# Effects of the interaction between an acid solution and pedogenic carbonates: the case of the Buenavista del Cobre Mine, Mexico

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**ABSTRACT**

The main purpose of this work was to study and understand the interaction that occurred between an acid solution spilled from Buenavista del Cobre Mine and the soils located in the Bacanuchi River area. The question put forward in this work was: if the soils of the area were able to cushion the impact of the acid solution?. Two soil profiles were examined: Profile 8A, was located on the riverbank and was affected by the spill, whilst Profile 8B, located on the first terrace of the river valley, remained intact . Both soils profiles were chemically characterized. An additional three surface samples (0–30 cm) were taken for geoavailability tests (RBI, SB2, belonging to Profile 8B, and SB3, belonging to Profile 8A). Two further samples, representing typical unaltered soils of profiles 8A and 8B, were taken for their micromorphological study. The results showed a difference between the two profiles, with profile 8A having more acidic pH, greater electrical conductivity, and higher concentrations of Fe, Pb, Cu and As than profile 8B. The geoavailability test showed that the elements enriched in SB3 were stable and not available to the aqueous phase. The soils of Bacanuchi River contain carbonates, which interacted with the acid solution and stabilized the potentially toxic elements presents in the spilled acid solution. This interaction with carbonates promoted a new minerals formation such as gypsum and copiapite. So, the release of contaminants from soil to surface and ground waters is improbable, unless the redox conditions change or a new spill occurs releasing the potentially toxic elements (PTE) to the environment. In this work we show the importance of pedogenic carbonates in soils of arid and semi-arid environments; these carbonates represent a natural geochemical barrier, that can prevent the migration of PTEs in mining areas.

Key words: soils; secondary carbonates; acid solution; potentially toxic elements.

**RESUMEN**

*El objetivo principal de este trabajo es estudiar y comprender la interacción que se produjo entre una solución ácida, derramada de la mina Buenavista del Cobre, y los suelos ubicados en el área del río Bacanuchi. La pregunta de investigación fue: ¿los suelos en el área fueron capaces de amortiguar el impacto del paso de la solución ácida?. Dos perfiles de suelo fueron estudiados y caracterizados químicamente. El perfil afectado, 8A, se encuentra en la ribera del río y el perfil no afectado, 8B, ubicado en la primera terraza del río. Además, se tomaron tres muestras superficiales (0–30 cm) RBI, SB2 (que pertenecen a 8B) y SB3 (que pertenece a 8A), para las pruebas de geodisponibilidad. Finalmente, se tomaron dos muestras inalteradas de los perfiles 8A y 8B para su estudio micromorfológico. Los resultados mostraron una diferencia entre los dos perfiles. El perfil 8A presentó un pH ácido, una conductividad eléctrica mayor y altas concentraciones de Fe, Pb, Cu y As en comparación con 8B. La geodisponibilidad mostró que los elementos enriquecidos de SB3 eran suficientemente estables y no estaban libres en la fase acuosa. La interacción con carbonatos presentes en los suelos formó nuevos minerales tales como yeso y copiapita. Los suelos del río Bacanuchi presentan carbonatos, los cuales interactuaron y estabilizaron a los elementos tóxicos presentes en la solución ácida. De acuerdo a los resultados obtenidos de geodisponibilidad, sería muy difícil que los elementos potencialmente tóxicos (EPT) se liberen a la fase acuosa; al menos, que las condiciones redox cambien o un nuevo derrame ocurra provocando la liberación de los EPT al ambiente. En este trabajo se muestra la importancia de los carbonatos pedogénicos en suelos de ambientes áridos y semiáridos; estos carbonatos representan una barrera geoquímica natural que puede prevenir la migración de los EPT en áreas mineras.*

*Palabras clave: suelos; carbonatos secundarios; elementos potencialmente tóxicos; solución ácida.*

## INTRODUCTION

Acid mine drainage (AMD), and its associated technical issues, is globally recognized as the most serious environmental problem related to the mining industry. AMD includes solutions characterized by low pH and high concentrations of heavy metals and other toxic elements that are generally persistent, non-degradable, and can severely contaminate the surface, including soils, and the groundwater (Akcil and Koldas, 2006; Islam and Park, 2012; Macias *et al.,* 2012). AMD generation is one of the main reasons for human-induced transformations in the soils of mining districts (Volke *et al.*, 2005; Arocena *et al.,* 2012).

In Mexico, the largest Cu deposits are located in the Cananea mining district in the state of Sonora. Production from this mining district accounts for 400000 tons of Cu per year (Valencia *et al.*, 2006). In this context, the Buenvista del Cobre Mine is considered to be the fourth most important mine in the world.

In 1984-1985 in the Cananea district, high concentrations of potentially toxic elements were reported from the surface water and sediments. Their presence was related to the dumping and infiltration of acid solutions from the mines into the riverbeds of the Bacanuchi and Sonora Rivers (Gómez *et al.*, 1990; Gómez *et al.*, 1993). These wastes promoted high levels of ions such as Cu, Pb, Zn, Mn and $SO_4^{2-}$, that exceeded the maximum permissible limits and these concentrations can cause health problems to the inhabitants who live near the river.

On 6 August 2014, about 40000 m³ of technical acid solution, for copper extraction, were spilled from the Tinajas 1 Dam, of the Buenavista del Cobre copper mine, into the Tinajas stream (17.6 km), the Bacanuchi River (64 km) and the Sonora River (190 km). Gutierrez-Ruiz y Romero (2015) mention that The Comisión Nacional del Agua (CONAGUA) reported the potentia+lly toxic elements (PTE) concentrations in the acid solution as: Fe = 1080 mg/L, Al = 461 mg/L, Cu = 114 mg/L, Mn = 98 mg/L, Zn = 51 mg/L, As = 42.7 mg/L, Ni = 11 mg/L, Cd = 7.8 mg/L, Pb = 2.5 mg/L, and Cr = 1.5 mg/L (Gutierrez and Romero, 2015). The private laboratory ABC Analytic (2014) also reported high concentrations of PTEs (Al, As, Ba, Cd, Cu, Cr, Fe, Mn, Hg, Ni, Pb, Sb, and Zn) in surface and groundwater samples obtained from the Sonora River basin after the spill. Three months later, all the PTEs concentrations were below the maximum permissible limits set by the Norma Oficial Mexicana NOM-127-SSA1-1994 (Mexican Official Norm NOM-127-SSA1-1994; ABC Analytic Report, 2014). The concentrations of Fe, Al, and Mn were high, but their concentrations were considered to be natural and associated with the clay fraction (≤ 0.45 μm).

Additionally, Rivera-Uria *et al.*, (2018) studied the micromorphology of the soils affected by the spill. These authors identified changes in color, acid pH and the precipitation of ferruginous material associated with the formation of gypsum. The micromorphometric quantification of this precipitation showed an increase associated with the effect of the acid solution from the mine. Herein, the working hypothesis is that carbonates present in the soils and sediments of the Bacanuchi River and its environment had the capacity to neutralize the spilled acidic waters. As a consequence, the heavy metals present in the acid solution were immobilized by different mechanisms, mainly precipitation, thus decreasing their concentrations in the solution.

There are quite few studies of contamination caused by the catastrophic mine spills of the scale comparable with that of Buenavista del Cobre mine in 2014. The investigations of these events focused on the metal concentrations in water and suspended sediments as a consequence of spills from acid mine drainage such as the case of the Gold King mine, New Mexico (Rodriguez-Freire, 2016) and de Zarza mine, Spain (Olias *et al.,* 2019). However, the role of the soil mantle and particularly of the soil components in the area affected by the spills were not investigated. Therefore, little is known about the interaction of a technical acid solution with different types of soils.

This paper considers the interactions of the acid solution released into the Bacanuchi River in the Cananea mining district during an operational collector leaching failure in August 2014 with the soils and surface sediments of the river valley. The purpose of the study was to determine the physicochemical changes in Bacanuchi River soils and sediments that were influenced by the interaction with the acid solution, and the mechanism of immobilization of PTEs from that solution.

## MATERIAL AND METHODS

### Environmental setting of the study area

The study area was located in the valley of the Bacanuchi River, a tributary of the Sonora River (Figure 1). The geology of the region includes a Proterozoic basement, overlain by Mesozoic plutonic, volcanic and sedimentary rocks (Anderson and Silver, 1979), with porphyry intrusions. During the Cretacic, magmatic activity produced the emplaced of magmatic/hydrothermal Cu–Mo and related deposits.

These deposits have been mined for several centuries, but such activities intensified since middle of the 20th century (Bracamonte *et al.*, 1997). One of the biggest and most important mining districts is Cananea, where the Buenavista del Cobre Mine is located. Here, the porphyry-related mineralization of Cu-Mo-W is most abundant (Valencia *et al.*, 2007), and accounting for 7,140 Mt of ore at 0.42 % Cu and 0.008 % Mo (Singer *et al.*, 2005). Additionally, Zn-Pb-Cu skarns and high-grade sulfide and Fe oxide deposits are present (Meinert, 1982).

The basin of the Sonora River has an area of 3,0913 km². The Bacanuchi River is located in the northern part of this basin, and extends for 64 km, forming a tributary that flows into the Sonora River. The climate of this region is semi-dry to dry. Predominant soils are Regosols and Leptosols, less common are Phaeozems, Calcisols, and Fluvisols.

### Fieldwork and sample collection

Samples of the acid solution and the sediment (SEDT1) from the Tinaja 1 Dam were collected 10 weeks after the August discharge event (on 23 October 2014). The acid solution was stored in a bottle composed of high-density polyethylene, having been filtered through with a 0.45 μm nitrocellulose membrane, and was chilled until the analysis.

The sediment, obtained from the deepest area of the Tinaja 1 Dam, was collected using a handled bottle. The liquid was discarded and the solid was preserved in a polyethylene bag.

Soil and sediment samples were collected along the first terrace of the Bacanuchi River. As reported by Rivera-Uria *et al.* (2018), one of the main observations made in the fieldwork was a change in soil color, whereby a yellow-orange color appeared on the surface of the soil profiles, which was not present in the natural (unaffected) surrounding soils. This was the first criterion used to distinguish between affected and unaffected sediments and soils as a guide in the sampling procedure.

Profile 8A and the sample SB3 were considered to represent affected soil, while the profile 8B and samples SB2 and RB1 were considered to be unaffected. The samples were taken from the river bank 8A and 8B (1.5 m from 8A, on the first river terrace) and from the center of the river channel RB1 (Figure 2a). At locations 8A and 8B, two profiles were dug to a depth of 70 and 100 cm, respectively. Samples from these profiles were taken every 10 cm. Additional surface samples (0–30 cm)
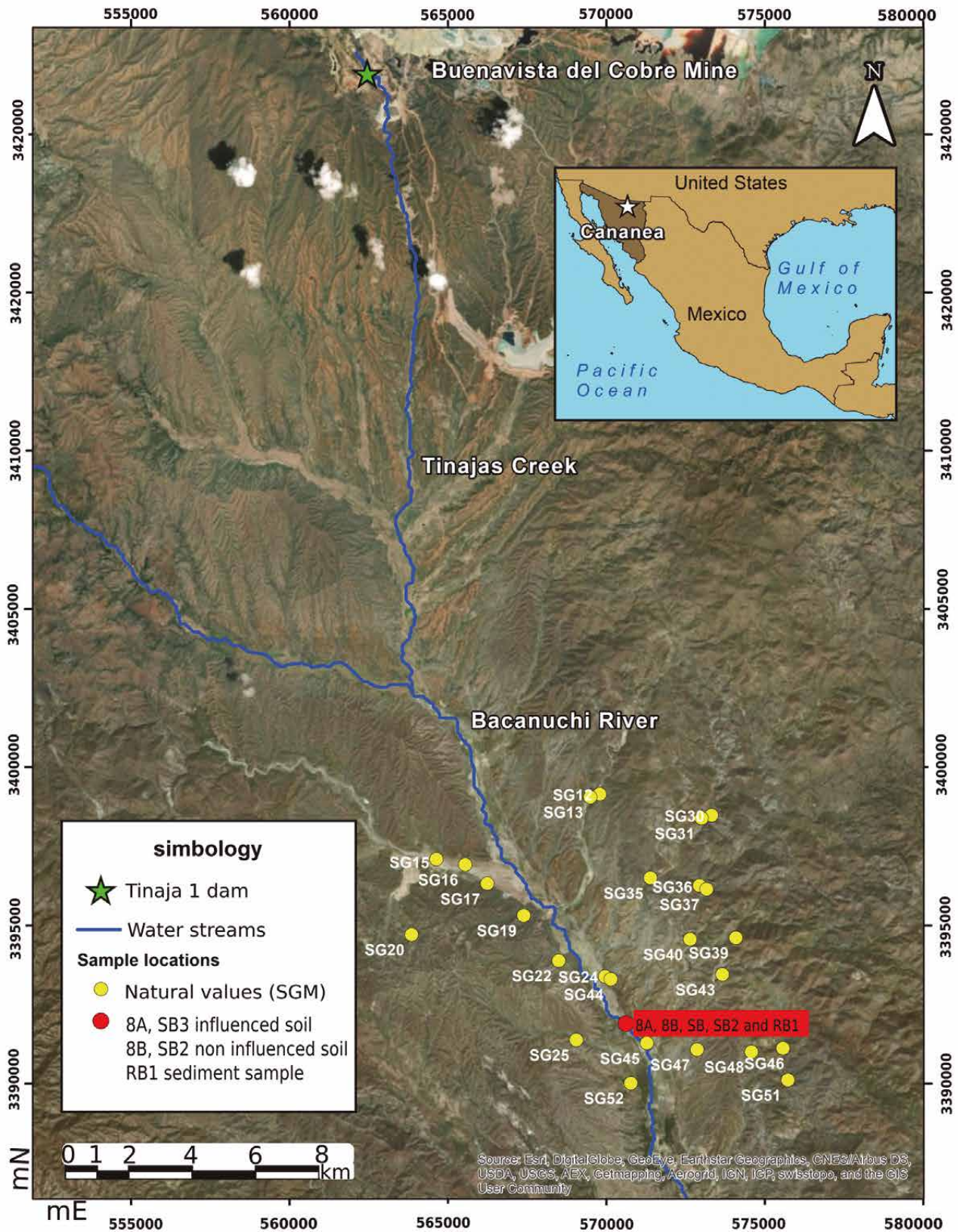
Figure 1. Study area: location Buenavista del Cobre Mine, profiles 8A, 8B, SB2, SB3, RB1. Points of the natural values according to SGM (2007). Location of the Tinaja 1 dam. Source: ESRIC, DigitalGlobe (2015) [Satellite Imaginery]. Software: ArcGis [GIS software]. Version 10.2 Redlands, CA: Environmental Systems Research Institute, Inc., 2014.
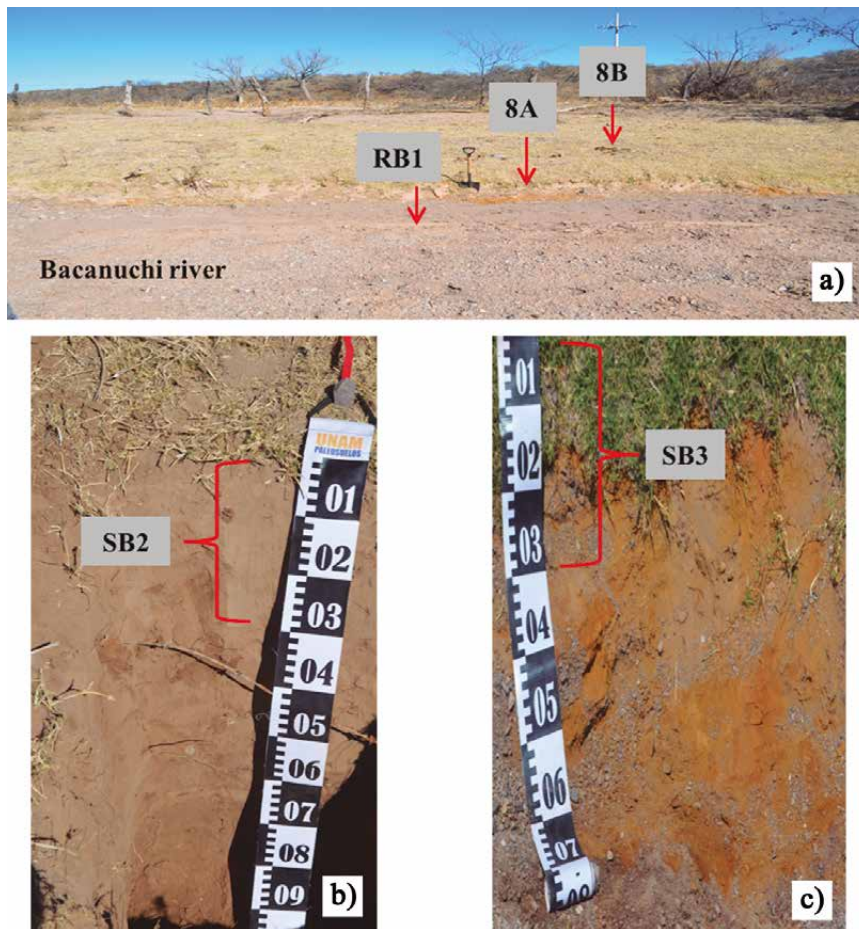
Figure 2. a) Landscape, Bacanuchi River and samples sites. b) Profile 8B and SB2 sample. c) Profile 8A and SB3 sample. Scale in cm.

were obtained from locations 8B and 8A, labeled SB2 (Figure 2b) and SB3 (Figure 2c), respectively. SB3 displayed the most contrasting colors, while SB2 showed similar colors to the soils in the neighboring areas.

**Microscopic techniques**

To produce fine thin-sections, two samples with original structure were taken from SB2 and SB3, air dried and subsequently impregnated with polyester resin. After their hardening, the blocks were cut to a thickness of 30 μm. Each thin-section was covered with glass coverslip. For the micromorphological analysis, an Olympus BX50 petrographic microscope was used.

In Addition, an elementary analysis was carried out on polished surfaces obtained from the two blocks of soil impregnated with resin. These were polished with diamond abrasives of 1 and then 0.5 μm, and then coated with graphite. For this analysis, a JEOL JXA-8900R scanning electron microscopy (SEM), equipped with energy dispersive X ray spectroscopy (EDS), was used. The results presented are in percentage weight.

**Geochemical characterization**

The soil and sediment samples were dried at room temperature and then sieved so as separate out the coarse fraction (> 2 mm). Subsequently, the < 2mm fraction was prepared for laboratory analysis.

The pH and electrical conductivity (EC) were determined directly from sample acid solution. For the soil and sediment, in a 1:5 mixture of soil:solution using ultrapure water; this was shaken for 1 h. The measure

of pH was determined using a calibrated pH-meter (Denver Instrument Ultrabasic) and the EC was measured using Oakton 700 equipment.

The concentrations of the PTEs (Al, As, Cd, Cr, Mn, Ni, Pb, and Zn) in the acid solution were determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using Perkin Elmer Model 8300DV equipment with a cyclonic spray chamber. The concentrations of the major ions ($Na^+$, $K^+$, $Ca^{2+}$, $Mg^{2+}$, $F^-$, $Cl^-$, $SO_4^{2-}$) were determined by ionic chromatography using a Metrohm 883 Basic IC Plus.

The Fe speciation was determined by spectrophotometry for complexes of $Fe^{2+}$, using 1,10-phenanthroline. Total $Fe^{3+}$ was determined to be the difference between the total Fe reduced by hydroxylamine and $Fe^{2+}$.

For the soils and sediments, the concentrations of the major elements and trace elements were determined by X-ray fluorescence. A Rigaku Primus II ZSX with pressed sample pellets was used for the major ion determination, and a portable Thermo Scientific Nitton FXL 959 was used for trace element determination.

For the mineralogical identification of the soils and sediments, X-ray diffraction (XRD) was employed, using an Empyrean diffractometer with Cu X-ray radiation was used. Prior to this analysis, the samples were ground and homogenized with an agate mortar.

**Geoavailability test and sequential extraction for determining the geochemical distribution of selected elements**

Geoavailability is the susceptibility and availability of a resident mineral phase(s) to alteration and weathering reactions (Smith and Huyck, 1999). The geoavailability of the soil and sediment samples was

estimated by soluble extraction in equilibrium with $CO_2$ at pH = 5.5, with agitation for 18 h at a ratio of 1:20 of soil:extractant, according to Norma Oficial Mexicana NOM-147-SEMARNAT/SSA1-2004 (Mexican Official Norm NOM-147-SEMARNAT/SSA1-2004). The extractant was filtered through a 0.45 μm nitrocellulose membrane, then refrigerated at 4 °C until analysis.

Trace element analysis was performed by ICP-OES. The major elements analysis was performed using ionic chromatography with an 883 Basic IC Plus Metrohm.

Prior to the sequential extraction, X-Ray Fluorescence (XRF) was used to determine the relative importance of the analyzed elements in the whole affected and unaffected samples (SEDT1, SB2 and SB3). Based on this pre-analysis, the elements selected for sequential extraction were As, Cu, Fe, Pb, Mn, and Zn.

For this analysis, the samples were dried at 40 °C for 72 h, then sieved to separate out the coarse fraction (> 2 mm). Subsequently the samples were ground in an agate mortar and homogenized.

For the extraction procedure, 1 g of sample was weighed in a centrifuge tube with a flat bottom (polypropylene, 50 mL). The sample was heated in a digestion system using an Environmental Express HotBlock to control the temperature. Between each successive extraction, separation was stimulated by centrifuging for 30 min at 5 °C in a Centurion Scientific Ltd Model Pro-Research. The supernatant was removed using a Pasteur pipette, and preserved in a refrigerator at 4 °C until analysis by ICP-OES. The only exception was for residual 2 (R2) (VII), which was analyzed by XRF using a portable Thermo Scientific Nitton FXL 959. The extraction process for the samples is shown in the Table 1.

## RESULTS

### Characterization of the acid solution, sediments, and soils

The acid solution had a reddish-yellow color (Munsell Color, 2013). The sediment (SEDT1) from the base of the dam also had a reddish yellow color and a clayey texture.

The affected soil from profile 8A comprised a 70 cm-thick AC horizon, with a sandy texture. It had a very friable granular-subangular blocky structure and did not show any reaction with 10 % hydrochloric acid (HCl), this latter qualitative result indicated an absence of $CaCO_3$.

The surface of the profile had a reddish-yellow color. After cleaning of the first 10 cm, this color changed into pale brown. The soil was classified in the field as a calcic Regosol.

The unaffected soil of the profile 8B contained A and AC horizons. The A horizon (0–10 cm) had a light brown color and a very friable granular structure, with very fine roots. The reaction with 10 % hydrochloric acid (HCl) was positive. The AC horizon (10–100 cm) was also light brown in color and had a loose sandy texture. The structure was poorly developed, and it was possible to observe alluvial layering. Soil material reacted with 10 % hydrochloric acid (HCl). The positive reactions in the two horizons indicated the presence of $CaCO_3$, the effervescence being from released $CO_2$ as demonstrated by the following reaction:

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O \qquad (1)$$
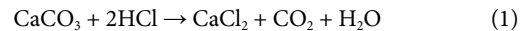
Based on these properties, profile 8B was classified as a calcic Fluvisol.

Sample RB1 from the riverbed had a coarse texture with large amounts of gravel and sand, and was mainly brown in color. There was no evidence of the reddish-yellow coloration associated with the spill. This sample showed a strong reaction with 10 % hydrochloric acid (HCl), confirming the presence of carbonates. Sample SB2 was sandy, had a light brown color, and a positive reaction with 10 % hydrochloric acid (HCl). In contrast, sample SB3 had a reddish-yellow color and a negative reaction to the 10 % hydrochloric acid (HCl), similar to the profile 8A.

The acid solution had a pH of 2.3 and an EC of 5910 μS/cm (Table 2) with the highest chemical concentrations ranked as: $SO_4^{2-}$ > $Fe^{3+}$ > Al > Cu > Mg > Mn > Ca > Zn; and lowest concentrations as: Cl > F > Na > K > Ni > Cd > As > Pb > Cr.

The sediment sample from Tinaja 1 (SEDT1) had chemicals properties similar to the acid solution, with a low pH value (2.9), high CE (5911 μS/cm) and relatively high concentrations of PTEs (Fe = 9.3 % w/w, As = 165 mg/kg, Cu = 1292 mg/kg, , Pb = 140 mg/kg, Mn = 1192 mg/kg and Zn = 551 mg/kg). The mineralogical assemblage identified by XRD included quartz, muscovite, labradorite, montmorillonite, alunite, anhydrite, jarosite, goethite, hematite, and birnessite (Table 3).

Profile 8A (affected soil) had acidic pH values, ranging from 4.5

Table 1. Procedure for sequential extraction used in this study.

| Geochemical fraction | Extractable agents and conditions | Reference |
|---|---|---|
| Exchangeable (I) | 8mL de 1 M NaOAc, pH= 8.2, orbital shaking 250 rpm, 60 min. | (Tessier *et al.*, 1979) |
| Acid soluble (II) (Bound to carbonate) | The residue from (I) was leached with 8 mL of buffer solution 1 M of $CH_3COO^-$/$CH_3COOH$, pH=5 with orbital shaking 250 rpm for 5 h. | (Tessier *et al.*, 1979) |
| Easily reducible (III) (Bound to Fe poorly crystalline) | The residue from (II) was leached with 20 mL of 0.25 M de $NH_2OH\cdot HCl$/ 0.25 HCl 50ºC for 30 min. | (Chao and Zhou, 1983) |
| Moderately reducible (IV) (Bound to crystalline Fe and Mn oxides) | The residue from (III) was leached with 20 mL of 0.25 M $NH_2OH\cdot HCl$ and 25 % de acetic acid with heating to 96 ºC with occasional agitation for 6 h. | (Tessier *et al.*, 1979) |
| Moderately and poorly oxidizable (V) (Bound to refractory organic compounds and sulfides) | To the residue from (IV) was added 3 mL 0.02 M de $HNO_3$ and 5 mL 30 % $H_2O_2$ adjusted to pH = 2 with heating to 85 ºC for 2 h with occasionally agitation. After that, 3 mL 30 % $H_2O_2$ was added and the sample was heated for 3 h. Finally, after cooling was added 5 mL of 3.2 M $NH_4OAc$ in 20 % de $HNO_3$ for 30 min. The sample was completed to 20 mL with ultrapure water. | (Gupta and Cheng, 1975) |
| Residual 1 (VI) (aqua regia extractable $HNO_3$/HCl)) | The residue from (V) was leached with 3mL HCl 37 % and 9 mL $HNO_3$ 70 % and heat by microwave at 180 ºC for 10 min. The extractable was filtrate with qualitative filter 5 and it was diluted to 50 mL | (US EPA, 1994) |
| Residual 2 (R2) (VII) Mineral lattices. Strongly bounded to silicates (R2) | The residue from (VI) was dried at 105 °C for 24 h. | (US EPA, 2007) |

Table 2. Comparison of geochemical characterization of acid solution spilled in this study and data reported by ABC Lab. (2014).

| Parameter | Concentration determined in this study (mg/L) | Concentration determined by ABC Lab., 2014 (mg/L) |
|---|---|---|
| $SO_4^{2-}$ | 5888.70 | ND |
| $Fe^{3+}$ | 1016.70 | 1080.00 |
| $Fe^{2+}$ | 12.00 | ND |
| Al | 392.80 | 461.00 |
| Cu | 320.80 | 114.00 |
| $Mg^{2+}$ | 184.00 | ND |
| Mn | 163.49 | 98.10 |
| $Ca^{2+}$ | 83.40 | ND |
| Zn | 72.19 | 51.00 |
| $Cl^-$ | 36.8 | ND |
| $F^-$ | 10.90 | ND |
| $Na^+$ | 9.22 | ND |
| $K^+$ | 3.66 | ND |
| Ni | 1.90 | 11.00 |
| Cd | 1.00 | 7.76 |
| As | 0.88 | 42.70 |
| Pb | 0.31 | 2.50 |
| Cr | 0.20 | 1.54 |

ND: no determined.

to 6.7, and a variable EC, ranging from 421 to 2390 μS/cm (Figure 3a and 3b). This profile also showed high concentrations of Fe from 4.07 to 6.4 % w/w (Figure 3c), Cu from 149 to 1387 mg/kg (Figure 3d), Pb from 53 to 69 mg/kg (Figure 3e), As from 30 to 120 mg/kg (Figure 3f), and Zn from 108 to 425 mg/kg (Figure 3g).

Sample SB3 (affected) had a pH of 5.6, and the EC was 1257 μS/cm; moreover, they had high concentrations of Fe = 5.7 % w/w, Al = 8.5 % w/w, As = 58 mg/kg, Cu = 647 mg/kg Cr = 161 mg/kg, Pb = 85 mg/kg, and Zn = 343 mg/kg.

The minerals identified by X ray diffraction were plagioclase, quartz, potassium feldspar, and phyllosilicates (peaks at 10 Å and 14 Å), but the most important detected neoformed minerals were gypsum and traces of copiapite (Table 3).

Profile 8B (unaffected), located just 1.5 m from 8A, showed quite a different composition. The pH was more basic, ranging from 7.9 to 8.4, and the EC was much lower (54–107 μS/cm). The chemical composition included low contents of Fe from 3.6 to 4.8 % w/w, Pb from 37 to 55 mg/kg, Cu from 63 to 112 mg/kg, and As from 24 to 30 mg/kg. In contrast, this profile had a high concentrations of Ca from 16856 to 34424.7 mg/kg (Figure 3h).

The samples SB2 and RB1 (unaffected) were more basic with pH values of 8.8 and 9.1, respectively, and EC values of 49.4 and 50.9 μS/cm, respectively. SB2 had low concentrations of Fe = 4.4 % w/w, Al = 7.7 % w/w, Pb = 81 mg/kg, As = 34 mg/kg, Cu = 100 mg/kg, Cr = 81 mg/kg, and Zn = 180 mg/kg. Similarly, RB1 also contained low concentrations of Fe = 3.8 % w/w, Al = 7.7 % w/w, Pb = 51 mg/kg, As = 25 mg/kg, Cu = 118 mg/kg, Cr = 85 mg/kg, and Zn = 160 mg/kg.

The mineralogical analysis of both samples revealed similar minerals: intermediate plagioclase, quartz, potassium feldspar, phyllosilicates (≈10 Å, 14 Å), and the presence of calcite (Table 3).

The values of the major and trace elements from sample SB3 along with those published by the Servicio Geológico Mexicano (2007), which analyzed samples from 25 locations around the area, in order to determine whether SB3 had above background level values are presented in the Figure 1. The comparison of the results showed high concentrations of the major elements Al, Fe, K, Na and Mg (Figure 4a) and trace elements: As, Cu, Cr, Zn and Pb (Figure 4b).

**Microscopic characterization of soil materials**

The micromorphological study in the sample SB3 (affected soil) displayed a subangular blocky structure, with evidence of micro-laminations, which were mainly presented in the fine fraction (silt and clay). Carbonates were not identified, but a very fine material with reddish-brown coloration was found surrounding the pores and minerals (Figure 5a).

By SEM-EDS analysis was identified Fe (88 % w/w), S (7.1 %), Al (1.7 %), Ca (0.6 %), and other elements (2.1 %) (see Figures 5b and 5c). The minerals detected here included: titanomagnetite ($Fe^{2+}(Fe^{3+}Ti)_2O_4$) with Fe (84.2 %), Ti (10 %), Si, (2.1 %), Ni (1.4 %), Ca (O.1 %), and other elements (2.2 %); barite ($BaSO_4$) with Ba (50.5 %), Ti (23 %), S (13.2 %), Si (6.2 %), Al (1.8 %), Fe (2.6 %), Ca (0.9 %), and other elements (1.8 %); illite (($K, H_3O) Al_2(Si_3Al) O_{10}(H_2O, OH)_2$) with Fe (32.1 %), Si (35.4 %), Al (16.5 %), K (6.6 %), Mg (5.05 %), Mn (1.8 %), Ca (0.7 %) and other elements (1.4 %). It is important to note that the Ca concentration was relatively much lower that of the unaffected soil (SB3).

The micromorphological study showed samples with a subangular blocky structure with granular areas and displayed fragments of fine carbonates in SB2 (unaffected; Figure 5d), as well as root fragments in varying degrees of degradation. Small areas of microlamination were also observed. The minerals, such as plagioclase and quartz, were mainly rounded with the coatings of Fe oxy-hydroxides and clay.

SEM-EDS analysis indicated high concentrations (% w/w) of Ca (46 %), Si (24.7 %), Al (17.1 %), Fe (4.6 %) K (3.2 %), and other elements (4.2 %) in the matrix of the soil (see Figure 5e and 5f). Minerals with high concentrations of Ca (98.8 %) and low concentrations of Mg (0.026 %), Al (0.137 %), Si (0.032 %), (0.26 %), Cr (172 %), and Mn (0.540 %) were also identified.

**Geoavailability test**

Following agitation, the pH in samples RB1 and SB2 fell from 9.1 and 8.8, respectively, to 7.7; thus, maintaining their basic characters. The EC increased from 50.9 and 49.4 mS/cm to 79.1 and 68.3 mS/cm, respectively.

The elements occurring in concentrations above the natural background values in sample SB3 (Al, As, Cr, Pb, and Zn) had fallen below

Table 3. Chemical and XRD Results.

| Sample | HCl 10 % | pH | CE mS/cm | color | X Ray Diffraction |
|---|---|---|---|---|---|
| RB1 | positive | 9.1 | 50.9 | 7.5 YR 6/6 | Intermediate plagioclase, quartz, potassium feldspar, phyllosilicates (≈10 Å, 14 Å) and calcite. |
| SB2 | positive | 8.8 | 49.4 | 7.5 YR 6/3 | Intermediate plagioclase, quartz, potassium feldspar, phyllosilicates (≈10 Å, 14 Å) and calcite. |
| SB3 | negative | 5.6 | 1257.0 | 7.5 YR 6/6 | Intermediate plagioclase, quartz, potassium feldspar, phyllosilicates (≈10 Å, 14 Å), gypsum and copiapite. |
| SEDT1 | negative | 2.9 | 5911.0 | 7.5 YR 6/5 | Quartz, muscovite, labradorite, montmorillonite, alunite, anhydrite, jarosite, goethite, hematite and birnessite. |
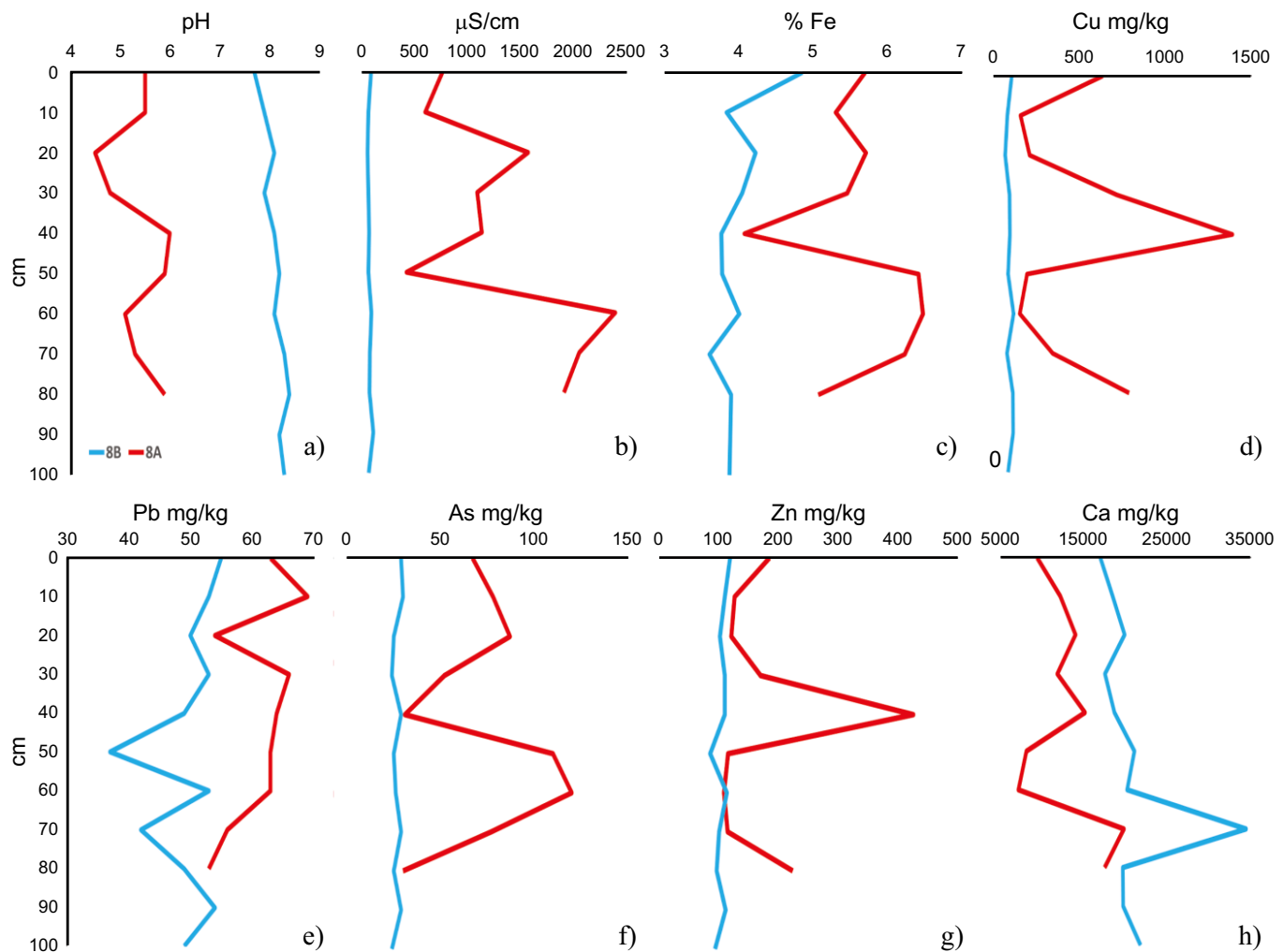
Figure 3. Chemical results of profiles 8A and 8B. Fe in % w/w.

the detection limit, suggesting stability to the solid phases. The Fe concentration was 0.009 mg/l, which was lower than that found in the RB1 and SB2 samples. Similarly, the Cu concentration of 0.007 mg/l was the same as in the sample SB2 but lower than in RB1. By contrast, the concentration of $SO_4^{2-}$ remained high in SB3 (6.34 mmol/L), compared to the other two samples 0.01 mmol/L (Table 4).

Finally, sample SEDT1 from the Tinaja 1 dam, showed the highest concentrations of Al (233.58 mg/L), Cd (0.318 mg/L), Fe (69.73 mg/L), Mn (40 mg/L), Ni (0.757 mg/L), and Zn (16.58 mg/L), indicating that all these elements had passed to the aqueous phase. In contrast, As, Cr and Pb were below the detection limit, and were thus not released to the aqueous phase during or after the test (see Table 4).

**Geochemical distribution of selected elements**

The distribution of the main elements associated with the acid solution from the spill in the geochemical fractions of soil and sediment samples is shown in Figure 6. The samples that were affected by the acid solution had a potentially high mobility of As (exchangeable, acid-soluble, oxidizable and easily and moderately reducible) in the range of 29.75–38.25 %; whereas, in the unaffected samples, the value was 16.34 % (Figure 6a). For the affected samples the potential mobility of Cu was in the range of 67.62–61.89 %, and was mainly associated with the moderately reducible, acid soluble and exchangeable fraction,

whereas in the unaffected samples, the mobilized fraction was only 22.21 % (Figure 6b).

For influenced samples, the potentially mobilized Fe was in the range of 23.22–38.25 %, while in the uninfluenced samples it was 15.89 %. The main differences occurred in the readily reducible fraction, which SB2 was 5.7 % less than in SB3, and in the presence of acid-soluble Fe of 0.61–4.03 % (Figure 6c).

For the affected samples, potentially high mobility of Mn was in the range of 36.73–71.69 %, while in the unaffected samples, it was 76.17 % (Figure 6e).

In the affected samples, potentially high mobility of Zn was in the range of 42.78–37.30 %, mainly associated with the moderately reducible, acid-soluble and exchangeable fraction, compared to 40.62 % in the unaffected samples (Figure 6f).

**DISCUSSION**

**Geochemical characterization of spilled acid solution**

The acid solution spilled in and around the Bacanuchi and Sonora Rivers showed similar concentrations of Fe and Al to those ABC Analytic report in 2014. In this solution, the sulfate anion was the most significant (5888.7 mg/L). The acid solution had a low pH of 2.3 a high
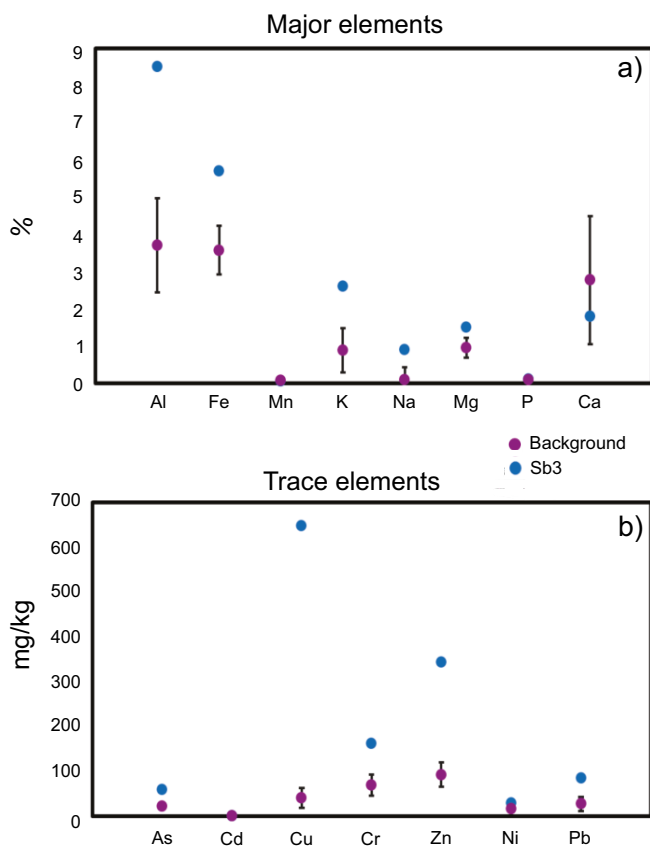
Figure 4. Average and standard deviation of the points of background values opposite impacted soil sample SB3. a) major elements (% w/w), b) trace elements.

EC values of 5910 μS/cm, similar to the composition of the AMD.

A change in the composition of the original acid solution, sampled 10 weeks after the event, was observed, including a decrease in the concentrations of Ni, Cd, As, Pb, and Cr. This can be attributed to the natural reactions of these elements producing precipitation, which was reported as the immobilization of Ni, Cd, As, and Pb in the presence of Fe and sulfate (jarosites, Fe oxides) by Zhixun *et al*. (1997), Lee and Sanders (2003) and Romero *et al*. (2010). We speculate that most of these reactions occur in the soils of the river basin affected by the spill and are manifested by the change of morphological, physical and chemical characteristics of profiles discussed below.

**Physicochemical differences between the properties in the of affected and unaffected soils**

The color is one of the most obvious differences between the affected and unaffected soils. Profile 8A, which was considered to be the most altered, exhibited orange colors in contrast to the light brown of the profile 8B (unaffected) profile; however, this difference is only qualitative, and should be viewed as only a preliminary criterion.

Profile 8A was acidic and had relatively very high EC with elevated concentrations of Fe, As, Cu, Pb and Zn and the micromorphology study indicated presence of fines precipitations of Fe coating minerals and infilling the pores. These fine precipitations are associated with concentrations of sulfur, according to the SEM study. On the contrary, the profile 8B had much lower concentrations of these mentioned elements and a lower electrical conductivity, while the pH was more basic.

Similar tendency of the downstream decrease of metal (Cu, Pb, Zn) concentrations was observed in the other contaminated semiarid catch-

ment area - Animas River valley (New Mexico), affected by the Gold King Mine spill (Rodriguez-Freire 2016). The authors also explained this phenomenon by co-precipitation of metals with the neo-formed iron oxides and jarosite, however they did not consider the possible role of soil components, especially carbonates, in this process. Similarly, another spill of acid mine drainage in the Zarza mine, Spain identified the decrease of toxic elements such as Fe, Cr, Pb and As along the Odiel river, suggesting processes of precipitation/co-precipitation and sorption by the sediments from the river (Olias *et al.,* 2019).

We assume that precipitation/co-precipitation processes responsible for decrease of dissolved forms of metal contaminants are to large extent provoked and controlled by the reaction between acid solution of the spill and carbonates present in the soils of the affected valley.

**Chemical reaction between pedogenic carbonates and acid solution**

Limestone ($CaCO_3$) is used as passive treatments for AMD and acid solutions, because it has a strong neutralizing effect, thereby promoting the precipitation of the PTEs (López *et al.*, 2002; Simate and Ndlovu, 2014). The limestone neutralizing effect has been proven in laboratory experiments via various methods. Offedu *et al.* (2015) neutralized synthetic acid leachates using limestone, demonstrating that the interaction between the limestone and the leachates promoted limestone dissolution, increased pH, the precipitated Fe and Al as oxyhydroxides, and the formed gypsum. Corrales and Romero (2013) precipitated Fe, Al, Si, As, and Cu from AMD from a silver mine in Taxco, Mexico. Their results also showed an increase in pH (from 2.6 to 7) and gypsum formation. In pedogenic carbonates, Rivera-Uria *et al.* (2018), demonstrated (using a column test) that the interaction of secondary carbonates and the acid solution promoted the precipitation of PTEs and the formation of secondary minerals, such as gypsum and jarosite.

The acid solution from the Buenavista del Cobre Mine was characterized by low pH, high EC, high sulfate, and high concentrations of PTEs. Thus providing an opportunity to show the effect of the carbonates on the precipitation of the PTEs in the natural environment. Profile 8A contained carbonates, as did profile 8B and sample RB1; however, contact with the acid solution caused changes in the soil. Interaction between the (basic) carbonates and the acid solution promoted the dissolution of the carbonates and increase in the pH of the solution, as represented in reaction (2). The micromorphology and XRD provided further evidence of the absence of carbonates (calcite) in sample SB3 (Table 3). On the other hand, the high concentrations of $SO_4^{-2}$ (from sulfuric acid) in the acid solution and the Ca liberated from calcite, promote the precipitation of gypsum, which was identified by XRD.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2 \qquad (2)$$
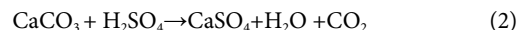
Copiapite was another mineral identified by XRD; however, it was only found in low concentrations. The copiapite group contains hydrated double sulfate of trivalent metals (Fe, Al) and divalent metals (Mg, Fe, Zn) and can precipitate by the hydrolysis of the $Fe^{3+}$. Chemically it is represented as $AFe^{3+}(SO_4)_6(OH)_2 \cdot 20H_2O$, where A = $Mg^{2+}$, $Cu^{2+}$, $Al^{3+}$ or $Fe^{3+}$ (Rull *et al.*, 2014).

On the other hand, during the carbonate dissolution (reaction 2) the immediate chemical effect was an increase in pH of the solution and the precipitation of metals. The strong link between metal solubility and the pH of the medium is well known, especially in oxidizing environments (Tack *et al.*, 1996). Kalin *et al.* (2006) document that Fe and Al precipitate at pH > 3, and Cu at pH > 5. The pH also promotes the adsorption and co-precipitation of As, Cr, Pb, and Zn (Cravotta and Kay, 1999). Sample SB3 displayed elevated concentrations of Al, Fe, As, Cu, Cr, Pb, and Zn that were related to the change in pH and subsequent precipitation.
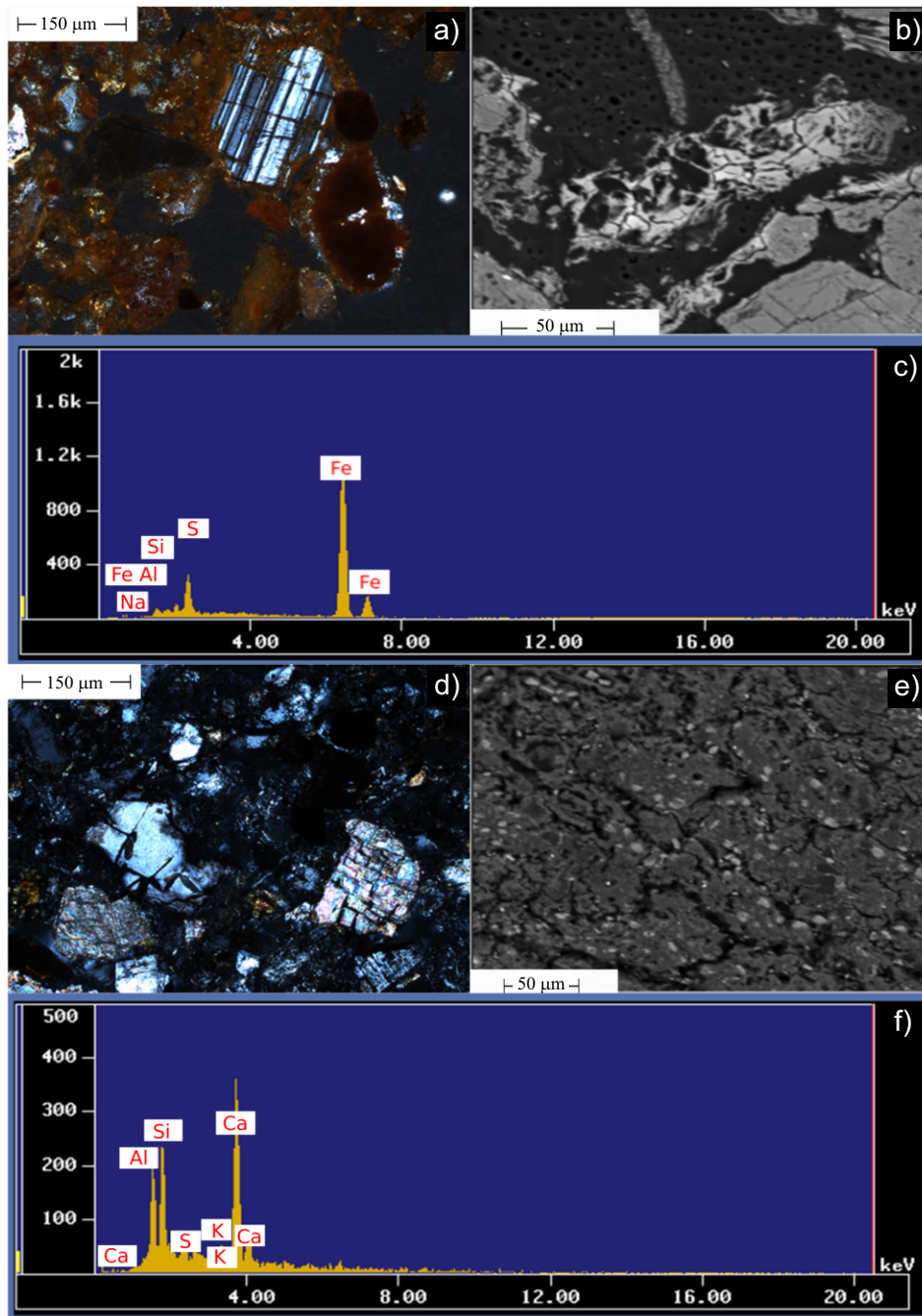
Figure 5. a) SB3, plagioclase coated with fines precipitations rich in Fe related to the acidic solution, photograph. b) SB3, fine precipitation in pore, SEM-EDS image of a fine precipitation in a pore. c) SB3, identifying the elements Fe, S, Al, Si with SEM-EDS. d) SB2, soil matrix rich in carbonates. e) SB2, fine matrix rich in calcium, SEM-EDS image. f) SB2, identifying the elements Ca, with SEM-EDS.

**Retention of contaminants in soils: limitations and possibilities of future mobilization**

The test of geoavailability confirmed that all the elements with above background values were stable and not released to the environment (Table 4). This confirms the results obtained by Gutierrez-Ruiz and Romero (2015), which showed that the concentrations of toxic elements were below the maximum allowable limits for drinking water (NOM-127) in the waters of the Bacanuchi River. The elements became stable under oxidizing chemical conditions and the pH buffering capacity, conditioned by the presence of carbonates in the soils and sediments close to the river. A change in the chemical conditions, however – perhaps from an influx of reducing agents or a change in environmental pH due to a new spill – would result in a future release of PTEs.

A similar case occurred in 1998 in the Aznalcóllar mine in Spain. The mine spilled 450000 m³ of mud and acid waters. Soils that were impacted contained carbonates. When the sludge had contact with the soil, it was observed that the penetration of the mud was very limited by the presence of the carbonates. The interaction caused the

Table 4. Results of Geo-availability.

| | SEDT1 (mg/L) | RSD % | RB1 (mg/L) | RSD % | SB2 (mg/L) | RSD % | SB3 (mg/L) | RSD % | Detection limit (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| As | <DL | ND | <DL | ND | <DL | ND | <DL | ND | 0.026 |
| Al | 233.58 | 2.0 | 0.191 | 6.0 | 0.217 | 3.8 | <DL | ND | 0.004 |
| Ba | 0.003 | 0.4 | 0.033 | 8.5 | 0.033 | 2.0 | 0.034 | 2.5 | 0.002 |
| Cd | 0.318 | 3.4 | <DL | ND | <DL | ND | <DL | ND | 0.003 |
| Cr | <DL | ND | <DL | ND | <DL | ND | <DL | ND | 0.002 |
| Cu | 0.002 | 0.4 | 0.010 | 2.6 | 0.007 | 6.4 | 0.007 | 8.5 | 0.002 |
| Fe | 69.732 | 2.5 | 0.105 | 2.0 | 0.109 | 3.4 | 0.009 | 33.5 | 0.002 |
| Mn | 40.007 | 0.9 | 0.013 | 1.2 | 0.014 | 1.8 | 0.078 | 2.7 | 0.002 |
| Ni | 0.757 | 2.9 | <DL | ND | <DL | ND | <DL | ND | 0.002 |
| Pb | <DL | ND | <DL | ND | <DL | ND | <DL | ND | 0.007 |
| Zn | 16.58 | 2.5 | 0.015 | 8.9 | 0.006 | 8.9 | <DL | ND | 0.003 |
| *Sulphate* | | | | | | | | | |
| $SO_4^{2-}$ mmol/l | 2156.4 | 8.0 | 0.01 | 5.3 | 0.01 | 5.0 | 6.34 | 7.0 | 0.009 |

<LD: below of limit detection; ND: no determined.

carbonates to neutralize the acidity and the rapid precipitation of Fe, Ca and sulfate forming the gypsum (Dorronsoro *et al.*, 2002). However, over the years (12 years of study) it was shown that sludge exposed to environmental conditions began to oxidize again and generate acid drainage interacting with carbonates. The resource of soil carbonates was finally exhausted and re-dissolution of many elements such as Ca, Cu, and Zn took place, releasing them towards the liquid phases (Madejon *et al.*, 2018).

As mentioned above, in 2015 the spill of a DAM occurred in the Animas River (US). The river was hit by high concentrations of PTEs such as Fe, Zn, Cu and Pb and low pH water. Downstream the concentrations of these elements were low, that was attributed to the association with metal-bearing jarosite and oxy-hydroxides of Fe. However, the authors suppose that the stability of jarosite can be affected and precipitated metals can be solubilized if biogeochemical changes occur and released the PTEs (Rodriguez-Ferire *et al.,* 2016).

In the sequential extraction, the identification and quantification of metals in the geochemical fraction of the soils were determined using reagents with increasing aggressiveness – a common approach for distinguishing species of trace elements according to their physicochemical mobility and potential bioavailability (Violante *et al.*, 2010). In this study, it was found that, in samples affected by the acid solution (SEDT1, SB3), the mobility of As increased in the moderately reducible and oxidized fraction (35.15 and 3.10 %, respectively) compared to the unaffected samples.

The Cu mobility increased from 22.21 % in unaffected samples (SB2) to 61.86 % in the affected sample (SB3), with a significant contribution in the exchangeable, acid-soluble and oxidized fraction, which can be attributed to the retention of Cu from the acid solution by $CaCO_3$ that occurred through the precipitation of hydroxide or hydroxycarbonate and organic matter (Rodriguez-Rubio *et al.*, 2003; Singh, 1971).

The mobile concentration of Fe grew from 15.89 % in the unaffected samples to 23.22 % in the affected samples, mainly in the easily and moderately reducible fraction, which can be attributed to the formation of the poorly-crystalline Fe oxy-hydroxides that coated the soil particles, and can be identified by micromorphology and SEM-EDS. There is no evidence that the mobility of Pb, Mn, or Zn can be affected by interaction with the acid solution in the soils surrounding the Bacanuchi River.

## CONCLUSIONS

The accidental discharge of the acid solution in the fall of 2014 led to leachate flowing into the Bacanuchi River. The soils in the area show evidence that they were able to cushion the impact, mainly via the interaction of minerals such as calcite with the acid solution, resulting in pH changes and the precipitation of the dissolved elements, forming new mineral products. As far as carbonates (both inherited from geological materials and neoformed/pedogenic) are common in the soils and surface sediments formed under conditions of water deficit, we conclude that the effect of mine spill neutralization and metal retention in the soil mantle should be expected in the arid and semiarid regions worldwide.

The results of sequential extraction provided evidence that the As, Cu, and Fe from the acid solution were incorporated into the soil in the geochemical fraction. This incorporation was stable, and leading to the formation of minerals with low solubility, as shown in the geoavailability test. These results confirm that all PTE were precipitated as very stable phases.

These phases were stabilized under the actual prevailing oxidizing environmental conditions; however, their stability could be at risk if the environmental conditions were to change as the result of a new spill that promoted changes in pH or water saturation over longer intervals, generating reduced soil environment (change Eh and pH). As a consequence, metallic contaminants trapped earlier by the soil material could be released.

The phenomenon of neutralization and metal retention from the spills by soils is supposed to have high spatial variability both in vertical (soil profile) and lateral (soil toposequences) direction. To document the latter denser sampling of the same soil horizons in the horizontal direction is needed. The first studies of that kind in the Cananea area are already in process (Romero-Lazaro *et al.*, 2019).

## ACKNOWLEDGEMENTS

## a) As distribution in geochemical fraction

## b) Cu distribution in geochemical fraction

## c) Fe distribution in geochemical fraction

## d) Pb distribution in geochemical fraction

## e) Mn distribution in geochemical fraction
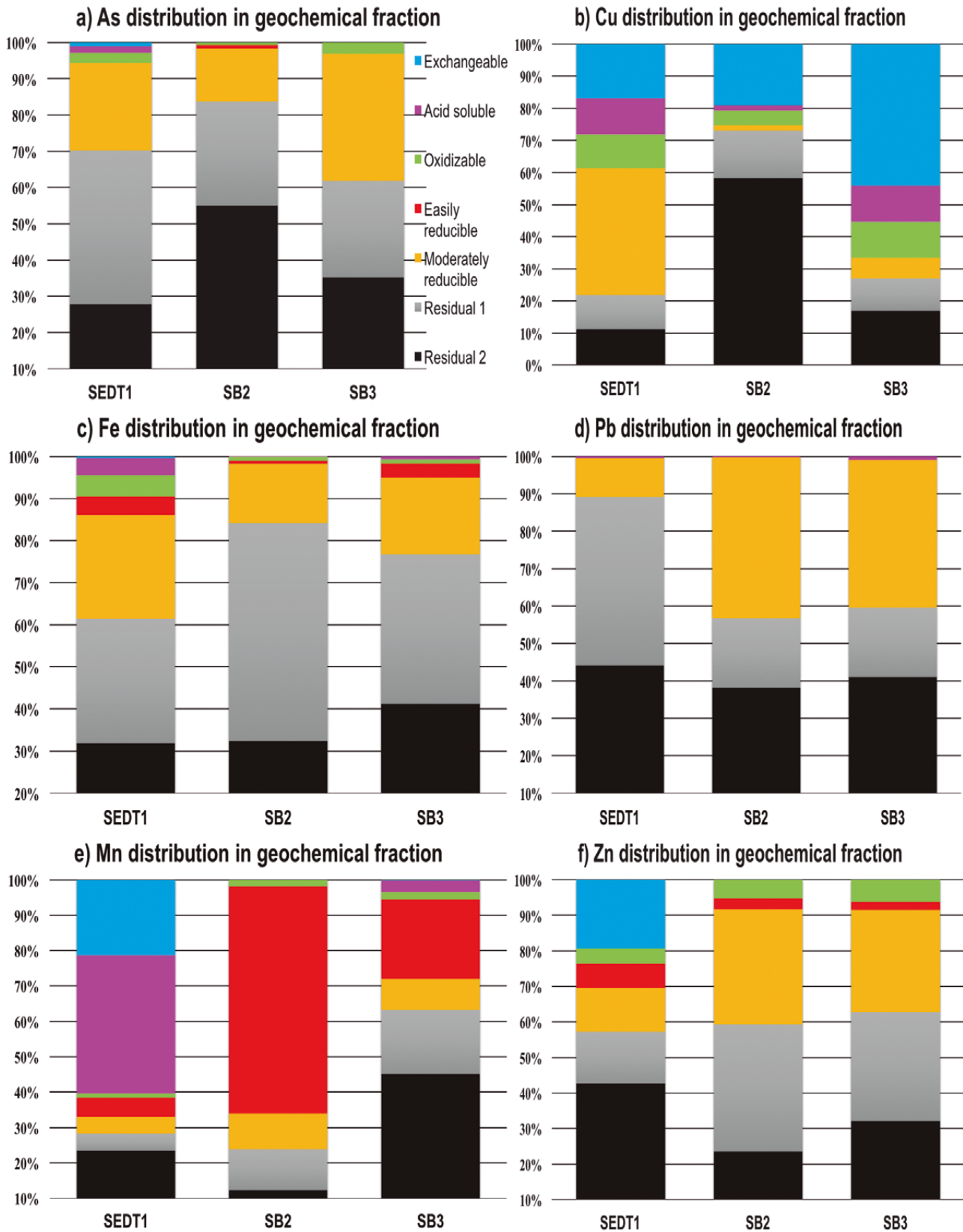
## f) Zn distribution in geochemical fraction

Figure 6. Distribution of main elements in geochemical fraction of samples impacted (SB3 and SEDT1) and non-impacted (SB2).

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