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MERCURY POLLUTION ASSESSMENT OF MINING WASTES AND SOILS FROM FORMER SILVER AMALGAMATION AREA IN NORTH-CENTRAL MEXICO

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Key words: patio process, tailings, reprocessing, solubility, bioaccessibility

ABSTRACT

Mining wastes and soils from Cedral, San Luis Potosí, Mexico, were studied to assess mercury (Hg) pollution in areas of historical silver (Ag) amalgamation and in areas where amalgamation mining wastes were recently reprocessed for Hg and Ag recovery. The total, soluble and bioaccessible Hg concentrations from eight mining waste and nine soil cores were determined at varying depths, which fluctuated from the surface up to 1.0 m depth. The total Hg concentrations in the mining wastes samples ranged from 8 to 548 mg/kg. The total Hg concentrations in the soil samples were lower (1 to 116 mg/kg) than those in the mining wastes. Eighty percent of the soil samples exceeded the maximum permissible limit for residential soils according to the Mexican regulations, demonstrating the impacts of the amalgamation process in Cedral. The soluble Hg concentrations were low, from 0.009 to 0.32 mg/kg in the mining wastes, and from 0.003 to 0.02 mg/kg in soils. The latter represents 0.007 % to 0.54 % and < 0.03 % of total Hg, from mining wastes and soils, respectively, indicating low aqueous Hg transport during rainfall events. The bioaccessible Hg concentrations in the mining waste samples (0.1 to 60 mg/kg) and soil samples (0.1 to 17 mg/kg), suggested that humans could be exposed to this toxic element through the accidental ingestion of mining wastes and soil particles. Although the total Hg concentrations in the mining wastes decreased after reprocessing, the soluble and bioaccessible Hg concentrations increased.

Palabras clave: beneficio de patio, jales, reprocesamiento, solubilidad, bioaccesibilidad

RESUMEN

Se estudiaron residuos mineros y suelos de Cedral, San Luis Potosí, México, para evaluar la contaminación por mercurio (Hg) en áreas de amalgamación histórica de plata (Ag) y de reprocesamiento reciente de residuos de amalgamación para la recuperación de Hg y Ag. Se obtuvieron ocho perfiles de hasta 1 m de profundidad de depósitos de residuos mineros y nueve de suelo, de los cuales se recolectaron muestras a diferentes profundidades para la determinación de concentraciones totales, solubles y bioaccesibles de Hg. Las concentraciones totales de Hg en residuos mineros variaron entre 8 y 548 mg/kg, mientras que en suelos las concentraciones se presentaron en un rango de entre 1 y 116 mg/kg. Se encontró que el 80 % de las muestras de suelo analizadas superaron el límite máximo permisible de Hg para suelo de uso residencial establecido en la normatividad mexicana, lo que demuestra el severo impacto de la amalgamación y del reprocesamiento de jales de amalgamación en Cedral. Con relación a las concentraciones solubles de Hg, en las muestras de residuos se obtuvieron de 0.009 a 0.32 mg/kg y de 0.003 a 0.02 mg/kg para suelos, lo que representa de 0.007 % a 0.54 % y < 0.03 % del total de Hg contenido en residuos mineros y suelos, respectivamente. Esto indica un bajo potencial de transporte de especies solubles de Hg durante eventos de lluvia. Finalmente, las concentraciones de Hg bioaccesible obtenidas en el estudio (0.1 a 60 mg/kg en residuos, 0.1 a 17 mg/kg en suelos), sugieren una exposición de la población humana a este elemento tóxico a través de la ingestión accidental de partículas de residuos mineros y de suelo. Además, quedó evidenciado que el reprocesamiento de residuos de amalgamación disminuyó las concentraciones totales de Hg, pero incrementó las concentraciones solubles y bioaccesibles de Hg.

INTRODUCTION

Mercury (Hg) occurs naturally in the Earth's crust and soils, with average concentrations typically not exceeding 0.07 mg/kg and 1.1 mg/kg, respectively (Kabata-Pendias 2011). However, human activities, including the production of Hg by mining or recycling activities, the use and production of products containing Hg, fossil fuel combustion, and the uncontrolled disposal of Hg-containing mining wastes, have increased environmental Hg concentrations sufficiently to result in its classification as a priority global contaminant. Hg is toxic and exhibits exceptional environmental behaviors, including transportation in the atmosphere and its transformation to highly bioavailable chemical forms that bioaccumulate once they enter the food chain (Ebinghaus 1999).

Hg has been used since ancient times. The first use of Hg in a large-scale industrial process consisted of recovering gold (Au) and silver (Ag) from low-grade ores by amalgamation with elemental Hg (Hylander and Meili 2003). The historical importance of the amalgamation process on the world's demand for Hg is clear because approximately one-fifth of the total recorded Hg production of 943 172 t before 2012 occurred between 1550 and 1900 (Hylander and Meili 2003, CEC 2013). Ag mines consumed most of the Hg produced between 1550 and 1900 (~196 000 t) in colonial Spanish America (CEC 2013). Therefore, the colonial amalgamation process not only encouraged Hg production and world trade but also contributed to a global increase in environmental Hg concentrations. Historically, the amalgamation process resulted in Hg emissions of between 87 750 t and 126 000 t to the atmosphere (Nriagu 1994, Camargo 2002). Additionally, a significant fraction of the Hg used in amalgamation in colonial Spanish America (5 % to 20 %) was accidentally or deliberately released into soils and water, and was primarily incorporated into mining wastes that were abandoned at the mining sites. Historical amalgamation is also likely responsible for the increased local environmental Hg concentrations at sites where it was practiced (Camargo 2002).

The fate of Hg in amalgamation mining wastes at most of the historical Ag mining sites from colonial America remains unknown. In the case of Mexico, it was recently estimated that 73 473 t of residual Hg could be contained in the amalgamation tailings produced from 1556 to 1900 (CEC 2013). Moreover, from 1890 to present, leaching methods without control measures for correctly managing reprocessed tailings were applied to reprocess amalgamation mining wastes and polluted soils to recover Au, Ag and Hg at some historical mining sites in Zacatecas, Guanajuato and San Luis Potosí (Ogura et al. 2003, Ramos-Arroyo et al. 2004, CEC 2013). Therefore, sites where metal amalgamation and the reprocessing of amalgamation tailings were practiced, must be considered as potentially contaminated with Hg.

Although Hg pollution persists at historical amalgamation sites, elevated Hg concentrations occur in "hot spots", and the soluble and bioavailable fractions of Hg at these sites are generally low (< 0.1 %). The latter because the predominant chemical species associated with the residual fraction are most likely elemental Hg and HgS (Lacerda 1997, Johnson and Whittle 1999, Lang 1999). However, elemental Hg is subjected to chemical transformations, such as oxidation, dissolution, amalgamation, precipitation and adsorption, which affect its chemical speciation during the amalgamation process (Slowey et al. 2005) and its transformations due to chemical weathering or biological activity (Navarro 2008). Moreover, the chemical transformations of Hg that occur when amalgamation mining wastes are reprocessed remain unknown. However, reprocessing these wastes could result in the chemical transformation of Hg to more soluble and bioavailable species, which would increase environmental and human health risks. This situation might be the case in Cedral in the state of San Luis Potosí, Mexico, where uncontrolled historical amalgamation tailings were reprocessed and abandoned in the vicinity of urban areas.

Therefore, the aim of this study was to assess the grade of Hg pollution of non-reprocessed and reprocessed mining wastes, and of soils within and outside of the former Ag amalgamation facilities in Cedral, San Luis Potosí, Mexico. The assessment of Hg pollution at this site includes the determination of total, soluble and bioaccessible Hg concentrations by using methods that have been developed for the extraction of contaminants from solid mining wastes and soils to predict potential effects on health and environmental impact. The solubility test used in this study was developed to assess the leaching potential of contaminants from solid mining wastes or soils in contact with simulated meteoric water (ASTM 2004), whereas bioaccessibility infers the fraction of a contaminant dissolved from soils or mining wastes under acidic gastric conditions and could be available for absorption through the gastrointestinal tract (Zagury et al. 2009). Solubility and bioaccessibility of Hg in mining wastes and soils are mainly controlled by the chemical species (Bloom et al. 2003, Zagury et al. 2009). Thus, the soluble and bioaccessible Hg concentrations, together with the total Hg concentration, would provide useful complementary information about the chemical speciation of Hg in mining wastes and soils of Cedral, reported previously by selective extraction methods (Morton-Bermea et al. 2015).

MATERIALS AND METHODS

Study site

The study site was located in the city of Cedral in northern San Luis Potosí, Central Mexico, at approximately 23º49´ N, 100º43´ W (**Fig. 1**). In 2010, the city of Cedral had 11 468 inhabitants (INEGI 2010). The climate is dry-temperate, with an annual average of temperature, precipitation and evaporation of 10.6 ºC, 405.1 mm and 2090 mm, respectively (SMN 2015). The regional geology consist of continental and marine sedimentary rocks that vary in age from the Middle Jurassic to the Upper Cretaceous, which belong to the Mesozoic Basin of Central Mexico. These geological units are covered indistinctly by continental sediments of the Cenozoic age represented by lacustrine deposits of Paleogene age, polymictic conglomerate of Neogene age, and silt-gravel and alluvium of the Quaternary. The igneous geological units are restricted to small basalt outcrops of Miocene age (SGM 2013). The regional soils are derived from sedimentary rocks, and the soils in the urban area of Cedral are predominantly classified as Gypsic Xerosols with overlapping calcrete hardpan or caliche layers of varying depths (INEGI 2009).

During the late 18th century, at least seven metallurgical facilities were installed in the urban area of Cedral to recover Ag from ores that were mined in the Real de Catorce mining area, 25 km southwest of Cedral. According to historical maps of the study area (Aguirre 1878), the former metallurgical facilities, called "haciendas de beneficio", were located at the southwest margin of the urban area of Cedral (**Fig. 1**). At these facilities, the amalgamation method known as "beneficio de patio" was used, which consisted of the following five sequential operations (Bargalló 1969): 1) the ore was crushed using stone mills, 2) the pulverized ore was spread on a large stone pavement court and common salt (NaCl) and magistral (roasted copper and iron sulfides) were added, 3) elemental Hg was thoroughly mixed with the pulverized ore before allowing the amalgamation reaction to occur for three weeks to five months, depending on the room temperature, 4) the Ag-Hg amalgam (pella) was recovered by adding elemental Hg to increase the fluidity before separating the low-density materials using a stream of water (in this step, major mining wastes and amalgamation tailings were produced and commonly dumped in surrounding areas), and 5) Hg was separated from the pella by heating in a retort to recover metallic Ag and some of the Hg by condensation. The total amount of Hg used in the amalgamation facilities installed in Cedral, remains unknown but it is estimated that, between 1773 and 1827, 5 000 t of Hg were approximately consumed in the Real de Catorce mining region, which includes Cedral (Ávalos-Lozano et al. 2007).

In 1905, only one "hacienda de beneficio" was operating in Cedral (Hornelas 1905). Soon after,

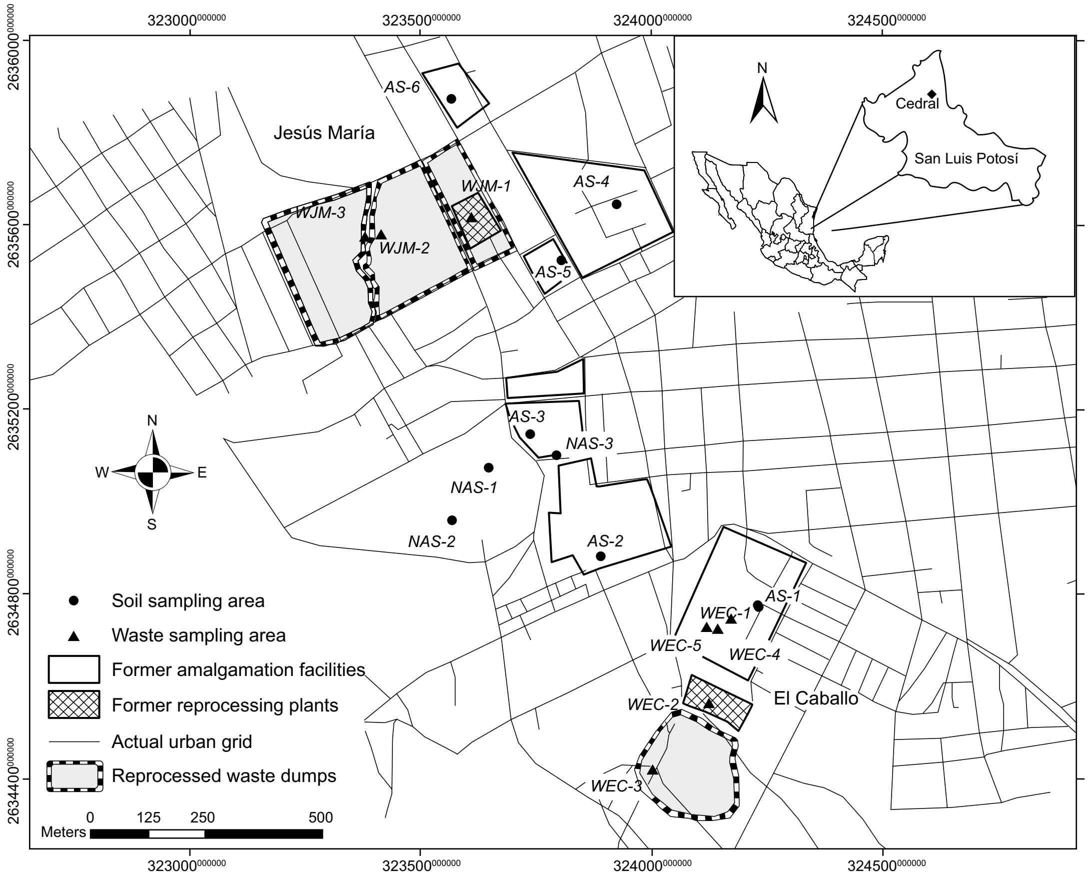

Fig. 1. Location of Cedral, San Luis Potosí, Mexico, and descriptive map of the mining waste sample areas at El Caballo (WEC) and Jesús María (WJM) reprocessing plants, and sample areas of indirectly affected soils (NAS) and directly affected soil (AS) at former amalgamation facilities

the production of Ag by amalgamation was stopped completely. Subsequently, the land occupied by the amalgamation facilities was gradually converted into recreational and residential land.

The amalgamation mining wastes (tailings) were reprocessed to recover Ag and Hg at two leaching plants that operated from 1920 to 1980 (**Fig. 1**). Static lixiviation with calcium thiosulfate (CaS_2O_3) was the method used to recover Ag and Hg. Considering the characteristics of the investigated facilities, the same process was most likely used at similar reprocessing plants that operated in Zacatecas, Mexico. In this process, elemental sulfur is burned in a conventional furnace and the exhaust gases are bubbled into a suspension of elemental sulfur and $Ca(OH)_2$ in water with vigorous stirring to produce a CaS_2O_3 solution. Next, the amalgamation tailings are dumped into leaching ponds where the tailings are lixiviated with the CaS_2O_3 solution. The Ag-Hg-rich solution is pumped to a tank for precipitation using copper scrap. Finally, the precipitate is heated in a retort to recover the metallic Ag and Hg (Ogura et al. 2003, CEC 2013).

The reprocessed amalgamation tailings were dumped near the facilities, which were abandoned after the closure of the reprocessing plants in Cedral. Therefore, within the urban area of Cedral, two primary reprocessed tailing dumpsites exist: El Caballo and Jesús María (**Fig. 1**).

Sampling and sample preparation

Seventeen sample areas were selected based on the locations of former amalgamation facilities according to historical maps from Cedral (Aguirre 1878, Hornelas 1905) and on the locations of abandoned leaching plants and reprocessed mining wastes dumps. Eight areas were selected for soils sampling (**Table I**), including three near former amalgamation facilities to represent soils that were affected indirectly by the amalgamation

TABLE I. DESCRIPTION OF SELECTED AREAS FOR INDIRECTLY AFFECTED SOIL (NAS) AND DIRECTLY AFFECTED SOIL (AS) SAMPLINGS

Sample area	Description
NAS-1	Indirectly affected soil outside former amalgamation facilities
NAS-2	Indirectly affected soil outside former amalgamation facilities
NAS-3	Indirectly affected soil outside former amalgamation facilities
AS-1	Directly affected soil within a former amalgamation facility
AS-2	Directly affected soil within a former amalgamation facility
AS-3	Directly affected soil within a former amalgamation facility
AS-4	Directly affected soil within a former amalgamation facility
AS-5	Directly affected soil within a former amalgamation facility

process (NAS-1 to NAS-3), and six inside former amalgamation facilities to represent soils that were affected directly by amalgamation (AS-1 to AS-6). In addition, five areas were selected at the mining wastes dumps at El Caballo (WEC-1 to WEC-5), and three at the Jesús María (WJM-1 to WJM-3) reprocessing site (**Table II**). Additionally, one area with low anthropogenic influence was used as a reference site. In **figure 1**, the locations of the sample areas are shown, except the reference sample area, which was located approximately 1.5 km southeast from the El Caballo site.

In each sample area, three soils or mining waste cores were obtained using a Pürckhauer sampler within a 1 m^2 area. The depths of the soils and mining waste cores fluctuated from the surface to 1.0 m, and each core was divided into sections measuring approximately 10 cm or more depending on the color and the texture of the material. Thus, 48 soils and 60 mining wastes samples were obtained, and each sample consisted of a composite of three sections from the same depth of three different soils or mining waste cores. The samples were stored and transported in sealed plastic bags before air-drying at room temperature and passing through a stainless steel ASTM No. 10 (< 2 mm) mesh sieve.

Four additional cores were collected at WEC-1, WEC-2, WEC-3 and AS-2 and they were not sectioned. These cores were used for bulk characterization of the mining wastes and soils, and are identified in the text as WEC-1B, WEC-2B, WEC-3B and AS-2B.

Mining wastes and soils characterization

In samples WEC-1B, WEC-2B, WEC-3B and AS-2B, the pH and the electrical conductivity (EC) were analyzed potentiometrically using an YSI Pro Plus multi-parameter in waste or soil suspension, prepared by mixing thoroughly solid samples with deionized water (1:1 ratio) for 10 min and let stand for 30 min. The organic matter (OM) content was determined by dichromate oxidation by the Walkley-Black method (Pansu and Gautheyrou 2006). In addition, the principal mineral phases were identified using X-ray diffraction analysis in a Rigaku D/ max 220 diffractometer (λ= 1.5406 κα Cu).

Analysis of total Hg in mining waste and soil samples

To determine the total Hg concentrations, the EPA method 3051A (USEPA 2007a) was used for the microwave-assisted acid digestion of 0.5 g of the soil or mining waste samples and was modified by using 20 mL of HNO_3 25 % - HCl 10 % as an extraction solution. Acid digestion was conducted in an MDS-2000 CEM microwave.

After sample digestion, total Hg concentrations were determined by atomic absorption spectrometry

TABLE II. DESCRIPTION OF SELECTED AREAS FOR MINING WASTES SAMPLING AT EL CABALLO (WEC) AND JESUS MARIA (WJM) REPROCESSING PLANTS

Sample area	Reprocessing plant	Description
WEC-1	El Caballo	Non-reprocessed tailings
WEC-2	El Caballo	Reprocessed tailings from a leaching pond
WEC-3	El Caballo	Reprocessed tailings from waste dump top
WEC-4	El Caballo	Non-reprocessed tailings
WEC-5	El Caballo	Non-reprocessed tailings
WJM-1	Jesús María	Reprocessed tailings from a leaching pond
WJM-2	Jesús María	Reprocessed tailings from waste dump top
WJM-3	Jesús María	Reprocessed tailings from waste dump toe

with the cold-vapor method (CV-AAS) in an Analyst 100 Perkin-Elmer spectrophotometer at 253.7 nm. The reductant solution used was $NaBH_4$ 0.2 % - NaOH 0.05 % through a flow-injected FIAS 100 Perkin-Elmer system. Before analysis, a drop of $KMnO_4$ 5 % solution was added to the extract aliquot to maintain an oxidizing medium.

The detection limit for Hg in the liquid phase was 0.2 µg/L, and with the 1:40 solid to solution ratio used in the acid digestion of solid samples, the lowest detectable total concentration of Hg in the soils and mining waste samples was 0.008 mg/kg. For quality assurance, blanks of a standard reference material (SRM) (2710a "Montana Soil" obtained from the National Institute of Science and Technology, USA) and duplicates were analyzed for all samples. The recovery of Hg based on the analysis of ten SRM samples ranged from 87 % to 103 %.

Determination of soluble Hg in mining waste and soil samples

To assess the Hg solubility, five soils and eight mining waste sample areas, accounting for a total of 78 samples, were selected depending on the changes in their total Hg concentrations with depth. Because of the available sample quantities, it was sometimes necessary to pool contiguous samples.

The soluble Hg obtained from the selected soils and mining waste samples was determined using the D-3987-85 method from ASTM (2004), which was consistent with the official Mexican guidelines for the characterization of metal-contaminated soils and mining wastes (SEMARNAT 2004, 2009). The procedure used to determine soluble Hg employed deionized water that was adjusted to pH 5.5 ± 0.1 by CO_2 addition to simulate the leachability of the solids in contact with meteoric water (ASTM 2004). Two grams of each solid sample (soils or mining wastes) were extracted in a 40 mL of solution for 18 ± 0.25 h in 50 mL high-density polyethylene (HDPE) vials at room temperature using a rotatory agitator at 30 rpm. After extraction, the samples were centrifuged for 20 min at 3000 rpm and the supernatant solutions were vacuum-filtered through disposable 0.45-µm nitrocellulose filters. The filtrated leachates were preserved by adding two drops of HNO_3 25 % solution and were stored at 4 ºC until the Hg analysis with CV-AAS was performed. Considering the 1:20 solid-to-solution ratio established in the extraction procedure for soluble Hg determinations and the detection limit of the Hg analysis method (0.2 µg/L), the lowest soluble Hg concentration that could be reliably detected in the soils and mining waste samples was 0.004 mg/kg.

Determination of bioaccessible Hg in mining waste and soil samples

The same soils and mining waste samples that were selected for the solubility assessment were used to evaluate Hg bioaccessibility. The bioaccessibility of Hg was determined using an in vitro method that was established to measure the fraction of a chemical solubilized from a solid sample under the simulated acidic conditions of the mammalian gastrointestinal tract (Kelley et al. 2002).

For the bioaccessibility assessment, 1.0 ± 0.05 g of the mining wastes or soils sample was extracted in 100 mL of a simulated stomach acid solution, which consisted of a 0.4 M glycine solution at 37 ºC that was adjusted to pH 1.5 ± 0.05 using HCl. The samples were mixed at 30 rpm in a rotatory agitator for 1 h in 125 mL HDPE bottles at 37 ± 2 ºC. After extraction, the samples were centrifuged for 20 min at 3000 rpm, and the supernatant solutions were vacuum-filtered through disposable 0.45-µm nitrocellulose filters. The filtrates were preserved by adding two drops of a HNO_3 25 % solution and were stored at 4 ºC until Hg analysis by CV-AAS. For quality control, 10 SRM (2711 "Montana Soil") samples were analyzed. The concentration of lead (Pb) extracted from the SRM ranged from 8.7 to 10.3 mg/L, which confirmed the accurate performance of the extraction method (USEPA 2007b). Based on the 1:100 solid to solution ratio used in the extraction procedure and the detection limit of the Hg analysis method (0.2 µg/L), the lowest bioaccessible Hg concentration that could be reliably detected in soils or mining waste samples was 0.02 mg/kg.

Data analysis

Statistical analyses were performed using SigmaPlot (v11.0, Systat Software Inc.). One-way ANOVA (with a 95 % confidence interval) was used to determine whether the total, soluble or bioaccessible concentrations of Hg in the soils and mining waste samples differed with depth. For statistical analysis, the resulting data were grouped based on the three following depths: 0-30 cm, 30-60 cm and 60-100 cm.

RESULTS AND DISCUSSION

Mining waste and soil characterization

The results from the bulk characterization of the mining waste and soil cores are summarized in **table III**. No differences were observed in the pH values between the mining waste and the soil samples. In addition, reprocessing the amalgamation mining

TABLE III. BULK CHARACTERIZATION OF SAMPLES FROM EL CABALLO WASTES (WEC) AND DIRECTLY AFFECTED SOIL SAMPLES (AS)

Sample	Description	pH	Electrical conductivity (μS/cm)	Organic matter (%)	Major (+++), middle (++) and minor(+) mineral phases		
					SiO_2	$CaCO_3$	$CaSO_4$•$2H_2O$
WEC-1B	Non-processed waste	7.9	1381	3.6	+++	+	++
WEC-2B	Reprocessed waste from leaching pond	8.2	3113	0.4	+++	++	+
WEC-3B	Reprocessed waste	7.8	4968	3.0	+++	++	+
AS-2B	Directly affected soil	7.6	2609	6.9	+	++	+++

wastes increased the EC of the mining waste samples. The relatively high EC value in AS-2B could be associated with the predominating soil type in Cedral, which corresponds to gypsic soils with more than 15 % saturated sodium within a depth of 125 cm (INEGI 1972). Thus, it is very likely that the EC in other soil samples is also relatively high. The mining waste samples had relatively high organic matter contents, particularly samples WEC-1B and WEC-3B, due to the presence of vegetation patches in the sampling areas. However, the organic matter contents in the mining waste samples were lower than that found in soil sample AS-2B.

The main components of the amalgamation mining waste sample (WEC-1B) that were observed by X-ray diffraction analyses were quartz (SiO_2), gypsum ($CaSO_4$•$2H_2O$) and calcite ($CaCO_3$) (in decreasing order of abundance). When analyzing the reprocessed mining wastes sampled at the leaching pond (WEC-2B) and at the reprocessed mining waste dump (WEC-3B), the same main minerals were identified, but calcite was more abundant than gypsum. These results agree with the mineralogical composition of the Au-Ag ore amalgamated in Cedral, where quartz and calcite represented the main gangue minerals for the deposits mined in Real de Catorce (CRM 1992). The relative abundance of gypsum in WEC-1B indicates that this sample consisted of a mixture of un-reprocessed mining wastes and soils because gypsum is mainly associated with the natural composition of the gypsic soils at the site, as shown by sample AS-2B.

Total Hg concentrations in the mining wastes and soils

The concentrations of Hg in the mining waste samples from the study area ranged from 8 to 548 mg/kg. These concentrations were similar to those from studies conducted worldwide, with residual Hg concentrations in the historical amalgamation tailings ranging from < 0.5 to 4900 mg/kg (Lacerda and Salomons 1999). In addition, these concentrations were similar to those found in amalgamation tailings at other historical mining sites in Zacatecas, with Hg concentrations ranging from < 0.08 to 264 mg/kg (Ogura et al. 2003). In most of these cases, the identification of "hot spots" with high Hg concentrations indicated that the mining wastes were potential long-lasting sources of contamination (Lacerda and Salomons 1999). This outcome likely occurred in Cedral because Hg levels as high as 548 mg/kg occurred in uncontrolled mining waste dumps; to our knowledge, this is the highest Hg concentration reported for this type of Hg source in Mexico.

Notable differences were observed in the variation of the Hg concentrations among the mining waste sampling areas (**Fig. 2**). According to the different characteristics among the mining waste sample sites (**Table II**), the differences in the total Hg concentrations were associated with Hg extraction during reprocessing. Therefore, a negative gradient of the Hg concentrations is observed from the not reprocessed tailings (WEC-1, 276 to 584 mg/kg), to the lixiviation pond of the reprocessing plant (WEC-2, 148 to 484 mg/kg), and to the reprocessed wastes (WEC-3, 18 to 36 mg/kg). Similar low Hg concentrations were observed in sample areas WJM-1 to WJM-3 from Jesús María dump (**Fig. 2B**). According to Ogura et al. (2003), the efficiency of the lixiviation method for reprocessing amalgamation tailings, as used in Cedral, could reach a Hg extraction efficiency of up to 72 %. Thus, a significant fraction of Hg persisted in the mining wastes even after reprocessing, as shown by the El Caballo (WEC-3) and Jesús María (WJM-1 to WJM-3) reprocessed mining waste samples.

The total mean Hg concentrations did not significantly differ (ANOVA, 95 % CI) with depth when considering depths of 0-30 cm (112 ± 33 mg/kg), 30-60 cm (157 ± 21 mg/kg) and 60-100 cm (130 ± 85 mg/kg). However, the Hg concentration profiles were different among the sample areas (**Fig. 2A**, **2B**). The sample areas with lower Hg concentrations

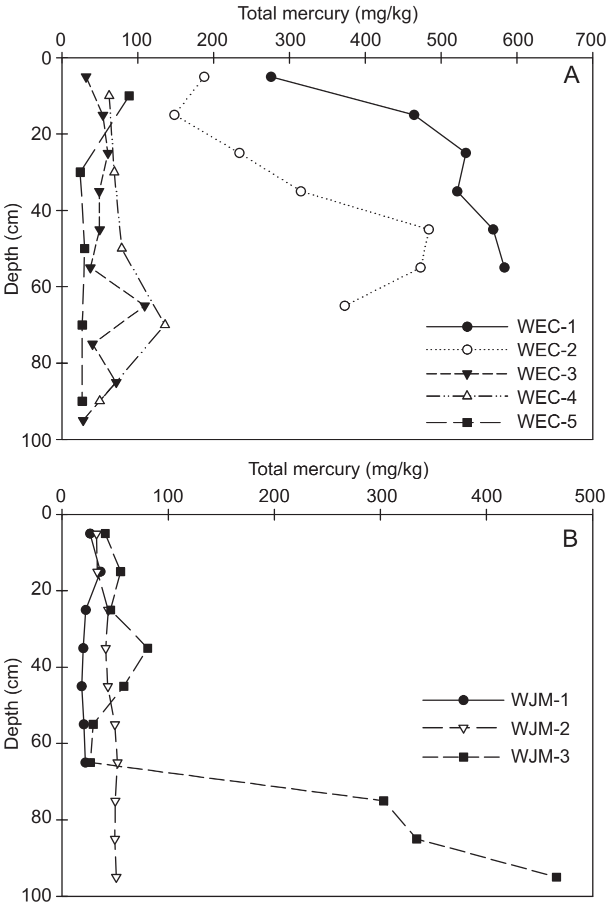

Fig. 2. Variations in the total mercury concentrations (mg/kg) with depth (cm) at the mining wastes sample areas. (A) El Caballo wastes (WEC), (B) Jesús María wastes (WJM)

(WEC-3 to WEC-5 and WJM-1 to WJM-3) showed little variation in the Hg concentrations with depth, and the concentrations ranged from 18 to 90 mg/kg, except for WEC-3 and WEC-4, which had noticeable Hg concentration peaks at depths of 60-70 cm (109 mg/kg) and 60-80 cm (136 mg/kg), respectively. Additionally, the WJM-3 sample area showed a significant increase in the Hg concentration from 27 mg/kg in the 60-70 cm section to 303 mg/kg in the 70-80 cm section, 334 mg/kg in the 80-90 cm section, and 466 mg/kg in the 90-00 cm section. The relative uniformity of the Hg concentrations could be explained by the homogenization of mining wastes due to stockpiling and reprocessing the amalgamation tailings. The anomalous Hg concentrations in the deepest sections of WJM-3 could be related to the specific conditions of the sample area because the WJM-3 samples were obtained at the toe of the Jesús María tailing dump. In contrast, the WJM-2 sample area (maximum Hg concentration of 52 mg/kg), was obtained at the top of the same mining waste dump.

For sample areas WEC-1 and WEC-2, the Hg concentration clearly increased with depth from 276 and 187 mg/kg in the first 10 cm to 584 mg/kg at 50-60 cm, and to 484 mg/kg at 40-50 cm, respectively. The Hg levels remained high in the deeper layers at WEC-1 and decreased in WEC-2. The lower levels of Hg in the surface sections from WEC-1 and WEC-2 potentially resulted from the release of elemental Hg vapor, particularly because amalgamation tailings were proposed to be an important source of atmospheric Hg emissions due to the presence of elemental Hg (Lacerda 1997). The Hg degassing rates depend on multiple climatic factors, such as temperature, solar radiation and rainfall events (Song and Van Heyst 2005, Moore and Castro 2012). Therefore, the semiarid conditions at the study site potentially promoted the release of Hg from the surfaces of the mining waste dumps (Navarro 2008).

Figure 3 shows the total Hg concentrations in soils at the Cedral sampling sites, which ranged from 1.0 mg/kg to 116 mg/kg and were lower than the concentrations observed in the mining waste sample areas. The observed Hg concentrations generally confirmed that metallurgical activities affected the soils because the Hg concentrations were higher than the regional background Hg concentrations, which ranged from 0.39 to 0.83 mg/kg, as previously reported for Cedral (Chiprés et al. 2008). Moreover, the Hg concentrations at the reference site were 9 mg/kg at 0-10 cm and 17 mg/kg at 10-20 cm, indicating that anthropogenic influence likely occurred at the soil surface. However, no anthropogenic influence was evident in the deeper sections where the Hg concentrations remained below the detection limit (< 0.008 mg/kg). Therefore, the results from the reference area indicate that past and distant Hg sources influenced the soil surface and that the Hg concentrations throughout the soil profile were consistent with surface deposition (Santos-Francés et al. 2011). In contrast with the soils at the reference site, the surface and deep soil samples from the study area had higher Hg concentrations, with 80 % of the soil samples exceeding the maximum permissible limit of 23 mg/kg for residential soils according to Mexican regulations (SEMARNAT 2004) and the USEPA (2014).

These results demonstrate severe Hg pollution in soils as a consequence of past metallurgical and recent reprocessing activities in the study area. Notably, the Hg concentrations in the deeper sections from the NAS-2, AS-1, AS-2 and AS-3 sample areas were higher than the levels allowed by Mexican

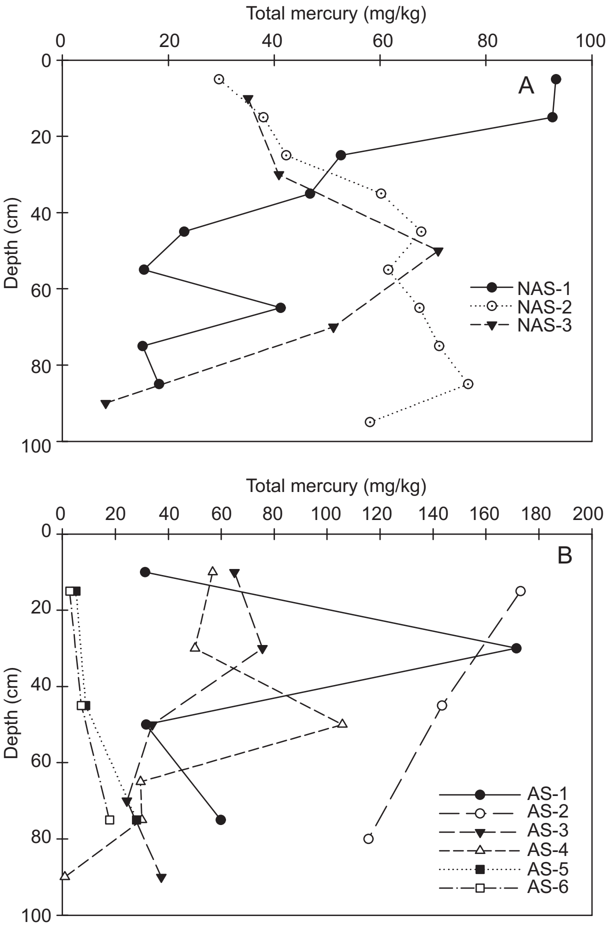

Fig. 3. Variations in the total mercury concentrations (mg/kg) with depth (cm) at the soil sample areas. (A) Indirectly affected soils (NAS), (B) directly affected soils (AS)

regulations, which suggested that the impacts of metallurgical activities most likely extended further into the soils than the maximum depth evaluated in this study (1.0 m).

Studies of soils from historical and modern amalgamation sites have reported Hg concentrations ranging from 0.13 to 542 mg/kg. These wide Hg concentration variations are potentially associated with the production capacity, operation time, extent of amalgamation processing, and pollution mechanisms. Higher Hg concentrations were reported in soils that were impacted by direct mining waste deposits rather than by pollution through surface deposition of mining wastes or elemental Hg after aeolian dispersion (Lacerda and Salomons 1999). Thus, the high Hg concentrations in the soils at the sample sites in Cedral primarily resulted from the direct impacts of the amalgamation process and the mining waste deposition. However, the dispersion of Hg particles by wind and/or water transport also enriched the soils, and these dispersion mechanisms are influenced by climate and topography conditions (Navarro 2008, Santos-Francés et al. 2011). The potential contributions of dispersion as a pollution mechanism in the study area were observed at sample sites NAS-1 and NAS-2, which were outside of the former amalgamation facilities. Thus, the Hg concentrations observed outside of the former amalgamation facilities were as higher as those observed inside of the former amalgamation facilities. Because the NAS-1 and NAS-2 sites were located on a floodplain, it was likely that the high Hg concentrations at these sites resulted from the accumulation of mining waste particles transported by discharge from upstream amalgamation facilities. Thus, the surface hydrological conditions at the site could play a role in controlling Hg dispersion during heavy seasonal rainfalls, which are distinctive in semiarid climates.

The Hg concentration profiles in the soil cores are presented in **figure 3**, and distinctive shapes and pronounced Hg concentration peaks are shown for sites NAS-3 (40-60 cm soil section), AS-1 (20-40 cm soil section) and AS-4 (40-60 cm soil section). The Hg concentrations varied less with depth at the other sampling sites. However, it was observed that the Hg concentrations slightly increased (NAS-2, AS-5 and AS-6) or decreased (NAS-1, NAS-3, AS-2 and AS-3) with increasing depth. The heterogeneity of the shapes of the Hg concentration profiles could be associated with soils cutting, filling and/or mixing in urbanized areas. The potential effects of urbanization on the compositions of surface and deep soils include the redistribution, homogenization and dilution of natural and anthropogenic elements (Meuser 2010).

The mean total Hg concentrations were significantly different (ANOVA, 95 % CI) among the soil samples obtained at depths of 0-30 cm (62 ± 16 mg/kg), 30-60 cm (55 ± 2 mg/kg) and 60-100 cm (44 ± 9 mg/kg), indicating that the Hg concentration decreased with increasing depth. Thus, the distribution of Hg in the soil profiles suggested that physical and chemical Hg transport processes affected the downward movement of Hg through the soil profile. The mobilization of Hg in soils is controlled by several factors, including Hg speciation, soils physical and chemical properties and climatic conditions, such as precipitation and evaporation (Navarro 2008).

Authors such as Nacht and Gustin (2004) and Liang et al. (2014) indicated that adding small amounts of water to dry soils without reaching saturation, results in the release of Hg from the soils to the atmosphere. These emissions arose from the displacement of elemental Hg by water infiltrating the soil pores. In addition, Hg(II) in soil can be dissolved in the soil water pores. Subsequently, once the soil dries and the water begins to evaporate, the elemental Hg and Hg(II) in the water migrate to the surface by mass flow. Once Hg(II) is adsorbed to the surface of soil particles, it can be photo-reduced to elemental Hg and released to the atmosphere (Gustin et al. 2003). Because evaporation exceeds precipitation in Cedral, the process described above could be an important mechanism of Hg transport in soils. Therefore, the Hg solubility was assessed by using simulated conditions of rainwater contact to evaluate the net potential effects of all controlling factors on the aqueous transport of Hg in mining wastes and soils at Cedral.

Concentration of soluble Hg in the mining wastes and soils

In this study, the operationally soluble Hg is all that could pass through a 0.45 µm diameter pore membrane as ions, molecules and bound to organic matter or colloidal mineral particles (Boszke et al. 2008).

The soluble Hg concentrations in the mining waste samples were significantly lower than the total Hg concentration, ranging from 0.009 to 0.32 mg/kg. Thus, the solubility of Hg under simulated rainwater contact conditions varied from 0.007 to 0.54 % of the total Hg found in the mining wastes. The latter in agreement with the soluble fraction of Hg (0.01 - 0.22 %) in the samples from the El Caballo and Jesús María dumps reported by Morton-Bermea et al. (2015). The data from other historical and modern amalgamation sites are consistent with the results from Cedral, which indicated that the aqueous solubility of Hg is low in amalgamation mining wastes (Lacerda and Salomons 1999). The concentrations of soluble Hg indicate that the transport of Hg resulting from Hg solubilization in rainwater is negligible during rainfall events in Cedral.

The differences in the soluble Hg concentrations among the mining waste sample areas are shown in **figure 4**. According to the different characteristics among the mining waste sample sites (**Table II**), the highest soluble Hg concentration was associated to the reprocessed waste. Therefore, reprocessed amalgamation tailings from the lixiviation pond site WEC-2 had the highest concentrations of soluble Hg at the surface (0.10 mg/kg) and at a depth of 40-50 cm (0.32 mg/kg). Notably, the concentrations of soluble Hg at non-reprocessed amalgamation tailings were near the detection limit of 0.004 mg/kg. In these samples, it was suspected that elemental Hg is the main chemical species responsible for the low Hg solubility in non-reprocessed mining wastes from Cedral. Elemental Hg has been reported as a major chemical species that causes low Hg solubility in amalgamation mining wastes (Bloom et al. 2003). In contrast, the WEC-2 site exemplified conditions of reprocessed tailings at the stage of lixiviation with CaS_2O_3 because it corresponded to the mining waste content in one pond from the El Caballo reprocessing plant. Therefore, the relatively higher concentrations of soluble Hg could be caused by the occurrence of soluble Hg compounds that were formed during the leaching of amalgamation residues (Ogura et al. 2003). The increase in the concentration of soluble Hg due to reprocessing was also observed in samples from reprocessed tailing dumps (WEC-3, WJM-1, WJM-2 and WJM-3).

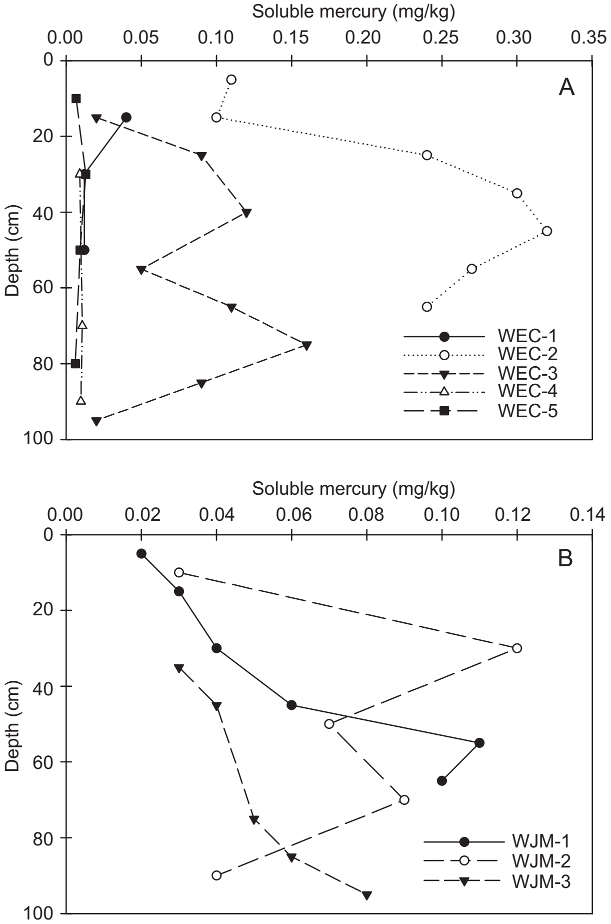

Fig. 4. Variations in the soluble mercury concentrations (mg/kg) with depth (cm) at the mining wastes sample areas. (A) El Caballo wastes (WEC), (B) Jesús María wastes (WJM)

The Hg solubility found in the reprocessed mining wastes from Cedral likely resulted from the prevalence of Hg sulfide (HgS), which was the main Hg species according to a previous study of the same reprocessed tailings from Cedral (Bayer 2013).

The depth-dependent variations in the concentrations of soluble Hg in the mining wastes showed clear differences among the sample sites (**Fig. 4**). Thus, the sample areas with lower soluble Hg concentrations (WEC-1, WEC-4 and WEC-5) showed low variation with depth. This trend was also observed in WJM-3, except for a small increase in the soluble Hg concentrations in the deeper sections. The samples from sites WEC-2, WEC-3, WJM-1 and WJM-2 had a noticeable peak of soluble Hg concentrations in the middle and deeper sections of the mining waste profiles.

The soluble Hg concentrations in the soils varied from 0.003 to 0.04 mg/kg (**Fig. 5**) and were lower than the soluble Hg concentrations observed in the mining waste samples. Soluble Hg represented < 0.03 % of the total Hg in the soil samples, which was consistent with data obtained from studies of soils near former amalgamation areas with mean soluble Hg concentrations of only 0.05 % of the total Hg concentration (Santos-Francés et al. 2011). However, the soluble Hg fraction was lower than the one reported previously (0.37 - 0.68 %) for two soil samples from Cedral (Morton-Bermea et al. 2015).

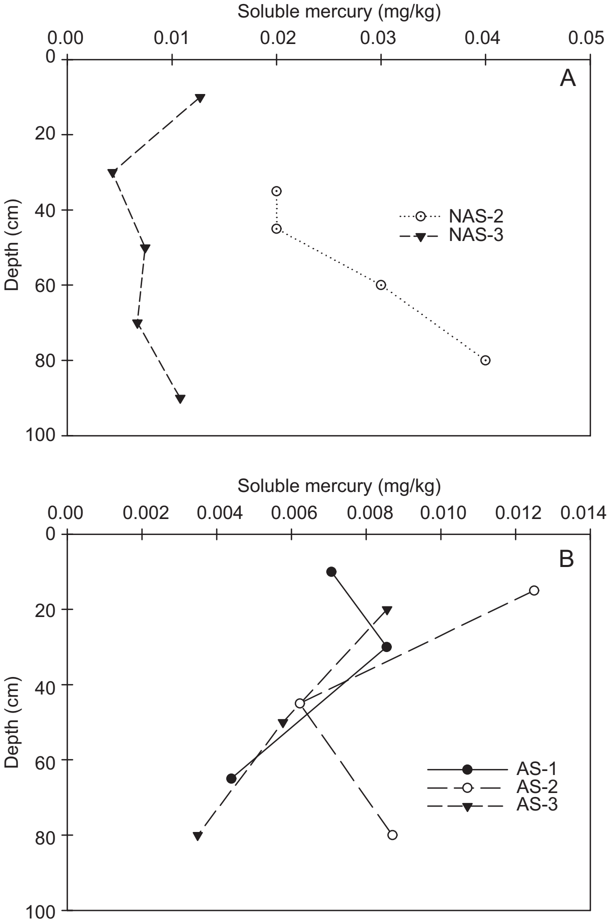

Fig. 5. Variations in the soluble mercury concentrations (mg/kg) with depth (cm) at the soil sample areas. (A) Indirectly affected soils (NAS), (B) directly affected soils (AS)

The soluble Hg concentrations among the soil sample sites were not high enough to detect significant differences (ANOVA, 95 % CI). Nonetheless, as shown in **figure 5A**, the soluble Hg concentrations in the NAS-2 soils were notably higher than those in the soils from the other sample sites and increased with depth from 0.02 to 0.04 mg/kg. Therefore the low solubility of Hg in the mining waste and soil samples under simulated rainwater contact conditions indicated that aqueous transport was a minor contributor to the vertical migration governed by soluble chemical Hg species. Thus, colloidal transport could play a major role in the downward migration of Hg in soils (Navarro 2008).

Bioaccessible Hg in the mining waste and soil samples

A previous study has shown that children from Cedral are exposed to Hg (Morton-Bermea et al. 2015). Taking into account that seafood is not an important dietary component in Cedral, the bioaccessible Hg concentrations were determined in order to evaluate if the accidental ingestion of mining wastes and polluted soil particles could be a major exposure route.

The concentrations of bioaccessible Hg in the mining waste samples are expressed in mg of bioaccessible Hg per kg of mining wastes, and range from 0.1 to 60 mg/kg (**Fig. 6**). These values were lower than the total Hg concentrations (**Fig. 2**) but higher than the soluble Hg concentrations (**Fig. 4**). The latter might be due to more acidic conditions, higher Cl^- concentrations and the presence of the organic functional groups of glycine in the extraction solutions (Ravichandran 2004, Jing et al. 2007).

The mining waste sample area WEC-2 had the highest values of bioaccessible Hg, ranging from 9 to 60 mg/kg. In contrast, the other sample areas had lower bioaccessible Hg concentrations that ranged from 0.1 to 22 mg/kg. The bioaccessibility of Hg is primarily controlled by its chemical speciation, which depends on the nature of the primary source and on the physical and chemical properties of the polluted soils (Zagury et al. 2009). The bioaccessible Hg concentrations at WEC-2 sample site represent less than 10 % of the total Hg concentration. The concentrations of bioaccessible Hg in the WEC-1, WEC-4 and WEC-5 non-reprocessed mining waste sites were less than 1 % of the total Hg concentration,

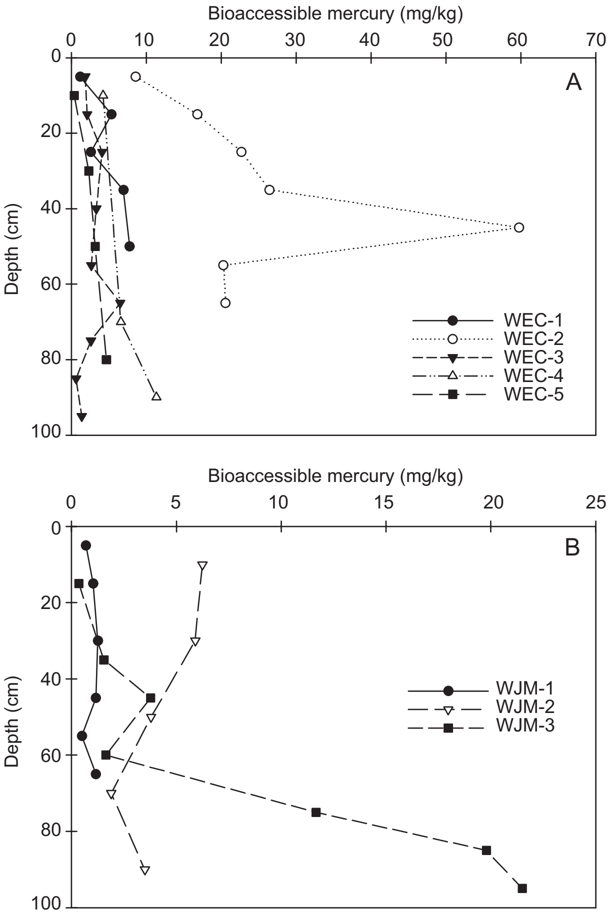

Fig. 6. Variations in the bioaccessible mercury concentrations (mg/kg) with depth (cm) in the mining wastes sample areas. (A) El Caballo wastes (WEC), (B) Jesús María wastes (WJM)

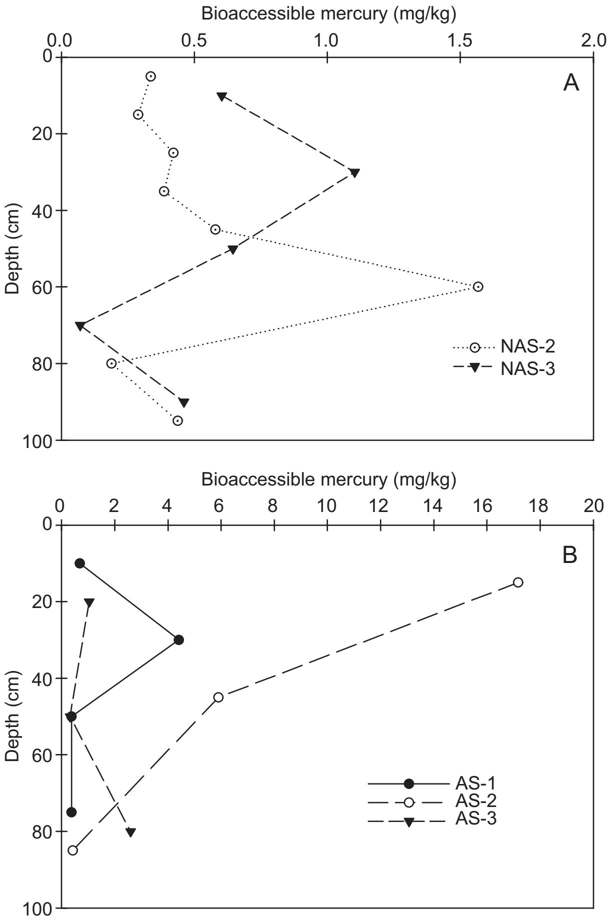

Fig. 7. Variations in the bioaccessible mercury concentrations (mg/kg) with depth (cm) at the soil sample areas. (A) Indirectly affected soils (NAS), (B) directly affected soils (AS)

as clearly observed at the WEC-1 sample site, which had the highest total Hg concentration. Thus, these results are supported by the predominant occurrence of HgS in reprocessed tailings (Bayer 2013), and they may be explained because elemental Hg is the primary chemical species in non-reprocessed mining wastes, since these Hg species present low bioaccessibilities in soils and mining wastes (Davis et al. 1997, Zagury et al. 2009).

Despite the limited bioaccessibility of Hg, the highest bioaccessible concentration of Hg observed in this study (60 mg/kg), exceeded the health-risk-based Mexican regulation of 23 mg/kg for residential soils by nearly three times, which suggests that ingestion of mining waste particles could be a major exposure pathway for Hg in the studied area.

Regarding the variations in the bioaccessible Hg concentrations with mining waste depth in the WEC-2 sample area, an important peak in the Hg concentration was observed, with concentrations of 26 mg/kg at 40-50 cm to 60 mg/kg at 50-60 cm, which coincided with the higher total and soluble Hg concentrations at the same sample site and in WJM-3 sample site. A notable increase in the concentration of bioaccessible Hg occurred with the bioaccessible Hg concentration reaching 22 mg/kg in the deepest sampled section (90-100 cm). Thus, the vertical distributions of bioaccessible Hg at the WEC-2 and WJM-3 mining waste sample sites were primarily controlled by the total Hg concentration. The shapes of the total, soluble and bioaccessible Hg profiles were similar for this sample area, which indicated a homogenous distribution of chemical Hg species throughout the sampled mining waste profile.

The bioaccessible Hg concentrations in soils ranged from 0.1 to 17 mg/kg and were notably different among the sample areas (**Fig. 7**). The samples from the NAS-2, NAS-3 and AS-3 areas had lower bioaccessible Hg concentrations of 0.1 to 3 mg/kg that varied slightly with depth. By contrast, site AS-1 had a significant peak of the bioaccessible Hg concentration of up to 4 mg/kg at a depth of 20-40 cm, and the AS-2 sample area had a distinctive bioaccessible Hg concentration profile that clearly decreased from 17 mg/kg at the surface to 0.4 mg/kg in the deeper sections. Similar patterns in the total (**Fig. 3**) and bioaccessible Hg (**Fig. 7**) concentrations were observed at the AS-1 and AS-2 sample sites, which indicated that the bioaccessibility of Hg were homogenous throughout the studied soil profiles.

CONCLUSIONS

This study confirmed the existence of Hg sources and soil pollution due to historical and recent metallurgical activities at the study site.

The most affected soils were those on which amalgamation activities were conducted. Besides, the Hg concentrations in soils determined at areas outside of the former amalgamation facilities, indicated that Hg was dispersed in the surrounding areas.

The high Hg concentrations observed at soil depths of up to 1.0 m indicated the severe impacts of metallurgical activities in these soils years after metallurgical activities were stopped, which highlights the importance of evaluating this site with more detail.

The soluble Hg concentration indicated that during a rainfall event the aqueous transport of dissolved Hg at the sample sites is negligible. In contrast, the observed bioaccessible Hg concentrations confirmed that humans could be exposed to Hg at these sites by accidentally ingesting mining wastes and soil particles.

The soluble and bioaccessible Hg concentrations in the non-reprocessed and reprocessed mining wastes indicated that the water solubility and bioaccessibility of Hg increased after reprocessing. Additional studies should be conducted to understand the effect of reprocessing on Hg speciation at this site.

A risk, not considered here, should be the possible atmospheric emissions of gaseous Hg from these wastes or contaminated soils. An assessment of this possibility should be important to evaluate the exposure of vapor Hg through inhalation in order to delimitate the areas with higher potential risks.

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