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

**Core ideas:**

Weathering processes increase lability of metals in mining wastes.

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

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

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

**The Labile Fractions of Metals and Arsenic in Mining Impacted Soils are Explained by  
Soil Properties and Metal Source Characteristics**

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**Abbreviations:** C, contaminated soil samples; DOM, dissolved organic matter; E, labile metal concentration; %E, labile metal fraction; eCEC, effective cation exchange capacity; (Fe/Al)<sub>ox</sub>, oxalate extractable Fe and Al; Fe<sub>ox</sub>, oxalate extractable Fe; FeOx, iron oxyhydroxides; GMS, Mexican Geological Survey (in Spanish); IA, isotopic abundance, ID, isotopic dilution; M<sub>tot</sub>, total metal concentration; MBC, mass bias correction; OC, organic carbon; TOC, total organic carbon; U, uncontaminated soil samples; W, waste samples.

This article has been accepted for publication and undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the [Version of Record](#). Please cite this article as [doi: 10.1002/jeq2.20055](https://doi.org/10.1002/jeq2.20055).

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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.

## 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  $\text{Ca}^{2+}$  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 (De Brouwere, K., et al. 2004; Marzouk, E., 2013; Buekers et al. 2007). Metal toxicity in mining impacted soils to plants revealed that the labile metal concentration indicates the toxicity rather well, pointing at the E-value as an acceptable index of the available metal in soils that can be used in risk assessment (Hamels et al. 2014; Smolders et al. 2009).

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

In environmental samples, trace elements are not added as soluble forms in most situations. For example, mining impacted soils have been contaminated with poorly soluble and non-labile ore minerals. Conceptually, the %E might first increase by weathering followed by a decrease due to gradual metal immobilization during soil ageing, however that concept has not been demonstrated in a longitudinal study. Surveys of environmentally contaminated soils have shown that the role of soil properties, such as pH, relate only poorly to the %E values of Zn, Cd, Pb and Cu and that %E is generally below that of the pH dependent labile fractions in soils that had been spiked with metal salts (Degryse, Buekers, and Smolders 2004; Marzouk et al. 2013b; Smolders et al. 2012). Multivariate models were fitted to data of %E of Cd, Cu, Ni, Pb and Zn of a set of 3 year aged metal salt amended soils (n=23) and a second set of urban contaminated soils (n=50) (Mao et al. 2017). In general, the contaminated soil samples exhibited similar trends between %E and soil properties as in metal salt spiked soils, but %E were lower than those in the metal salt amended soils illustrating the role of the contamination source on metal lability. Marzouk et al. (Marzouk et al. 2013b) studied %E of Cd, Pb and Zn in a Pb mining affected catchment in England and found that soil pH, organic matter and total metal content strongly affected the %E values. The relationship between %E and total metal concentrations showed a binary trend, increasing at low doses followed by a

decrease at larger doses. The former trend was interpreted from saturation of high affinity fixation sites and the latter trend indicating the presence of non-labile ore minerals in soil. Surprisingly limited data exist on labile fractions of As in mining-impacted soils despite the fact that it is the primary suspected toxic element in several metal mines worldwide. As far as known, no study has yet surveyed a wide range of mining-impacted soils around mines to test variability in labile fractions due to contrasting characteristics of the metal source.

At a world scale, Mexico is the first producer of silver, the second place in mercury production, is among the top five producers of cadmium, molybdenum, bismuth, lead and zinc, and among the top 10 producers of gold and copper (Reichl et al. 2018). This study was primed by a survey of mining impacted soils in Mexico where As is the suspected primary toxic agent as judged from the total concentrations. The objective of this study was to survey the labile fractions of potentially toxic elements in soils of different mining impacted regions. The sampling was designed to better identify the role of the ore type, ore lithology, main extracted metals and metals mineralogy, relative to that of the properties of the receiving soils in determining the labile fractions in soil. The premise was that sampling a wide range of metal mines with contrasting mineralogical characteristics will help to untangle effects of source versus soil properties. Hence, labile fractions of five metals (Ni, Cu, Zn, Cd and Pb) and As were determined by isotopic dilution in soils and wastes samples from several Mexican mining sites and these fractions were statistically related to soil properties and metal-contamination source characteristics .

## **MATERIALS AND METHODS**

### **Sampling**

Eleven locations with intense actual or former metal mining activity were selected within the central region of Mexico (Table 1 and Figure S11). Each location had a different mine. Mine-specific characteristics of metal source were obtained from the Mexican Geological Survey

(Servicio Geológico Mexicano (SGM) 2003) or from interviews with mine managers and included: the main extracted metals (those mined with economical interest), the ore type (according to SGM classification, verified on geological maps), the mineralogy of the metals (main chemical form of metals in the original ore), the ore lithology (type of material enclosing the ore), the treatment or not of the mining waste and the oxidation of the waste (scored by apparent color at the moment of collection). At each location, one or two pairs of uncontaminated and contaminated soil samples were collected (Table 1). Where possible, mining wastes were collected as well. A total number of 32 soil and 10 waste samples were collected between February and May 2014 (Table 1). Additional relevant information on the sampling locations is shown in (Table SI1). The uncontaminated soil samples were consistently collected at a minimal uphill distance of 100 m from the mining dam edge, preferably at undisturbed places, while contaminated soil samples were collected at the border of waste dams. The uncontaminated and contaminated soil samples consisted of about 20 kg of top soil (0–20 cm depth) taken after cleaning the shallow litter. Mining waste, about 5 kg, was collected directly inside the dams at a minimal distance of 5 m from the dam border. All samples (n=42) were air dried and sieved at 4 mm. Each sample was mixed to ensure homogeneity. The soils were stored at room temperature, in dry and dark conditions until further analyses.

**Table 1.** Selected properties of the 11 locations where soils and mining wastes were collected. The sampling locations, sample numbers and sample types are given in Figure S11.

Samples		Mining district	Economic interest metals <sup>a</sup>	Ore type <sup>a</sup>	Mineralogy <sup>a,b</sup>	Lithology <sup>a</sup>	Soil pH range <sup>c</sup>	Soil OC range (%) <sup>c</sup>
Location	Number							
I	1 and 2	Zimapan	Cu, Pb, Zn	Mesothermal	S, Ox, CO <sub>3</sub> , SO <sub>4</sub> , AsO <sub>4</sub>	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 <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ))	7.4-8.2	0.2
XI	16	Bernal	Ag, Au	Epithermal	S, Ox, CO <sub>3</sub>	Black limestone	6.7-7.4	2.0-2.8

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

<sup>b</sup>S=sulphidic; Ox=oxides; CO<sub>3</sub>=carbonates, AsO<sub>4</sub>=arsenates; SO<sub>4</sub>=sulphates.

<sup>c</sup>Experimental data obtained from soils samples <2 mm (wastes excluded).

### 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 (CaCO<sub>3</sub>) and aqua regia soluble metal concentrations. The analytical details are specified in Table S12. 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; Marzouk et al. 2013b).

The stable isotope dilution was based on quadrupole ICP-MS analysis of the isotope ratios of  $^{60}\text{Ni}/^{62}\text{Ni}$ ,  $^{63}\text{Cu}/^{65}\text{Cu}$ ,  $^{66}\text{Zn}/^{70}\text{Zn}$ ,  $^{108}\text{Cd}/^{111}\text{Cd}$  and  $^{204}\text{Pb}/^{208}\text{Pb}$ . The first isotope of each pair (e.g.  $^{60}\text{Ni}$ ) is termed here the reference isotope, the second (e.g.  $^{62}\text{Ni}$ ) is the spike isotope, except for Cd and Pb where spike isotopes are  $^{108}\text{Cd}$  and  $^{204}\text{Pb}$ . Enriched stable isotopes of  $^{62}\text{Ni}$ ,  $^{70}\text{Zn}$  and  $^{108}\text{Cd}$  were purchased from TRACE-Sciences International. The  $^{65}\text{Cu}$  and  $^{204}\text{Pb}$  isotopes were gratefully supplied by the School of Biosciences (The University of Nottingham, UK, 2013). All metallic isotopes were dissolved in ultrapure 5%  $\text{HNO}_3$ . The specified isotopic abundance (IA) of each enriched isotope was verified under the experimental conditions of each measurement (Table SI3).

The total metal concentrations among the samples spanned  $>2$  orders of magnitude and required that the ID method used different doses of the added isotopes. The doses to be added need to be sufficiently large to obtain a significant shift in the natural abundance but need to be sufficiently low to avoid that the soil equilibrium is not disturbed and that soils are not acidified from the acid spike solutions. Soils were grouped in two categories based on total Zn concentrations since this metal exhibited the highest total concentration compared to the other metals in a molar basis. For samples with total Zn concentrations below  $300 \text{ mg Zn kg}^{-1}$ , samples were spiked with a low spike solution, above that threshold, spiking was with a high spike solution (Table SI4). The spiking solutions at two concentration levels were initially prepared from original individual solutions of enriched isotopes with nominal concentrations of  $120 \text{ mg } ^{62}\text{Ni L}^{-1}$ ,  $200 \text{ mg } ^{65}\text{Cu L}^{-1}$ ,  $600 \text{ mg } ^{70}\text{Zn L}^{-1}$ ,  $20 \text{ mg } ^{108}\text{Cd L}^{-1}$  and  $250 \text{ mg } ^{204}\text{Pb L}^{-1}$  in a background solution of 5 %  $\text{HNO}_3$  (65% ultrapure acid, EDM Millipore

Corporation, Germany) to prevent isotope precipitation. With this background, the total acidity added by spiking was about  $34 \mu\text{mol H}^+ \text{g}^{-1}$  soil, which is well below the recommendation made by Garforth (2015); with maximal acidity addition of  $54 \mu\text{mol H}^+ \text{g}^{-1}$  soil.

Four replicates of  $1.0 (\pm 0.05)$  g soil or waste were weighed in 40 mL polypropylene tubes to which 30 mL of  $10 \text{ mmol L}^{-1} \text{Ca}(\text{NO}_3)_2$  was added. Then, samples were shaken end-over-end (28 rpm) for 24 hours. Next, two out of four replicates of each sample were spiked with 200  $\mu\text{L}$  of spike enriched isotope solution. The last two replicates were left un-spiked to determine the natural abundance of the metal isotopes. The suspensions were shaken 24 hours in the end-over-end shaker, centrifuged for 15 minutes at  $1830 g$  and supernatants were filtered using a  $0.45 \mu\text{m}$  disposable filter. Supernatants were then diluted 1:50 in 1%  $\text{HNO}_3$ , and isotopes were measured using a quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS, Agilent 7700x) using  $^{45}\text{Sc}$  as internal standard for Ni, Cu, Zn and Cd isotopes in the He mode with quadrupole dwell times of 3.0 ms. For Pb isotopes,  $^{193}\text{Ir}$  was used as an internal standard in the No Gas mode with quadrupole dwell time of 1.0 ms. Additionally,  $^{103}\text{Rh}$  was used as internal standard in the He and the No Gas modes and isotopes  $^{107}\text{Ag}$  and  $^{202}\text{Hg}$  were measured just below the lightest Cd and Pb isotopes, respectively, to give the quadrupole sufficient time to locally stabilize. External multi-element standards were used for instrument calibration. Mass bias correction (MBC) factors of isotope pairs were determined from the ratio of isotope signals and that of the natural ratio using not enriched calibration standard solutions ( $10$  and  $50 \mu\text{g elements L}^{-1}$ , Certipur®Merk) and certified reference solutions (NIST 1640a diluted and SPS-SW2). The MBC-factor varied  $<5\%$  of the average values along different measurement and concentrations.

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

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

where:

- $AM_{\text{ref}}$  and  $AM^*$  are the average atomic masses of the reference and spiked isotopes, respectively,
- $C_{\text{sp}}$  is the concentration ( $\text{mg L}^{-1}$ ) of the multielement spike solution,
- $V_{\text{sp}}$  is the spiking volume (L),
- $W_{\text{samp}}$  is the dry mass of soil sample (kg),
- $IA_{\text{sp}}^*$ ,  $IA_{\text{sp\_soil}}^*$  and  $IA_{\text{soil}}^*$  are the isotopic abundances of the spike isotope in the spike solution (sp), the spiked soil solution (sp\_soil) and the un-spiked soil solution (soil),
- $IA_{\text{sp}}^{\text{ref}}$ ,  $IA_{\text{sp\_soil}}^{\text{ref}}$  and  $IA_{\text{soil}}^{\text{ref}}$  are the isotopic abundances of the reference isotope at the three former solutions.

The  $IA^*$  values were derived from the measured isotopes (spike and reference isotope) and assuming that the unmeasured isotopes have an identical ratio to the reference isotopes as the natural ratio.

For testing accuracy and reproducibility of the E-values determined by this method, several steps were taken. First, two internal soil samples (low and high Zn soils; Table SI5) were included in each batch of samples. Second, an external reference soil sample was obtained

from the School of Biosciences, The University of Nottingham, UK where the E-values of the five studied metals had been determined previously by Garforth, (unpublished data, 2015). Finally, a standard addition test was made in which soils were amended with metal salts and the E value subsequently determined in amended and not amended samples (see SI for more details).

### Determination of As E-values

The As lability was determined on a subset of samples with total As concentrations above 500 mg kg<sup>-1</sup> (10 soils and 6 wastes, see Table SI9) using the <sup>73</sup>As radio isotope (as As(V), Oak Ridge National Laboratory, U.S.) and following De Brouwere et al. (De Brouwere et al. 2004).

About 2.5 g of air-dried sample were weighed into a centrifuge tube. Then, 24 mL of background electrolyte solution (0.005 M Ca(NO<sub>3</sub>)<sub>2</sub>) was added, followed by 1 mL of carrier-free <sup>73</sup>As spike. Initial concentrations of <sup>73</sup>As in the spiking solution varied from 1.7 to 17 kBq mL<sup>-1</sup>, depending on expected solid-liquid concentration ratio K<sub>D</sub>. After 7 days of equilibration in an end-over-end shaker, the samples were centrifuged at 3200 g for 30 minutes. Next, 2 mL of the supernatant were analysed for γ activity (Packard, COBRA Auto-gamma A5003; 15-70 keV). For the same sample, dissolved As concentration ([As]<sub>l</sub>, mg As L<sup>-1</sup> solution) was measured with ICP-MS. All measurements were made by duplicate.

The radio labile E-values (mg As kg<sup>-1</sup> soil) were calculated as:

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

where L/S is the liquid solid ratio and K<sub>D</sub> is obtained by:

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

with γ<sub>i</sub> and γ<sub>f</sub>, the total initial and final activity of the added <sup>73</sup>As in solution, W the weight of the air-dry soil and V the final volume of the solution.

### Data analysis

Statistical analyses were carried out with JMP® Pro 13.1 (Copyright© 2016, SAS Institute). Chemical properties, total metal(loid) concentrations and labile fractions in contaminated soil and mining waste were compared relative to the uncontaminated soils by the Dunnett test, thereby using mine location as a random effect factor. Metal(loid) lability was expressed as the fraction of the total metal concentration that is labile (%E, i.e. E divided by total metal concentrations in %). Using the %E rather than E values allows to compare metal lability, i.e. speciation, among soils with different total concentrations. The %E indicates the fraction of the total concentrations that contributes to the solid-liquid distribution and is an improvement over total concentration to indicate metal mobility (Degryse et al. 2009), the %E values have also been used to estimate the fraction of total metal concentrations that are toxic and, therefore, have been used in risk assessment (Smolders et al. 2009). The %E is typically used to develop mathematical models relating soil properties to the fractions of total metal concentrations that are labile (Marzouk et al. 2013; Mao et al. 2017). The effects of soil properties and metal contamination source characteristics on the metal(loid) labile fractions (%E) were evaluated through consecutive analyses. First, the metal(loid) labile fractions (%E) in the soils samples (mean of duplicate analytical data for each sample, n=32) were related to single soil properties at a time (pH, total organic carbon, carbonate content, eCEC and total metal concentration) by standard least squares regression to obtain linear models. Second, an ANOVA was performed to relate the metal(loid) %E to factors that indicate the characteristics of the metal contamination source. The source characteristics are those given in Table 1 and were: the group of extracted metals, the dominant mineralogy, the ore type and the lithology of the ores. In both analyses samples from different locations were considered as independent observations. Third, a combination of the first two analyses was made with stepwise regression. For that analysis, two steps were made: first, %E values were related to

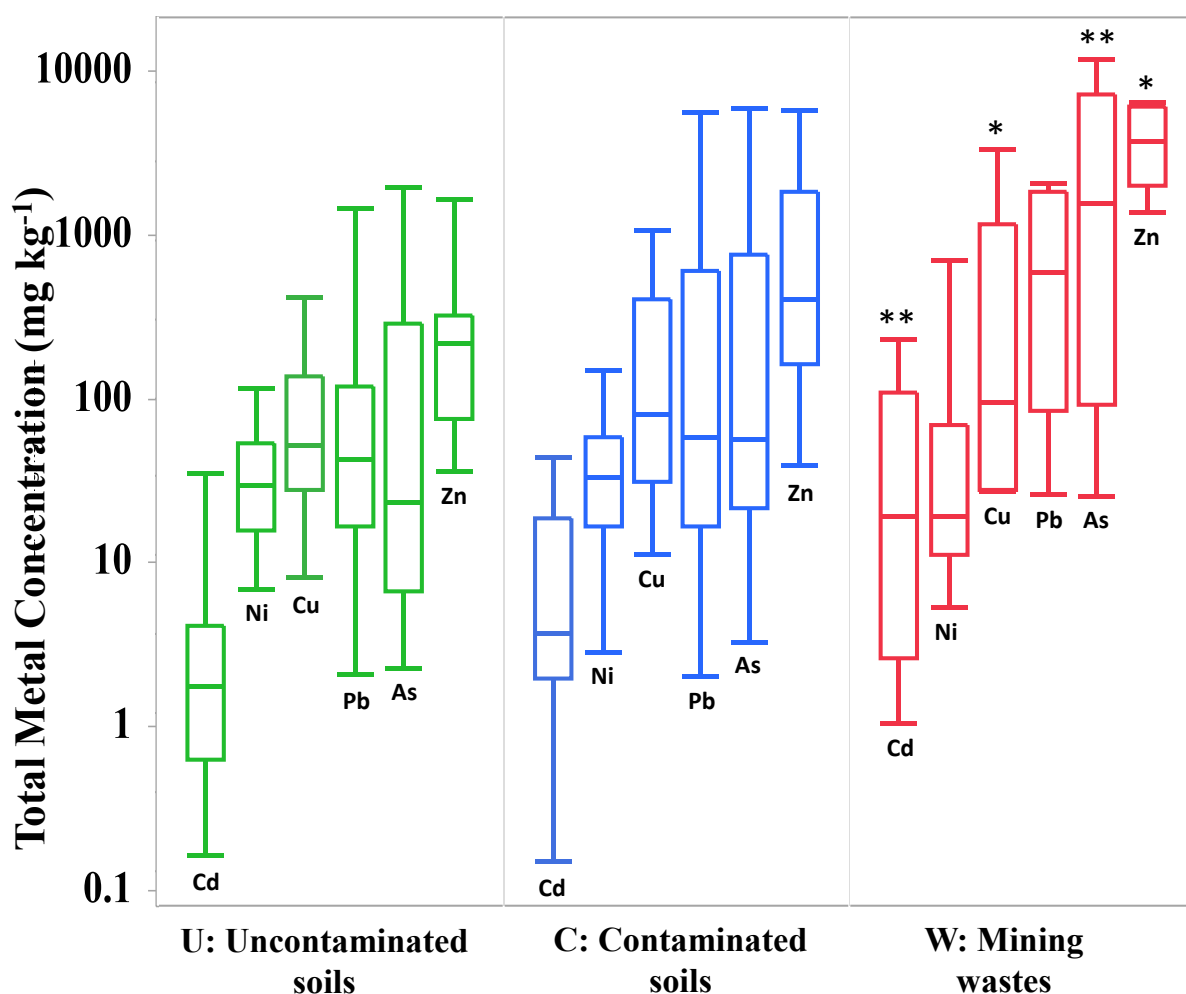
several important soil properties (continuous variable), to identify the significant soil parameters in a multivariable regression. Second, these soil parameters were combined with the contamination source characteristic (categorical variables: only the type of extracted metals and lithology as these were the only significant ones). The selection method to enter or leave the regression model was based on statistical significance set at  $p < 0.05$ . No interactions between soil properties and contamination source characteristics were tested, i.e. the models effectively linearly related the %E to soil parameters allowing for different intercepts, not different slopes, depending on source characteristics. This was selected due to the limited number of different samples and to allow testing effects and interactions. Selected tests for interactions showed only very few and inconsistent significant effects (details not shown).

## RESULTS

The 11 sites covered a wide range in type of extracted metals and ore types (Table 1). Plant cover was present on all the uncontaminated soils and in 12 (> 50%) of the contaminated soils. Selected properties of soil and waste samples are given in Table SI8. Almost all soils and treated mining wastes were pH neutral, ranging between pH 6-8, while only two sulfidic ore derived wastes were acid (pH 2.5 and 5.1), corresponding to locations where waste was reported to be not treated (Figure SI1 and Table SI8). All soils contained detectable  $\text{CaCO}_3$  and average % $\text{CaCO}_3$  concentrations were about 10%. In general, uncontaminated soils had higher organic C content and lower % $\text{CaCO}_3$  content than the contaminated ones.

Arsenic, zinc and lead showed the highest elemental total concentrations, with As concentrations reaching up to  $15 \text{ g As kg}^{-1}$  in contaminated soils (Figure 1, Table SI8). Total metal concentrations ranked uncontaminated < contaminated < waste, with statistically significant differences only present between soil and waste samples ( $p < 0.05$  for Cu and Zn,  $p < 0.01$  for Cd and As), except for Pb probably due to the presence of a highly contaminated

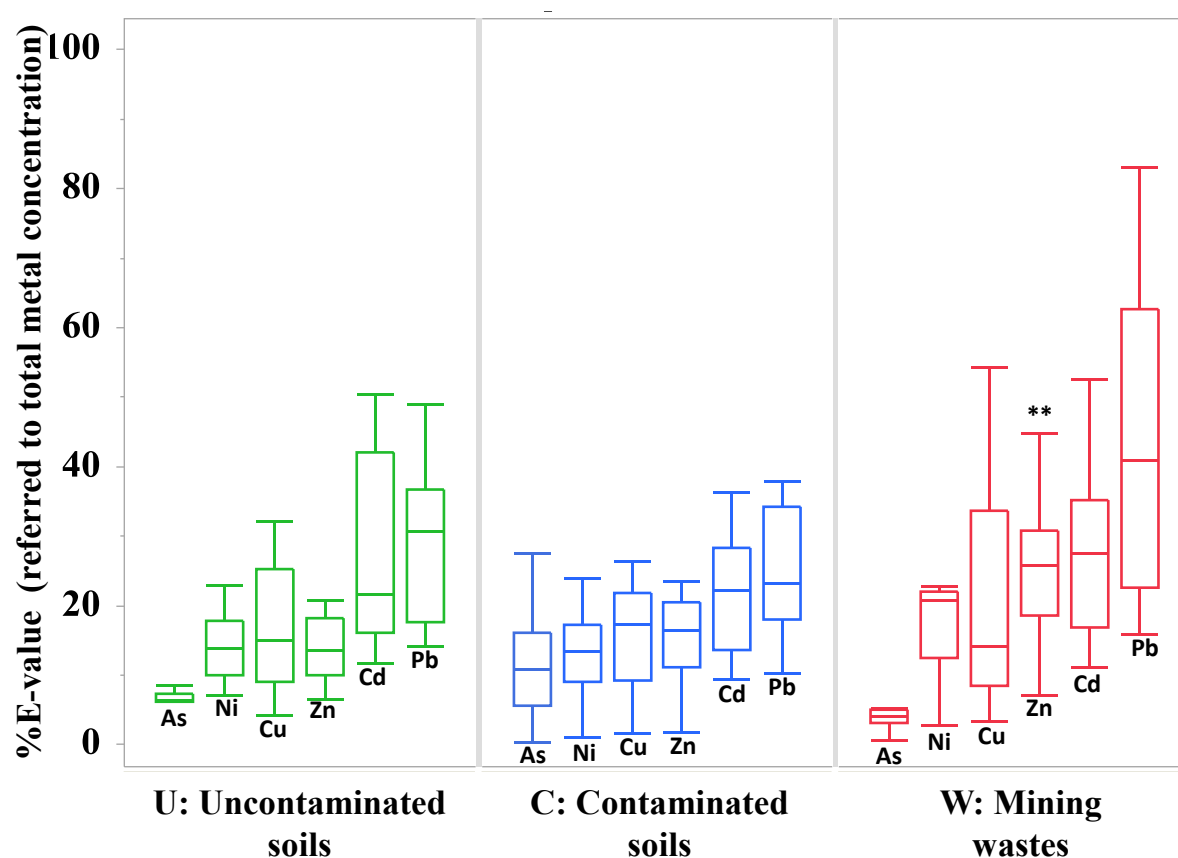
soil sample (4C) and for Ni that was present in relatively low concentrations in all sample types, most likely because no Ni is mined in any of the mines (Table SI8).



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

The labile fractions (E as % of total) in the soils ranked, (with median values in brackets, considering uncontaminated and contaminated soils): Pb (22) > Cd (18) > Cu (15) > Ni~Zn (13) > As (9). The mean %E of the studied elements were unaffected by the sample type (uncontaminated soil, contaminated soil or wastes), except for %E of Zn, which was larger for wastes than for soils (Figure 2, full data in Table SI9). The coefficient of variation of E-

values among different analytical replicates was about 13% with highest mean values for Pb (16%) and lowest for Cu (12%). The % E values of Pb, Zn, Ni and Cu in the external reference sample deviated less than 10% from the corresponding values determined by Garforth (School of Biosciences, The University of Nottingham, UK, unpublished data, 2015). For Cd deviation was of 28% (Table SI7) from the reference value. Finally, the % recovery of the amended metals in the labile pools in a standard additions test ranged 100-121% depending on soil and was deemed acceptable (Table SI6).



**Figure 2.** Visual representation by box-whisker plot of Ni, Cu, Zn, Cd, Pb and As labile fractions (% E) in different Mexican sample types. Horizontal lines show the median. Box edges correspond to the upper boundaries of the first and third quartile. Whiskers extend to the furthest data point within  $1.5 \times$  box heights. The marks above the whiskers are added if the %E values in contaminated soils or mining wastes were different from the corresponding uncontaminated soils (Dunnett's test, with \* for  $p < 0.05$  and \*\* for  $p < 0.01$ ).

The labile Ni and Zn fractions decrease with increasing pH. Cu and Cd increase with increasing %OC and those of Pb increase with increasing total Pb concentrations (Table 2).



The %E of Zn related to total soil Zn in a biphasic pattern, increasing with total concentration up to about 2000 mg Zn kg<sup>-1</sup> followed by a negative variation of %E with the increase of total concentration (Figure SI2), a pattern also found by Marzouk et al. 2013 (Marzouk, et al. 2013). No such biphasic patterns are found for the other elements. The %E value of As increased with soil Fe content, however the limited sample number and high leverage effect of a single observation (sample 4C with As %E= 30 and Fe=140mmol kg<sup>-1</sup>) suggest that this trend should be treated with caution.

**Table 2.** Model R<sup>2</sup> values for the linear regression between labile fractions (%E) of Ni, Cu, Zn, Cd, Pb, and As and soil chemical properties or for the ANOVA of %E related to contamination source attributes. Bold values indicate that the corresponding regression variables or factors are statistically significant ( $p < 0.05$ ). Italic values denote that the effects (slope) are negative. M<sub>tot</sub>: total metal concentration (mg kg<sup>-1</sup>); OC: organic carbon concentration (% w/w); eCEC: effective cation exchange capacity (cmol<sub>c</sub> kg<sup>-1</sup>); CaCO<sub>3</sub> carbonates concentration (g kg<sup>-1</sup>); (Fe/Al)<sub>ox</sub>: oxalate extractable Fe or Al (mg kg<sup>-1</sup>). For source attributes see Table 1. For the parameters and RMSE of 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	<i>0.44</i>	<i>0.30</i>	<i>0.38</i>	<i>0.05</i>	<i>0.09</i>	0.08
M <sub>tot</sub>	<b>0.19</b>	0.09	0.08	<b>0.15</b>	<b>0.63</b>	<0.01
OC	0.08	<b>0.63</b>	<b>0.17</b>	<b>0.62</b>	<b>0.18</b>	<0.01
eCEC	0.02	0.1	0.06	<b>0.12</b>	0.01	<i>0.21</i>
CaCO <sub>3</sub>	<0.01	0.04	0.03	0.02	0.1	<i>0.11</i>
Fe <sub>ox</sub>	<0.01	0.05	0.09	<0.01	0.14	<b>0.83</b>
Al <sub>ox</sub>	<b>0.25</b>	0.22	0.05	<b>0.26</b>	0.14	<i>0.48</i>
Extracted metals <sup>a</sup>	<b>0.57</b>	<b>0.68</b>	<b>0.49</b>	<b>0.57</b>	<b>0.59</b>	0.25
Mineralogy <sup>a</sup>	0.08	0.26	0.18	0.29	0.11	0.11
Ore type <sup>a</sup>	0.25	0.39	<b>0.21</b>	0.26	0.10	0.25
Ore structure <sup>a</sup>	0.12	0.36	<b>0.25</b>	0.16	0.14	0.24
Ore lithology <sup>a</sup>	<b>0.39</b>	<b>0.58</b>	<b>0.50</b>	<b>0.39</b>	0.26	0.25

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

When labile fractions were related to individual metal source characteristics the %E values were strongly affected by the type of extracted metals (Table 2), a term referring to the type of metals mined at each site, with 9 different defined groups (Table 1), suggesting a large effect of the sample location since only 11 mine sites were surveyed. However, when soil

properties and metal contamination source characteristics were included together in the analysis, the effects of the ore lithology (the ore enclosing material) were more relevant than the other metal-source characteristics. Stepwise multiple regression yielded a multivariate linear model in the form:

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

where  $b$  is the intercept and  $m_1$  to  $m_4$  are the corresponding slopes for different soil properties:  $pH_{CaCl_2}$ ; total metal concentration ( $M_{tot}$ ,  $mg\ kg^{-1}$ ); organic carbon content (OC, %); oxalate extractable Fe ( $Fe_{ox}$ ,  $mg\ kg^{-1}$ ).

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

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

Element	n	b	$m_1^*$	$m_2$	$m_3$	$m_4$	Model $R^2$	RM SE	Additional metal source characteristic	Improved Model $R^2$	RM SE	r (pred to obs)
Ni	32	66 (9)	<b>-7.9</b> (1)	0.08 ( $<0.01$ )			0.67	3.5	Ore lithology <sup>1</sup>	0.73	2.9	0.89
Cu	32	49 (10)	-6 (1.4)	<b>0.01</b> (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)		<b>0.15</b> (0.1)	5.5 (0.8)		0.69	5.78				0.83
Pb	32	17 (2)		0.01 (0.001)	<b>3.3</b> (0.9)		0.75	6.37				0.87
As	10	2 (2)				<b>0.004</b> (0.001)	0.83	3.83	Ore lithology	0.99	3.1	0.91

\*Corresponding slopes for different soil properties:  $m_1$   $pH_{CaCl_2}$ ;  $m_2$  total metal concentration ( $M_{tot}$ , mg  $kg^{-1}$ );  $m_3$  organic carbon content (OC, %);  $m_4$  oxalate extractable Fe ( $Fe_{ox}$ , mg  $kg^{-1}$ ).  
<sup>1</sup> See Table 1.

## DISCUSSION

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

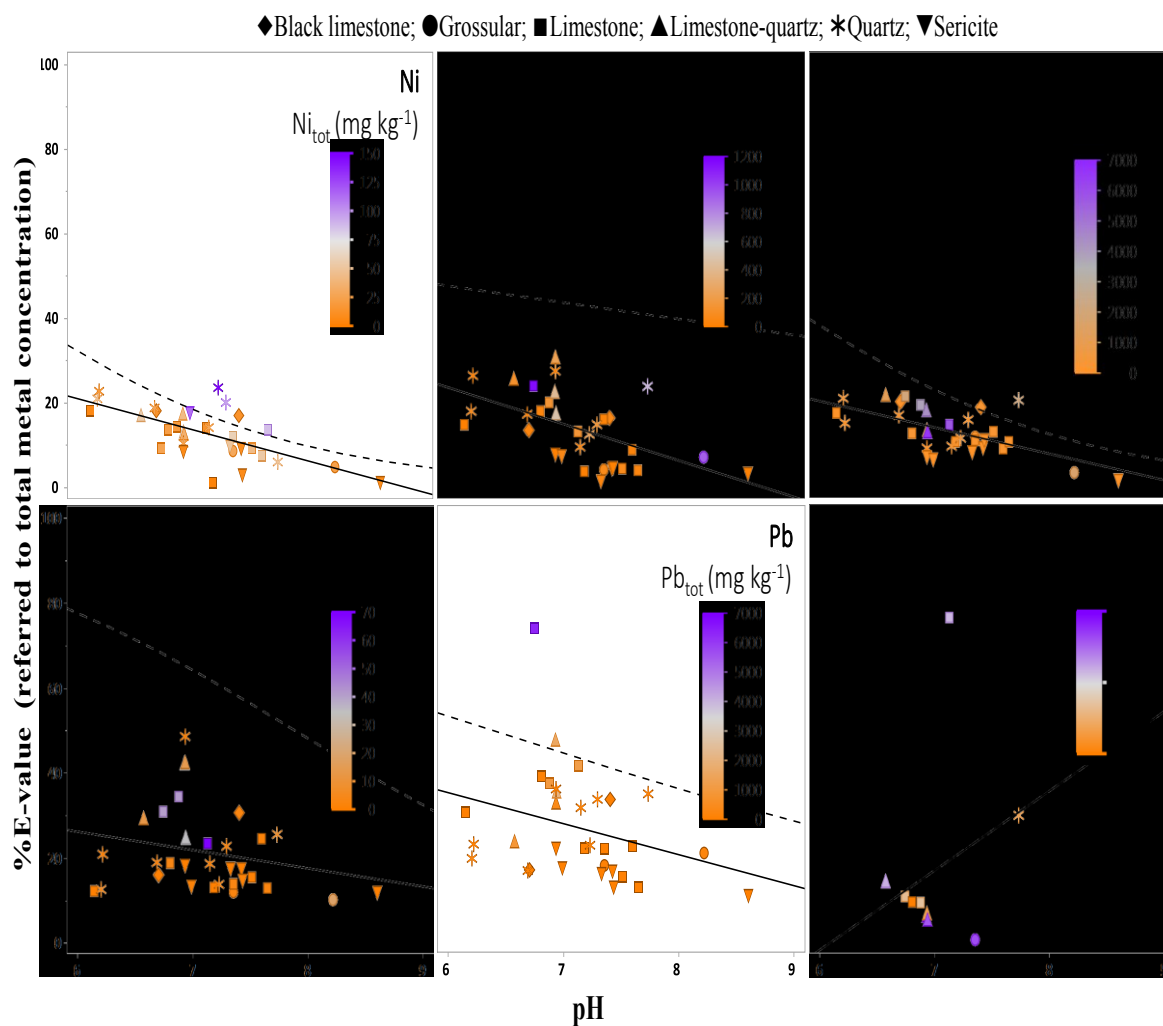
At four locations (I, II, IV and X), the concentrations in uncontaminated soils even exceeded such baseline values, e.g. 1100 mg Zn  $kg^{-1}$  and 890 mg As  $kg^{-1}$ , respectively, with values

largely higher than median background concentrations for Mexican soils ( $47 \text{ mg Zn kg}^{-1}$  and  $4.8 \text{ mg As kg}^{-1}$ , (Gutiérrez-Ruiz et al. 2009)). This illustrates that the soils located within about 100 m from the mining dam edge still contained the signature of a metal enrichment and, therefore, that the uncontaminated samples do not truly represent the background soils conditions at a large scale. Total Zn and As concentrations in contaminated soils peak to about  $7000 \text{ mg kg}^{-1}$  for both elements, in agreement with reported values for those locations (Duarte-Zaragoza et al. 2015; Morton-Bermea et al. 2013; Santos-Jallath et al. 2013).

The element lability in contaminated soils and mining wastes is a more relevant indicator for environmental risk than total concentrations (Hamon et al. 2008). The median %E of Cu, Zn and Cd for the soil samples were 10 to 20 percent lower than the median of previously reported values for Cu (17%, n=87), Zn (23%, n=101) and Cd (30%, n=105) obtained using the same protocol (Buekers et al. 2007; Garforth et al. 2016; Hamon et al. 2008; Marzouk et al. 2013b). Ni and Pb labile fractions were very comparable with the same set of reported values. A main reason for the discrepancies is, of course, the type of sampled analyzed, as in the case of Buekers et al. (2007), were high fractions of labile Cu and Cd correspond to control-uncontaminated soils. When field contaminated soils are analyzed (as in Garforth et al. 2016 and Marzouk et al. 2013b) the discrepancies are more related to soil chemical properties, mainly to lower pH values and  $\text{Fe}_{\text{ox}}$  contents compared to the values of the present work. Median As %E values are in good agreement with the median of reported values in contaminated soils (8.2, n=27) determined with similar protocols (De Brouwere et al. 2004). However, the median %E of As obtained using a different extracting solution (mainly  $\text{H}_2\text{PO}_4^-$ ) is about 4 times higher than the one in this study, probably due to the dissolution of the non-labile fraction to some extent, as it has been observed for some cationic metals with strong extractant solutions (Hamon et al. 2004; Stroud et al. 2011; Tye et al. 2002). The higher metal lability in mining wastes (W) compared to that in soil samples is in contrast with

earlier findings (Degryse et al. 2004; Marzouk et al. 2013b; Rahman et al. 2017), and may be the result of the prolonged weathering time of the collected mining wastes, generating acid drainage after oxidation of remaining mineral sulphides in the wastes.

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



**Figure 3.** Element labile fraction (% E) as a function of pH for uncontaminated and contaminated soils related to different ore lithologies. The dashed lines are previously established relationships of labile fractions in well-equilibrated metal salt amended soils derived from Mao et al., 2017 (Mao et al. 2017).

In the data here, the %E of Cd increases with increasing %OC in soil, this contrasts observation of Degryse et al. in a study where Cd lability decreased with increasing organic carbon associated to progressive sludge loadings to soil (Degryse et al. 2004). However, in that case it was assumed that the negative trend was more related to the dilution of the most labile Cd fraction in the original soil with less labile Cd in the amendment. Here, it is possible that increased %OC in soil enhances Cd mobility through complexation of  $Cd^{2+}$  in soil solution with dissolved organic matter, thereby limiting Cd fixation. Indeed, it is well known that  $Cd^{2+}$  has a high affinity to form complexes with dissolved organic matter (DOM). The labile Pb

fraction increased here with total Pb concentration, suggesting that there is only a minor presence of non-labile Pb mineral forms (like galena or pyromorphite) that normally restrict Pb lability (Atkinson et al. 2011). The high affinity of Pb for organic functional groups in DOM may explain the sensitivity of Pb labile fraction to changes in soil organic content. At high TOC contents such higher affinity could obscure the effects of pH on Pb lability more than on Zn resulting in different variables explaining the %E of Zn and Pb. Marzouk (2013) found a strong effect of total Pb concentration on labile Pb fractions: increasing %E with total Pb at total concentrations  $<2000 \text{ mg kg}^{-1}$  and decreasing %E with total Pb at total concentrations  $>2000 \text{ mg kg}^{-1}$  (Marzouk et al. 2013b). The first trend is the one observed in our data set in which total Pb concentration range of 1.7 to 2100  $\text{mg kg}^{-1}$  excluding one outlier at 6400  $\text{mg kg}^{-1}$ .

*Effect of metal source characteristics in the models.* Among the metal-source characteristics, only ore lithology explained the labile fractions of Zn in the multivariate models, while the model improvement for Ni labile fractions was only marginal and that for As labile fraction needs to be treated with caution due to a lack of large data number (Table 3). Differently from the other metal source characteristics, the ore lithology is not exclusively related with the ore but it is extensive to the original geological material. It is probable that the effect of the ore lithology (the main material enclosing the ore) on %E in the soil samples reflects the influence of the parent rock on the soil formation process for the uncontaminated soils, while for the contaminated soils it could reflect the influence of the mining waste as a source of contamination.

For Zn, it was observed that the lowest %E-values was about 9% (at pH=7 and  $e\text{CEC}=20 \text{ cmol}_c \text{ kg}^{-1}$ ) in mines where sericite (mica group) and grossular (garnet group) ore lithologies occur, both mainly composed of silicates, whereas highest %E-values were about 15% (at equal soil properties as above) in mines dominated by the black-limestone ore lithology. The

sericite and grossular silicate ore lithologies are here associated with polymetallic extraction mines, including Au, Ag, Cu, Pb and As in the form of sulphides in the mineral. The silicate ore lithology may explain the lower end of labile Zn fractions in such mines: Zn speciation in mining impacted soils showed that kerolite, a trioctahedral phyllosilicate, was a major host of Zn in soils with high Zn contamination from either smithsonite ( $\text{ZnCO}_3$ ), hemimorphite ( $\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2\text{H}_2\text{O}$ ) and willemite ( $\text{Zn}_2\text{SiO}_4$ ) and the labile fraction of Zn in such soils is very low (Van Damme 2010). The labile fractions of Zn were slightly higher where the black-limestone occurs, exclusively in areas used for gold and silver extraction from sulfidic and oxide ores, but the reasons behind such larger %E associated to those samples are unclear.

Earlier studies in well equilibrated metal salt amended soils have revealed empirical trend lines between metal labile fractions and soil pH. Such models have been taken forward to regulations (Smolders et al. 2009). Selected empirical trend lines are added in Figure 3 (Mao et al. 2017). In general, these lines are on the higher end of labile fractions observed here, pointing that the labile fractions in the mine impacted soils are lower than in the metal salt impacted soils and that some non-labile metal may originate from the ore lithology. However, the differences in average labile fractions at equivalent pH is less than factor 2, except for Cd and Cu (maximally factor 4) but these metals are unlikely be of risk concern due to their low concentrations. These lability data suggests that the mineral weathering/alteration in these mining impacted soils has already proceeded rather far, especially for Ni, Zn and Pb. Such also suggests that, in a risk assessment context, the differences with equilibrated metal salt amended soils are not very large and that the earlier generic trends of major soil properties explaining labile fraction adequately describe the data in such mining waste impacted soils, with some bias to the conservative (protective) prediction of metal(loid) lability.



## CONCLUSIONS

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

The necessity to ensure the sustainability of the mining production also involves the control of soil contamination derived from the mining activities, not only in México but at many other important mining regions in developed and developing countries as China, Spain, Australia, Papua New Guinea, Canada, Botswana, Mozambique, South Africa, Guinea, Chile, Peru, Argentina, Kazakhstan or India. Many of these countries share climatic, geological and edaphic characteristics and production practices with mining places in Mexico.

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

## ADDITIONAL INFORMATION

**Author Contributions:** Investigation, formal analysis, and original draft preparation: G.G. R. Review, text improvement, map elaboration: N. V. M. V. Supervision, conceptualization, and resources: E.S.

**Funding:** This research was partially funded by Consejo Nacional de Ciencia y Tecnología (Conacyt, Mexico) grant number 359484.

**Conflicts of Interest:** The authors declare no conflict of interest. The founding sponsors had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; and in the decision to publish the results.

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**Tables**  
(Next page)

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

Samples		Mining district	Economic interest metals <sup>a</sup>	Ore type <sup>a</sup>	Mineralogy <sup>a,b</sup>	Lithology <sup>a</sup>	Soil pH range <sup>c</sup>	Soil OC range (%) <sup>c</sup>
Location	Number							
I	1 and 2	Zimapan	Cu, Pb, Zn	Mesothermal	S, Ox, CO <sub>3</sub> , SO <sub>4</sub> , AsO <sub>4</sub>	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	Hypothermal	S	Limestone	6.1-7.2	0.8-1.2
VII	10	Guanajuato	Ag, Au	Hypothermal	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 <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ))	7.4-8.2	0.2
XI	16	Bernal	Ag, Au	Epithermal	S, Ox, CO <sub>3</sub>	Black limestone	6.7-7.4	2.0-2.8

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

<sup>b</sup>S=sulphidic; Ox=oxides; CO<sub>3</sub>=carbonates, AsO<sub>4</sub>=arsenates; SO<sub>4</sub>=sulphates.

<sup>c</sup>Experimental data, obtained from soils samples <2 mm (wastes excluded).

**Table 2.** Model  $R^2$  values for the linear regression between labile fractions (%E) of Ni, Cu, Zn, Cd, Pb, and As and soil chemical properties or for the ANOVA of %E related to contamination source attributes. Bold values indicate that the corresponding regression parameters or factors are statistically significant ( $p < 0.05$ ). Italic values denote that the effects (slope) are negative.  $M_{\text{tot}}$ : total metal concentration ( $\text{mg kg}^{-1}$ ); OC: organic carbon concentration (% w/w); eCEC: effective cation exchange capacity ( $\text{cmol}_c \text{ kg}^{-1}$ );  $\text{CaCO}_3$  carbonates concentration ( $\text{g kg}^{-1}$ );  $(\text{Fe/Al})_{\text{ox}}$ : oxalate extractable Fe or Al ( $\text{mg kg}^{-1}$ ). For source attributes see Table 1. For the parameters and RMSE of 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	<b>0.44</b>	<b>0.30</b>	<b>0.38</b>	<i>0.05</i>	<i>0.09</i>	0.08
$M_{\text{tot}}$	<b>0.19</b>	0.09	0.08	<b>0.15</b>	<b>0.63</b>	<i>&lt;0.01</i>
OC	0.08	<b>0.63</b>	<b>0.17</b>	<b>0.62</b>	<b>0.18</b>	<0.01
eCEC	0.02	0.1	0.06	<b>0.12</b>	0.01	<i>0.21</i>
$\text{CaCO}_3$	<0.01	0.04	0.03	0.02	0.1	<i>0.11</i>
$\text{Fe}_{\text{ox}}$	<i>&lt;0.01</i>	0.05	0.09	<0.01	0.14	<b>0.83</b>
$\text{Al}_{\text{ox}}$	<b>0.25</b>	0.22	0.05	<b>0.26</b>	0.14	<i>0.48</i>
Extracted metals <sup>a</sup>	<b>0.57</b>	<b>0.68</b>	<b>0.49</b>	<b>0.57</b>	<b>0.59</b>	0.25
Mineralogy <sup>a</sup>	0.08	0.26	0.18	0.29	0.11	0.11
Ore type <sup>a</sup>	0.25	0.39	<b>0.21</b>	0.26	0.10	0.25
Ore structure <sup>a</sup>	0.12	0.36	<b>0.25</b>	0.16	0.14	0.24
Ore lithology <sup>a</sup>	<b>0.39</b>	<b>0.58</b>	<b>0.50</b>	<b>0.39</b>	0.26	0.25

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

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

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)	<b>-7.9</b> (1)	0.08 ( $<0.01$ )			0.67	3.5	Ore lithology <sup>1</sup>	0.73	2.9	0.89
Cu	32	49 (10)	-6 (1.4)	<b>0.01</b> (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)		<b>0.15</b> (0.1)	5.5 (0.8)		0.69	5.78				0.83
Pb	32	17 (2)		0.01 (0.001)	<b>3.3</b> (0.9)		0.75	6.37				0.87
As	10	2 (2)				<b>0.004</b> (0.001)	0.83	3.83	Ore lithology	0.99	3.1	0.91

\*Corresponding slopes for different soil properties:  $m_1$  pH<sub>CaCl2</sub>;  $m_2$  total metal concentration ( $M_{tot}$ , mg kg<sup>-1</sup>);  $m_3$  organic carbon content (OC, %);  $m_4$  oxalate extractable Fe ( $Fe_{ox}$ , mg kg<sup>-1</sup>).

<sup>1</sup> See Table 1