

1 *Labile fractions of metals and As in mining impacted soils.*

2 **Core ideas:**

3 Weathering processes increase lability of metals in mining wastes.

4 Soil properties rather than ore lithology explained the labile fractions of Pb, Cd, Cu, and Ni in
5 mining contaminated soils.

6 Ore lithology was the dominant factor explaining labile fractions of Zn and As.

7 Earlier generic models adequately explain metal lability in mining waste impacted soils.

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9 **The Labile Fractions of Metals and Arsenic in Mining Impacted Soils are Explained by Soil**

10 **Properties and Metal Source Characteristics**

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17 **Abbreviations:** C, contaminated soil samples; DOM, dissolved organic matter; E, labile metal

18 concentration; %E, labile metal fraction; eCEC, effective cation exchange capacity; (Fe/Al)_{ox},

19 oxalate extractable Fe and Al; Fe_{ox}; oxalate extractable Fe; FeOx, iron oxy-hydroxides; GMS,

20 Mexican Geological Survey (in Spanish); IA, isotopic abundance, ID, isotopic dilution; M_{tot}, total

21 metal concentration; MBC, mass bias correction; OC, organic carbon; TOC, total organic carbon;

22 U, uncontaminated soil samples; W, waste samples.

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ABSTRACT

Isotopically exchangeable metals in soil, also termed labile metals, are reversibly bound to soil surface and are a better index of the environmental risk of the metals than are their total concentrations. In this study, labile fractions of potentially toxic elements were surveyed in metal mining impacted soils of Mexico to test the relative importance of either soil properties (pH, eCEC, OM, etc.) or attributes of the mines (ore type and lithology, metal mineralogy, etc.) on the fractions of labile elements. Mining waste impacted soils, corresponding uncontaminated soils and mining waste were collected around 11 metal mines in Mexico presenting contrasting ore types. Pseudo-total concentrations and labile fractions of Cd, Ni, Zn, Pb, Cu and As were determined by aqua regia digestion and isotope dilution, respectively. Pseudo-total concentrations of these elements ranked: waste>contaminated soil>uncontaminated soils, and Zn and As dominated the concentrations of toxic elements. The labile fractions (% of total) in the soils ranked, with median values in brackets, Pb (22)>Cd (18)>Cu(15)>Ni~Zn(13)>As(9). The labile fractions of waste samples were slightly higher than those of soil samples suggesting either a high weathering of mining wastes or the stabilization of heavy metals by soil. Stepwise multiple regression showed that soil properties rather than source attributes primarily explained the %E of most elements, except for Zn and As for which the ore lithology was the dominant factor. This study showed that earlier generic models explain metal lability adequately in mining waste impacted soils.

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Introduction

The dispersion of toxic metals and metalloids by wind and water is of major environmental concern in regions with intense metal mining. This dispersion process is accelerated where the sites are devoid of plant cover due to metal toxicity. Therefore, a realistic estimation of phytotoxic doses of these elements in soil is required as a first step towards effective site remediation. It is well established that total concentrations of metals in soil are poor indices for toxicity to plants, since a significant fraction of the toxic trace metals might be present as unweathered, poorly soluble minerals (Hamels et al. 2014). The bioavailability and, hence, environmental risk, partially depends on their solubility in soils (Allen 1993; Plette et al. 1999). However, soil solution concentrations of metals are not unequivocal toxicity indices, since metal toxicity is also affected by the presence of competing ions such as protons and Ca^{2+} during their uptake by plant roots, this concept is the basis of the terrestrial Biotic Ligand Model for toxicity (Thakali et al. 2006). A systematic assessment of toxic thresholds of cationic metals revealed that metal toxicity to plants is primarily mitigated by soil cation exchange capacity and secondly ageing reactions that take place after soil spiking and before the toxic threshold is derived (Smolders et al. 2009). The metal ageing process can be addressed by the metal(loid) concentration that is isotopically exchangeable in soil (the labile metal concentration, also termed E-value or %E when it is referred to total concentrations). The labile metal is conceptually equivalent to the metal concentration involved in the solid-liquid partitioning of a freshly spiked soil with a soluble metal salt. It has been demonstrated that ageing reduces the %E of Cu, Zn, Cd and As added to soils as soluble salts from initially 100% to lower fractions in the subsequent months (Crout et al. 2006; Smolders et al. 2012; Tye et al. 2002). After ageing, %E values strongly relate to soil properties, likely due to pH dependent fixation of metals in amorphous Fe&Al oxyhydroxides and/or organic matter

65 ^{[14],[15]},(Buekers et al. 2007). Metal toxicity in mining impacted soils to plants revealed that the
66 labile metal concentration indicates the toxicity rather well, pointing at the E-value as an
67 acceptable index of the available metal in soils that can be used in risk assessment (Hamels et al.
68 2014) (Smolders et al. 2009).

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70 Isotopic dilution (ID) is well recognized as a reference method to determine metal and metalloid
71 E-values in soils using whether radioactive or stable isotopes, the latter allowing multi-element
72 determination in single-step extractions (Garforth et al. 2016). In contrast to other labile metals
73 single extractions, the ID is robust across different types of electrolytes, solid:liquid ratios, pre-
74 equilibration times, separation methods, and it is measured at native soil pH and ionic strength
75 with minimum solid phase disturbance (Hamon, Parker, and Lombi 2008; Young et al. 2006). The
76 E-value is, however, operationally defined by the time-specific exchange in a soil suspension
77 (Rodriguez et al. 2005; Young et al. 2000).

78
79 In environmental samples, trace elements are not added as soluble forms in most situations. For
80 example, mining impacted soils have been contaminated with poorly soluble and non-labile ore
81 minerals. Conceptually, the %E might first increase by weathering followed by a decrease due to
82 gradual metal immobilization during soil ageing, however that concept has not been demonstrated
83 in a longitudinal study. Surveys of environmentally contaminated soils have shown that the role
84 of soil properties, such as pH, relate only poorly, to the %E values of Zn, Cd, Pb and Cu and that
85 %E is generally below that of the pH dependent labile fractions in soils that had been spiked with
86 metal salts (Degryse, Buekers, and Smolders 2004; E. Marzouk et al. 2013b; Smolders et al. 2012).
87 Multivariate models were fitted to data of %E of Cd, Cu, Ni, Pb and Zn of a set of 3 year aged

88 metal salt amended soils (n=23) and a second set of urban contaminated soils (n=50)(L. Mao et al.
89 2017). In general, the contaminated soil samples exhibited similar trends between %E-and soil
90 properties as in metal salt spiked soils, but %E were lower than those in the metal salt amended
91 soils illustrating the role of the contamination source on metal lability. Marzouk et al. (2013) (E.
92 Marzouk et al. 2013b) studied %E of Cd, Pb and Zn in a Pb mining affected catchment in England
93 and found that soil pH, organic matter and total metal content strongly affected the %E values.
94 The relationship between %E and total metal concentrations showed a binary trend, increasing at
95 low doses followed by a decrease at larger doses. The former trend was interpreted from saturation
96 of high affinity fixation sites and the latter trend indicating the presence of non-labile ore minerals
97 in soil. Surprisingly limited data exist on labile fractions of As in mining-impacted soils despite
98 the fact that it is the primary suspected toxic element in several metal mines worldwide. As far as
99 known, no study has yet surveyed a wide range of mining-impacted soils around mines to test
100 variability in labile fractions due to contrasting characteristics of the metal source.

101
102 At a world scale, Mexico is the first producer of silver, the second place in mercury production,
103 is among the top five producers of cadmium, molybdenum, bismuth, lead and zinc, and among the
104 top 10 producers of gold and copper (Reichl C. et al. 2018). This study was primed by a survey of
105 mining impacted soils in Mexico where As is the suspected primary toxic agent as judged from
106 the total concentrations. The objective of this study was to survey the labile fractions of potentially
107 toxic elements in soils of different mining impacted regions. The sampling was designed to better
108 identify the role of the ore type, ore lithology, main extracted metals and metals mineralogy,
109 relative to that of the properties of the receiving soils in determining the labile fractions in soil.
110 The premise was that sampling a wide range of metal mines with contrasting mineralogical

111 characteristics will help to untangle effects of source versus soil properties. Hence, labile fractions
112 of five metals (Ni, Cu, Zn, Cd and Pb) and As were determined by isotopic dilution in soils and
113 wastes samples from several Mexican mining sites and these fractions were statistically related to
114 soil properties and metal-contamination source characteristics .

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MATERIALS AND METHODS

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Sampling

119 Eleven locations with intense actual or former metal mining activity were selected within the
120 central region of Mexico (Table 1 and Figure SI1). Each location had a different mine. Mine-
121 specific characteristics of metal source were obtained from the Mexican Geological Survey (SGM)
122 (Servicio Geologico Mexicano (SGM) 2003) or from interviews with mine managers and included:
123 the main extracted metals (those mined with economical interest), the ore type (according to SGM
124 classification, verified on geological maps), the mineralogy of the metals (main chemical form of
125 metals in the original ore), the ore lithology (type of material enclosing the ore), the treatment or
126 not of the mining waste and the oxidation of the waste (scored by apparent color at the moment of
127 collection). At each location, one or two pairs of uncontaminated and contaminated soil samples
128 were collected (Table 1). Where possible, mining wastes were collected as well. A total number
129 of 32 soil and 10 waste samples were collected between February and May 2014 (Table 1).
130 Additional relevant information on the sampling locations is shown in (Table SI1). The
131 uncontaminated soil samples were consistently collected at a minimal uphill distance of 100 m
132 from the mining dam edge, preferably at undisturbed places, while contaminated soil samples were
133 collected at the border of waste dams. The uncontaminated and contaminated soil samples

134 consisted of about 20 kg of top soil (0–20 cm depth) taken after cleaning the shallow litter. Mining
135 waste, about 5 kg, was collected directly inside the dams at a minimal distance of 5 m from the
136 dam border. All samples (n=42) were air dried and sieved at 4 mm. Each sample was mixed to
137 ensure homogeneity. The soils were stored at room temperature, in dry and dark conditions until
138 further analyses.

139

140 **Table 1.** Selected properties of the 11 locations where soils and mining wastes were collected. The sampling locations, sample numbers
 141 and sample types are given in Figure S1.

Location	Samples		Mining district	Economic interest metals ^a	Ore type ^a	Mineralogy ^{a,b}	Lithology ^a	Soil pH range ^c	Soil OC range (%) ^c
	Number								
I	1 and 2		Zimapan	Cu, Pb, Zn	Mesothermal	S, Ox, CO ₃ , SO ₄ , AsO ₄	Limestone-quartz	6.6-6.9	2.0-4.5
II	3 and 4		Taxco	Ag, Au, Cd, Cu, Pb, Zn	Epithermal	S	Limestone	6.7-7.1	1.5-2.5
III	5		Zacualpan	Ag, Cu, Pb, Zn	Mesothermal	S	Quartz	6.1-6.2	0.5-2.3
IV	6 and 11		Pozos	Ag, Au, Cu, Pb, Zn	Epithermal	S	Quartz	6.7-7.7	1.0-4.7
V	7 and 8		Guanajuato	Ag, Au, Pb, Zn	Epithermal	S	Sericite	6.9-8.6	0.3-0.9
VI	9		Guanajuato	Ag, Au, Pb, Zn	Hipothermal	S	Limestone	6.1-7.2	0.8-1.2
VII	10		Guanajuato	Ag, Au	Hipothermal	S	Quartz	7.2-7.3	1.2-2.1
VIII	12		Guanajuato	Au, Ag, Cu	Epithermal	S	Sericite (colorless mica)	7.0-7.3	0.1-0.7
IX	13 and 14		Molango	Mn	Oxic-epithermal	S, Ox	Limestone	7.5-7.6	0.1-3.0
X	15		Maconi	As, Au, Cu, Pb, Zn	Metasomatic	S	Grossular (Ca ₃ Al ₂ (SiO ₄))	7.4-8.2	0.2
XI	16		Bernal	Ag, Au	Epithermal	S, Ox, CO ₃	Black limestone	6.7-7.4	2.0-2.8

^a Source: SGM, <https://www.gob.mx/sgm>

^bS=sulphidic; Ox: oxides; CO₃: carbonates, AsO₄: arsenates; SO₄: sulphates.

^cExperimental data, obtained from soils samples (wastes excluded) < 2 mm.

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Soil characterization

Selected soil properties were determined on 2 mm sieved subsamples, including the soil pH, effective cation exchange capacity (eCEC), oxalate extractable iron oxy-hydroxides (FeOx), organic carbon (OC), calcium carbonate content (CaCO₃) and aqua regia soluble metal concentrations. The analytical details are specified in Table SI2. Reference soil materials were included for quality assurance.

Determination of cationic metal E-values

The E values of Cd, Zn, Ni, Pb and Cu were measured with a single step (multi-element) stable isotope dilution (ID) method following procedures described by Garforth and Marzouk et al. (Garforth 2015; E. Marzouk et al. 2013b).

The stable isotope dilution was based on quadrupole ICP-MS analysis of the isotope ratios of ⁶⁰Ni/⁶²Ni, ⁶³Cu/⁶⁵Cu, ⁶⁶Zn/⁷⁰Zn, ¹⁰⁸Cd/¹¹¹Cd and ²⁰⁴Pb/²⁰⁸Pb. The first isotope of each pair (e.g. ⁶⁰Ni) is termed here the reference isotope, the second (e.g. ⁶²Ni) is the spike isotope, except for Cd and Pb where spike isotopes are ¹⁰⁸Cd and ²⁰⁴Pb. Enriched stable isotopes of ⁶²Ni, ⁷⁰Zn and ¹⁰⁸Cd were purchased from TRACE-Sciences International. The ⁶⁵Cu and ²⁰⁴Pb isotopes were gratefully supplied by the School of Biosciences (The University of Nottingham, UK, 2013). All metallic isotopes were dissolved in ultrapure 5% HNO₃. The specified isotopic abundance (IA) of each enriched isotope was verified under the experimental conditions of each measurement (Table SI3).

165 The total metal concentrations among the samples spanned >2 orders of magnitude and required
166 that the ID method used different doses of the added isotopes. The doses to be added need to be
167 sufficiently large to obtain a significant shift in the natural abundance but need to be sufficiently
168 low to avoid that the soil equilibrium is not disturbed and that soils are not acidified from the acid
169 spike solutions. Soils were grouped in two categories based on total Zn concentrations since this
170 metal exhibited the highest total concentration compared to the other metals in a molar basis. For
171 samples with total Zn concentrations below 300 mg Zn kg⁻¹, samples were spiked with a low spike
172 solution, above that threshold, spiking was with a high spike solution (Table SI4). The spiking
173 solutions at two concentration levels were initially prepared from original individual solutions of
174 enriched isotopes with nominal concentrations of 120 mg ⁶²Ni L⁻¹, 200 mg ⁶⁵Cu L⁻¹, 600 mg ⁷⁰Zn
175 L⁻¹, 20 mg ¹⁰⁸Cd L⁻¹ and 250 mg ²⁰⁴Pb L⁻¹ in a background solution of 5 % HNO₃ (65% ultrapure
176 acid, EDM Millipore Corporation, Germany) to prevent isotope precipitation. With this
177 background, the total acidity added by spiking was about 34 μmol H⁺ g⁻¹ soil, which is well below
178 the recommendation made by Garforth (2015); with maximal acidity addition of 54 μmol H⁺ g⁻¹
179 soil.

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181 Four replicates of 1.0 (±0.05) g soil or waste were weighed in 40 mL polypropylene tubes to which
182 30 mL of 10 mmol L⁻¹ Ca(NO₃)₂ was added. Then, samples were shaken end-over-end (28 rpm)
183 for 24 hours. Next, two out of four replicates of each sample were spiked with 200 μL of spike
184 enriched isotope solution. The last two replicates were left unspiked to determine the natural
185 abundance of the metal isotopes. The suspensions were shaken 24 hours in the end-over-end
186 shaker, centrifuged for 15 minutes at 1830 g and supernatants were filtered using a 0.45 μm
187 disposable filter. Supernatants were then diluted 1:50 in 1% HNO₃, and isotopes were measured

188 using a quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x)
 189 using ^{45}Sc as internal standard for Ni, Cu, Zn and Cd isotopes in the He mode with quadrupole
 190 dwell times of 3.0 ms. For Pb isotopes, ^{193}Ir was used as an internal standard in the No Gas mode
 191 with quadrupole dwell time of 1.0 ms. Additionally, ^{103}Rh was used as internal standard in the He
 192 and the No Gas modes and isotopes ^{107}Ag and ^{202}Hg were measured just below the lightest Cd
 193 and Pb isotopes, respectively, to give the quadrupole sufficient time to locally stabilize. External
 194 multi-element standards were used for instrument calibration. Mass bias correction (MBC) factors
 195 of isotope pairs were determined from the ratio of isotope signals and that of the natural ratio using
 196 not enriched calibration standard solutions (10 and 50 μg elements L^{-1} , Certipur®Merk) and
 197 certified reference solutions (NIST 1640a diluted and SPS-SW2). The MBC-factor varied <5% of
 198 the average values along different measurement and concentrations.

199
 200 The isotopically exchangeable metal concentration (mg kg^{-1}), also called E-value (E, mg/kg soil),
 201 was determined in soil suspension applying Eq. 1 adapted from Gabler et al. to each individual
 202 metal (Gabler et al. 1999).

$$E = \left(\frac{AM_{\text{ref}}}{AM^*} \right) \cdot \left(\frac{C_{\text{sp}} V_{\text{sp}}}{W_{\text{samp}}} \right) \cdot \left(\frac{IA_{\text{sp}}^* - \left(\frac{IA_{\text{sp_soil}}^*}{IA_{\text{sp_soil}}^{\text{ref}}} \right) IA_{\text{sp}}^{\text{ref}}}{\left(\frac{IA_{\text{sp_soil}}^*}{IA_{\text{sp_soil}}^{\text{ref}}} \right) IA_{\text{soil}}^{\text{ref}} - IA_{\text{soil}}^*} \right) \quad [1]$$

203 where:

- 204 · AM_{ref} and AM^* are the average atomic masses of the reference and spiked isotopes,
 205 respectively,
- 206 · C_{sp} is the concentration (mg L^{-1}) of the multielement spike solution
- 207 · V_{sp} is the spiking volume (L),

- 208 · W_{samp} is the dry mass of soil sample (kg),
- 209 · IA_{sp}^* , $IA_{\text{sp_soil}}^*$ and IA_{soil}^* are the isotopic abundances of the spike isotope in the spike
- 210 solution (sp), the spiked soil solution (sp_soil) and the un-spiked soil solution (soil),
- 211 · $IA_{\text{sp}}^{\text{ref}}$, $IA_{\text{sp_soil}}^{\text{ref}}$ and $IA_{\text{soil}}^{\text{ref}}$ are the isotopic abundances of the reference isotope at the tree
- 212 former solutions.

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214 The IA^* -values were derived from the measured isotopes (spike and reference isotope) and

215 assuming that the unmeasured isotopes have an identical ratio to the references isotopes as the

216 natural ratio.

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218 For testing accuracy and reproducibility of the E-values determined by this method, several steps

219 were taken. First, two internal soil samples (low and high Zn soils; Table SI5) were included in

220 each batch of samples. Second, an external reference soil sample was obtained from the School of

221 Biosciences, The University of Nottingham, UK where the E-values of the five studied metals had

222 been determined previously by Garforth, (Garforth, unpublished data, 2015). Finally, a standard

223 addition test was made in which soils were amended with metal salts and the E value subsequently

224 determined in amended and not amended samples (see SI for more details).

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226 **Determination of As E-values**

227 The As lability was determine on a subset of samples with total As concentrations above 500 mg

228 kg^{-1} (10 soils and 6 wastes, see Table SI9) using the ^{73}As radio isotope (as As(V), Oak Ridge

229 National Laboratory, U.S.) and following De Brouwere et al. (De Brouwere et al. 2004).

230 About 2.5 g of air dried sample were weighed into a centrifuge tube. Then, 24 mL of background
231 electrolyte solution (0.005 M Ca(NO₃)₂) was added, followed by 1 mL of carrier-free ⁷³As spike.
232 Initial concentrations of ⁷³As in the spiking solution varied from 1.7 to 17 kBq mL⁻¹, depending
233 on expected solid-liquid concentration ratio K_D. After 7 days of equilibration in an end-over-end
234 shaker, the samples were centrifuged at 3200 g for 30 minutes. Next, 2 mL of the supernatant were
235 analysed for γ activity (Packard, COBRA Auto-gamma A5003; 15-70 keV). For the same sample,
236 dissolved As concentration ([As]_l, mg As L⁻¹ solution) was measured with ICP-MS. All
237 measurements were made by duplicate.

238

239 The radio labile E-values (mg As kg⁻¹ soil) were calculated as:

$$E = [As]_l \{K_D + L/S\} \quad [2]$$

240 where L/S is the liquid solid ratio and K_D is obtained by:

$$K_D = \frac{(\gamma_i - \gamma_f)/W}{\gamma_f/V} \quad [3]$$

241 with γ_i and γ_f, the total initial and final activity of the added ⁷³As in solution, W the weight of the
242 air-dry soil and V the final volume of the solution.

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Data analysis

245 Statistical analyses were carried out with JMP® Pro 13.1 (Copyright© 2016, SAS Institute).

246 Chemical properties, total metal(loid) concentrations and labile fractions in contaminated soil and

247 mining waste were compared relative to the uncontaminated soils by the Dunnett test, thereby

248 using mine location as a random effect factor. Metal(loid) lability was expressed as the fraction of

249 the total metal concentration that is labile (%E, i.e. E divided by total metal concentrations in %).

250 Using the %E rather than E values allows to compare metal lability, i.e. speciation, among soils

251 with different total concentrations. The %E indicates the fraction of the total concentrations that
252 contributes to the solid-liquid distribution and is an improvement over total concentration to
253 indicate metal mobility (Degryse et al. 2009), the %E values have also been used to estimate the
254 fraction of total metal concentrations that are toxic and, therefore, have been used in risk
255 assessment (Smolders et al. 2009). The %E is typically used to develop mathematical models
256 relating soil properties to the fractions of total metal concentrations that are labile (Marzouk et al.
257 2013; Mao et al. 2017). The effects of soil properties and metal contamination source
258 characteristics on the metal(loid) labile fractions (%E) were evaluated through consecutive
259 analyses. First, the metal(loid) labile fractions (%E) in the soils samples (mean of duplicate
260 analytical data for each sample, n=32) were related to single soil properties at a time (pH, total
261 organic carbon, carbonate content, eCEC and total metal concentration) by standard least squares
262 regression to obtain linear models. Second, an ANOVA was performed to relate the metal(loid)
263 %E to factors that indicate the characteristics of the metal contamination source. The source
264 characteristics are those given in Table 1 and were: the group of extracted metals, the dominant
265 mineralogy, the ore type and the lithology of the ores. In both analyses samples from different
266 locations were considered as independent observations. Third, a combination of the first two
267 analyses was made with stepwise regression. For that analysis, two steps were made: first, %E
268 values were related to several important soil properties (continuous variable), to identify the
269 significant soil parameters in a multivariable regression. Second, these soil parameters were
270 combined with the contamination source characteristic (categorical variables: only the type of
271 extracted metals and lithology as these were the only significant ones). The selection method to
272 enter or leave the regression model was based on statistical significance set at $p < 0.05$. No
273 interactions between soil properties and contamination source characteristics were tested, i.e. the

274 models effectively linearly related the %E to soil parameters allowing for different intercepts, not
275 different slopes, depending on source characteristics. This was selected due to the limited number
276 of different samples and to allow testing effects and interactions. Selected tests for interactions
277 showed only very few and inconsistent significant effects (details not shown).

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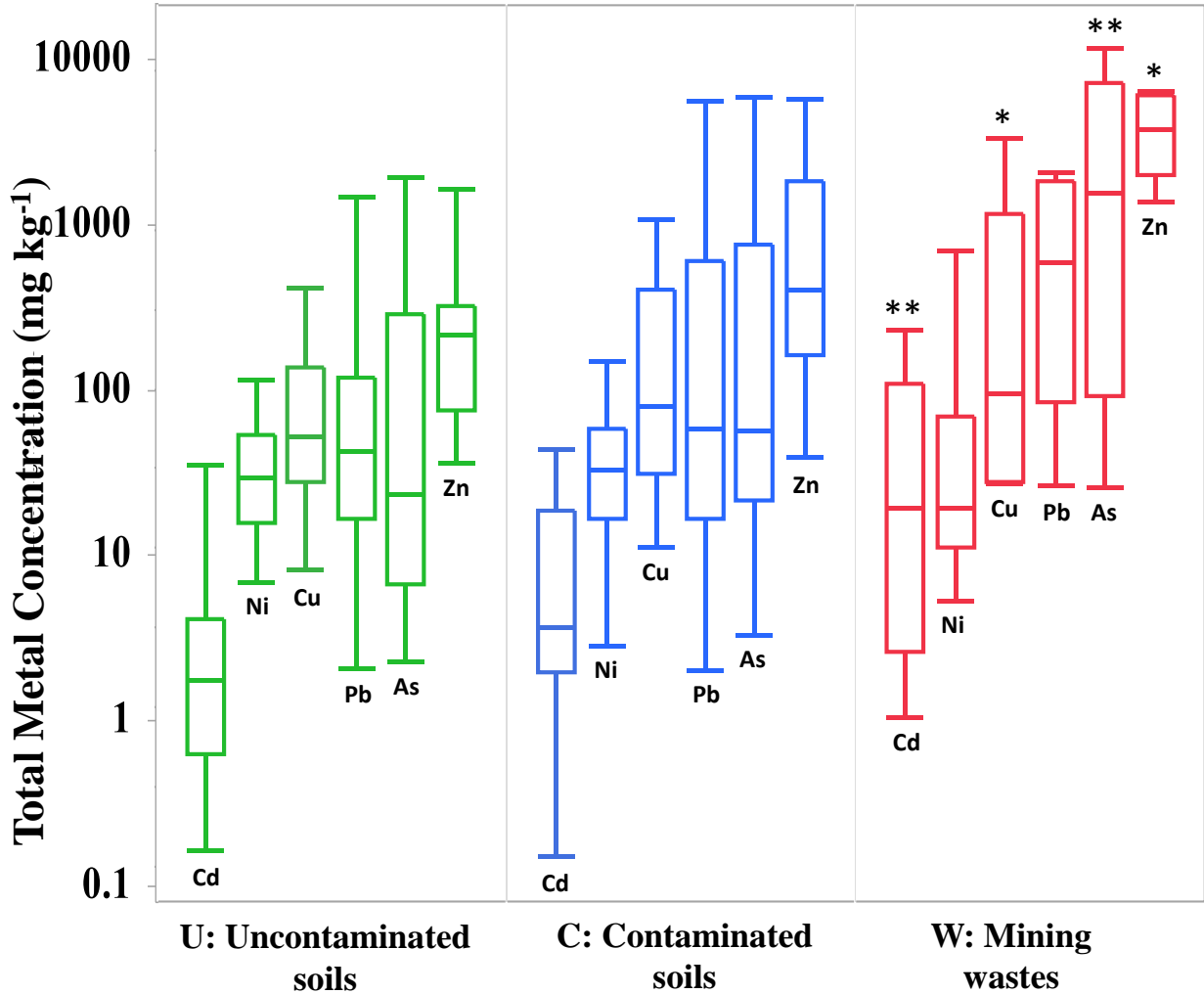
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RESULTS

280 The 11 sites covered a wide range in type of extracted metals and ore types (Table 1). Plant cover
281 was present on all the uncontaminated soils and in 12 (>50%) of the contaminated soils. Selected
282 properties of soil and waste samples are given in Table SI8. Almost all soils and treated mining
283 wastes were pH neutral, ranging between pH 6-8, while only two sulfidic ore derived wastes were
284 acid (pH 2.5 and 5.1), corresponding to locations where waste was reported to be not treated
285 (Figure SI1 and Table SI8). All soils contained detectable CaCO_3 and average % CaCO_3
286 concentrations were about 10%. In general, uncontaminated soils had higher organic C content
287 and lower % CaCO_3 content than the contaminated ones.

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289 Arsenic, zinc and lead showed the highest elemental total concentrations, with As concentrations
290 reaching up to 15 g As kg⁻¹ in contaminated soils (Figure 1, Table SI8). Total metal concentrations
291 ranked uncontaminated < contaminated < waste, with statistically significant differences only
292 present between soil and waste samples ($p < 0.05$ for Cu and Zn, $p < 0.01$ for Cd and As), except for
293 Pb probably due to the presence of a highly contaminated soil sample (4C) and for Ni that was
294 present in relatively low concentrations in all sample types, most likely because no Ni is mined in
295 any of the mines (**Table SI 8**).



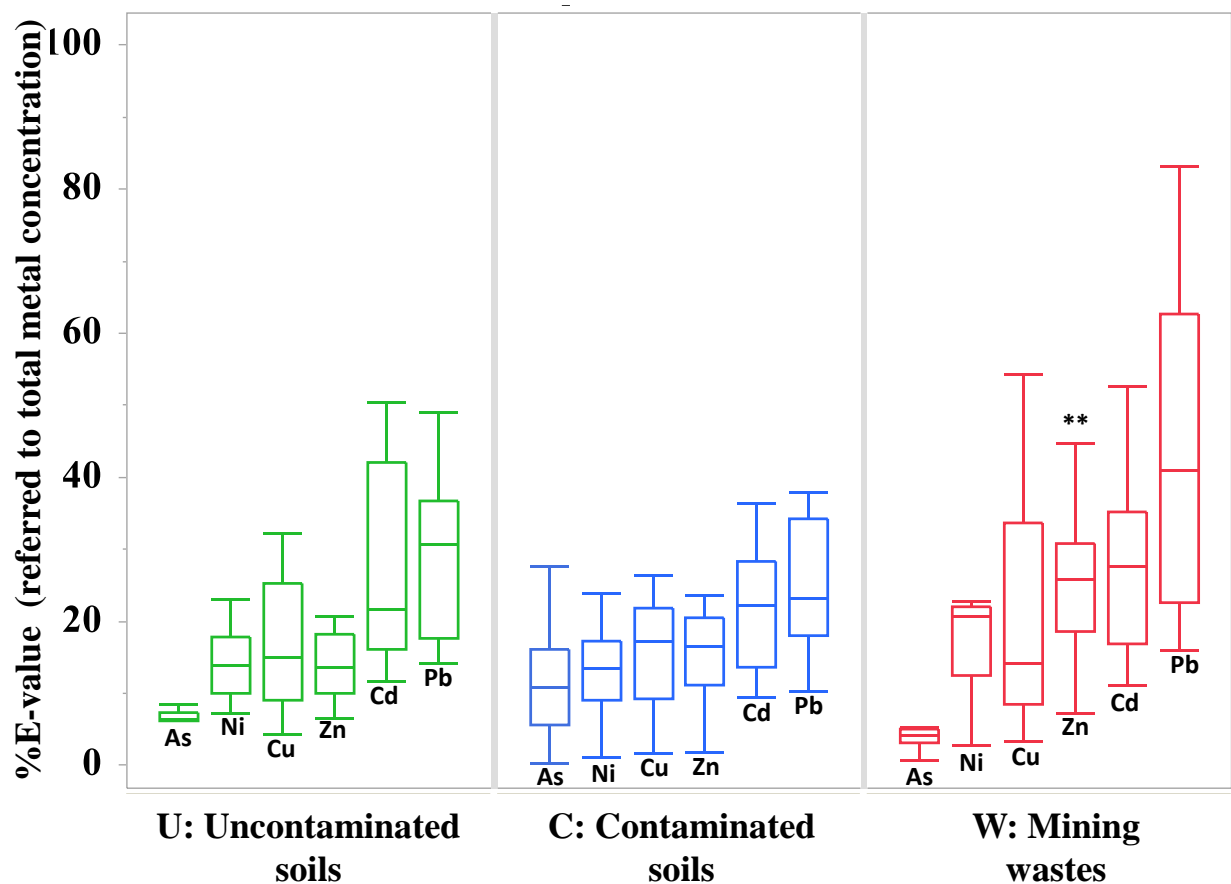
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297 **Figure 1.** Visual representation by box-whisker plot of Ni, Cu, Zn, Cd, Pb and As total
 298 concentration of (mg, kg⁻¹ dry mass) in different Mexican sample types. Horizontal lines show the
 299 median values. Box edges correspond to the upper boundaries of the first and third quartile.
 300 Whiskers extend to the furthest data point within 1.5× box heights. The marks above the whiskers
 301 are added if the concentrations in contaminated soils or mining wastes were different from the
 302 corresponding uncontaminated soils (Dunnett's test, with * for p<0.05 and **for p<0.01).

303

304 The labile fractions (E as % of total) in the soils ranked, (with median values in brackets,
 305 considering uncontaminated and contaminated soils): Pb (22) > Cd (18) > Cu (15) > Ni~Zn (13)
 306 > As (9). The mean %E of the studied elements were unaffected by the sample type
 307 (uncontaminated soil, contaminated soil or wastes), except for %E of Zn, which was larger for

308 wastes than for soils (Figure 2, full data in Table SI9). The coefficient of variation of E-values
 309 among different analytical replicates was about 13% with highest mean values for Pb (16%) and
 310 lowest for Cu (12%). The % E values of Pb, Zn, Ni and Cu in the external reference sample
 311 deviated less than 10% from the corresponding values determined by Garforth (School of
 312 Biosciences, The University of Nottingham, UK, unpublished data, 2015). For Cd deviation was
 313 of 28% (Table SI 7) from the reference value. Finally, the % recovery of the amended metals in
 314 the labile pools in a standard additions test ranged 100-121% depending on soil and was deemed
 315 acceptable (Table SI 6).



316
 317 **Figure 2.** Visual representation by box-whisker plot of Ni, Cu, Zn, Cd, Pb and As labile fractions
 318 (% E) in different Mexican sample types. Horizontal lines show the median. Box edges correspond
 319 to the upper boundaries of the first and third quartile. Whiskers extend to the furthest data point
 320 within 1.5× box heights. The marks above the whiskers are added if the %E values in contaminated

321 soils or mining wastes were different from the corresponding uncontaminated soils (Dunnett's test,
 322 with * for $p < 0.05$ and **for $p < 0.01$).

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324 The labile Ni and Zn fractions decrease with increasing pH. Cu and Cd increase with increasing
 325 %OC and those of Pb increase with increasing total Pb concentrations (Table 2). The %E of Zn
 326 related to total soil Zn in a biphasic pattern, increasing with total concentration up to about 2000
 327 mg Zn kg⁻¹ followed by a negative variation of %E with the increase of total concentration (Figure
 328 SI2), a pattern also found by Marzouk et al. 2013 (E. R. Marzouk, Chenery, and Young 2013). No
 329 such biphasic patterns are found for the other elements. The %E value of As increased with soil
 330 Fe content, however the limited sample number and high leverage effect of a single observation
 331 (sample 4C with As %E = 30 and Fe=140mmol kg⁻¹) suggest that this trend should be treated with
 332 caution.

333

334 **Table 2.** Model R² values for the linear regression between labile fractions (%E) of Ni, Cu, Zn,
 335 Cd, Pb, and As and soil chemical properties or for the ANOVA of %E related to contamination
 336 source attributes. Bold values indicate that the corresponding regression variables or factors are
 337 statistically significant ($p < 0.05$). Italic values denote that the effects (slope) are negative. M_{tot}:
 338 total metal concentration (mg kg⁻¹); OC: organic carbon concentration (% , w/w); eCEC: effective
 339 cation exchange capacity (cmol_c kg⁻¹); CaCO₃ carbonates concentration (g kg⁻¹); (Fe/Al)_{ox}: oxalate
 340 extractable Fe or Al (mg kg⁻¹). For source attributes see Table 1. For the parameters and RMSE of
 341 the significant univariate regression models see Table SI10.

Regressor	Ni n=32	Cu n=32	Zn n=32	Cd n=32	Pb n=32	As n=10
pH	0.44	0.30	0.38	<i>0.05</i>	<i>0.09</i>	0.08
M _{tot}	0.19	0.09	0.08	0.15	0.63	<0.01
OC	0.08	0.63	0.17	0.62	0.18	<0.01
eCEC	0.02	0.1	0.06	0.12	0.01	<i>0.21</i>
CaCO ₃	<0.01	0.04	0.03	0.02	0.1	<i>0.11</i>
Fe _{ox}	<0.01	0.05	0.09	<0.01	0.14	0.83
Al _{ox}	0.25	0.22	0.05	0.26	0.14	<i>0.48</i>
Extracted metals ^a	0.57	0.68	0.49	0.57	0.59	0.25
Mineralogy ^a	0.08	0.26	0.18	0.29	0.11	0.11

Ore type ^a	0.25	0.39	0.21	0.26	0.10	0.25
Ore structure ^a	0.12	0.36	0.25	0.16	0.14	0.24
Ore lithology ^a	0.39	0.58	0.50	0.39	0.26	0.25

^a Source: Mexican Geological Survey <https://www.gob.mx/sgm>

342
343 When labile fractions were related to individual metal source characteristics the %E values were
344 strongly affected by the type of extracted metals (Table 2), a term referring to the type of metals
345 mined at each site, with 9 different defined groups (Table 1), suggesting a large effect of the sample
346 location since only 11 mine sites were surveyed. However, when soil properties and metal
347 contamination source characteristics were included together in the analysis, the effects of the ore
348 lithology (the ore enclosing material) were more relevant than the other metal-source
349 characteristics. Stepwise multiple regression yielded a multivariate linear model in the form:

$$\%E = b + m_1pH + m_2M_{tot} + m_3\%OC + m_4Fe \quad [4]$$

350
351 where *b* is the intercept and *m*₁ to *m*₄ are the corresponding slopes for different soil properties:
352 pH_{CaCl2}; total metal concentration (*M*_{tot}, mg kg⁻¹); organic carbon content (OC, %); oxalate
353 extractable Fe (Fe_{ox}, mg kg⁻¹).

354
355 The obtained model parameters (Table 3) showed that soil properties rather than source attributes
356 primarily explained the %E of most metals, except for Zn and As for which the ore lithology (6
357 types) was the dominant factor. The %E of Zn was lowest in locations where the ore lithology was
358 sericite (a fined grained mica) and highest where it was black limestone. For As, the ore lithology
359 also dominated the %E values but, again, such data need to be taken with caution as only 10
360 samples were analyzed. The relative roles of soil pH, total metal concentration and organic carbon
361 explaining %E variation are given graphically in Figures 3, SI2 and SI3, including the related ore
362 lithology.

363

364

365 **Table 3.** Significant ($p < 0.01$) linear regression parameters (m_1 to m_4) from stepwise multivariate analysis of labile fractions (%E) of Ni,
 366 Cu, Zn, Cd, Pb, and As as a function of soil chemical properties and contamination source attributes. Parameters in bold explain the
 367 most of the variance, according to the model in equation [4]. Standard errors of regression parameters are shown between brackets.
 368

Element	n	b	m_1^*	m_2	m_3	m_4	Model R^2	RMSE	Additional metal source characteristic	Improved Model R^2	RMSE	r (pred to obs)
Ni	32	66 (9)	-7.9 (1)	0.08 (<0.01)			0.67	3.5	Ore lithology ¹	0.73	2.9	0.89
Cu	32	49 (10)	-6 (1.4)	0.01 (0.003)	4 (0.6)		0.81	3.85				0.9
Zn	32	50 (10)	-5.5 (1.4)				0.48	4.08	Ore lithology	0.62	3.35	0.62
Cd	32	11 (2)		0.15 (0.1)	5.5 (0.8)		0.69	5.78				0.83
Pb	32	17 (2)		0.01 (0.001)	3.3 (0.9)		0.75	6.37				0.87
As	10	2 (2)				0.004 (0.001)	0.83	3.83	Ore lithology	0.99	3.1	0.91

* Corresponding slopes for different soil properties: m_1 -pHCaCl₂; m_2 -total metal concentration (M_{tot}, mg kg⁻¹); m_3 -organic carbon content (OC, %); m_4 -oxalate extractable Fe (Fe_{ox}, mg kg⁻¹).

¹ See Table 1.

369

DISCUSSION

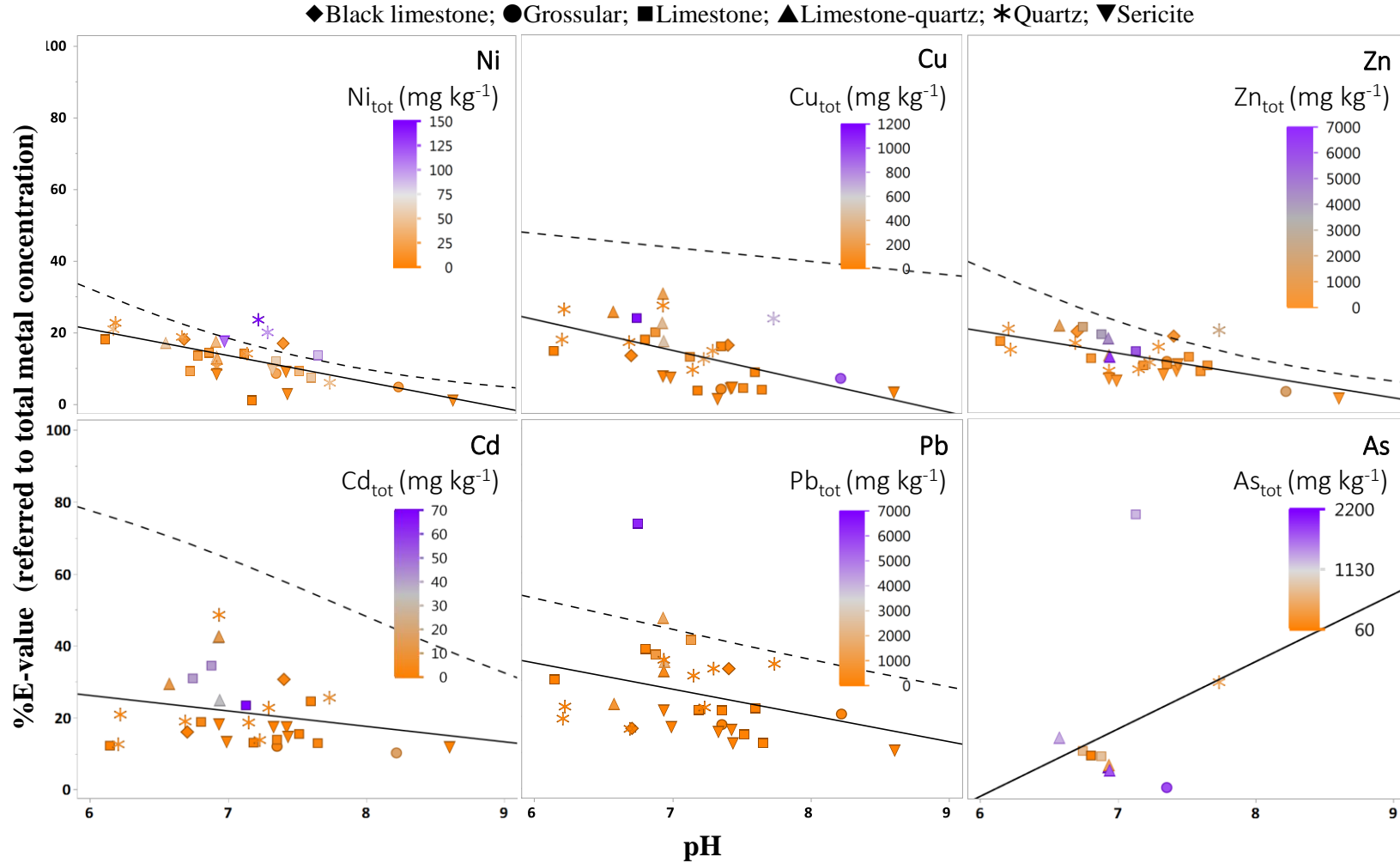
370
371 *Total and labile metal concentrations.* Total metal concentration in uncontaminated soils were
372 most often larger than estimated median values of geological background values in large regional
373 surveys (Gutiérrez-Ruíz et al. 2009; Holmgren et al. 1993). For example, the median
374 concentrations of aqua regia soluble metals in the uncontaminated soils were (in mg kg⁻¹): 1.5
375 (Cd), 27 (Ni), 51 (Cu), 40 (Pb) and 223 (Zn) whereas corresponding median concentrations
376 in cropland soils from the USA are 0.2, 18, 19, 11 and 53, respectively (Holmgren et al. 1993).

377
378 At four locations (I, II, IV and X), the concentrations in uncontaminated soils even exceeded such
379 baseline values, e.g. 1100 mg Zn kg⁻¹ and 890 mg As kg⁻¹, respectively, with values largely higher
380 than median background concentrations for Mexican soils (47 mg Zn kg⁻¹ and 4.8 mg As kg⁻¹,
381 (Gutiérrez-Ruíz et al. 2009)). This illustrates that the soils located within about 100 m from the
382 mining dam edge still contained the signature of a metal enrichment and, therefore, that the
383 uncontaminated samples do not truly represent the background soils conditions at a large scale.
384 Total Zn and As concentrations in contaminated soils peak to about 7000 mg kg⁻¹ for both
385 elements, in agreement with reported values for those locations (Duarte-Zaragoza et al. 2015;
386 Morton-Bermea et al. 2013; Santos-Jallath et al. 2013).

387
388 The element lability in contaminated soils and mining wastes is a more relevant indicator for
389 environmental risk than total concentrations (Hamon et al. 2008). The median %E of Cu, Zn and
390 Cd for the soil samples were 10 to 20 percent lower than the median of previously reported values
391 for Cu (17%, n=87), Zn (23%, n=101) and Cd (30%, n=105) obtained using the same protocol
392 (Buekers et al. 2007; Garforth et al. 2016; Hamon et al. 2008; Marzouk et al. 2013b). Ni and Pb

393 labile fractions were very comparable with the same set of reported values. A main reason for the
394 discrepancies is, of course, the type of sampled analyzed, as in the case of Buekers et al. 2007,
395 were fractions high fractions of labile Cu and Cd correspond to control-uncontaminated soils.
396 When field contaminated soils are analyzed (as in Garforth et al. 2016 and Marzouk et al.2013b)
397 the discrepancies are more related to soil chemical properties mainly to lower pH values and Feox
398 contents compared to the values of the present work. Median As %E values are in good agreement
399 with the median of reported values in contaminated soils (8.2, n=27) determined with similar
400 protocols (De Brouwere et al. 2004). However, the median %E of As obtained using a different
401 extracting solution (mainly H_2PO_4^-) is about 4 times higher than the one in this study , probably
402 due to the dissolution of the non-labile fraction to some extent, as it has been observed for some
403 cationic metals with strong extractant solutions (Hamon et al. 2004; Stroud et al. 2011; Tye et al.
404 2002). The higher metal lability in mining wastes (W) compared to that in soil samples is in
405 contrast with earlier findings (Degryse et al. 2004; E. Marzouk et al. 2013b; Rahman et al. 2017),
406 and may be the result of the prolonged weathering time of the collected mining wastes, generating
407 acid drainage after oxidation of remaining mineral sulphides in the wastes.

408
409 *Single and multiple variable regressions using soil properties.* The negative correlation between
410 %E and soil pH was found for all metals (Table 2), and is attributed to the effect of increased pH
411 on increasing the negatively charged sorption sites at the soil surface, the preferential adsorption
412 of metal on hydroxide groups, the metal-hydroxide complex formation or different interactions
413 (surface precipitation or diffusion) with carbonate minerals. For Pb and Cd, such trend was weaker
414 compared to that for Ni or Zn, in agreement with the results obtained by Gabler et al. 1999, Degryse
415 et al. 2004 and Mao et al. 2017 (Degryse et al. 2004; Gabler et al. 1999; L. C. Mao et al. 2017).



416

417 **Figure 3.** Element labile fraction (% E) as a function of pH for uncontaminated and contaminated soils related to different ore lithologies.

418 The dashed lines are previously established relationships of labile fractions in well equilibrated metal salt amended soils derived from

419 Mao et al., 2017 (L. Mao et al. 2017).

420 In the data here, the %E of Cd increases with increasing %OC in soil, this contrasts observation
421 of Degryse *et al.* in a study where Cd lability decreased with increasing organic carbon associated
422 to progressive sludge loadings to soil (Degryse et al. 2004). However, in that case it was assumed
423 that the negative trend was more related to the dilution of the most labile Cd fraction in the original
424 soil with less labile Cd in the amendment. Here, it is possible that increased %OC in soil enhances
425 Cd mobility through complexation of Cd²⁺ in soil solution with dissolved organic matter, thereby
426 limiting Cd fixation. Indeed, it is well known that Cd²⁺ has a high affinity to form complexes with
427 dissolved organic matter (DOM). The labile Pb fraction increased here with total Pb concentration,
428 suggesting that there is only a minor presence of non-labile Pb mineral forms (like galena or
429 pyromorphite) that normally restrict Pb lability (Atkinson et al. 2011). The high affinity of Pb for
430 organic functional groups in DOM may explain the sensitivity of Pb labile fraction to changes in
431 soil organic content. At high TOC contents such higher affinity could obscure the effects of pH on
432 Pb lability more than on Zn resulting in different variables explaining the %E of Zn and Pb.
433 Marzouk (2013) found a strong effect of total Pb concentration on labile Pb fractions: increasing
434 %E with total Pb at total concentrations <2000 mg kg⁻¹ and decreasing %E with total Pb at total
435 concentrations >2000 mg kg⁻¹. The first trend is the one observed in our data set in which total Pb
436 concentration range of 1.7 to 2100 mg kg⁻¹ excluding one outlier at 6400 mg kg⁻¹.

437
438 *Effect of metal source characteristics in the models.* Among the metal-source characteristics, only
439 ore lithology explained the labile fractions of Zn in the multivariate models, while the model
440 improvement for Ni labile fractions was only marginal and that for As labile fraction needs to be
441 treated with caution due to a lack of large data number (Table 3). Differently from the other metal
442 source characteristics, the ore lithology is not exclusively related with the ore but it is extensive to

443 the original geological material. It is probable that the effect of the ore lithology (the main material
444 enclosing the ore) on %E in the soil samples reflects the influence of the parent rock on the soil
445 formation process for the uncontaminated soils, while for the contaminated soils it could reflect
446 the influence of the mining waste as a source of contamination.

447

448 For Zn it was observed that the lowest %E-values was about 9% (at pH=7 and eCEC=20 cmol_c kg⁻¹)
449 ¹) in mines where sericite (mica group) and grossular (garnet group) ore lithologies occur, both
450 mainly composed of silicates, whereas highest %E-values were about 15% (at equal soil properties
451 as above) in mines dominated by the black-limestone ore lithology. The sericite and grossular
452 silicate ore lithologies are here associated with polymetallic extraction mines, including Au, Ag,
453 Cu, Pb and As in the form of sulphides in the mineral. The silicate ore lithology may explain the
454 lower end of labile Zn fractions in such mines: Zn speciation in mining impacted soils showed that
455 kerolite, a trioctahedral phyllosilicate, was a major host of Zn in soils with high Zn contamination
456 from either smithsonite (ZnCO₃), hemimorphite (Zn₄Si₂O₇(OH)₂H₂O) and willemite (Zn₂SiO₄)
457 (Van Damme et al. 2010) and the labile fraction of Zn in such soils is very low (Van Damme
458 2010). The labile fractions of Zn were slightly higher where the black-limestone occurs,
459 exclusively in areas used for gold and silver extraction from sulfidic and oxide ores, but the reasons
460 behind such larger %E associated to those samples are unclear.

461

462 Earlier studies in well equilibrated metal salt amended soils have revealed empirical trend lines
463 between metal labile fractions and soil pH. Such models have been taken forward to regulations
464 (Smolders et al. 2009). Selected empirical trend lines are added in Figure 3 (L. Mao et al. 2017).
465 In general, these lines are on the higher end of labile fractions observed here, pointing that the

466 labile fractions in the mine impacted soils are lower than in the metal salt impacted soils and that
467 some non-labile metal may originate from the ore lithology. However, the differences in average
468 labile fractions at equivalent pH is less than factor 2, except for Cd and Cu (maximally factor 4)
469 but these metals are unlikely be of risk concern due to their low concentrations. These lability data
470 is suggesting that the mineral weathering/alteration in these mining impacted soils has already
471 proceeded rather far, especially for Ni, Zn and Pb. Such also suggests that, in a risk assessment
472 context, the differences with equilibrated metal salt amended soils are not very large and that the
473 earlier generic trends of major soil properties explaining labile fraction adequately describe the
474 data in such mining waste impacted soils, with some bias to the conservative (protective)
475 prediction of metal(loid) lability.

476

477

CONCLUSIONS

478 Labile fractions were determined in a set of soils unaffected/affected by mining activities,
479 including mining wastes samples with different underlying source characteristics. Most of the
480 labile fraction variation can be sufficiently described-predicted by multivariate regression models
481 based on routinely determined soil chemical characteristics, across a wide range of samples with
482 a common contamination source. The role of metal source attributes determining metals lability
483 was limited and only provided consistent explanation for labile fractions of Zn where silicate
484 minerals are the main matrices. Such suggests that the earlier generic trends of major soil properties
485 explaining labile fraction adequately describe the data in such mining waste impacted soils.

486

487 The necessity to ensure the sustainability of the mining production also involves the control of soil
488 contamination derived from the mining activities, not only in México but at many other important

489 mining regions in developed and developing countries as China, Spain, Australia, Papua New
490 Guinea, Canada, Botswana, Mozambique, South Africa, Guinea, Chile, Peru, Argentina,
491 Kazakhstan or India. Many of these countries share climatic, geological and edaphic characteristics
492 and production practices with mining places in Mexico.

493
494 In this sense, the present research contributes to the development of models that allow the
495 environmental risk assessment associated to the mining activities, the planification of waste
496 treatment and management and monitored control of the treated wastes and recovered soils”

497

498 SUPPLEMENTAL MATERIAL

499 The following are available online at <http://www.xxxxxxxxxxxxxxxxxxxxxxxxxxxxxx>. **Mexican soil**
500 **samples and chemical characterization.** Figure SI1: The 11 visited locations and associated
501 sample numbers and types. Table SI2: Analytical methods used to determine selected
502 characteristics of the soil samples. **Experimental remarks on stable isotopic dilution.** Table SI3:
503 Isotopic Abundance data of enriched isotopes in the multi-element spike. Table SI4: Concentration
504 of enriched stable isotopes at different spike solutions. Table SI5: Aqua-regia metal concentrations
505 of reference soils. Table SI6: Added and recovered metal concentrations in the standard addition
506 test. Table SI7: Metal lability in reference soils samples. **Isotopic dilution: Mexican soil samples**
507 **results.** Table SI8: Selected properties of Mexican soil samples. Table SI9: Labile fraction of
508 metals and As in Mexican samples. **Metal lability affected by soil properties and metal source**
509 **characteristics.** Figure SI1: Variation of labile fraction with organic carbon for different total
510 metal and As concentrations and ore lithology source. Figure SI2: Variation of labile fraction with
511 total concentration for different ore lithology source.

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ADDITIONAL INFORMATION

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636 **Tables**

637 **(Next page)**

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640 **Table 1.** Selected properties of the 11 locations where soils and mining wastes were collected. The sampling locations, sample numbers
 641 and sample types are given in Figure S1.

Samples		Mining district	Economic interest metals ^a	Ore type ^a	Mineralogy ^{a,b}	Lithology ^a	Soil pH range ^c	Soil OC range (%) ^c
Location	Number							
I	1 and 2	Zimapan	Cu, Pb, Zn	Mesothermal	S, Ox, CO ₃ , SO ₄ , AsO ₄	Limestone-quartz	6.6-6.9	2.0-4.5
II	3 and 4	Taxco	Ag, Au, Cd, Cu, Pb, Zn	Epithermal	S	Limestone	6.7-7.1	1.5-2.5
III	5	Zacualpan	Ag, Cu, Pb, Zn	Mesothermal	S	Quartz	6.1-6.2	0.5-2.3
IV	6 and 11	Pozos	Ag, Au, Cu, Pb, Zn	Epithermal	S	Quartz	6.7-7.7	1.0-4.7
V	7 and 8	Guanajuato	Ag, Au, Pb, Zn	Epithermal	S	Sericite	6.9-8.6	0.3-0.9
VI	9	Guanajuato	Ag, Au, Pb, Zn	Hipothermal	S	Limestone	6.1-7.2	0.8-1.2
VII	10	Guanajuato	Ag, Au	Hipothermal	S	Quartz	7.2-7.3	1.2-2.1
VIII	12	Guanajuato	Au, Ag, Cu	Epithermal	S	Sericite (colorless mica)	7.0-7.3	0.1-0.7
IX	13 and 14	Molango	Mn	Oxic-epithermal	S, Ox	Limestone	7.5-7.6	0.1-3.0
X	15	Maconi	As, Au, Cu, Pb, Zn	Metasomatic	S	Grossular (Ca ₃ Al ₂ (SiO ₄))	7.4-8.2	0.2
XI	16	Bernal	Ag, Au	Epithermal	S, Ox, CO ₃	Black limestone	6.7-7.4	2.0-2.8

^a Source: SGM, <https://www.gob.mx/sgm>

^bS=sulphidic; Ox: oxides; CO₃: carbonates, AsO₄: arsenates; SO₄: sulphates.

^cExperimental data, obtained from soils samples (wastes excluded) < 2 mm.

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648 **Table 2.** Model R² values for the linear regression between labile fractions (%E) of Ni, Cu, Zn,
649 Cd, Pb, and As and soil chemical properties or for the ANOVA of %E related to contamination
650 source attributes. Bold values indicate that the corresponding regression parameters or factors are
651 statistically significant (p<0.05). Italic values denote that the effects (slope) are negative. M_{tot}:
652 total metal concentration (mg kg⁻¹); OC: organic carbon concentration (% w/w); eCEC: effective
653 cation exchange capacity (cmol_c kg⁻¹); CaCO₃ carbonates concentration (g kg⁻¹); (Fe/Al)_{ox}: oxalate
654 extractable Fe or Al. For source attributes see Table 1.

Regressor	Ni n=32	Cu n=32	Zn n=32	Cd n=32	Pb n=32	As n=10
pH	<i>0.44</i>	<i>0.30</i>	<i>0.38</i>	<i>0.05</i>	<i>0.09</i>	0.08
M _{tot}	0.19	0.09	0.08	0.15	0.63	<0.01
OC	0.08	0.63	0.17	0.62	0.18	<0.01
eCEC	0.02	0.1	0.06	0.12	0.01	<i>0.21</i>
CaCO ₃	<0.01	0.04	0.03	0.02	0.1	<i>0.11</i>
Fe _{ox}	<0.01	0.05	0.09	<0.01	0.14	0.83
Al _{ox}	0.25	0.22	0.05	0.26	0.14	<i>0.48</i>
Extracted metals ^a	0.57	0.68	0.49	0.57	0.59	0.25
Mineralogy ^a	0.08	0.26	0.18	0.29	0.11	0.11
Ore type ^a	0.25	0.39	0.21	0.26	0.10	0.25
Ore structure ^a	0.12	0.36	0.25	0.16	0.14	0.24
Ore lithology ^a	0.39	0.58	0.50	0.39	0.26	0.25

^a Source: Mexican Geological Survey <https://www.gob.mx/sgm>

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669 **Table 3.** Determination coefficients (R^2) of stepwise multivariate analysis of labile fractions (%E)
 670 of Ni, Cu, Zn, Cd, Pb, and As in soils as a function of soil chemical properties and contamination
 671 source attributes. Variables in bold explain the most of the variance. M_{tot} : total metal concentration;
 672 OC: organic carbon concentration; eCEC: effective cation exchange capacity; Fe_{ox} : oxalate
 673 extractable Fe; ore lithology: see Table 1.

Metal	n	Soil properties only		Soil properties and metal source characteristics	
		Significant variables ($p < 0.01$) ^a	Model R^2	Significant variables ($p < 0.01$) ^a	Model R^2
Ni	32	pH ; M_{tot}	0.67	pH ; M_{tot} ; Ore lithology	0.73
Cu	32	OC ; pH; M_{tot}	0.81	OC ; pH; M_{tot}	0.81
Zn	32	pH	0.38	Ore lithology ; pH; eCEC	0.62
Cd	32	OC ; M_{tot}	0.69	OC ; M_{tot}	0.68
Pb	32	M_{tot} ; OC	0.75	M_{tot} ; OC	0.75
As	10	Fe_{ox}	0.83	Ore lithology ; pH	0.99

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