

MERCURY IN THE ENVIRONMENT OF THE MINERALIZED ZONE IN SAN JOAQUÍN, QUERÉTARO, MEXICO

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RESUMEN

La explotación minera del cinabrio (HgS) durante más de dos mil años al sur de la Sierra Gorda, México, ha liberado grandes cantidades de mercurio a los ecosistemas, dando lugar a una contaminación generalizada de su paisaje. Esta actividad minera es la principal fuente de emisiones contaminantes al aire, transportando y depositando el elemento en la región. Su uso extenso durante el último siglo, ha incrementado el potencial de exposición en la población general y en el medio ambiente. Por lo tanto, la zona sur de la Sierra Gorda ofrece la oportunidad de estudiar al mercurio desde varios puntos de vista. Durante seis años, un grupo de investigadores de México y Hungría ha estado trabajando en el área de San Joaquín, Estado de Querétaro. Como parte de esta vinculación y la conjunción de varias disciplinas, se presentan algunos resultados obtenidos entre 2008 y 2013. El mercurio es el eje central del proyecto, iniciando su estudio con el antecedente geológico general de la Sierra Gorda; la actividad minera del Hg a través de muchos siglos, ha afectado a los sistemas terrestres (agua, suelo, aire y biota); el secuestro de carbono en el suelo ha sido alterado por las actividades mineras y el cambio de uso de la tierra; también se presenta un enfoque de flujo de las interacciones totales de Hg en estos sistemas terrestres. Estos resultados constituyen la base para la implementación de un monitoreo permanente del mercurio en la zona y que sirvan de referencia para llamar la atención a las autoridades correspondientes,

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sobre este problema del medio ambiente y de salud pública.

Palabras clave: mercurio, sistemas terrestres, medio ambiente, Sierra Gorda, Querétaro, México.

ABSTRACT

The continuous cinnabar (HgS) mining exploitation for over two thousand years in Southern Sierra Gorda, Mexico, have released large amounts of mercury (Hg) into the ecosystem and also resulted in a widespread contamination. The HgS mining activity is the main source of airborne emissions, transportation and deposition in the region. The extensive use of Hg in the last century has increased its potential for exposure in the general population and in the environment. Therefore, the southern area of the Sierra Gorda offers the opportunity to study Hg from several points of view. For six years, a mercury research group from Mexico and Hungary worked in San Joaquin area of Queretaro, Mexico, involving several disciplines. Some of the research results from 2008 to 2013 are presented in this study. Hg is the main focus in this study and it starts from the geological background of Sierra Gorda. For centuries, Hg mining activities has affected terrestrial systems (water, soil, air and biota); soil carbon sequestration has been altered by mining activities and land use changes. An approach of flow of total Hg interactions within the terrestrial systems was presented as well. These efforts constituted the basis for constructing permanent Hg monitoring in the area and pay attention to the authorities because of environment and public health problems.

Key words: Mercury, terrestrial systems, environment, Sierra Gorda, Querétaro, México.

INTRODUCTION

Mercury (Hg) is found naturally as cinnabar (HgS), but human activities such as mining increases its presence within the atmospheric, terrestrial, biotic and aquatic systems (Mason and Sheu, 2002; Selin, 2009). The effect of the HgS mining represents an environmental concern since abandoned and enriched open air mining tailings are considered permanent sources of atmospheric Hg emissions. The mine drainage could contain high levels of Hg that affects the water and biota quality; therefore, HgS tailings increase the Hg content of soils and sediments of hydrographic watershed (Rytuba, 2000; Kocman and Horvat, 2011). The effect on the environment through diverse processes such as rock weathering, erosion, leaching, oxidation and transportation is very important. Hg can be transported across great distances, thus becoming a legacy associated to soil, sediments and plants. Even after many years of mining inactivity, high amounts of Hg can be found in the environment (Parsons and Percival, 2005; García-Sánchez et al., 2009). On the other hand, man can be a receptor of Hg through

air particles inhalation, direct contact or ingestion through the accumulation of this element in the trophic chain. These mechanisms have operated in past and present times (Wasserman et al., 2003; Pyatt et al., 2005).

Throughout history, San Joaquin has been converted to a highly sensitive area to Hg inputs, where the ecosystem characteristics play a significant role in determining the Hg sensitivity of any potential monitoring location. In addition to monitoring changes in Hg concentrations, an additional and permanent measure such as atmosphere, climate, soil chemistry parameters, etc., are necessary to interpret trends and dynamics of Hg. On the other hand, spatial distribution and long-term trends in Hg concentrations in each ecosystem compartments including concepts such as watersheds and wildlife are necessary to be implemented. The process by which Hg deposits in the watersheds, transforms to methylmercury (MeHg) and magnifies in food webs is complex, thus requiring monitoring of all components of the Hg cycle to assess how changing emissions and deposition affect fish, wildlife,

and people (Parsons and Percival, 2005). It is proven by archaeological findings that people of the Chichimecas culture exploited HgS in the surroundings of Ranas and Toluquilla archaeological sites, from the 3rd Century BC (Herrera-Muñoz, 1994). Mining ceased before the Spanish conquest, and was hidden during the colonial period, but it became significant again in the XX century. The exploited material was deposited in spoils that were altered through oxidation, and was partially dissolved and accumulated in the soil and young sediments of the surrounding landscape and was transported by streams. Due to the complex geological setting, direct dissolution of near- surface rocks bearing Hg cannot be excluded either. The present Hg distribution can thus be the result of Prehispanic, colonial and modern mining activities as well as the specific natural geological processes of the area.

The framework of this study exhibits a certain structure and sequential linkage of diverse subjects. The draft interpretation starts from the geological background of the Sierra Gorda and ores that are the sources of pollution. Mining activities altered the natural quality of soils and sediments in the area; changing

many of their initial natural properties and transforming the soils and their sediments which contains different levels of Hg, hence altering some of the soil characteristics (Scharek et al., 2010; Martínez-Trinidad et al., 2013). The Hg mining activities through many centuries affected terrestrial systems. Vegetation cover reduced as a result of these past and present activities. Also, forest conversion into agriculture practices is a common practice and they are the main causes of changing land use system in the region (Hernández-Silva et al., 2013).

The ancient and modern population of the region has been affected in their health as well (Hernández-Silva et al., 2009). An investigation on the flow of Hg interactions in the landscape is presented in a bid to define the extent of Hg translocations in the different compartments of the terrestrial systems that affect man and the environment (Martínez-Trinidad et al., 2013). On the other hand, personnel from the Geological Institute of Hungary through Geochemical Laboratory (Bartha and Varga-Berna, 2002; Bartha et al., 2009) and Environmental Geology (Scharek et al., 2010) supported this project with specific

topics. The aim of this study was to determine the total Hg contents in the terrestrial systems, derived from HgS mining activities in an area with over 2000 years of HgS mining exploitation.

METHODOLOGY

The study area is 172 km² and is localized between longitude 99°40' and 99°30' W, and latitude 21°10' and 20°50' N . As a study unit, the hydrological micro basin concept was used. Its limit takes into consideration the ecosystems and the interdependence with hydrological cycle since it allows detection of multiple functions and alterations that take place on them (Sarukhan and Maas, 1990). The region is composed of several Mesozoic marine formations deformed and folded during the Laramid orogen cycle. Mineralization of Hg is associated with magmatic rocks that take place in the area and the types of mineralization are hydrothermal Hg deposits and skarn Zn-Cu-Pb-Ag deposits (Vassallo and Solorio, 2009). The predomination of limestone, marlstone and lutites rocks from the Upper Jurassic (Suter, 1987) have been eroded and the region has been shaped with the physiographic and morphological features that characterize it.

These characteristics are marked by the stark contrast between high peaks whose summits exceed 3000 m altitude and deep depressions where the main streams are at an altitude of 900 m. It has a climate ranging from sub-humid to semi-dry temperate and sub-humid semi-warm. The mean annual temperature is 14°C with a mean annual rainfall of 800 mm. The predominant soil types are chromic Luvisol, chromic Cambisol, calcareous Regosol, and Leptosol. The vegetation is mesophyll woods, deciduous woods, and pine-oak, as well as sub-montane shrubs and xerophytes. Area delimitation for the study was done by criterion of the hydrological basin, considering it as a reference framework for the selection of sampling sites (Hernandez-Silva et al., 2009) (Fig. 1).

METHOD ANALYSIS

SOILS, SEDIMENT AND TAILINGS

A systematic random sampling scheme was used to select the material sampling site, using soils and sediment as strata (Gilbert, 1987). Soils were collected in control plots with 5 sub-samples at distances of 50 m each and at depths of 25 cm. Sediment samples were randomly collected from sections of approximately 100 m along the stretch,

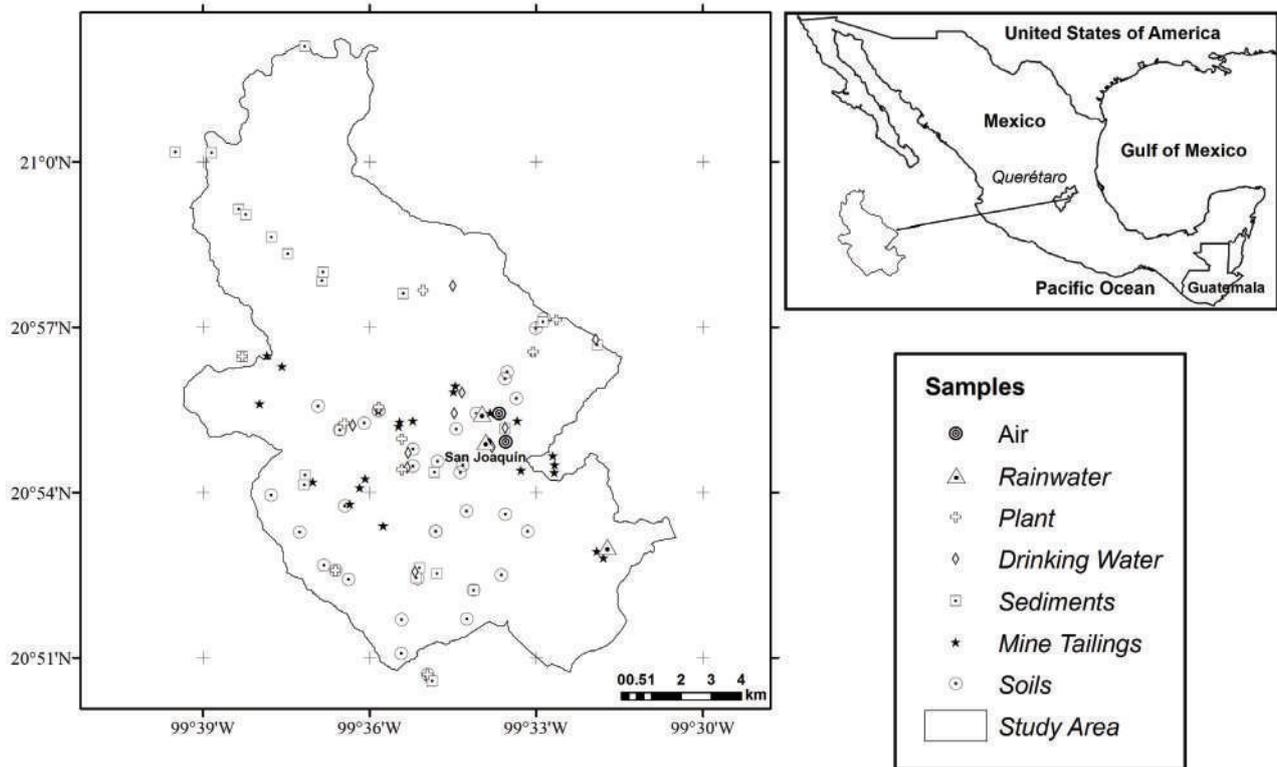


Figure 1. Sampling sites for air, rainwater, drinking water and soils in the San Joaquin region.

streams, rivers, bottom sediments, flood plains and small alluvial terraces. Each site represents a compound sample with an average of 5 sub-samples, with a maximum depth of 25 cm. In the tailing materials, 5 sub samples were taken on a distance of 10 to 50 m (depending on the tailing size) between them and at three exposed depths of 5 m each. The samples were perfectly mixed and a portion of 2 kg was kept at 4°C. The end result was a set of 103 georeferenced sites (Fig. 1). For the Hg analysis of soil, the sediments and tailing samples

were not digested. The total Hg content was analyzed by a direct AAS mercury analyzer (AMA 254 Advanced Mercury Analyzer) with detection limit of 0.01 ng Hg. For checking the solution calibration of the AMA 254, the standard used were MOSTAR Hungarian stream sediment standard (recommended value: 0.2245 ppm); Slovakian reference material (ISE 982) (recommended value: 0.020 ppm); WEPAL monitor sample (ISE 921) and a recommended value of 1.210 ppm. Accuracy was verified by analyzing two repetitions for

each sample. More than 98% recovery was reached for Hg analysis.

MAIZE PLANTS

The sampling was made at the time of harvesting in three different years at the same sampling site in October 2006, November 2007 and 2010. Maize plants were collected from agricultural lands, and separated by structures into root, stalk, leaf, and grain, obtaining 15 samples from the roots, 17 from stems, 11 from leaves, and 18 from grains (Fig. 1). Each structure was washed with HNO₃ diluted to 10%, rinsed with deionized water, and dried at room temperature (22° to 25°C). The plant material was ground and sifted until achieving particle size under 0.13 mm. Then, 0.1 g was weighed and 5 ml concentrated HNO₃ was added for digestion through a MARSPRESS microwave oven. Some drops of concentrated HCl were added to the digestion and the volume was taken to 200 ml with 18.2 µS/cm deionized water. They were kept at 4°C until measurement was taken. Total Hg quantification was made through induction coupled plasma mass spectrometry (ICP-MS) equipment Thermos Series.

RAINWATER

At the micro-watershed of Agua de Venado, Agua de León and Pondejhe of the study zone, rainwater collectors were installed for total Hg quantification (Fig. 1). Information was also collected from a nearby meteorological station in order to determine the predominance of the wind directions. Sample collection of rainwater was compound; each sample includes water from all the events in a month. 24 samples were collected from December 2009 to June 2010. The rainwater samples were filtered through a polycarbonate membrane with 0.4 µm pores, using a magnetic filtration system (Gelman 47-mm). The filtrate was acidified to pH 1.8 with 0.016N HNO₃, and 60 ml from the sample was transferred to high density polyethylene bottles thus, the soluble fraction was obtained. The insoluble fraction is the part that remained on the filters used for the filtration process of the soluble fraction. These filters were subjected to acid digestion using 15 ml of 3M HNO₃ with a digestion time of 45 min in a MARSPRESS microwave oven. The digested samples were filtered and the volume was adjusted to 25 ml with deionized water, obtaining a final HNO₃ acidity of 0.45N. Both fractions (soluble and insoluble) were refrigerated and kept at 4°C

until quantification. Total Hg concentration was determined through inductively coupled plasma optical emission spectrometry (ICP-OES) equipment 710-ES Axial.

DRINKING WATER

Drinking water was sampled from nine settlements in the San Joaquin's municipality in the month of March and November, 2007, obtaining a total of 18 samples (Fig. 1). The samples were collected in decontaminated Nalgene bottles. Preservation of the samples was done with INSTRA nitric acid and refrigerated at 4°C until measurement. Total Hg quantification was done through induction coupled plasma mass spectrometry (ICP-MS) equipment Thermo Series X2.

AIR

The atmospheric Hg concentrations (elemental mercury in vapor phase) were measured in two sampling sites (Fig. 1); the first one was established within the San Joaquin community and the samples were taken in a continuous manner through 17 days (March 2011); while the second type which was measured for 21 days was located at the Agua de Venado area (April-May 2011). TEKRA 2537A model was

the equipment used to determine the ultra-trace Hg vapor facilitated by CENICA, INE.

CARBON SEQUESTRATION

Organic matter is the most important soil component controlling Hg²⁺ absorption and desorption processes, affecting its retention and release in the environment (Zhang et al., 2009). In organic matter properties, colloidal characteristics of humic substances (HS), permits their interaction with diverse cations, helping or restricting their mobilization through soils. As a result, HS forms stable compounds with Hg, and reduces its mobility and availability for other systems (García-Calderón et al., 2012). The methodology used includes the available data in the study area: % SOC, pH, % base saturation, and diagnostic horizons (ISRIC, 2002). Hence, a parametric approach method was used, allowing a methodical arrangement in the CS classification. Consequently, each sampling site was classified in three categories of CS (low, medium and high). Finally, a CS distribution map was constructed with a software R, v. 2.11.1 (R Development Core Team, 2010) and final edition with software ArcGIS version 10 (Fig.5).

MAPPING

Mapping provides the means to characterize and quantify spatial variability to use this information for rational interpolation, and to estimate the variance of the interpolated values (White et al., 1997). Knowledge of the spatial distribution of a contaminant is essential for site assessment and any subsequent risk assessment (Markus and McBratney, 2001). Although it is time consuming and expensive to obtain enough samples for this kind of studies, the use of an interpolated map can be useful. Such a map of the element in the studied area was constructed and was used to describe dispersion patterns. This map synthesizes a great amount of field data, as well as laboratory and statistical analyses. Map processing was made by Micro Station 95 SE used in the Geological Institute of Hungary. Polygons were compiled by the software family MGE of Integraph Co. The map was converted into ArcView 32 shapes for publication (Fig. 2).

STATISTICAL ANALYSIS

Descriptive statistical analyses for total Hg content in the database coming from mining tailings, soils, sediments, maize plants, rainwater and air samples were taken into

consideration. This analysis allows determining the extent of contamination by Hg within each environmental component, as well as the detection of its maximum and minimum threshold. For a better understanding of Hg distribution in each component, box and whiskers diagrams were used through STATISTICA Version 10 software.

RESULTS AND DISCUSSIONS

Hg in soils and sediments

The boundaries on the map (Fig. 2) represent the different levels of Hg content and the extent under the entire superficial area studied. The site sequence farther from the mines could be assigned the domain between 2.5 to 25.0 mg/kg, showing the background value of the territory (Bartha et al., 2009) (Fig. 3). The Hg content of the soil samples overlying the Soyatal Formation remains commonly under 2.5 mg/kg similar to the sediments of the river Gatos upstream of Bucareli. The domain between 25.0 and 250.0 mg/kg of t-Hg content is covered by the geological formations of Las Trancas and Tamaulipas and occurs in zones affected by hydrothermal processes (Bartha et al., 2009; Scharek et al., 2010). The areas with the highest levels of total Hg content (>250

TOTAL MERCURY CONTENTS IN SOILS, SEDIMENTS AND TAILINGS (mg/kg)

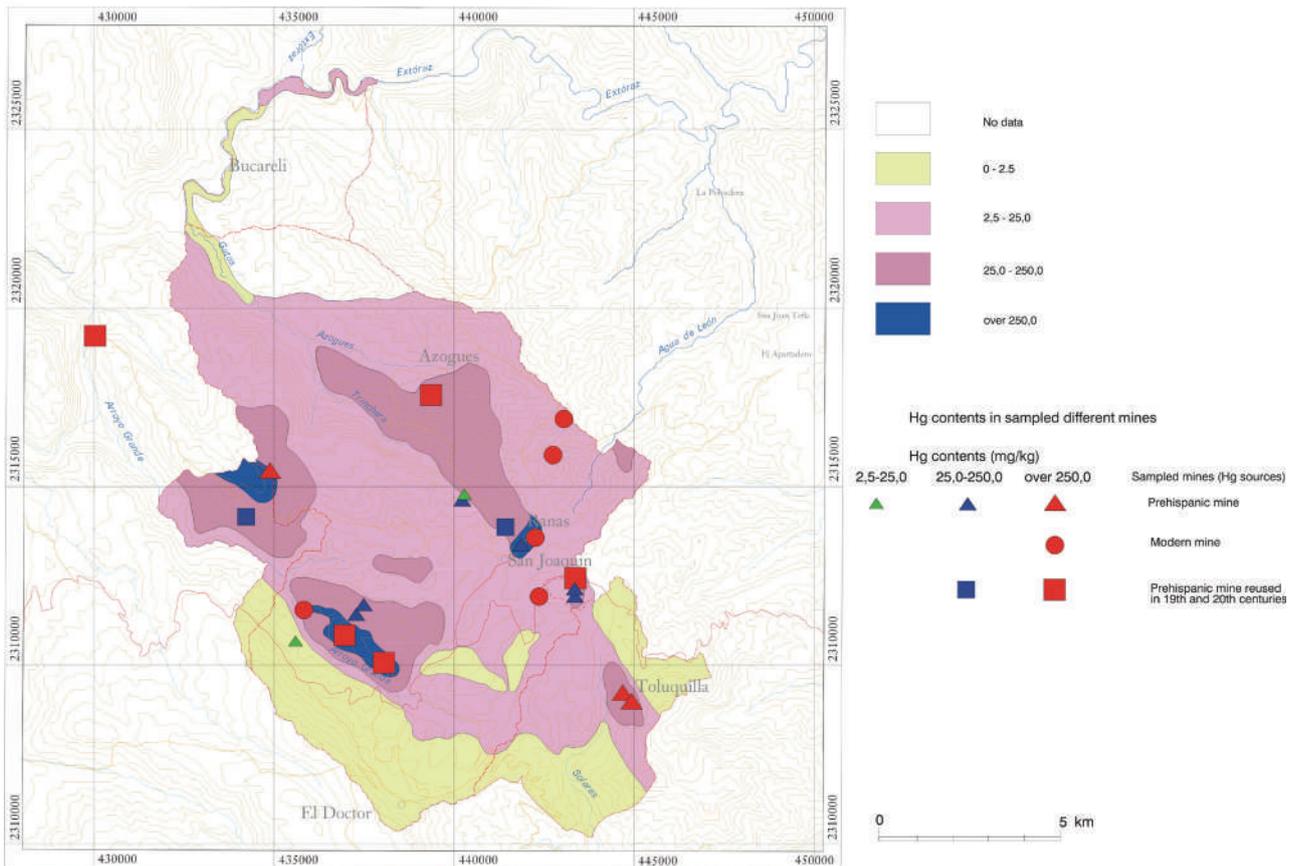


Figure 2. Dispersion map showing four levels of total mercury and the highest areas in blue color (mg/kg).

mg/kg) were found in three areas that include groups of several Hg mines from different sizes, period and types of exploitation:

- an area of Arroyo Grande micro basin.
- Calabacillas area, in both cases predominating present and mixed origin mining.
- the surroundings of Ranas archaeological site are mostly with ancient mining (blue color in Fig. 2). By means of association of the three areas, we see the results of HgS exploitation

and its accumulation in the landscape for over 2000 years (Hernández-Silva et al., 2009).

Total Hg concentration in agricultural soils is distributed in a wide range of 0.5 to 314 mg/kg (Table 1), where the highest registered value clearly indicates a great Hg incorporation into the landscape soils. According to the NOM 2004, 46% of the soil samples analyzed showed that Hg concentrations are greater than the maximum limit established for agricultural use (23 mg/kg). The results show that the median

values of total Hg content decreases as follows: agricultural soils (16 mg/kg) > sediments (14 mg/kg) > forest soils (2.8 mg/kg) (Table 1). Since time immemorial, agricultural soils are associated to mining activities; sediments permanently collect the HgS remainders from the surroundings tailings in forest soils. The soil organic carbon content is higher than the other materials; this SOC plays a very important role through the colloidal character of the humic substances that reduce the mobility and availability of Hg (Hernandez-Silva et al., 2013).

The land relief of the study region could be an important factor in Hg distribution, given that the forest areas are in a slope $>15^\circ$, which makes them more susceptible to erosion processes, while agricultural areas are next to forest areas, and therefore are receptors of the Hg eroded by surface runoff. Almeida (2005) mentions that hydric erosion favors re-mobilization of Hg in the surface soil layer. Sediments are a natural means of transportation of Hg loads, causing its dispersion into the drainage network. Several authors (Hines et al., 2000; Feng and Qiu et al., 2008; Lin et al., 2010) point out that mercury concentrations in sediments tend to decrease as they are farther away from

the source of contamination.

MERCURY IN MINING TAILING

Hydrothermal tailings show total Hg contents ranging from 2.4 to 4164 mg/kg. It can be seen that the range is quite extended. However, most concentrations are somewhere around the median (233 mg/kg), being the upper limit an extreme value in the region. As it was expected, the tailings skarn type presented a lower Hg concentration than the hydrothermal, since they present concentrations from 3.7 to 25.6 mg/kg. Over time, the tailings get mixed with the soil and showed high content of total Hg from 14.6 to 1448 mg kg⁻¹ (Table 2). These amounts of Hg could be due to the inefficient and incomplete HgS processing, possible re-absorption of Hg, and direct exposure of the chimney in several years (Biester et al., 1999; Navarro et al., 2009).

Nevertheless, considering the NOM (2004) with regard to concentration levels to be considered as contaminated soil (> 23.0 mg/kg), it is observed that 37% of the tailing samples analyzed showed Hg concentrations greater than the limit allowed for industrial use (310 mg/kg). Hg concentration in tailings gives to the San Joaquin region a high level

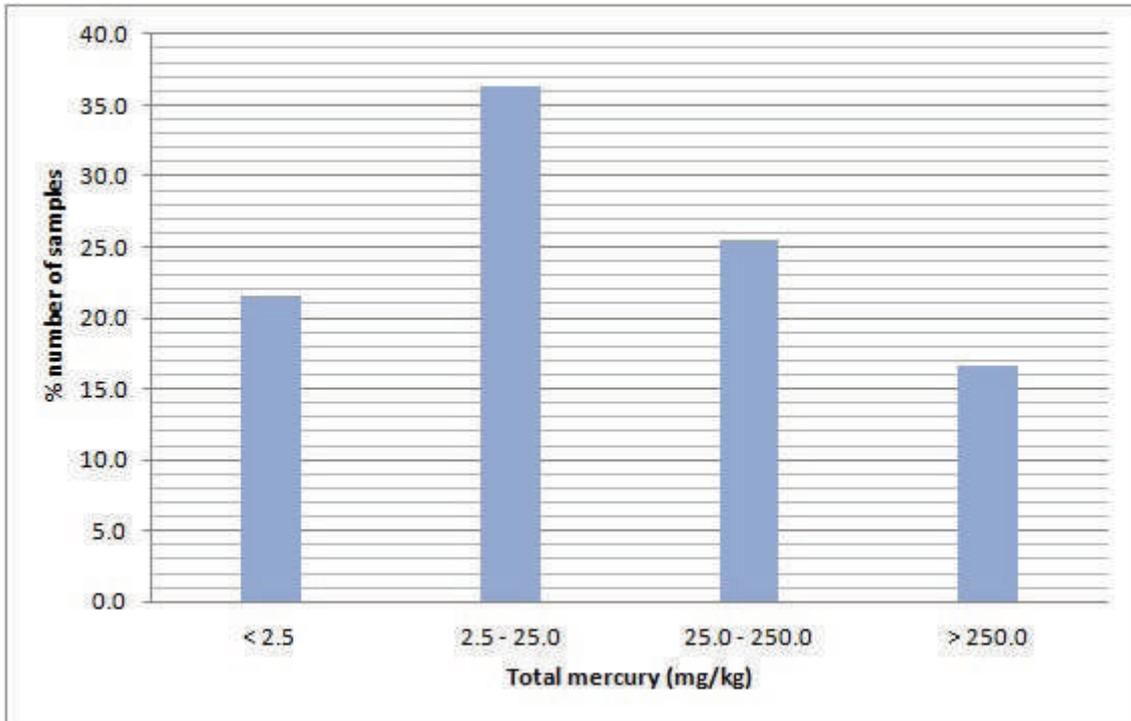


Figure 3. Percentage of the number of samples taken with its levels in total mercury.

of contamination, which is one reason why its exploitation and use is currently forbidden. In this region, there exists great amounts of open air mine tailings located in the surrounding areas of the abandoned mines, thus becoming a serious risk to the underground water (Gray et al., 2004; Li et al., 2008). The highest total Hg concentration (4164 mg/kg) was similar to that reported by Qiu et al., (2005, 2006) in the mining district of Guizhou, China (4400 mg/kg), but lower than that of Almadén, Spain (34,000 mg/kg), considered as the most contaminated

place by Hg on Earth (Higuera et al., 2003).

MERCURY IN MAIZE PLANTS

The concentrations of total Hg in the different structures of the maize plants are shown in Table 3. The structures (root, stalk and leaves) showed the highest Hg concentration in maize plants. Nevertheless, plants close to the mines presented a higher concentration of total Hg than those located farther away, while in the maize grain, maximum and median values showed small differences

between near and far away from mines (maximum of 0.8 and 0.9 mg/kg and median of 0.1 and 0.2 mg/kg, respectively). This was because different soil types, plant species, and growing conditions contributed to divergent influences of soil contamination on trace elements status in plants (Trudgill, 1988). The fate and phytoavailability of Hg depend on soil chemical and physical properties that may influence the transportation of Hg to the plants (Kabata-Pendias and Pendias, 1992). A direct relationship between Hg content in the soils and the concentration in the plants does not always exist (Molina et al., 2006).

On the other hand, plants assimilate organic and inorganic Hg through their radicle system and transport it to the foliage (Hanson et al., 1995). Temmerman et al., (2009) indicated that Hg absorption through the plant roots is proportional to the exposition concentration in the soil. Stamenkovic and Gustin (2009) suggested that Hg absorption in foliage occurs through the stomas, and the accumulation is positively correlated to Hg atmospheric concentration. Hg dissolved in water and incorporated into foliar tissue, is another other absorption mechanism of Hg (Rea et

al., 2004). Atmospheric contamination could be the cause for Hg accumulation in most plants (Patra and Sharma, 2000; Temmerman et al., 2009). The concentrations of Hg in the maize grain were of 0.04 to 0.9 mg/kg, which was a higher value than that reported (0.5 mg/kg) by the World Health Organization (2004) of, which is the maximum limit for Hg contaminated food and cannot be sold for human consumption. In the study region, the maize plant stalk and leaf are used as cattle forage. Sierra et al., (2009) mentioned that the European legislation establishes a limit of 0.1 mg/kg of Hg for animal feed. In this work, higher concentrations than this limit were found; e.g., for the stalk a 2.0 mg/kg and for leaf, an 8.2 mg/kg was discovered. Bioaccumulation of Hg in maize crops is an entrance source of Hg into the food chain, through foliage consumption by cattle or grains by humans (Rothenberg et al., 2007).

MERCURY IN RAINWATER

Total Hg concentrations in rainwater ranged from 1.5 to 339 $\mu\text{g l}^{-1}$, with a mean of 96 $\mu\text{g l}^{-1}$; corresponding to the insoluble fraction of 60 and 36 $\mu\text{g l}^{-1}$ to the soluble fraction (Patiño, 2011), (Table 4). The removal of a contaminant

from the atmosphere can happen through precipitation (wet deposition) or by dry deposition (Duce et al., 1983). This agrees with Kocman et al. (2011) since Hg combined with atmospheric particles represents over 50% of the total Hg in the deposition, and the remaining part is dissolved in rainwater. Duce and Hoffman (1976) concluded that particle removal by rain is approximately twice that of dry deposition. Guo et al. (2008) and Kocman et al. (2011) reported concentrations from 0.19 to 36 ng l⁻¹ and 3.15 to 24.4 ng l⁻¹ total Hg in the rainfall of mining zones, being lower those found in this study. This behavior is because samples were collected in 3 to 17 rain events, involving a higher accumulation of particulate material coming from the wind erosion. The sampling sites close to the mines and the wind regressive trajectories at 500 m of elevation, indicate that the air masses can drag the particles from the mine tailings, transporting and depositing them, thereby enriching the soils with this pollutant (Table 4). Kocman et al. (2011) observed an increase in Hg concentration in the rainfall samples due to the presence of HgS particles as result of eolian erosion of the surfaces that containing HgS in the area. Nevertheless, the particles (aerosols)

are not uniformly distributed in the atmosphere neither spatially nor temporally. This results in differences in Hg deposition, which could explain the variations in the Hg concentration in each rain event. The results in this study are in agreement with those reported by Guo et al. (2008) who found a positive correlation between precipitation and Hg concentration, establishing that in the rainy season, there is a greater wet deposition of Hg. The climatic and orographic conditions of the region favor changes in humidity, temperature, and solar radiation, causing high Hg volatilization in land systems (Gustin et al., 2003; Johnson et al., 2003), which could be contributing to the concentrations of atmospheric Hg.

MERCURY IN DRINKING WATER

The total Hg concentrations in drinking water ranged from 10 to 170 ng l⁻¹ (Table 4). These contents are below the maximum limit (0.001 mg l⁻¹) established by the NOM (1994) and WHO (2005) guideline value of 6 µg l⁻¹. This indicates that there is no problem in its use for human consumption in the studied area. Grandjean (2008) mentioned that in drinking water, the Hg concentrations are usually 5 to 100 ng l⁻¹, resulting to a minor public health

concern. But the presence of Hg in the water phase in the environment can lead to serious problems, e.g., the intoxication occurred at the Minamata Bay, Japan in 1953 as a result of the ingestion of fish containing MeHg coming from polluted waters (Harada, 1995; UNEP, 2002). Cabrera-Vique et al., (2007) suggested a strict vigilance of Hg content in drinking water given the alimentary habits of human beings, since they could be drinking great amounts of water.

The MeHg is the result of the methylation of the inorganic Hg by the microorganisms that are present in the freshwater and saltwater bodies; this MeHg produced is capable to enter the aquatic feeding chain and can be bio-accumulated within the fish muscular tissues (Mason et al., 2005).

MERCURY IN AIR

Measurements of total gaseous mercury (TGM) in the air ranges between 40 and 100 ng/m³ and the daily average during the 38 days of measuring was of 67 ng/m³ (Table 4). When comparing these concentrations with those reported by Grandjean (2008) in remote areas, 2 to 3 ng/m³ in winter allows observing the amount of volatilization that exists within the

study area. The WHO (2002) indicated that the Hg levels in air are in a range of 2 to 10 ng/m³. The Hg values of 40 to 100 ng/m³ obtained in this study indicates that the San Joaquin population is exposed to a high concentration of Hg in air, which may be a health hazard.

The gaseous elemental Hg is the main chemical Hg species released to the atmosphere. It is characterized for being very stable and having low water solubility; it volatilizes at room temperature and is relatively inert to chemical reactions with other atmospheric components. Its residence time is about one year. Therefore, once it is released to the atmosphere, it can be dispersed or transported to greater distances before being re-deposited in the terrestrial and aquatic ecosystems (Schroeder and Munthe, 1998).

The chemical reactions and the partitioning of Hg in gas and aqueous phases appear to determine Hg residence in the atmosphere and its deposition at various latitudes (Grandjean, 2008). Kocman et al. (2011) mentioned that the Hg space distribution depends on the wind conditions (direction, velocity). On the other hand, the emissions of Hg of the contaminated surfaces depend on the temperature. Boening (2000) mentioned that the environmental

variables such as pH, redox potential, water chemicals composition, soil type and geology affect Hg absorption.

AN APPROACH OF FLOW OF TOTAL MERCURY INTERACTIONS WITHIN THE TERRESTRIAL SYSTEMS

Fig. 4 shows a total Hg cycle of the four interconnected compartments: atmospheric, terrestrial, aquatic and biotic in the studied area of San Joaquin (Martinez-Trinidad et al., 2013). Each compartment is linked to others through series of biogeochemical cycles that control the speciation and flux of Hg and ultimately its toxicity (Krabbenhoft et al., 2005). This figure establishes the insertion dynamics of Hg in the different components. Hg concentrations in each component change substantially, and it can be seen that the greatest contamination source of Hg is found in the open air mining tailings, adding a deficient processing of HgS. These tailings are exposed to climatic conditions as well as air and water erosion, which transports Hg particles to the atmospheric and terrestrial landscape. This has repercussions on the concentration levels of Hg present in air, rainwater, forest soils, agricultural soils and sediments. The presence

of crops, especially maize, near the entrance of the mines is very common, and in some cases on the tailings. Thus the plant is exposed to Hg accumulating in the different structures (roots, stems, leaves, and grains).

CARBON SEQUESTRATION MAP

Table 5 shows the soil organic carbon (%) and total Hg content (mg/kg). The mean of agricultural soil was 2.5, sediments, 1.2; while in forest soils was 2.8. The highest Hg sequestration (2 to 10) is shown in the less altered areas with land use of forest soils (beige color in Fig 5). The lowest Hg sequestration (24 to 48) are located in the punctual tailing areas, surrounding a group of mines at Calabacillas, Santa Rita and La Lana areas (brown color in Fig. 5). Nevertheless, most of the studied area corresponds to a medium immobilization of Hg, ranging from 11 to 23 (pine nut color in Fig. 5). This area suggests that most of the regions' carbon sequestration potential decreased mainly due to land use changes and introduction of agricultural and mining activities in a region of forest natural vocation.

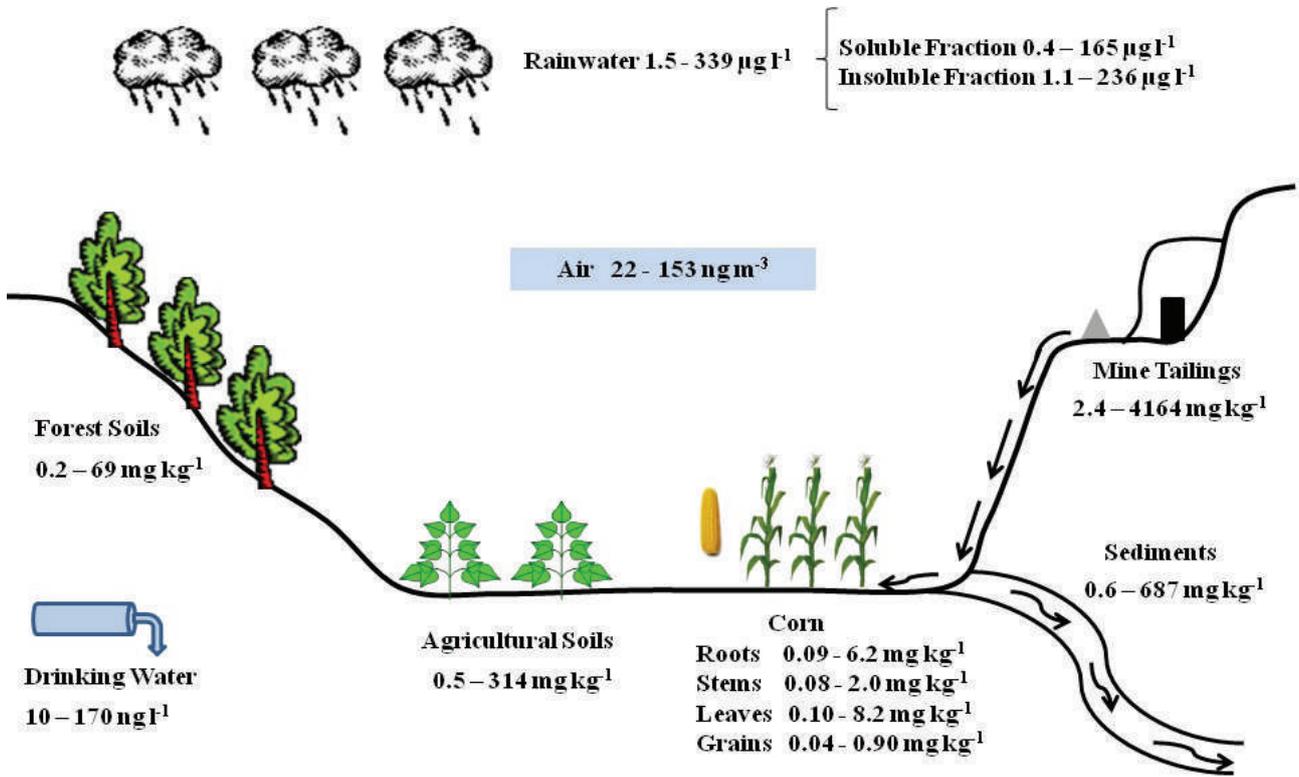


Figure 4. Distribution of total mercury content in the different compartments of the San Joaquin's mining region.

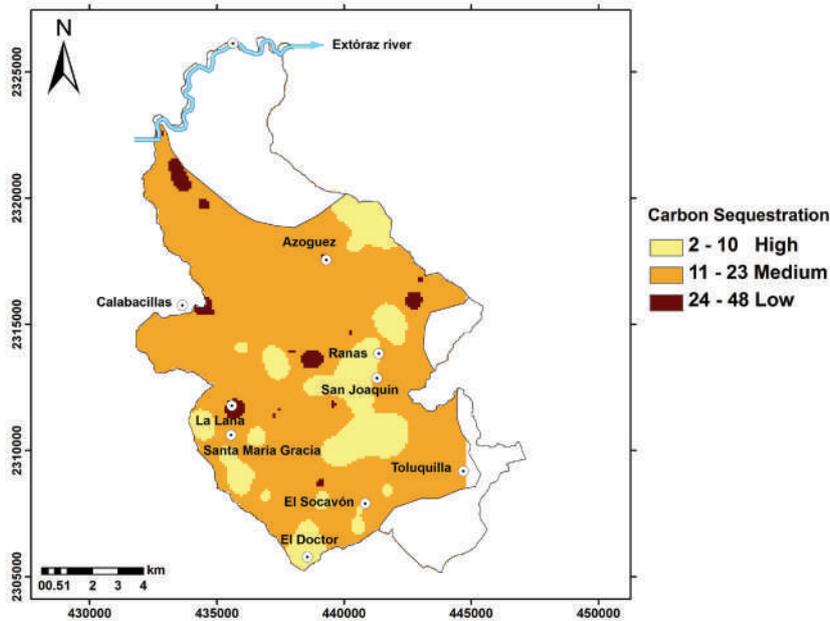


Figure 5. Carbon sequestration map.

CONCLUSIONS

The HgS mining exploitation in different periods for over 2000 years, have resulted in large amounts of Hg that have been released into the environment in Southern Sierra Gorda. The dispersion map of total Hg content shows that the highest Hg content in soils and sediments are associated to three groups of mining tailings in the study area (>250 mg/kg): At the center of Arroyo Grande micro-basin, the Calabacillas area, and in the surroundings of Ranas archaeological site. They represent three groups of several HgS mines with a mixture of Pre-Hispanic HgS mines and mines reused in the last century associated with a long period of exploitation.

A wide range of total Hg in agricultural soils is present, from 0.5 to 314 mg/kg; in addition, 46% of the soil samples showed Hg concentrations greater than the maximum limit established for agricultural use (23 mg/kg, according to NOM-2004). Hg in sediments presented a wide range as well, the highest content (687.0 mg/kg) corresponding to the maximum concentration in mining tailings (4164.0 mg/kg) where the management and a deficient processing of the HgS have been a constant situation. The results obtained suggest that, Hg in soils and

atmosphere are the origin of Hg accumulation in maize plants. The concentrations of Hg in the maize grain (0.04 to 0.9 mg/kg) were higher than the values reported by the WHO (2004) which establishes a limit of 0.1 and 0.5 mg/kg, respectively of Hg for animal feed. In this study higher concentrations were found than these limits: for the stalk a 2.0 mg/kg and for leaf an 8.2 mg/kg. Bioaccumulation of Hg in maize crops is an entrance source of Hg into the food chain, through foliage consumption by cattle or grains by humans. The maize plants close to the mines presented a higher concentration of total Hg than those located farther from them, while in the maize grain there was no a significant difference.

Total Hg concentrations found in San Joaquin rainwater ranged from 1.5 to 339 $\mu\text{g l}^{-1}$, with a 96 $\mu\text{g l}^{-1}$ mean. The atmospheric particles represented over 50% of the total Hg in the deposition, and the remaining part is dissolved in rainwater. The Hg levels were higher compared with rainwater concentrations in a pristine area of 1-2 $\mu\text{g l}^{-1}$ (Grandjean, 2008) or from 3 to 40 $\mu\text{g l}^{-1}$ in the Upper Midwest, USA (Glass and Sorensen, 1999). Only 17 drinking water samples were analyzed coming from different seasons and years, resulting in

a value below the accepted limit allowed by NOM-1994.

The levels of total Hg found in air showed an extremely high content, from 5.3 to 415.8 $\mu\text{g}/\text{m}^3$, taking into consideration the reference values of 1 $\mu\text{g}/\text{m}^3$ (WHO, 2002) and 0.3 $\mu\text{g}/\text{m}^3$ (UNEP, 2002). Due to continuous volatilization of Hg-enriched soils and HgS tailings, the inhabitants of the region keep a constant direct contact with Hg^o through inhalation. These emissions favor the metal accumulation within the structures as maize crops.

The land use changes, mostly from introduction of agricultural and mining activities, resulting to a decrease in the Hg immobilization through carbon sequestration. The previous results demonstrated a major public health concern for San Joaquín's population. The environment exhibits a constant exposure to the pollution of Hg coming from the open HgS tailings. A high percentage of agricultural soils are above the permitted limit. Therefore, a constant monitoring of Hg emissions is necessary in a long term to determine the scope and to detect trends that might be attributable to mining remains and accounting for baseline conditions that vary in space and time.

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