1	Predicting trace metal solubility and fractionation in urban soils from isotopic
2	exchangeability.
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10	ABSTRACT
11	Metal-salt amended soils (MA, n = 23), and historically-contaminated urban soils from two English
12	cities (Urban, $n = 50$), were investigated to assess the effects of soil properties and contaminant source
13	on metal lability and solubility. A stable isotope dilution method, with and without a resin purification
14	step, was used to measure the lability of Cd, Cu, Ni, Pb and Zn. For all five metals in MA soils, lability
15	(%E-values) could be reasonably well predicted from soil pH value with a simple logistic equation.
16	However, there was evidence of continuing time-dependent fixation of Cd and Zn in the MA soils,
17	following more than a decade of storage under air-dried conditions, mainly in high pH soils. All five
18	metals in MA soils remained much more labile than in Urban soils, strongly indicating an effect of
19	contaminant source on metal lability in the latter. Metal solubility was predicted for both sets of soil by

21 metal solution concentrations, over-estimation of Cd, Ni and Zn solubility was associated with binding

the geochemical speciation model WHAM-VII, using E-values as an input variable. For soils with low

- to the Fe oxide fraction while accurate prediction of Cu solubility was dependent on humic acid content. Lead solubility was most poorly described, especially in the Urban soils. Generally, slightly poorer estimation of metal solubility was observed in Urban soils, possibly due to a greater incidence of high pH values. The use of isotopically exchangeable metal to predict solubility is appropriate both for historically contaminated soils and where amendment with soluble forms of metal is used, as in toxicological trials. However, the major limitation to predicting solubility may lie with the accuracy of model input variables such as humic acid and Fe oxide contents where there is often a reliance on
- 29 relatively crude analytical estimations of these variables.

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31 Capsule:

Trace metal reactivity in urban soils depends on both soil properties and the original source material;
 the WHAM geochemical model predicts solubility using isotopically exchangeable metal as an input.

34

35 **1. INTRODUCTION**

36 Accurate assessment of risk from heavy metal contamination of the environment requires consideration of metal 'reactivity' or 'lability' in soils (Fairbrother et al., 1999; Lock and Janssen, 2001). Published 37 38 literature (Degryse et al., 2004, Tack, 2010, Hammer et al., 2006) generally suggests that the lability of 39 trace metals in soils is the net result of three factors: (i) soil properties, including soil physicochemical 40 characteristics such as pH (e.g. McBride et al., 2006; Bonten et al., 2008) and redox potential (Borch et 41 al., 2010) and the proportions of soil constituents such as Fe/Mn hydroxide and organic matter present 42 (Tipping et al., 2003; Rodrigues et al., 2010); (ii) metal sources, which may vary greatly in their intrinsic 43 metal lability (e.g. Atkinson et al., 2011; Mao et al., 2014) and (iii) soil-metal contact time, because 44 there is a time-dependency to both metal fixation in soils (e.g. Tye et al., 2003; Ma et al., 2006b) and 45 the release of trace metals from contaminant sources in soils (Kaste et al., 2006; Atkinson et al., 2011). 46 Generally, low metal lability is more likely in soils with high pH values and following long contact 47 times. Recent studies have focused on the concentrations and origins of heavy metals in the urban 48 environment (Manta et al., 2002; Cheng et al., 2014; Wei and Yang, 2010), but the effects on lability 49 arising from characteristics of the original contaminant source are usually difficult to assess (Mao et al., 50 2014).

A range of techniques have been developed to measure the lability of trace element fractions in soils, 51 52 among which isotope dilution is perhaps the most appropriate method (Degryse et al., 2009). This 53 approach defines an amount of metal, distributed between the solution and solid phases, which is 54 isotopically exchangeable, known as the E-value or M_E (Smolders et al., 1999; Young et al., 2000). 55 Measurement is achieved by adding a small 'spike' of an enriched isotope of the analyte of interest into a pre-equilibrated soil suspension and measuring the isotopic abundance of the spike isotope in the 56 57 separated solution phase. The extent to which the spike isotope has been able to mix with the indigenous 58 soil metal quantifies the 'isotopically exchangeable' metal pool in the soil. The method has been 59 modified to correct for the presence of non-labile metal in sub-micron colloidal particles (SCP-metal) 60 by adding a resin purification step (Lombi et al., 2003). E-values can then be used as input variables to geochemical speciation models, such as WHAM (Windermere Humic Aqueous Model, Tipping et al., 61 62 2003) to predict metal fractionation and speciation in the solid and solution phases of soils respectively (Tipping et al., 2003; Shi et al., 2008; Almas et al., 2007; Buekers et al., 2008b; Marzouk et al., 2013b). 63

64 The primary aims of this study were to investigate how trace metal *lability* and *solubility* are affected 65 by (i) soil properties, (ii) ageing and (iii) variable contamination sources in urban soils. To achieve this, 66 objectives focussed on determination of the isotopically exchangeable fractions of Cd, Cu, Ni, Pb and 67 $Zn(M_E)$ in two distinct sets of soil samples. These included (i) soils, chosen for their range of land uses 68 and soil properties, that had been incubated with metal nitrate salts (Cd, Cu, Ni, Pb and Zn) for several 69 years and (ii) urban contaminated soils, from Nottingham and Wolverhampton (UK), chosen for their 70 range of metal contaminant concentrations and sources. To reveal the effect of contaminant source, the 71 'lability' of soils from the two datasets were compared by normalising values of %M_E against soil pH;

- ⁷² logistical models for describing metal lability with pH were parameterised. Secondary objectives ⁷³ included: (i) testing for non-labile SCP-metal (<0.22 μ m) by comparing values of M_E with equivalent ⁷⁴ values following a resin cleaning procedure (M_{Er}); (ii) testing for metal *fixation* in air dried soil stored ⁷⁵ for more than a decade, (iii) comparing a sequential fractionation scheme with fractionation by isotopic ⁷⁶ exchangeability and (iv) assessing the performance of the geochemical model, WHAM VII, to predict
- 77 Cd, Cu, Ni, Pb and Zn solubility in both sets of soils.
- 78

79 **2. MATERIAL AND METHODS**

80 2.1 Soil sampling

Two sets of soils were used in this study. The first set comprised 23 metal-amended topsoils (MA soils), 81 82 from sites with contrasting land uses and parent material, to provide a wide range of soil properties (pH, 83 soil organic matter, mineral (hydr)oxides content and texture). These soils were collected for a previous study of trace metal fixation and solubility (Tye et al., 2003; Tye et al., 2004) and had been amended 84 85 with metal nitrate salts to the limits prescribed by the UK Sludge Regulations (MAFF, 1993) (Cd = 3, Cu = 135, Ni = 75, Pb = 300 and Zn = 300 mg kg⁻¹) before being incubated at 16°C and 80% field 86 capacity (FC) for ~3 years (Tye et al., 2003), air-dried, and then stored for ~12 years prior to the current 87 88 study. The second set (Urban soils) consisted of 50 topsoils collected in the cities of Wolverhampton 89 (WV) and Nottingham (NG), UK. Site selection included consideration of historical and recent 90 industrial and domestic land use and locations included brownfield sites, rail transport sidings, urban 91 roadsides, waste disposal facilities, recreational areas, gardens, urban nature reserves and woodland and 92 parkland areas. Data relating to these soils has been published previously in an investigation of metal 93 speciation and bioavailability in risk assessment (Thornton et al., 2008; Hough et al., 2005).

94 2.2 Soil characterization

95 Some of the soil properties originally determined were re-measured to identify changes during storage 96 and to provide a more complete input dataset for subsequent modelling (Section 2.6). Soil pH was 97 measured on suspensions (1 g soil: 30 mL of 0.01 M Ca(NO₃)₂) using a pH meter with combined 98 Ag/AgCl glass electrode (Model pH 209, HANNA Instruments, Bedford, UK). Total organic matter 99 content was estimated using a LECO combustion analyser (Tye et al., 2003) for MA soils. For Urban 100 soils total organic matter content was calculated from the difference between total soil carbon (SC) 101 content measured using an Elemental Analyser (CE Instruments model Flash EA1112) and calibrated 102 using a range of certified soils, and carbonate content determined by manometric assay using the Collins' 103 calcimeter method (Piper, 1954). Alkaline extraction was used to determine humic acid (HA) and fulvic 104 acid (FA) content in all soils. Organic carbon content in HA and FA was measured using a Shimadzu TOC-Vcp analyser. Clay content (%) was estimated from the soil texture classification provided by 105 Tye et al. (2003) for MA soils. Iron, Al and Mn oxide concentrations were determined following 106 107 extraction with a mixture of sodium dithionite, sodium citrate and sodium bicarbonate (DCB extraction,

- 108 Anschutz et al., 1998). Total Cd, Cu, Ni, Pb and Zn concentrations in soil were determined following
- 109 digestion of 200 mg of finely ground soil with HF (40% AR), HNO₃ (70% TAG), HClO₄ (70% AR)
- and 2.5 mL H₂O in a block digester (Model A3, Analysco Ltd, Chipping Norton, UK). Iron, Al and
- 111 Mn in DCB extractants and trace metals in acid digests were analysed by Inductively Coupled Plasma-
- 112 Mass Spectrometry (ICP-MS; Thermo-Fisher Scientific X-Series^{II}) operating in 'collision cell mode'
- 113 (7% hydrogen in helium) to reduce polyatomic interferences.

114 2.3 Cadmium, Cu, Ni, Zn, and Pb lability measured by isotopic dilution (E-value)

115 Sample preparation

116 The stable isotopic dilution method used in this study was adapted from Atkinson et al. (2011). Soils were pre-equilibrated in 0.01 M Ca(NO₃)₂ (1 g: 30 mL) on an end-over-end shaker for 3 days; 4 117 suspensions were made for each soil. An aliquot (0.4 mL) of enriched stable isotope stock solution 118 119 (ISOFLEX, San Francisco CA, USA) in ~2% HNO₃, with known isotopic abundances (IA) for ¹⁰⁸Cd 120 (IA = 69.7%), ⁶⁵Cu (IA = 99.0%), ⁶²Ni (IA = 98.2%), ²⁰⁴Pb (IA = 98.8%) and ⁷⁰Zn (IA = 92.7%) was added to two of the suspensions and the other two were used as control samples to derive the natural 121 122 isotopic abundance of the labile metal. The spike isotopes used were, with the exception of 65 Cu, chosen 123 because they have relatively low natural isotopic abundance (De Bievre and Barnes, 1985). Therefore, 124 only a small addition to the system was required to produce a significant increase in IA from the background level. To reduce the number of individual operations and to avoid adding different amounts 125 126 of isotopes to each soil, the samples were classified into several groups according to their soil metal 127 content. The level of isotope tracer to be added was determined from the highest concentration of metal 128 in each group to ensure that the difference in isotopic ratio between the spiked and un-spiked samples 129 was at least 20 %. After spiking, the suspensions were shaken for a further 3 days; the solution and solid 130 phases were then separated by centrifugation (2200 g) and then filtration ($\leq 0.2 \mu m$). For several Urban soils, where the native and/or spike metal concentrations in $0.01 \text{ M Ca(NO_3)}_2$ suspension were judged 131 to be too low to provide reliable isotopic ratios (Midwood, 2007), a suspending solution of 1×10^{-5} M 132 EDTA was used to shift the labile metal equilibrium in favour of the soil solution while presenting 133 134 minimal risk of mobilizing non-labile metal, as shown by Atkinson et al., (2011) and Nazif et al., (2015).

135 ICP-MS settings for measuring isotopic abundances and calculation of E-value

Isotopic ratios in supernatant solutions were measured by ICP-MS in 'collision cell with kinetic energy 136 discrimination' (CCT-KED) mode to avoid interference from the chlorine dimer (³⁵Cl-³⁵Cl), and other 137 polyatomic species, on ⁷⁰Zn (Malinovsky et al., 2005; Stenberg et al., 2004). Quadrupole dwell times 138 were short to reduce plasma flicker: ¹⁰⁸Cd (10 ms), ¹¹¹Cd (2.5 ms), ⁶³Cu (2.5 ms), ⁶⁵Cu (10 ms), ⁶⁰Ni 139 (2.5 ms), ⁶²Ni (10 ms), ²⁰⁴Pb (10 ms), ²⁰⁶Pb (2.5 ms), ²⁰⁷Pb (2.5 ms), ²⁰⁸Pb (2.5 ms), ⁶⁶Zn (2.5 ms) and 140 ⁷⁰Zn (10 ms). The isotopes ⁵⁹Co, ¹⁰⁷Ag and ²⁰²Hg were also measured, as quadrupole settle points 141 (Marzouk et al., 2013a). It is well known that the relative abundance of Pb isotopes varies according 142 143 to the sources of Pb present in the soil (Komarek et al., 2008). Therefore, instead of relying on assumed

- 144 relative abundances of naturally occurring isotopes, the apparent isotopic ratio in un-spiked samples
- 145 (blanks) was also determined for all five elements. To avoid the electron multiplier detector tripping to
- analogue mode, all the sample solutions were diluted appropriately.

A source of error when analysing stable isotopes is mass discrimination: isotopes with greater mass are measured by ICP-MS with greater sensitivity and so the measured ratio of CPS for two isotopes is not equal to their true isotopic ratio. External mass discrimination correction was therefore applied using a certified isotopic standard reference material (NIST, SRM 981) for Pb and a mix of single ICP-MS calibration standards for Cd, Cu, Ni, and Zn. The mixed standard ($25 \ \mu g \ L^{-1}$) was used to calculate a correction factor (K-Factor) (**Eq. 1**):

$$153 \quad K - factor = \frac{IR}{CR} \tag{1}$$

where IR and CR are the true isotopic ratio and the measured ratio of CPS for the isotopic standard respectively. For individual samples, the K-factor for each isotopic ratio (e.g. ²⁰⁴Pb/²⁰⁸Pb, ²⁰⁶Pb/²⁰⁸Pb, ²⁰⁷Pb/²⁰⁸Pb) was estimated by linear interpolation between the K-factor measured for standards run at intervals of eight samples.

158 Concentrations of isotopically exchangeable metal (M_E ; mg kg⁻¹) were calculated for Cd, Cu, Ni, Pb 159 and Zn from **Eq. 2** adapted from Gabler et al. (1999):

160
$$M_E = \left(\frac{Am_{Msoil}}{W}\right) \left(\frac{C_{spk}V_{spk}}{Am_{Mspk}}\right) \left(\frac{s^{pk}IA_{spike} - bg_{IA_{spike}}R_{ss}}{bg_{IA_{soil}}R_{ss} - s^{pk}IA_{soil}}\right)$$
(2)

where Am_{Msoil} and Am_{Mspk} are the average atomic masses of Cd, Cu, Ni, Pb or Zn in the soils and the spike isotope solution respectively, W is the weight of the soil (kg), C_{spk} is the gravimetric concentration of the metal in the spike solution, V_{spk} is the volume of spike added (L), IA is the isotopic abundance and R_{ss} is the ratio of isotopic abundances, spiked (spk): background (bg), for the two isotopes in the spiked soil solution. For comparative purposes, lability is often expressed as a percentage of the total metal content of the soil (%M_E)

167 A 'resin purification' test for the presence of non-labile metal in suspended colloidal particles (SCP-168 metal; $< 0.2 \,\mu$ m), first described by Lombi et al. (2003), was undertaken. Analytical grade Na-Chelex-100 resin (Bio-Rad laboratories, UK) was converted to the Ca^{2+} form by equilibrating in 0.5 M Ca(NO₃)₂ 169 170 for 2 hours. The resin was then washed twice with MilliQ water (18.2 M Ω cm) to remove remaining 171 Na⁺ ions. An aliquot of Ca-Chelex resin (c. 100 mg) was introduced into 10 mL of filtered ($\leq 0.2 \mu m$) 172 solution from both spiked and un-spiked soil suspensions. After equilibration for 2 hours, the resin was rinsed with MilliQ water three times to remove colloidal particles. Metals were then eluted from the 173 resin with 0.5 M HNO₃ and the measured isotopic ratio used to calculate the labile pool (M_{Er} ; mg kg⁻¹). 174 Results were compared with M_E measured directly on the filtered solution phase to test for the presence 175

176 of non-labile SCP-metal.

- 177 Comparison with radio-labile metal fraction measured in October 1999
- 178 A comparison was made between values of Cd_E and Zn_E measured in this study in August and
- 179 September 2011, and the 'radio-labile' fraction (M_E^*) measured by Tye et al. (2003) on the same soils
- 180 in October 1999 shortly after collection of the Urban soils but following 818 d incubation at 80% field
- 181 capacity in the case of the MA soils. The objective was to investigate possible further aging of Cd and
- 182 Zn in MA and Urban soils following 12 years of soil storage under air dry conditions. In the study of
- 183 Tye et al., the radio-isotopes ¹⁰⁹Cd and ⁶⁵Zn were used to determine Cd_{E}^{*} and Zn_{E}^{*} .

184 2.4 Analysis of soil solution

Elemental concentrations of dissolved major (Al, Ca, K, Mg and Na) and trace (Cd, Cu, Ni, Pb and Zn) cations were measured in 0.01 M Ca(NO₃)₂ suspensions with 1 g soil in 30 mL solution using ICP-MS, as described in Section 2.2. Dissolved organic carbon (DOC) and inorganic carbon (DIC) were determined in the suspensions using a Shimadzu TOC-Vcp analyser. For modelling purposes, an estimate of FA concentration in solution was made assuming that dissolved organic matter (DOM) contains 50% C and that 65% of DOM consists of active FA (Buekers et al., 2008b; Cheng et al., 2005).

191 **2.5** Describing lability ($%M_E$) as a function of soil properties

192 Two types of empirical model for predicting $\%M_E$ from measured soil properties were assessed. The 193 first was a multiple linear regression model where the simplicity of the equation allows inclusion of a 194 large number of variables. Values of $\%M_E$ were correlated with a range of soil characteristics including 195 pH, %SOC, %Clay, Al, Fe and Mn oxide contents (mg kg⁻¹) and total Cd, Cu, Ni, Pb, Zn concentration 196 (M_{total} ; mg kg⁻¹). The significance of each variable was determined (Minitab vs 16.2.2) and only those 197 that were significant (p < 0.05) in predicting $\%M_E$ were included in the model (**Eq. 3**). The constants 198 were optimized using the *Solver* function in Microsoft Excel.

199
$$\%M_E = k_0 + k_1 (pH) + k_2 (\%SOC) + k_3 (FeOx) + k_4 (MnOx) + k_5 (AlOx) + k_6 (\%Clay) + k_7 (M_{total})$$
 (3)

The second model was a logistic (sigmoid) equation based on the assumption that pH is likely to be the primary determinant of $\%M_E$ (**Eq. 4**). A similar function has been shown to describe trace metal *adsorption* on soil binding phases (Sinitsyn et al., 2000; Lamy et al., 1993). Metal lability was therefore predicted assuming that $\%M_E$ was controlled only by pH and that the pH at which 50% of the metal was labile (*pH*₅₀) was metal specific (**Eq. 4**).

205
$$\% M_E = \frac{100}{1 + exp[k_M(pH - pH_{50})]}$$
 (4)

In Eq. 4, the 'spreading factor' (k_M) controls the slope of the model trend across the pH range and is probably unique to a particular soil-metal combination. Therefore, an attempt was made to refine Eq. 4 by making k_M a function of other soil characteristics (S) describing the role of likely metal adsorbents (e.g. %SOC, metal oxide concentration and clay content); a power function (n) was added because it achieved a better fit to the data in practice (Eq. 5).

211
$$\% M_E = \frac{100}{1 + exp[k_M S^n(pH - pH_{50})]}$$
 (5)

A further simplification was to combine the measured oxide phases into a single variable, allowing for differences in the molecular weight for Al_2O_3 , $Fe_2O_3 \cdot H_2O$ and MnO_2 , resulting in three variables (%SOC, mineral (hydr)oxides and clay). Only one of the three variables was assumed to control the spread of %M_E values with pH (**Eq. 5**) for each metal. The constants in **Equations 4** and **5** were optimized, using the *Solver* function in Microsoft Excel, to assess the performance of each model.

217 **2.6** *Predicting trace metal solubility and speciation by WHAM-VII*

The geochemical speciation model WHAM-VII was used to predict Cd, Cu, Ni, Pb and Zn concentration in the solution phase of soil suspensions. Measured values of M_E were used as inputs to WHAM, representing the total reactive trace metal fraction in the soil suspensions. The modelled metal concentration in solution was compared with measured values to assess the model performance. Speciation in solution and fractionation in the soil solid phase were derived from the model output. Model parameters and variables are listed in **Appendix 1**.

224 **3. RESULTS**

225 3.1 Soil characteristics

226 Full details of soil properties for the MA and Urban soils are provided as supplementary material 227 (Appendices 2&3). Soil pH values covered a wide range, from < 4 to ~ 8 ; the Urban soils were slightly 228 more alkaline with 60% of pH values > 6.0. All the soils can be categorized as mineral soils (%SOC < 229 20%) with two possible exceptions; Urban soils with 20.5% and 25.1% SOC, one sampled in a public 230 park and the other near a railway line, both had evidence of coal in the soil. Urban soils from brownfield 231 sites typically had the lowest %SOC (Appendix 2). Iron oxide content (FeOx) in both sets covered a 232 wide range of values (5.4 - 43 g kg⁻¹); concentrations of Mn oxides (MnOx) were much lower than 233 FeOx $(0.16 - 3.01 \text{ g kg}^{-1})$, but the two variables were strongly correlated (p < 0.01). Iron oxides strongly 234 adsorb trace metals at neutral and high pH values (Tack, 2010) whereas Mn oxides are more important at lower pH values due to their lower pzc (Dong et al., 2003; Trivedi and Axe, 2001). For the MA 235 soils, uniformly amended with five trace metals, there was a relatively small variation in total metal 236 concentration resulting from native soil metal content (Tye et al., 2003; Tye et al., 2004). Total metal 237 concentrations in the Urban soils covered a much wider range as a consequence of historical 238 239 contamination. Some individual metal concentrations in Urban soils were strongly correlated implying 240 contamination from the same source (p-values < 0.05). Copper, Ni, Pb and Zn concentrations were 241 positively, but weakly, correlated with %SOC ($r_{Cu}=0.36$, $r_{Ni}=0.40$, $r_{Pb}=0.45$, $r_{Zn}=0.43$,), FeOx ($r_{Cu}=0.47$, $r_{Ni}=0.41$, $r_{Pb}=0.37$, $r_{Zn}=0.43$) and MnOx ($r_{Cu}=0.48$, $r_{Ni}=0.39$, $r_{Pb}=0.32$, $r_{Zn}=0.38$) possibly as a result of 242 243 their accumulation in soils with strong binding phases (Rieuwerts et al., 2006; Zimdahl and Skogerboe, 244 1977). Cadmium concentration was less affected by soil properties, only showing a very weak 245 correlation with AlOx ($r_{Cd}=0.34$).

246

247 3.2 Measured metal lability in soils

248 Values of %M_E for Cd, Cu, Ni, Pb and Zn are shown in **Fig. 1**. For Urban soils the average %M_E values 249 were 47.2% (Cd), 20.5% (Cu), 6.28% (Ni), 21.1% (Pb) and 18.1% (Zn) emphasising the need to consider metal lability (i.e. M_E, mg kg⁻¹), rather than just total soil metal content, when assessing risk 250 251 and mobility in brownfield sites. Values of metal lability in the MA soils were significantly greater than in the Urban soils with average $\%M_E$ values of 74.4% (Cd), 48.7% (Cu), 36.2% (Ni), 54.1% (Pb) 252 253 and 41.5% (Zn) despite three years incubation of MA soils at 80% field capacity and a further 12 years 254 of storage under air dry conditions. In both sets of soils, the relative lability of the five metals followed the same sequence $(Cd > Pb \ge Cu > Zn > Ni)$. 255

The presence of a non-labile fraction of metal in suspended colloidal particles (SCP-metal) in the submicron filtered (< 0.22 μ m) supernatant solutions from the soil suspensions used to measure M_E values was investigated by comparing M_E and M_{Er} (**Appendix 3**). For most of the soils, SCP-metal had only a very small effect on measured E-values. There was a strong correlation between %M_E and %M_{Er} and an average difference of less than 2% for all five metals; a significant difference was only observed

- 261 for Cu in the soils investigated. The ratio of Cu_E : Cu_{Er} against soil pH and %Cu_E (Fig. 2a & 2b) clearly
- suggests the presence of SCP-Cu, despite filtration to $< 0.22 \,\mu$ m, especially at low levels of %M_E and high pH values in the Urban soils.

264 3.3. Predicting metal lability from soil properties

The effects of soil properties on values of $%M_E$ were described in two ways: a multiple-regression model, which has the advantage of being able to include many variables, and a simple logistic model with soil pH as the primary determining factor.

- 268 In the current study, seven variables were available to predict values of M_E from Eq. 3. Metal lability 269 in the Urban soils is likely to have been affected by factors other than soil properties, especially metal 270 source characteristics. Therefore, Eq. 3 was parameterized using data from the MA soils only in which 271 the added metal was from a single, initially dissolved, source. The goodness of fitting was evaluated 272 from the values of RSD and correlation co-efficient (r). A good level of prediction was achieved for Cd 273 (r=0.92, RSD=6.3), Ni (r=0.97, RSD=5.85) and Zn (r=0.95, RSD=7.7), but Cu and Pb were less 274 successfully modelled, with correlation co-efficient equals to 0.83 and 0.85 respectively. Soil pH was 275 negatively correlated with $M_{\rm E}$ for all five metals and accounted for the largest proportion of the total 276 variance in %M_E in the MA soils: 63.2%, 25.5%, 73.1%, 53.3% and 66.1%, for Cd, Cu, Ni, Pb and Zn
- 277 respectively. The optimized constants, RSD values and correlation co-efficients (r) are summarized in
- **Appendix 4**.
- Although linear regression modelling can provide reasonable predictions of metal lability where %M_E 279 280 is largely a function of soil characteristics and a single contaminant source predominates, as in the MA soils, the application of this model is limited to the range of data used to parameterise the model. 281 282 Extending 'prediction' of lability outside this range can result in physically impossible outcomes in 283 which modelled values of $%M_E$ may be negative, or > 100%. By contrast, a sigmoidal model (Eq. 4) 284 offers more realistic boundaries to model outcomes ($%M_{\rm E} = 0 \sim 100\%$). The sequence of optimized 285 pH_{50} values was Cd > Pb > Cu > Zn > Ni, and covered nearly three pH units, in agreement with the expected order of metal lability. The exponential factor k_M is related to the range of pH values over 286 which the major change in %M_E occurs. Inclusion of each of the adsorption phases (OM, oxides, and 287 clay) was then used to try and refine prediction of %M_E according to Eq. 5. For Cd, Ni and Zn, the best 288 289 prediction, lowest RSD and highest value of r, was achieved by including total oxide content within Eq. 290 5 (S value) to control the spread of predicted %M_E values as a function of pH. For Cu and Pb, including 291 total oxide content also improved prediction of %M_E, but the lowest RSD was obtained by including 292 clay and organic matter content respectively. Copper produced the lowest k_M value (0.16) and so only gradually undergoes transition from labile to a fixed state over a relatively large range of pH values, 293 294 whereas Ni and Zn were labile over a more restricted range of pH values with k_M values equal to 0.76 295 and 0.72 respectively. The optimized values of pH₅₀ and the exponential constant k_M in Eq. 4 & 5, together with the results of modelling for the MA soils are shown in Appendix 5. 296

297 3.4. Metal lability in MA and Urban soils solely as a function of soil pH

Measured values of %M_E for Cd, Cu, Ni, Pb and Zn in MA and Urban soils, as a function of pH value, 298 299 are shown in Fig. 3 with model lines derived from Eq. 4. In the MA soils, for all five metals, there was 300 no obvious bias in model prediction across the pH range. Measured values of Cu lability were only 301 weakly correlated with pH. Although Cd and Pb also showed a restricted range of %M_E values, lability exceeded 90% and 80%, respectively, below pH 4.0. Zinc and Ni in the MA soils both showed 302 substantially greater variation in %M_E with pH compared to the other three metals. Only small and non-303 304 significant differences between predicted values of %M_E were achieved by substituting Eq. 5 for Eq. 4 305 (p > 0.05) which implies no advantage in considering an effect of geocolloidal adsorption phase in the 306 sigmoidal equation. The values of pH_{50} optimized using Eq. 4 were very similar to those for Eq. 5 and 307 followed the observed sequence of relative metal lability in soils (Appendix 5). The measured values 308 for the Urban soils are shown for comparison with the MA soils in Fig. 3. Soil pH affected metal lability 309 in the Urban soils with a trend qualitatively similar to that of the MA soils but M_E values were greatly 310 over-predicted by the model (Eq. 4 parameterised using the MA soils) in all cases.

Possible source effects were investigated by calculating the deviation from the model line as a proportion (%) of the modelled E-value ($\%\Delta M_E$); the model being parameterized solely from the MA soils for each element. No correlation between $\%\Delta M_E$ and pH or %C was observed with the exception of Pb where a trend with pH was apparent (r = 0.602) suggesting either a pH effect on the *source* of Pb or a continuing effect of soil-metal contact time (greater for the Urban soils). Thus, overestimation of %M_E values for Pb was greater for soils with high pH and low metal lability.

317 3.5 Changes in Cd and Zn lability in air dried soils during storage

For the MA soils, a paired t-test showed that the difference between M_E and M_E^* measured using radio-318 isotopes by Tye et al. (2003) was significant for Zn (p = 0.007), but not for Cd (p = 0.416). However, 319 320 for the Urban soils, there was a significant difference for both Zn and Cd (p < 0.001) with, generally, $%M_E^* > %M_E$ (Fig. 4a). It is notable, for example, that the difference between M_E and M_E* 321 was more pronounced in high pH soils than in acidic soils (Fig. 4b). However, only a very small 322 323 difference between M_E and M_E^* was observed in MA soils; the average ratio M_E : M_E^* was 0.93 and 1.00 for Zn and Cd respectively. In contrast, for the Urban soils the ratios were 0.71 and 0.69 for Zn 324 and Cd. 325

326 3.6 WHAM-VII prediction of metal solubility and fractionation

The ability of the geochemical speciation model, WHAM-VII, to predict Cd, Cu, Ni, Pb and Zn concentration in solution is shown in **Fig. 5** as modelled against measured solubility on a $-\log_{10}$ scale (pM_{soln}). Values of M_E were input to the model to represent the reactive metal pool in the soil suspensions (Appendix 1). Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils. The values of RSD were less than 1 (pM_{soln} unit) for all five metals although the

- average absolute bias ($\Delta p(M_{soln})$) differed between metals. Summary of model outcomes comparing the
- measured and the predicted are provided in the Appendix 6.
- 334 Predictions of Cu, Ni, Cd and Zn solubility were only slightly better for MA soils than for the Urban 335 soils but the difference for Pb was greater: r values for Pb were 0.96 and 0.78 for MA and Urban soils respectively. Among the five metals, the model gave the best prediction for Cd and Ni with relatively 336 337 low scatter around the 1:1 line (RSD = 0.51 and 0.63 respectively) and a high correlation coefficient (r 338 = 0.94 for both metals). The high RSD value for Zn (0.83) occurred because the model substantially overestimated the solution concentration for several Urban soils with high pH values (6.93 to 8.08) and 339 very low Zn concentrations in solution. Prediction of Cu solubility was reasonably good (RSD = 0.45; 340 341 r = 0.74) but with some Urban soil outliers. Lead solubility was most poorly predicted by WHAM-VII 342 (RSD=0.64; r=0.85). However, splitting the Pb dataset between MA and Urban soils, it was clear that, 343 although there was less average bias compared to the other metals, the poor correlation coefficient and 344 large RSD value was due to the Urban soils (RSD = 0.73, r = 0.78, $\Delta pPb_{soln} = -0.08$), whereas solubility for the MA soils was more accurately predicted although with very slightly greater bias (RSD = 0.35, r 345
- 346 = 0.96, $\Delta pPb_{soln} = 0.11$).
- 347 Trace metal fractionation in the solid phase is provided by WHAM-VII as an output. Therefore, metal 348 adsorption on different binding phases was investigated by interrogation of the WHAM-VII output data 349 to determine whether particularly large deviations between measured and predicted metal solubility 350 were associated with predominant sorption on particular binding phases. Average fractionation was modelled using WHAM-VII and includes six particulate geocolloidal fractions and a single pool for the 351 352 solution phase, including 'colloidal' (dissolved) fulvic acid. Figure 6 illustrates the average proportions 353 of labile Cd, Cu, Ni, Pb and Zn predicted to be held in different soil phases alongside with changes in 354 metal lability as a function of soil pH for both MA and Urban soils, as a combined dataset. For all five metals, Figure 6 suggests that the relative importance of Fe-oxides for metal binding increases with pH, 355 whilst that of organic matter (HA and FA) decreases. The WHAM model predicted that, on average, 356 357 96% of the Pb was adsorbed on Fe and Mn oxides for the MA and Urban soils; Mn oxides were more important below pH 6.5. By contrast, organic matter was most important for Cu across the pH range 358 359 studied. Non-specific adsorption of Cd, Ni and Zn on clay was only significant in soils with very low pH values (pH 3.5 – 4.5) and low organic matter contents - less than 2.3%, 2.4% and 2.1% respectively. 360
- Various factors may affect WHAM model performance in predicting metal solubility including soil pH and solid binding phase. The influence of soil pH value on model performance was statistically significant for Cd, Cu, Ni and Zn (p < 0.01), but not for Pb. Overestimation of metal solubility (log scale) increased with soil pH to give a positive correlation coefficient between ΔpM_{soln} (i.e. bias between the predicted and measured solubility by WHAM on –log scale) and pH. For Cd, Ni and Zn, the bias (ΔpM_{soln}) observed seemed to be mainly associated with the (modelled) proportion of labile metal bound to Fe oxides—especially for Cd and Zn in the high pH range (positive correlation coefficient). In the

368 case of Cu, bias was affected by Cu binding to particulate Mn oxides, and HA and colloidal (solution

369 phase) FA. There was less over-prediction of solubility with increase in the proportion of Cu bound

- 370 with HA and greater over-prediction with binding to colloidal FA-Cu. Prediction bias for Pb was
- 371 relatively unaffected by soil pH or by the proportion bound to either Fe or Mn oxides; the range of bias
- 372 was greater for the Urban soils. Correlation (r) between $\Delta p M_{soln}$ and soil pH or percentage binding with
- 373 an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA) are
- 374 presented in Appendix 7.
- 375

376 4. DISCUSSION

377 4.1 The effect of soil properties and metal source on metal lability

378 Greater metal lability in the MA soils (**Fig. 1**) may partly reflect different soil-metal contact times for 379 the two soil datasets, but it seems very likely that the characteristics of the original metal source are 380 also responsible for lowering the lability in Urban soils. A similar conclusion regarding Cd lability in 381 field contaminated soils was also made by Degryse et al. (2004) comparing radio-labile Cd in soils 382 sampled adjacent to a smelter and 'metal salt incubated soils' but with a much shorter period of 383 incubation.

384 The relative lability of the five metals in both MA and Urban soils followed the sequence $Cd > Pb \ge$ 385 Cu > Zn > Ni which agrees with the observations of Gabler et al., (2007) who measured the lability of these five metals on 115 unpolluted soil samples using a stable isotope dilution approach. In the MA 386 387 soils, where metal ions were originally added in solution, the difference in lability of the five metals 388 only partly reflects their expected rates of fixation into soil constituents, based on a negative correlation 389 with ionic radius, i.e. Ni \ge Cu > Zn > Cd \sim Pb (Degryse et al., 2009; Degryse et al., 2007). The relatively 390 larger proportion of Zn and Ni fixed may have been due to substitution for Fe in oxyhydroxides 391 (Buekers et al., 2008a; Manceau et al., 2000), a mechanism which is less likely for larger ions such as 392 Cd and Pb (Buekers et al., 2008a; Xu et al., 2006). However, the lower lability of Pb compared to Cd 393 may be due to Pb precipitation as pyromorphite in phosphate-rich soils (Dermatas et al., 2008). Copper 394 is predominantly bound with organic matter which may result in a slightly higher lability compared to 395 Zn sorbed within Fe oxides.

396 For Ni and Zn, a smaller range of lability was seen in the Urban soils than in the MA soils. This may 397 be counter to expectation because the Urban soils had a larger range of metal contaminant sources and 398 the *range* of soil pH values (a major determinant of $%M_E$) in the MA and Urban soils were broadly 399 similar (Appendix 2). However, the lower lability of metal sources in the Urban soils also probably 400 acts to limit the range of $M_{\rm E}$ values in comparison with the MA soils. A restricted range of low $M_{\rm E}$ values have also been reported for Pb in calcareous minespoils soils (Degryse et al., 2004; Marzouk et 401 402 al., 2013a) and for Cd and Zn in soils contaminated with smelter wastes (Degryse et al., 2004). However, 403 the greater lability of Cd in the Urban soils, relative to other metals, does not necessarily indicate that

the original source of Cd was more soluble. It has been shown that Cd and Zn added to soil in identical
(isomorphically substituted) forms (e.g. sphalerite) nevertheless end up with quite different labilities
following prolonged exposure to soil processes (Marzouk et al., 2013a; Degryse et al., 2004).

407 4.2 Prediction of metal lability

408 Poor prediction of %M_E for Cu and Pb compared to Cd, Ni and Zn (Appendix 4) may arise from several 409 factors. It is widely recognised that adsorption on humus dominates Cu dynamics in soils (Weng et al., 410 2001) but no significant correlation was found between Cu lability and %SOC in this study (p > 0.05). 411 Another possible explanation is a failure to include factors which might promote strong Cu binding 412 phases in the model, such as sulphide content (Du Laing et al., 2009). In some soils Pb is likely to 413 precipitate in non-labile mineral forms such as chloropyromorphite (Pb₅(PO₄)₃Cl) (Lang and 414 Kaupenjohann, 2003); fractionation of Pb in soils is generally less well described by current geochemical models (Gustafsson et al., 2011). 415

416 The importance of pH as a predictor of lability (Appendix 4) is in agreement with previous studies (Rieuwerts et al., 2006; Marzouk et al, 2013b). Stronger adsorption of metals is certainly expected with 417 increasing pH, partly due to the increase in negative charge on all adsorption surfaces. Metal *fixation* is 418 419 not necessarily linked directly to strength of adsorption, but it seems reasonable to assume that factors 420 that increase adsorption strength will also reduce isotopic exchangeability. Other processes may also explain the influence of pH on lability, including preferential adsorption of metal hydroxide complexes 421 (Basta and Tabatabai, 1992) and precipitation as carbonate phases, (e.g. Gambrell, 1994; Charlatchka 422 423 and Cambier, 2000). In calcareous soils, diffusion into carbonate minerals (Hamon et al., 2002; Collins 424 et al., 2003; Buekers et al., 2007; Ahmed et al., 2008), or surface precipitation reactions (Ma et al., 425 2006b; Nazif et al, 2015) are important. The significance of individual soil properties in predicting $%M_E$ was metal-specific; a positive coefficient (Eq. 3) may suggest that the adsorbent holds 426 427 labile metal and a negative coefficient may indicate a source of metal fixation. Thus the addition of 428 FeOx improved the prediction for Ni and Zn possibly suggesting that an important mechanism for metal 429 fixation is diffusion into Fe oxide micropores (Jacquat et al., 2009; Manceau et al., 2000; Degryse et 430 al., 2011). Although MnOx was correlated with the lability of all five metals (Appendix 4), it explained 431 \leq 0.4% of total variance in predicting %M_E for Cd, Ni and Zn. For Cu and Pb, MnOx was more 432 important, accounting for 4.8 and 8.2% of the total variance in $M_{\rm E}$ with a negative coefficient, which 433 is in agreement with previous studies (Bonten et al., 2008; Weng et al., 2001). The contribution from clay content was extremely limited; only a very small proportion of 'isotopically labile' trace metal ions 434 are normally exchangeable with a neutral alkali-earth salt (Nakhone and Young, 1993). The correlation 435 436 with clay content may reflect a general association with soil mineral geocolloid content, rather than implying that Zn and Ni are fixed within alumino-silicate clay minerals. Nevertheless, specific 437 adsorption of Zn within hydroxyl-interlayered clays in acidic soils has been demonstrated by Degryse 438 439 et al. (2011). Finally, there was a negative correlation between total Cd, Ni amd Zn and content and

440 values of $%M_E$, probably because the larger content of native metal in the Urban soils (especially Zn)

441 was less labile than the (fixed amount of) metal ions added as soluble salts to the MA soils.

The logistic model performance was generally slightly poorer than the fit achieved with multiple linear regression (**Appendix 4** and **5**). However, **Eq. 4** has parameters (pH_{50} ; k_M) that are more clearly related to the mechanisms that control trace metal lability and provides extrapolative predictions that remain realistic. Therefore, the simple logistic equation, expressing %M_E solely as a function of pH, is perhaps a more robust model for predicting metal lability solely and more useful than regression coefficients for comparative purposes.

- 448 Over-prediction of %M_E values in the Urban soils compared to the MA soils probably reflects the 449 characteristics of the contaminant source on metal lability. This conclusion is further supported in Fig. 3 by the greater scatter of %M_E values for the Urban soils seen for Cu and Cd and perhaps also the 450 451 flatter trend with pH seen for Ni and Zn in Urban soils suggesting a primary mineral source less affected 452 by pH-dependent adsorption strength. In the Urban soils set, more than half of the high pH soils (> 6.5) were associated with old industrial sites, i.e. brownfield, wasteland, etc. (Appendix 2), where metals 453 454 probably entered the soils in a relatively non-soluble form. Secondary formation of poorly soluble 455 minerals in calcareous soils (Degryse, et al., 2009) or Pb minerals (e.g. cerussite or chloropyromorphite) 456 would also contribute to the trend seen. For example, the average measured lability of Pb in two phosphate-rich sewage farm soils (NG14 & NG15, 13.8%) was much less than that predicted by the 457 458 MA-parameterized model (50.0%) suggesting precipitation of Pb phosphate minerals either in the soil or during the processing of the sewage sludge. However, it was difficult to identify any specific effects 459 of historical or current land use on lability as, for example, soils from 'brownfield sites' produced values 460 461 of $%M_E$ for Cu ranging from 5.6% – 30.5% (NG19 and NG18, Appendix 2).
- No effect of pH on $\% \triangle M_E$ was identified for Ni or Zn. A potential explanation is that Ni in these soils 462 463 may be mostly attributable to parent material; this is supported by the low total Ni concentrations found (mean = 38.5 mg kg^{-1} ; SD = 18.4 mg kg^{-1}). Only two soils had substantially higher Ni concentrations 464 465 (Fig. 3). These were both from a sewage farm (NG14 and NG15) and had the highest values of %Ni_E (34.4% and 42.9%, respectively), suggesting that Ni lability in the sludge was high and that the soil-466 contaminant interaction was closer to the behaviour seen in the MA soils. It has been suggested 467 previously that metal lability can be more dependent on the characteristics of the sludge than properties 468 469 of the soil (Stacey et al., 2001). For example immobilization of soft acids such as silver, by soft bases 470 such as sulphide has been recognized in biosolids (Donner et al., 2015; Donner et al., 2013). This suggests that Ni, as an intermediate metal cation, will be more strongly held by carboxyl groups in the 471 472 organic matter of the sludge and remain labile. In contrast to Ni, total Zn concentrations in the Urban soils (mean = 283 mg kg⁻¹; SD = 178 mg kg⁻¹) were generally higher than in most soils in England and 473 Wales in which Zn is typically $<100 \text{ mg kg}^{-1}$ unless contaminated by minespoil (Rawlins et al., 2012). 474 475 Therefore it can be assumed that the Urban soils received Zn from sources other than parent material.

It is difficult to summarize the effect of land use on metal lability for the whole dataset because of the complex range of Zn sources. For example, from field notes, metals in soil WV20 were probably associated with canal dredgings whereas soil WV25 was contaminated from its location in an industrial estate and proximity to a railway - but both soils had similar values of %Zn_E (27.7% and 20.6% respectively). There was only one sample where Zn lability was, unexpectedly, underestimated by the MA-parameterized model and fell slightly outside of the RSD range: soil WV3 was a slightly acidic woodland soil (pH = 6.1) with very high DOC concentrations (180 mg L⁻¹ in 0.01 M CaCl₂, 1g: 30 mL).

483 4.3 Aging of Cd and Zn in air dried soils during storage

The difference between values of M_E measured in the current study and M_E* measured by Tye et al. 484 485 (2003) for Cd and Zn may be a consequence of processes occurring within the soils or it may be the 486 result of analytical artefacts in either of the two methods (Fig. 4). Only a limited number of studies have compared the measurement of metal lability using both radio-isotopes and stable isotopes. Sterckeman 487 et al. (2009) compared Cd lability measured using ¹¹¹Cd (stable; M_E) and ¹⁰⁹Cd (radioactive; M_E*) and 488 489 found that the results were equivalent but that M_E data were more repeatable. Considering the range of properties of the MA soils, continuing fixation of Zn may have occurred in some soils. Even in air-dried 490 491 soils, particles may have thin films of surface hydration which could mean that the soil remains 492 sufficiently chemically reactive to allow solid phase matrix- and surface-diffusion processes.

493 The greater difference between M_E and M_E* for the Urban soils was surprising as there was no 494 expectation of measureable metal fixation during the 12 years of air dry storage prior to measurement 495 of M_E in August and September 2011 whereas further slow fixation in the MA soils was expected. This result may indicate a methodological difference. Values of ME* were determined using flame-AAS 496 and graphite furnace-AAS measurement of Cd and Zn combined with radio-assay of ¹⁰⁹Cd and ⁶⁵Zn in 497 solution following centrifugation of soil suspensions at 2200 g. Values of M_E were determined solely 498 499 by ICP-MS following additional filtration to $< 0.22 \,\mu m$. Thus, the (large) values of M_E* measured in 500 1999 may have been more susceptible to the influence of non-labile metal in suspended submicron 501 particles (Lombi et al., 2003) - an effect which is enhanced at (i) higher pH values, (ii) lower soluble metal concentrations and (iii) lower values of %M_E - which are all characteristics of the Urban soils. 502

503 4.4 Effect of non-labile soil colloidal particles on measured E-value

A strong correlation between %M_E and %M_{Er} was expected because as metal lability increases there is 504 505 less scope for a substantial effect from non-labile SCP-metal as M_{Er} gradually approaches the value of M_E at 100% lability. The increase in Cu_E/Cu_{Er} with pH (Fig. 2b) is in agreement with previous 506 explanations of more mobile geocolloidal particles in the soil solution at higher pH values (Lombi et 507 al., 2003; Nolan et al., 2009; Marzouk et al., 2013b). The presence of non-labile soluble Cu has also 508 509 been shown to arise from strong adsorption of Cu on humic acid (Mao et al., 2015) whereas other trace metal ions (Cd, Ni, Pb and Zn) are more likely to be associated with colloidal Fe, Al and Mn oxides 510 (Lombi et al., 2003; Ma et al., 2006a; Nolan et al., 2009). However, in this work no significant 511

512 correlation (p > 0.05) was observed between the ratio of M_E:M_{Er} and solution concentration of Fe, Al,

513 Mn or DOC measured in 0.01 M Ca(NO₃)₂ (solid: solution ratio 1 g : 30 mL).

514 4.5 Prediction of metal solubility and fractionation with WHAM-VII

515 *Metal binding*

For all five metals the relative importance of Fe-oxides for metal binding appeared to increase with increasing pH whilst that of organic matter (HA and FA) decreased (**Fig. 6**). The pH-dependency of metal adsorption to Fe oxide is stronger than that of organic matter (Weng et al., 2004) and Fe oxide appeared to control metal binding at high pH (> pH 7), except in the case of Cu where organic matter was most important. Most of the Cu (> 91.0%) and Pb (> 92.3%) were absorbed by the soil across the pH range, even at low pH values, although there were substantial differences in their affinity for particular binding phases.

523 Errors associated with modelling

524 Errors in prediction of metal solubility may arise for reasons originating in both modelling and 525 measurement. Model shortcomings may include poor parameterisation of the 'pure' geocolloidal metal 526 binding parameters and failure to include all binding phases. The default constants in WHAM were 527 originally parameterized on single geocolloidal systems and the most comprehensive datasets used in 528 the sub-model employed (Model VII) were from studies of metal binding by purified humic and fulvic 529 acids. Therefore it is likely that soils in which humus is the dominant adsorption surface are likely to perform better than those with complex assemblages of organic and mineral geocolloids. As suggested 530 531 by Smith et al. (2004) the properties of the cation binding sites of humic substances in peat appear very similar to those of isolated humic substances. It has also been shown in other studies that prediction of 532 533 the trace metal solubility with multi-surface geochemical models is more successful when solid \rightleftharpoons 534 solution partitioning is controlled mainly by soil organic matter (Weng et al., 2002; Cances et al., 2003).

535 In contrast to Model VII for HA and FA, the surface complexation model for describing metal speciation 536 on mineral oxides may be less rigorous in (i) combining all soil oxide adsorbents into just three types (Al, Mn and Fe oxides) and (ii) using a single parameter to describe heterogeneity for all metals (Lofts 537 538 and Tipping, 1998) and oxides (default setting). Such simplifications are reasonable to avoid the need 539 for a large parameter database limiting the applicability of the model. However, it may also be the 540 reason for greater deviation from measured values in predicting solubility in high pH soils in which 541 oxides are the dominant metal binding phases. Soils will have a range of oxide minerals, which vary in 542 surface charge characteristics, surface morphology/area, crystallinity and degree of surface 543 contamination with adsorbed anions and humus acids. All of these factors together will generate a range of adsorption strengths for metal cations. As pH rises, a greater range of metal oxides contribute 544 545 to cation binding and so the *diversity* of oxide surfaces involved in metal adsorption will increase. 546 Therefore, if a speciation model generates error in predicting metal binding on oxides surfaces, the effect is likely to be more significant in high pH soils as there is an accumulation of error contributed 547

548 by each oxide phase. In addition, there are other binding phases in soils which may actively adsorb 549 metal cations especially in high pH soils. For example, calcite (CaCO₃) and hydroxyapatite 550 $(Ca_5(PO_4)_3(OH))$, which are only likely to be present in soils with high pH (> 7.0 and > 6.0 respectively), can adsorb metal cations by surface replacement of Ca^{2+} on mineral surface sites (Davis et al., 1987; 551 Ahmed et al., 2008; Bailey et al., 2005). The exclusion of these phases in the WHAM model may 552 553 contribute to the general over-prediction of solution metal concentration at high pH. Alternative 554 explanations offered within the literature include a failure to account for (i) synergistic effects 555 associated with adsorption on mixed oxide-humic surfaces (Heidmann et al., 2005; Pedrot, et al., 2009); 556 (ii) the existence of highly specific sites on Fe oxides with much greater intrinsic stability constants 557 than used in the general surface complexation model (Buekers et al., 2008b; Linde et al., 2007) or (iii) formation of discrete solid phases such as chloropyromorphite ($Pb_5(PO_4)_3Cl$) (Degryse et al., 2009), 558 which is likely to affect Pb dynamics in some of the Urban and sewage sludged soils. 559

560 Errors associated with measurement

561 Reasons for over-estimation and scatter in predicted solubility may lie not only with model limitations but also with the measurements undertaken to provide model inputs. Using reactive trace metal 562 concentrations based on M_E values instead of 'total' improves the model prediction (Marzouk et al., 563 564 2013b). However, poor model input data is also likely to arise from the various 'proxies' that are used 565 to represent geocolloidal binding phases. For example soil organic carbon is typically used to estimate soil humic and fulvic acid while the Fe, Al and Mn oxide phases are rather crudely represented by 566 567 elemental extraction with a reducing reagent such as dithionite-citrate-bicarbonate solution. A 568 significant underestimation of measured solubility (> RSD) was seen for a small number of soils (e.g. 569 WV7 for Ni, Cu and Pb; WV10 for Pb, Figure 5). This may be a result of overestimation of some of 570 the binding phases. For example, for soil WV7, WHAM predicted 70%, 83% and 97% of binding on Fe oxides for Cu, Ni and Pb, and the bias was-1.62, -0.83, and -2.25 respectively; this implies over 571 572 prediction of metal binding on Fe oxides. Given that generally the model algorithms underestimate 573 metal binding on mineral oxides, overestimation of metal binding suggests that, for these soils, the DCB 574 method extracted more Fe than was actually present in the Fe oxides phase, leading to an overestimation 575 of the Fe oxide content.

576 Bias in prediction of metal solubility in Urban soils

WHAM prediction of solubility in Urban soils generally produced a poorer correlation than that for MA 577 578 soils. This may be the result of slightly higher pH values in Urban soils as a consequence of the presence 579 of alkaline wastes such as cement, concrete etc. (Bridges, 1991; Rosenbaum et al., 2003). The higher 580 metal sorption capacity seen in some brownfield soils, compared to non-urban soils, is thought to 581 involve processes of both sorption and precipitation (Markiewiez-Patkowska et al., 2005; Mclean and 582 Bledsoe, 1992). Some particular examples include (i) a large bias (ΔpM) observed for Zn and Pb with values of 1.7 and 1.8 respectively in soil WV21; (ii) extremely low metal solution concentrations which 583 584 lead to greater experimental error in some urban soils - e.g. Zn in NG13 with pH 7.0 and total Zn

585 concentration 26 mg kg⁻¹; (iii) a very high binding capacity in sewage farm soils, possibly due to 586 extremely high phosphate concentrations from the sewage sludge resulting in overestimation of Cd 587 solution concentrations in NG14 and NG15.

588 5. CONCLUSIONS

589 For all five metals, lability in the MA soils was significantly greater than in the Urban soils, although 590 the relative lability of the five metals followed the same sequence $(Cd > Pb \ge Cu > Zn > Ni)$ in both 591 sets of soils. Lower metal lability in the Urban soils may reflect longer soil-metal contact times but also 592 strongly suggests that metal source characteristics are more important. In the MA soils, a good 593 prediction of %E-value was achieved using both linear and logistic models with pH value as clearly the 594 most important soil property. Lability of Cu was least affected by soil properties. The addition of FeOx 595 improved the prediction for Ni and Zn lability, while MnOx was important for Pb at pH values < 5.5. 596 However, although the performance of the logistic model was no better than the linear one, it offers 597 more realistic boundaries to model outcomes (${}^{\%}M_{\rm E} = 0 - 100\%$) and is therefore perhaps a more robust 598 model for predicting metal lability solely from soil properties and more useful than regression 599 coefficients for comparative purposes. Soil pH affected metal lability in the Urban soils in a trend 600 qualitatively similar to that of the MA soils. However, in all cases, the effect of contaminant source was 601 evident from gross over-prediction of %E-value in Urban soils using logistic models parameterized with 602 data from the MA soils. Continuing fixation of Cd and Zn may have occurred during soil storage. A 603 more pronounced difference between M_E and M_E* was observed in high pH soils than in acidic soils. 604 However, the difference between lability measured in 1999 and in the current study may also be due to 605 the influence of non-labile SCP-metal in the earlier measurement.

Overall WHAM-VII predicted trace metal solubility reasonably well for both sets of soils and bias was 606 607 observed mainly in soils with low metal solubility and relatively high soil pH values. For Cd, Ni and 608 Zn, the bias observed was primarily associated with the proportion of labile metal predicted to bind to 609 Fe oxides. In the case of Cu solubility, prediction bias was affected by Cu binding to particulate Mn 610 oxides, and HA and colloidal (dissolved) FA. Of the five metals, Pb solubility was most poorly 611 described. Solubility of all metals was predicted more accurately in the MA soils than in the Urban 612 soils. This was likely to be the result of slightly higher pH values in the Urban soils or could indicate 613 that the influence of metal source was not completely eliminated by using isotopically exchangeable 614 metal as our best estimate of the labile metal pool required as input to WHAM VII. The poorer 615 performance of WHAM-VII in predicting metal solubility in high pH soils may be the result of errors in modelling, including the exclusion of potential adsorption surfaces such as CaCO₃, or simplicity of 616 617 the sub-model describing metal binding with mineral oxides. However there must also be considerable error associated with the simplistic representation of binding phases by measurement of 'extractable' 618 619 Fe and bulk soil organic carbon.

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Figure 1: Box and whisker plot showing lability of Cd, Cu, Ni, Pb and Zn ($\% M_E$) for MA soils (23) and Urban soils (50); the mean value (×) is also shown and outliers are marked as an asterisk.



Figure 2: Ratio of M_E : M_{Er} as a function of M_E (a) and pH (b) for Cu in MA (•) and Urban (Δ) soils.



Figure 3: Measured values of $%M_E$ (Cd, Cu, Ni, Pb and Zn) for MA (\bullet) and Urban (Δ) soils. The solid line represents the predicted trend in $%M_E$ from Equation 4.



Figure 4: (a) Comparison of $\%M_E$ (this study) and $\%M_E^*$ (Tye et al., 2003) for Zn and Cd in MA (•) and Urban (Δ) soils; the solid line is the 1: 1 line. (b) The ratio of $M_E : M_{Rad}$ as a function of pH.



Figure 5: Solution concentrations ($pM_{soln} = -log_{10}(M_{soln})$) of Cd, Cu, Ni, Pb and Zn predicted by WHAM-VII against measured values for MA (\bullet) and Urban (Δ) soils suspended in 0.01 M Ca(NO₃)₂ (1 g: 30 mL). M_E was used as the input variable for reactive metal concentration. The solid line represents the 1:1 relation, and the dashed lines represent ± 1 RSD for the model. Values of RSD and correlation coefficients (r) are also shown.



Figure 6: The first column shows fractionation by isotopic exchange into labile and non-labile metal (Cd, Cu, Ni, Pb and Zn) as a % of total soil metal content in MA (n=23) and Urban (n=50) soils, grouped by pH class. The second column shows the predicted distribution of the labile metal, only, between particulate humic and fulvic acid (HA and FA), Fe, Mn and Al oxides (FeOx, MnOx and AlOx), clays and the solution phase (Soln). Fractionation of labile metal was predicted using WHAM-VII parameterized using M_E as input (Appendix 1).

Appendix 1: Summary of the variables, parameters and settings for WHAM-VII modelling of trace metal solution concentration, speciation and fractionation.

Variable	Settings
Suspension condition	
Suspended particulate matter (SPM)	33.33 g L ⁻¹
Temperature (K)	288.15 K (15°C)
PCO ₂ (atm)	Measured bicarbonate concentration (DIC)
Soil pH	Measured in 0.01 M Ca(NO ₃) ₂ soil suspensions.
Charge balance options	No charge balance imposed i.e. a fixed (measured) pH value was used
Adsorption phase (g L^{-1})	
Clay content	MA soils: estimated from soil texture
-	Urban soils: measured by laser granulometry
Fe, Al and Mn oxides	DCB extraction; converted to Fe ₂ O ₃ .H ₂ O, Al ₂ O ₃ and MnO ₂
Humic and fulvic acid	Measured by alkaline extraction
Colloidal fulvic acid	Estimated from measured DOC
Major cation and anion concentration (mol L^{-1})	
Dissolved major cations	Concentration in filtered soil suspensions (0.01 M Ca(NO ₃) ₂)
(Na, Mg, Al, K and Ca)	<i>Precipitation option for Al:</i> One mole of precipitated Al(OH) ₃ forms 87 g of the binding phase within the particulate soil phase.
Fe ³⁺ activity	<i>Precipitation option for Fe:</i> assumes that Fe^{3+} activity is controlled by $Fe(U)(OH)$ solubility – calculated within the model
Dissolved nitrate (NO_2^{-})	Solution concentration estimated as 0.02 M in the suspension
Total dissolved carbonate (all species)	Estimated from total inorganic carbon measured in solution
Total dissolved carbonate (all species)	Estimated from total morganic carbon measured in solution
Trace reactive metal concentration in soil susper	nsion (mol L ⁻¹)
Total concentration	Estimated from E-values (M _E)
Ni, Cu, Zn, Cd and Pb	
Other settings	
Activity coefficient correction	Debye-Hückel
WHAM parameter data sets	Default master, solute and binding phase data bases.
-	

Soil series*	рН	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*
		%	g kg⁻¹	g kg⁻¹	g kg⁻¹	%	mg kg⁻¹	mg L ⁻¹				
Bardsey	3.57	3.18	19.9	0.16	1.44	35.0	69.6	134	273	2.5	343	48.1
Wick	3.76	4.47	17.9	0.22	1.26	10.0	82.1	158	327	2.7	346	58.1
Iveshead	3.79	6.55	16.3	0.20	2.99	5.0	73.8	147	328	3.1	345	46.0
Pwelliperian	4.69	3.03	14.6	0.47	3.44	35.0	97.7	161	498	3.1	341	26.0
Rivington	5.27	3.36	10.4	0.40	0.65	5.0	71.1	133	324	2.9	311	29.7
Braunshweig	5.36	2.28	5.4	0.61	0.10	15.0	73.3	138	318	2.8	292	18.0
Woburn	5.61	1.00	20.1	0.24	0.24	5.0	76.5	136	287	2.7	294	15.4
Fladbury	5.67	4.66	24.8	0.86	0.94	70.0	111	155	385	3.3	328	21.9
Ticknall	5.72	5.20	20.9	0.48	1.76	15.0	86.9	150	437	3.0	572	16.6
Cottam	5.76	2.08	15.6	0.61	0.67	15.0	92.1	161	365	3.5	332	12.9
Rosemaund	5.84	1.86	10.8	0.74	0.56	35.0	124	153	351	2.9	297	9.9
Arrow	6.06	2.08	15.9	0.57	0.64	10.0	83.1	156	347	3.2	323	10.3
Watlington	6.11	1.24	18.2	0.81	0.22	10.0	88.5	146	335	3.1	304	13.1
Insch	6.20	4.13	27.4	0.78	7.38	17.5	79.2	140	293	2.8	268	29.4
Newport	6.31	1.03	15.8	0.51	0.55	10.0	83.3	157	350	2.9	314	13.5
Gleadthorpe	6.45	1.68	8.8	0.35	0.41	10.0	75.2	145	341	3.0	306	13.8
Denchworth	6.78	4.42	18.9	0.77	1.07	70.0	98.0	155	316	2.8	300	10.8
Ragdale	6.78	4.10	29.8	0.79	1.60	35.0	107	154	404	3.3	321	13.3
Bridgets	6.91	2.38	28.7	2.68	3.01	35.0	108	142	377	4.3	306	7.1
Marian	6.95	7.06	15.8	2.54	0.15	35.0	93.6	172	417	3.2	377	16.3
Worcester	7.08	2.88	15.4	0.79	0.00	35.0	124	166	436	3.3	339	5.2
Hanslope	7.08	4.39	27.6	0.77	1.41	35.0	93.6	139	360	2.9	285	16.2
Evesham	7.12	2.38	22.0	0.98	1.11	70.0	97.6	155	337	3.0	312	7.6

Appendix 2 a): Summary of soil properties and total Ni, Cu, Zn, Cd and Pb concentration following metal amendment in MA soils.

*Soil Survey of England and Wales classification of soil series.

**DOC determined in suspension (1 g soil: 30 mL water).

Sample	рН	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*	Grid Ref.	Landuse
		%	g kg ⁻¹	g kg⁻¹	g kg ⁻¹	%	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg⁻¹	mg kg ⁻¹	mg L ⁻¹		
WV1	4.63	3.43	8.4	0.24	0.81	20.4	18.3	35.4	134	0.4	56.7	35.8	391030 301170	Grassland (golfcourse)
WV2	3.92	2.81	9.7	0.44	1.08	22.5	12.1	19.4	61.5	0.3	53.2	40.6	388450 300860	Grassland (golfcourse)
WV3	6.11	10.99	18.2	1.26	1.59	15.7	55.3	403	1050	3.7	266	59.4	393690 297700	Park
WV4	5.87	3.35	13.8	0.46	1.07	19.8	22.9	69.1	313	0.6	109	23.0	392180 297280	Grassland (open land)
WV5	6.46	13.28	26.3	0.84	1.16	14.6	77.9	233	588	1.3	227	8.0	393730 296530	Old industrial (gas works)
WV6	6.84	9.81	38.5	1.52	2.50	18.6	300	2200	4170	26.1	746	8.0	394490 295160	Wasteland (old landfill)
WV7	7.41	5.40	23.1	0.67	0.88	16.9	83.3	493	1170	3.6	590	3.2	394960 295960	Grassland
WV8	5.64	10.07	19.7	0.92	4.47	16.4	57.4	158	553	2.1	358	17.7	397060 296980	Woodland
WV9	5.56	4.39	16.8	0.62	1.66	18.4	32.3	134	300	0.9	273	17.5	390170 301290	Grassland
WV10	7.07	8.01	19.9	0.84	0.94	18.3	66.9	298	1100	4.1	1050	9.7	391330 301090	Old industrial (tyre factory)
WV11	4.46	3.68	14.9	0.38	1.80	22.9	25.3	87.7	514	1.9	173	28.9	390810 296710	Domestic garden
WV12	5.79	2.73	11.1	0.51	0.75	18.9	15.0	30.4	270	0.7	199	22.9	388240 295750	Grassland
WV13	5.54	3.83	12.6	0.64	0.71	24.4	25.4	51.1	308	1.0	131	22.1	392760 295760	Park
WV14	5.22	25.08	20.3	0.55	0.68	5.1	58.4	265	1190	5.1	332	16.2	392830 299710	Nature reserve (railway)
WV15	7.12	11.17	19.2	3.01	0.55	11.8	47.6	101	290	1.1	140	24.7	388910 299580	Nature reserve (railway)
WV16	4.01	14.46	7.1	0.27	5.10	16.8	29.1	89.1	135	0.7	88.4	18.0	392380 295460	Vegetated colliery spoil heap
WV17	5.64	2.76	11.1	0.52	0.87	19.4	26.9	73.8	239	0.6	141	50.3	391240 297580	Old industrial (disused factory)
WV18	4.63	5.49	16.7	0.51	2.49	22.6	39.8	204	524	1.7	150	26.3	395120 299290	Grassland (not maintained)
WV19	5.37	5.19	12.6	0.41	0.01	19.1	45.8	58.7	192	0.5	48.7	11.6	395150 299140	Grassland
WV20	4.14	4.54	10.8	0.25	2.36	15.3	15.1	77.6	105	0.5	85.7	30.4	396720 301130	Grassland
WV21	6.41	2.85	13.5	0.48	0.00	24.0	54.5	48.7	102	0.2	31.9	7.8	393960 299860	Brownfield
WV22	8.08	2.50	12.3	0.35	0.00	21.3	43.1	90.0	154	0.3	45.9	7.3	394390 299860	Brownfield
WV23	7.63	1.37	12.8	0.29	0.02	19.0	65.6	79.0	267	0.7	78.8	19.4	395400 299670	Brownfield
WV24	7.22	2.64	14.1	0.45	0.43	21.1	33.6	82.3	605	1.2	351	12.3	394680 299830	Brownfield
WV25	4.05	11.36	20.1	0.70	3.84	13.8	55.2	188	356	1.8	217	20.7	394210 298970	Grassland (park)
WV26	6.60	2.70	9.9	0.28	0.00	20.6	20.0	52.6	133	0.5	63.3	23.2	394600 298750	Grassland
WV27	7.67	3.16	28.7	0.54	0.29	20.5	39.1	160	279	0.6	177	15.3	392800 298520	Brownfield
WV28	7.25	5.85	21.1	0.44	0.66	18.8	44.8	150	281	0.6	156	10.6	391700 310630	Brownfield
WV29	6.87	20.50	27.4	1.03	0.64	20.0	94.1	338	739	3.3	429	10.4	391680 300080	Deciduous woodland
WV30	6.32	3.60	13.5	0.34	0.26	18.6	24.0	82.3	158	0.6	109	18.3	391780 300120	Grassland (park)

Sample	рН	SOC	FeOx	MnOx	AlOx	Clay	Total Ni	Total Cu	Total Zn	Total Cd	Total Pb	DOC*	Grid Ref.	Landuse
		%	g kg⁻¹	g kg⁻¹	g kg ⁻¹	%	mg kg⁻¹	mg kg⁻¹	mg kg ⁻¹	mg kg⁻¹	mg kg⁻¹	mg L ⁻¹		
NG1	4.75	5.00	40.6	1.67	3.81	24.6	49.5	51.4	340	1.8	194	29.9	455470 336660	Grassland (football field)
NG2	5.52	4.77	14.9	0.86	2.33	28.7	24.4	50.0	229	1.1	412	18.6	455280 338770	Churchyard
NG3	6.47	5.10	34.4	1.14	1.60	21.4	44.1	26.5	111	0.3	60.9	29.1	453760 341550	School
NG4	6.29	5.25	18.8	0.49	1.24	18.3	37.1	224	881	2.5	1300	7.0	454700 343720	Domestic garden
NG5	6.99	3.26	14.6	0.47	0.38	20.1	31.6	57.9	439	1.1	353	14.6	457360 342370	Domestic garden
NG6	6.78	10.70	39.5	0.81	1.36	19.8	60.1	161	459	2.0	406	14.6	458720 339210	Railway
NG7	7.00	5.31	21.4	0.85	0.88	18.8	59.0	129	359	1.5	385	13.0	458500 339110	Grassland (imported)
NG8	4.15	7.90	38.2	1.32	4.52	18.0	62.6	65.2	374	1.6	352	63.5	459710 339170	Grassland (racecourse)
NG9	6.27	4.81	14.6	0.38	1.50	20.5	28.2	47.6	169	0.6	205	14.5	453570 344310	Vegetated colliery spoil heap
NG10	6.53	5.21	18.5	0.79	1.38	21.7	35.2	54.4	301	0.8	257	11.7	455170 342480	Vegetated colliery spoil heap
NG11	7.25	8.56	25.3	1.30	1.83	14.8	228	1260	1690	2.1	1110	6.4	455770 338590	Disused factory
NG12	7.38	13.49	43.0	2.31	3.32	12.1	380	3190	2520	5.6	1240	6.9	455760 338550	Disused factory
NG13	7.02	1.28	15.6	0.35	0.03	20.7	20.3	26.0	26.0	0.1	18.5	8.0	453570 344210	Grassland (amenity)
NG14	6.54	11.41	16.7	0.59	3.59	13.0	370	644	1740	38.2	600	22.4	464120 340530	Sewage Farm
NG15	5.99	6.86	15.5	0.30	2.79	20.7	199	382	1020	19.2	337	21.1	464130 340810	Sewage Farm
NG16	7.57	5.03	25.0	0.93	0.61	18.9	44.0	92.9	223	0.9	121	7.3	462830 340800	Brownfield
NG17	6.34	18.25	27.7	1.06	1.33	11.6	99.0	274	634	1.1	1410	16.9	462770 340730	Brownfield
NG18	6.78	3.35	22.2	1.13	0.60	20.1	43.7	35.7	216	1.4	79.2	11.2	462900 340700	Brownfield
NG19	6.93	2.98	34.8	1.43	2.19	18.7	32.3	31.7	132	0.4	65.9	12.3	446800 339730	Brownfield
NG20	6.68	3.00	31.0	0.70	1.01	24.0	32.2	52.9	299	0.7	90.0	19.6	447040 339240	Brownfield

Appendix 2 c): Summary of soil properties, sampling location, land use and total Ni, Cu, Zn, Cd and Pb concentration in Urban soils (Nottingham).

	Ni	Cu	Zn	Cd	Pb
ΔM_{E}	-0.14	1.76	-0.52	-0.35	-1.59
RSD	0.79	4.84	28.22	0.13	15.49
r	0.999	0.997	0.973	0.997	0.963
p-value	>0.05	<0.01	>0.05	>0.05	>0.05
SE%me	0.371	0.873	1.218	2.167	1.216
SE _{%MEr}	0.468	0.666	0.636	1.189	1.854

Appendix 3: Average difference between $\%M_E$ and $\%M_{Er}$ (ΔM_E), RSD, R², p-values for correlations between $\%M_E$ and $\%M_{Er}$ and standard error of the mean for replicate estimates of $\%M_E$ and $\%M_{Er}$.

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Appendix 4: Linear regression model coefficients, RSD and r values for model prediction of $%M_E$. The regression (see Eq. 3) was parameterized from $%M_E$ (mg kg⁻¹) measured on MA soils. Values in brackets are the % of total variance, *n.s = not significant*.

	Constant	рН	%С	FeOx	MnOx	AlOx	Clay	Total metal	RSD	r
				(g kg-1)	(g kg-1)	(g kg-1)	(%)	content		
								(mg kg⁻¹)		
Ni	176	-14.7**	-0.96	0.20*	0.90**	-4.42	0.02*	-0.55**	5.85	0.97
		(73.1)		(10.8)	(<0.10)		(<0.10)	(1.90)		
Cu	99.7	-4.87*	-1.20	0.38	-1.34*	-3.46*	-0.01	-0.13	5.20	0.83
		(25.5)			(4.80)	(24.7)				
Zn	180	-14.6**	0.53	0.04*	1.49**	-4.68	-0.19*	-0.13*	7.70	0.95
		(66.1)		(5.5)	(<0.10)		(<0.10)	(10.9)		
Cd	185	-11.5**	-0.39	0.12	3.10**	-3.39	0.06	-13.2**	6.30	0.92
		(63.2)			(0.40)			(7.70)		
Pb	75.9	-7.02**	-1.08	0.57	-7.26**	-0.76	-0.01	0.06	6.91	0.85
		(53.3)			(8.20)					

** significant (p< 0.01), * significant (p< 0.05)

Appendix 5: Values of model parameters (pH_{50} , k_M , n), RSD, r values and Δ %M_E (average deviation of predicted %M_E from measured value) from sigmoidal model prediction of %E-value using Eq. 4 and Eq. 5 applied to MA soils only. The values in bold italic are the best fit of the measured %M_E.

		Ni	Cu	Zn	Cd	Pb
Equation 4:						
	pH₅o	5.06	5.55	5.36	7.89	6.33
	kм	0.76	0.16	0.72	0.66	0.35
	RSD	11.5	7.59	13.2	8.73	8.97
	r	0.85	0.51	0.81	0.77	0.72
	Δ%Μ _Ε	-0.39	-0.01	0.01	0.13	0.12
Equation 5:						
pH + %SOC	pH₅₀	4.94	5.17	5.02	7.59	6.27
	kм	0.54	0.07	0.23	0.38	0.12
	n	0.28	0.57	0.95	0.86	0.86
	RSD	11.2	7.66	13.3	11.5	8.53
	r	0.86	0.50	0.81	0.65	0.76
	Δ%Μ _Ε	0.18	0.66	1.43	0.37	0.74
pH + Ox	pH₅₀	4.99	5.47	5.29	8.03	6.40
	kм	0.16	0.06	0.12	1.19	0.13
	n	0.83	0.57	0.95	-0.40	0.55
	RSD	10.4	7.45	12.3	8.06	8.80
	r	0.88	0.53	0.84	0.81	0.73
	Δ%Με	0.15	0.40	1.08	0.06	-0.02
pH + %Clay	pH₅₀	5.01	5.70	5.16	7.22	6.46
	kм	0.20	0.03	0.03	0.10	0.02
	n	0.41	0.57	0.95	0.86	0.86
	RSD	10.0	7.17	14.5	11.8	11.4
	r	0.89	0.58	0.77	0.65	0.51
	Δ%Με	1.05	0.12	2.75	0.19	2.04

Appendix 6: Summary of model outcomes comparing predicted and measured solution concentrations of Ni, Cu, Zn, Cd and Pb using E-values (M_E) as input variables to WHAM-VII (Appendix 1; Fig. 5).

	Ni	Cu	Zn	Cd	Pb
	0.51	0.45	0.82	0.62	0.64
KSD	0.51	0.45	0.83	0.63	0.64
r	0.94	0.74	0.94	0.94	0.85
Δp(M)	0.40	0.23	0.58	0.56	-0.02
slope	0.82	0.73	0.54	0.78	0.80
intercept	0.77	1.53	2.08	1.11	1.70

Appendix 7 a): Correlation (r) between ΔpM_{soln} (the bias between measured and modelled solubility by WHAM on a –log scale) and soil pH or percentage binding with an important particulate phase (FeOx, MnOx, AlOx, HA) or colloidal (dissolved) phase (FA).

r	Ni	Cu	Zn	Cd	Pb
рН (p<0.01)	0.431	0.354	0.751	0.749	
FeOx (p<0.05)	0.284		0.744	0.532	
MnOx (p<0.05)	0.270	0.342			
HA (p<0.05)		-0.414			
Colloidal-FA		0.510			

Appendix 7 b): Difference between measured and predicted Pb solubility (ΔpPbsoln) as a function of (a) soil pH and fractional sorption by (b) FeOx and (c) MnOx.

