack of statistical  
434 difference in the reactive fraction between these sources, as leaching is expected to reduce reactive  
435 fraction in spiked aged soils as compared to non-leached aged soils (Ma et al., 2006). This may  
436 suggest that in some cases aged spiked soils can be used to approximate reactive fraction for  
437 anthropogenic metals. To test this, we systematically assessed the performance of published kinetic  
438 aging models that were developed for soluble salts for prediction of reactivity for anthropogenic  
439 contaminations in soils (see Appendix A, Section A4). The comparison of measured concentrations  
440 of reactive metal and concentrations predicted by published kinetic aging models shows that even if  
441 infinite aging time is assumed, the calculated bias (that is, mean of residuals) is positive, indicating  
442 that the models overestimate reactive concentration (and thus reactive fraction) of anthropogenic  
443 metals. This highlights the need for considering differences in metal reactivity between spiked soils  
444 and man-made metal contaminations soils in characterization of metal accessibility in soils.





446 Fig. 2. Left panel: reactive fraction ( $f_{\text{reactive}}$ , in  $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) of Cd, Co, Cu, Ni, Pb and Zn measured in soils spiked  
447 with soluble metal salts and in soils contaminated with various anthropogenic or geogenic metals; boxes with bars  
448 indicate the 5th, 25th, 50th, 75th, and 95th percentiles and black dots indicate minimum and maximum values; numbers  
449 of data points per emission source are shown above the boxes. Right panel: reactive fraction of Cd, Co, Cu, Ni, Pb and  
450 Zn measured in soils spiked with soluble metal salts (black crosses) and in soils contaminated with various  
451 anthropogenic metals (where all anthropogenic emission sources are combined; red circles) in relation to aging time in  
452 soil. Note, that the data presented are not corrected for geogenic background. Please see Table A1 and A2 for data  
453 corrected for geogenic background that are available for some spiked soils.

454 Table 1. The analysis of the effects of metal source, soil properties, and aging on the reactive fraction and proposed  
 455 reactivity rankings based on pairwise Tukey HSD or WILCOX comparisons (please see Tables Ax and Ay for details). The  
 456 symbols < and > both indicate statistically significant difference between sources; ≈ indicates either no statistically  
 457 significant difference or that comparison could not be done (because standardized residuals are related to the covariate or  
 458 because Q-Q plot for standardized residuals shows unacceptable deviations from 1:1 line); < ≈ > indicate that statistical  
 459 significance and direction of the difference depend on soil pH (for Zn) or soil organic carbon (for Co) values.

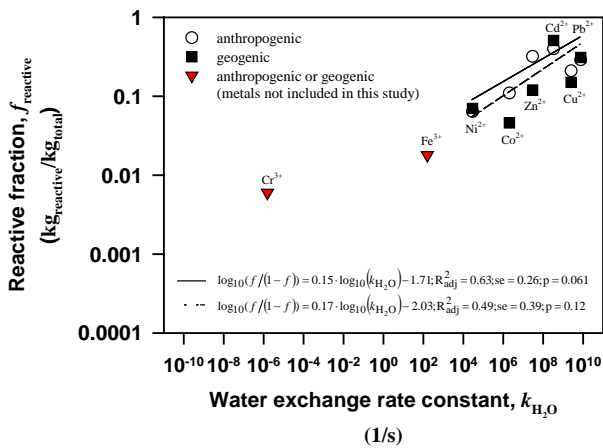
F statistics for one-way ANCOVA models		Proposed reactivity ranking based on pairwise Tukey HSD and WILCOX comparisons
<b>Geogenic and anthropogenic sources irrespective of aging time:<sup>1</sup></b>		
<b>Cadmium</b>		
pH <sub>H2O</sub>	F <sub>1,218</sub> =22.7, p=3e-06	m&w ≈ organic ≈ other < airborne ≈ geogenic
Source	F <sub>4,218</sub> =7.04, p=2e-05	
Source×pH <sub>H2O</sub>	F <sub>4,218</sub> =4.87, p=0.0009	
<b>Cobalt</b>		
log <sub>10</sub> (OC) <sup>4</sup>	F <sub>1,23</sub> =5.39, p=0.29	geogenic < airborne
Source <sup>4</sup>	F <sub>1,23</sub> =6.03, p=3e-5	
<b>Copper<sup>4</sup></b>		
pH <sub>H2O</sub> <sup>4</sup>	F <sub>1,181</sub> =33.6, p=3e-8	geogenic ≈ organic < other
Source <sup>4</sup>	F <sub>2,181</sub> =34.5, p=2e-13	
<b>Nickel</b>		
log <sub>10</sub> (OC) <sup>5</sup>	F <sub>2,85</sub> =12.7, p=0.0006	geogenic ≈ m&w ≈ airborne
<b>Lead</b>		
pH <sub>H2O</sub> <sup>5</sup>	F <sub>1,66</sub> =67.2, p=1e-11	geogenic ≈ m&w ≈ airborne ≈ other
<b>Zinc</b>		
pH <sub>H2O</sub> <sup>4</sup>	F <sub>1,171</sub> =67.2, p=1e-11	geogenic < airborne < other ≈ organic
Source <sup>4</sup>	F <sub>3,171</sub> =14.2, p=3e-8	
<b>Spiked soils and anthropogenic sources as influenced by aging time:<sup>2</sup></b> aging time for spiked soils: I (0-0.5 yr); II (0.5-2.5 yr) aging time for anthropogenic sources: 1 (0-20 yr); 2 (20-50 yr); 3 (50-100 yr); 4 (100-150 yr); 5 (150-220 yr)		
<b>Cadmium</b>		
models were not developed		airborne(3) ≈ airborne(2) ≈ spiked(II) < ≈ > spiked(I)
<b>Cobalt</b>		
models were not developed		airborne(2) < ≈ > spiked(I) not corrected
<b>Copper</b>		
models were not developed		organic(1) < spiked(II) < spiked(I) other(3) ≈ spiked(II) < spiked(I)
<b>Nickel</b>		
models were not developed		airborne(2) < spiked(I)
<b>Lead</b>		
models were not developed		airborne(2) ≈ airborne(1) < spiked(I) m&w(4) < m&w(5) < spiked(I)
<b>Zinc</b>		
models were not developed		airborne(3) < ≈ > airborne(2) < spiked(II) ≈ spiked(I) other(1) ≈ spiked(II) ≈ spiked(I)

460 <sup>1</sup> m&w, organic and other represent the “mining and industrial waste”, “organic-related” and “other anthropogenic” metal  
 461 sources, respectively

462 <sup>2</sup> soils spiked with Co and Pb are not corrected for geogenic background due insufficient number of data points for which  
 463 such correction could be done to make the comparison possible.

464 *3.3. Metal Reactivity In Relation to the Intrinsic Kinetic Lability of Metal Ions*

465 According to the conceptual aging model presented in Fig. 1, the size of reactive fraction depends  
466 on the exchange rate constants for the fixation and weathering reactions. The fixation rate constants  
467 are mainly determined by soil pH (Buekers et al., 2008b; Crout et al., 2006; Ma et al., 2013, 2006;  
468 Wendling et al., 2009). However, while the pH can also influence weathering kinetics, the  
469 weathering rate constants are expected to be mainly determined by the kinetic lability of metal ions  
470 as it determines the speed of a metal to undergo substitution reaction and thus desorption from the  
471 solid phase (Martell, 1978). Laird et al. (2011) already showed that metal bioaccessibility for  
472 gastrointestinal uptake from contaminated soils was related to a metal-specific property, the water  
473 exchange rate constant on metal aqua complexes ( $k_{H_2O}$ ), whereas Owsianiak et al. (2014) showed  
474 that a parameter related to the  $k_{H_2O}$  was related to metal absorption efficiency in terrestrial worms  
475 exposed to aged soil contaminations. In this study, the  $k_{H_2O}$  can explain 63 and 49% of variability in  
476 average (geometric mean) reactive fraction of anthropogenic and geogenic metal forms,  
477 respectively (Fig. 3). Because the mechanism by which a cation leaves a dissolving mineral surface  
478 is similar to the mechanisms of water exchange in the hydrated complex, the observed relation is  
479 expected to hold for those metals and contamination forms, for which the major chemical bond in  
480 the contamination material is that between metal and oxygen (Casey and Westrich, 1992; Casey et  
481 al., 1993; Ludwig et al., 1996; Pokrovsky and Schott, 2002). Indeed, the average reactive fraction of  
482 anthropogenic or geogenic  $Fe^{3+}$  and  $Cr^{3+}$  in soils agrees with predictions of the two reactivity –  
483 lability relationships if extrapolated outside the six studied metals (Fig. 3). We thus suggest that  
484 regression models based on  $k_{H_2O}$  and can be developed to estimate reactive fraction for metals  
485 which form metal-oxygen bonds in soils. Their performance could potentially be improved by  
486 taking into account molecular diffusion of a metal ion along surface site in the soil, which could be  
487 related to acidity constants or radii of the metal ions (Axe and Anderson, 1997; Bruemmer et al.,  
488 1988). By contrast, any relationship based on  $k_{H_2O}$  is not expected to hold for metals, which do not  
489 tend to form metal-oxygen bonds in soils. Indeed, the average reactivity of Ag measured by  
490 Settimo et al. (2014) in soils spiked with soluble Ag salt aged for up to 6 months was smaller (from  
491 50 to nearly 0%) than reactivity that could be expected based on the very large ( $>1 \times 10^{10}$ ),  
492 unmeasurable  $k_{H_2O}$  of  $Ag^+$ . This can be explained by the fact that the dominant forms of Ag in their  
493 soils were Ag bonded with S species, AgCl, and metallic Ag.



494

495 Fig 3. Relation between  $\log_{10}$ -transformed water exchange rate constant for metal aqua complexes,  
 496  $k_{\text{H}_2\text{O}}$  (in 1/s) and logit-transformed, average (geometric mean) reactive fraction,  $f_{\text{reactive}}$  (in  
 497  $\text{kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ) of Cd, Co, Cu, Ni, Pb, and Zn measured in soils contaminated with anthropogenic  
 498 forms of the metals (white dots and solid line) and geogenic metals (black squares and dashed line).  
 499 Red triangles show reactive fraction measured by Gabler et al. (1999) for  $\text{Cr}^{3+}$ ; and reactive fraction  
 500 estimated for  $\text{Fe}^{3+}$  based on the data presented in Collins and Waite (2009) (averaged across 21  
 501 samples of an iron-rich acid sulfate soil, assuming that  $C_{\text{total}} = 0.05 \text{ kg}_{\text{total}}/\text{kg}_{\text{soil}}$ , which is in lower  
 502 range of expected values; Richard Collins, personal communication). The  $k_{\text{H}_2\text{O}}$  for metal ions were  
 503 from Helm and Merbach (1999) except of  $\text{Pb}^{2+}$ , which was not available in the latter study, and was  
 504 from Martell (1978).

505

### 506 3.4. Implications for Inventory Analysis and Reporting for Anthropogenic Metal Emissions

507 In current inventory practice of LCA and chemical hazard assessment, emissions of metals are  
 508 reported as the element and its oxidation state (Pettersen and Hertwich, 2008; Pizzol et al., 2011)  
 509 However, for four out of six metals we found statistically significant effect of the metal source on  
 510 the reactive fraction, which suggests that for cationic metals the current practice may be insufficient  
 511 to support the characterization of bioavailability and terrestrial toxicity. Therefore, to eliminate the  
 512 potential error associated with using emission source-independent ACFs in calculation of CTP  
 513 values of metals in soils, we propose that inventory procedures for metal emissions, such as applied  
 514 in the LCI analysis phase of an LCA, should provide information about the metal emission source if  
 515 that source is known. The proposed classification of emission sources into archetypes based on their  
 516 expected differences in metal reactivities, may be used as guidance. The classification offers a  
 517 compromise between on the one hand the unrealistic option of creating inventories of each chemical

518 species within a metal source (that would then have to be matched with metal species-specific  
519 CTPs), and on the other hand the currently prevailing practice of completely ignoring differences in  
520 the ACF (and thus CTP) between emission sources.

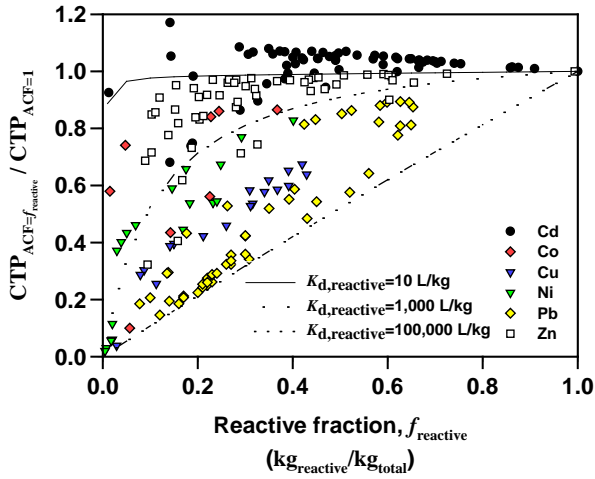
521

### 522 *3.5. Implications for Impact Assessment of Metals on Terrestrial Environments*

523 Our results suggest that at time scales of decades to centuries, the influence of aging on reactivity  
524 for anthropogenic metal sources is difficult to capture and is statistically uncertain. Thus, for  
525 calculating CTPs of cationic metals in soils we recommend using time-horizon independent ACFs  
526 derived from time-independent reactive fractions, combined with FFs calculated using time-horizon  
527 independent  $K_d^{\text{total}}$  values. If the emission source is known, ACFs should be derived from source-  
528 specific reactive fractions. If the emission source is unknown, ACFs can be derived from the  
529 geometric mean of the reactive fraction measured across all geogenic and anthropogenic  
530 contaminations in the study. Such a time-horizon independent ACF it is in practice equal to the  
531 (time-independent) reactive fraction and can be derived from values presented in Tables A1 and A2.

532 The implications of considering differences in reactive fraction on both fate and accessibility of  
533 the metals at the CTP level are presented in Fig. 4. For the metals Pb and Cu, the reduction in the  
534 CTP correlates almost linearly with the reduction in reactive fraction. These two metals are so  
535 strongly associated with the solid phase of the soil that their fate (residence time) in the soil is  
536 determined mainly by removal together with the solid phase, and this translates directly into the  
537 CTP (see eq 5). The CTP of Co and Ni is also reduced when reactive fraction decreases, particularly  
538 for the values below  $0.5 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ , whereas for Zn the reactive fraction is only important in the  
539 lower range of values ( $< 0.2 \text{ kg}_{\text{reactive}}/\text{kg}_{\text{total}}$ ). For these metals, both leaching and erosion determine  
540 metal residence time in soils, and a decrease in ACF can partly be compensated by an increase in  
541 the FF. For Cd, a reduction in the reactive fraction (and thus ACF) has no influence on the CTP  
542 because its fate is determined primarily by leaching and a decrease in ACF is fully compensated by  
543 an increase in the FF. Note, that a USEtox-default value of  $0.03 \text{ mm/yr}$  was assumed for the soil  
544 erosion rate in calculation of fate factors. This value lies within the wide range of values determined  
545 for various soils (Montgomery, 2007), and implies that about 3300 years are required for a 10-cm  
546 top soil layer to exchange completely as a result of erosion and run-off loss to surface water. As  
547 many metals have strong affinity to soil constituents, this removal process is important in the  
548 overall fate, and further research should focus on providing solid data for soil erosion rates under  
549 different environmental conditions.

550  
551



552

553 Fig. 4. Influence of the accessibility factor (ACF), as determined by the size of reactive fraction  
554 ( $f_{\text{reactive}}$ ), on the comparative toxicity potential (CTP) of anthropogenic Cd, Co, Cu, Ni, Pb, and Zn  
555 in soils. Black solid and dashed lines represent three hypothetical cases for metals with  $K_{d,\text{reactive}}$   
556 equal to (i) 10; (ii) 1,000; and (iii) 100,000  $L_{\text{pore water}}/kg_{\text{soil}}$ .

557

### 558 3.6. Limitations

559 The data set for anthropogenic sources is limited to contaminations aged for up to two centuries,  
560 and furthermore there is uncertainty in estimating the age. In the typically infinite time perspective  
561 applied in LCIA, aging processes may gain more importance by strengthening the binding of the  
562 metal in the soil and reducing its reactivity.. Considering the effort put into the literature search, it is  
563 questionable, however, whether a better data set can be compiled from the open literature, so it is  
564 not likely that such an aging effect can be demonstrated in this way. An alternative approach could  
565 be based on a repeated sampling experiment over centuries, but this is also not straight forward. On  
566 the other hand, in the assessment of CTPs for use in LCIA, the residence time of the metal in the  
567 soil may be restricted by the residence time of the soil solids in the soil compartment of the fate  
568 model, in which case even the aging over very long time perspectives will have small influence on  
569 the CTP values

570

571 Studies on metal reactivity in soils for other metals are scarce, which makes the estimation of  
572 reactive fraction, or any reactivity-age relationship, for the other metals virtually impossible.  
573 Reactive fraction could be potentially predicted using a structure-reactivity relationship, as  
demonstrated in this study for Cr and Fe. Alternatively, our conceptual aging model can be used to

574 determine shape of reactivity curve, provided that fixation and weathering rate constants are either  
575 measured or predicted for dominant soil minerals (Bearup et al., 2012; Brantley, 2008). A  
576 problematic issue is the estimation of the fixation rate constant between the inert and nonreactive  
577 (but chemically labile) metal pools, as is the potential for very slow release of metal from the inert  
578 pool that is not considered in our model and that may occur for some slowly-reacting minerals  
579 (Degryse et al., 2009).

580

## 581 **4. Conclusions**

582

583 We occasionally found the effect of the emission source on the solid-phase reactivity of the studied  
584 metals. The effect of contamination age in soil was not apparent, but the uncertainties in estimating  
585 the age do not allow drawing definite conclusions about the influence of aging time on the reactivity  
586 of anthropogenic metal sources in soils. We therefore recommend including the effect of the  
587 emission source and disregarding the role of aging in assessment of comparative terrestrial toxicity  
588 of anthropogenic Cd, Co, Cu, Ni, Pb and Zn. Our framework for including aging in calculation of  
589 fate and accessibility factors of metals in soils can, however, be used if aging is found to play a role  
590 in reactivity of other anthropogenic metals in terrestrial systems and if reactivity-age relationship  
591 can be estimated.

592

## 593 **Appendix A. Supplementary data**

594 Supplementary data related to this article can be found at [http:// dx.doi.org/](http://dx.doi.org/)

595

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601

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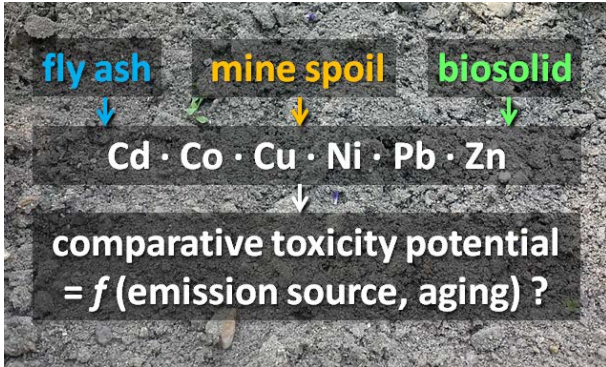
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## Graphical abstract



**Highlights**

- we found an effect of source on reactivity of anthropogenic metals in soils
- the influence of aging on reactivity of anthropogenic metals was not consistent
- we recommend including source and disregarding aging in calculation of CTPs values