Article

J. Mex. Chem. Soc. **2006**, *50(2),* 57-63

ISSN 1870-249X

Analysis of Arsenic, Lead and Mercury in Farming Areas with Mining Contaminated Soils at Zacatecas, Mexico

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Recibido el 18 de noviembre del 2005; aceptado el 12 de mayo del 2006.

Abstract. This study was conducted in order to identify the concentration of heavy metals (As, Pb & Hg) in contaminated soil in the county of Guadalupe, Zacatecas in order to have elements for decision making by authorities and to identify exposition routes and further research activities to evaluate and reduce environmental and health risks in the site. Analysis were developed using EPA methods: SW 846: 3050B/6010B for arsenic and lead (FLAAS); and EPA SW 846: 7471A for total mercury (CVAAS). Compared to a recommended concentration in soil of 20 mg/kg for arsenic and mercury and 100 mg/kg for lead (PROFEPA Interim Criteria of 2001), the concentration of heavy metals was found to be up to 8 times higher for the metals analyzed. With this information a dispersion model was run in order to get iso-concentration curves and to establish risk zones. From the data, two hot spots were identified (towns of *La Zacatecana* and *Osiris*) where mercury, lead and arsenic total concentration is higher enough to justify future speciation studies to evaluate the risk to the population within the area.
Keyword: Heavy metals; soil contamination; mining wastes; dispersion model

Resumen. Este estudio se llevó a cabo para identificar las concentraciones de los metales pesados (As, Pb y Hg) en suelos contaminados del municipio de Guadalupe, Zacatecas, con el fin de obtener elementos de decisión para las autoridades referentes a la identificación de rutas de exposición y a la realización de investigaciones adicionales para la evaluación y reducción de los riesgos ambientales y de salud en la zona. Los análisis fueron desarrollados usando los procedimientos EPA: SW 846: 3050B/6010B para arsénico y plomo (FLAAS); y EPA SW 846: 7471A para el mercurio total (CVAAS). Comparado con la concentración recomendada en suelo de 20 mg/kg para arsénico y mercurio, y 100 mg/kg para plomo (Criterios de PROFEPA para 2001), se encontró que la concentración de los metales pesados es 8 veces mayor. Con esta información, se corrió un modelo de dispersión para obtener las curvas de isoconcentración y para establecer las zonas de riesgo. A partir de los datos, se identificaron dos puntos sobresalientes: las ciudades de *La Zacatecana* y *Osiris*, donde las concentraciones de mercurio, plomo y arsénico son suficientemente altas para justificar estudios de especiación adicionales para la evaluación del riesgo para la población en el área.
Palabras clave: metales pesados, contaminación de suelos, desechos de minería, modelo de dispersión.

Introduction

Some of the main human activities that release large amounts of heavy metals into the global environment include: fossil fuel combustion; metal mining and smelting; chemical production; wastes incineration; and mercury amalgamation for gold mining [1].

Amalgamation for silver extraction, commonly called *patio process*, was introduced into Latin America shortly after 1550, and consisted in adding elemental mercury to the silver ore in order to get a silver amalgam as the final product [2]. This process was made obsolete by the use of cyanide in the early 20th century. During the colonial period, the most important mining centers included the states of Zacatecas and Guanajuato in Mexico, and Potosí in Bolivia [3,4].

The loss of mercury into the environment due to silver production between 1580 and 1900 totaled 196,000 tonnes in Latin America and 61,380 tonnes in the Unites States. Between 60 and 65% of the mercury is thought to have been released into the air, and from 35 to 40% into the soil and water [2].

The state of Zacatecas represents the most important contributor to silver production in Mexico, and amalgamation was used extensively throughout the period from 1570 to 1820. Most of the heavy metals lost via amalgamation were carried by rivers and deposited in the plain areas of the Zacatecan valley in the Guadalupe County [1,5,6]. Most of these areas are currently used for crop farming since there are no restrictions imposed by the Mexican authorities.

The Commission of Environmental Cooperation of North America (CEC) conducted a preliminary study to evaluate contamination from arsenic, lead, mercury and six other metals in soil and crops of the mining area of Zacatecas, Mexico. As result, the concentration of mercury and lead found was up to 10 times higher than Ontario's recommended levels for agricultural soil, but no clear conclusions on health and environmental risk were drawn [6 ,7]

Levels of lead in blood were studied by the Autonomous University of Zacatecas (UAZ) in the population of *La Zacatecana*. This study concluded that there was no evidence of health effects caused by levels of lead found in soil [8].

Several studies have shown different degrees of metal uptake by crops farmed in contaminated soils. This represents a health hazard for human consumption of those crops or cattle fed with crops or plants with high content of metals [9-13].

All the research previously conducted in the site was developed for specific limited purposes and were not designed on a systematic basis in order to evaluate the risk to health or environment of the crop-farming activities on the contaminated sites in the Guadalupe County in the state of Zacatecas, Mexico.

This study was devised, considering a systematic sampling design in a carefully delimited research area and considering quality control systems, in order to identify the concentration of the three most hazardous metals (arsenic, lead and mercury according to its concentration) identified as priority in agricultural soil in the Guadalupe County in the state of Zacatecas, Mexico and was carried out from November 2003 to March 2004.

Methods

Description of the Area

The site selected for this study is located in the natural floodlands of the Zacatecan valley, and covers an area of 180 sq km in the Guadalupe County. It is located within the coordinates 102º12´ to 102º55´ West (Longitude) and 22º37´ to 23º15´ North (Latitude) and is bounded by the towns of *San Joaquin* and *Tacoaleche* to the south and north respectively, and the mountains of *Zacatecas* and *Veta Grande* to the east and west respectively. This area is rich in natural deposits of arsenic and lead and enjoys major agricultural and cattle-raising activities because of the floods coming from the mountains and the influence of the *Plata* River, which flows into the *La Zacatecana* basin. (Table 1 and Figure 1) [14,15].

Soil sampling

The number of samples n was calculated with the formula: $n = [Za^2 * p * (1-p)] / d^2$ as established by McBean [16]. For this, a confidence of 95% (1-a) was established and a Za of 1.96 was obtained. From a pilot sampling programme in Zacatecas [6, 8], it was observed that 5% of the samples had a higher concentration than the recommended value of 20 mg/kg for arsenic and mercury, which represent a proportion value p of 0.05; it was also established a precision factor d of 8.5% for this study, with this, the number of samples n was calculated as 25.26 samples. From the previous calculation, twenty six soil samples (identified as G-1 to G-26) were collected in a regular pattern on the points on a 2 X 3 km grid covering a distance of 20 km at the south-north direction, and a distance of 9 km in the east-west direction, within the study area (Table 1).

This pattern was chosen in order to have a complete coverage of the area and to reduce errors in the interpolation modeling of data (IDW interpolation model) [17, 18]. The grid sampling program was focused on farm fields where crops were being grown in order to provide information on potential crops uptake and human and animal exposure resulting from contaminated soils.

Soil samples were collected at a depth of 0-15 cm in order to identify the surface contamination profile in terms of arsenic, lead and mercury uptake by crops farmed in the area. This depth was selected since it represents the normal agricultural tillage depth [19,20].

Table 1. Sampling sites and geographic coordinates for arsenic, lead and total mercury analysis in the County of Guadalupe-Zacatecas

Soil Sample	Latitude, longitude & altitude	Soil sample	Latitude, longitude & altitude
G-1	N22-42-36.96, W102-31-21.24 A.S.L. 2268.7 m	G-14	N22-46-03.86, W102-29-53.47 A.S.L. 2253.45 m
G-2	N22-43-32.96, W102-30-49.06 A.S.L. 2257.8 m	G-15	N22-47-19.60, W102-29-15.85 A.S.L. 2252.24 m
G-3	N22-44-26.15, W102-29-36.04 A.S.E. 2237 m	G-16	N22-47-24.72, W102-25-58.56 A.S.L. 2154.9 m
G-4	N22-43-07.01, W102-29-59.79 A.S.L. 2235.8 m	G-17	N22-47-22.45, W102-27-37.41 A.S.L. 2197.4 m
G-5	N22-43-38.74, W102-29-29.58 A.S.L. 2219.5 m	G-18	N22-45-42.13, W102-26-05.33 A.S.L. 2159.95 m
G-6	N22-42-51.62, W102-28-10.16 A.S.L. 2201.9 m	G-19	N22-45-06.43, W102-27-09.86 A.S.L. 2174.6 m
G-7	N22-42-13.40, W102-27-46.98 A.S.L. 2215.6 m	G-20	N22-46-56.91, W102-28-15.22 A.S.L. 2220.5 m
G-8	N22-44-36.94, W102-28-18.04 A.S.L. 2194.0 m	G-21	N22-40-24.86, W102-32-13.35 A.S.L. 2308.0 m
G-9	N22-44-14.22, W102-28-27.84 A.S.L. 2190.3 m	G-22	N22-41-18.32, W102-31-31.72 A.S.L. 2291.4 m
G-10	N22-44-47.27, W102-25-23.13 A.S.L. 2184.6 m	G-23	N22-39-56.14, W102-29-40.97 A.S.L. 2256 m
G-11	N22-44-40.92, W102-26-58.50 A.S.L. 2185.6 m	G-24	N22-40-11.13, W102-28-50.41 A.S.L. 2243 m
G-12	N22-46-03.28, W102-27-27.20 A.S.L. 2175.3 m	G-25	N22-41-13, W102-29-52.92 A.S.L. 2255 m
G-13	N22-46-16.05, W102-28-32.97 A.S.L. 2213.4 m	G-26	N22-48-38.43, W102-29-18.86 A.S.L. 2252.3 m

A.S.L. = Above Sea Level
na = Not available
Samples were taken at 0-15 cm depth
Sample size was calculated by using a significance (Za) of 1.96 (q = 95%); proportion (p) of 5%; and precision (d) of 8%: n = (Za2*p*q) / d2

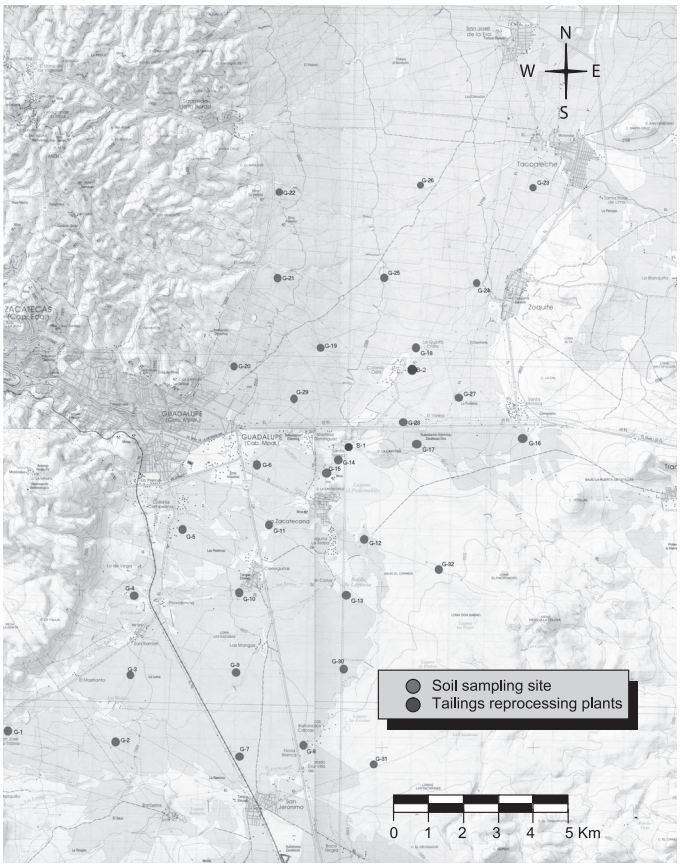


Fig. 1. Sampling of soil in Guadalupe, Zacatecas

A topographic map was used to get as close as possible to the sampling sites identified within the grid (Figure 1). Sampling preference was given to areas under active agricultural cultivation but in cases in which there were no fields under cultivation located on the sampling site, the area showing the least amount of visual disturbance was selected for sample collection. Coordinates of the sampling sites were verified in a Global Positioning System as well as the altitude in meters above sea level.

A stainless steel hand trowel was used to remove any soil that might have come in contact with the pick or shovel and to prepare a vertical side-wall for sampling. Soil samples were placed in a stainless steel bowl and gently disaggregated to ensure that a representative sample was collected from the sampling point, and placed directly into a previously labeled, polyethylene plastic bag. Upon completion of the sampling activities, all sampling equipment was thoroughly scrubbed with bottled water and sprayed with methanol to remove any particles that might have remained after the cleaning process with water [17].

At the end of each day, sample bags were double-wrapped, sealed in new plastic bags and stored in a container with ice until they could be transported to the laboratory.

Analytical methods

Samples were dried, open to the air, for 48 h or more if necessary, crushed in a mortar and then passed through a 2 mm mesh. Arsenic analysis was developed by Hydride Generation Flame Atomic Absorption Spectrometry (HGFLAAS); total mercury was analyzed by Cold Vapor Atomic Absorption Spectrometry (CVAAS); and lead was analyzed by Flame Atomic Absorption Spectrometry (FLAAS). For mercury and lead analysis, a microwave digestion was applied using 3 ml of concentrated HNO_3 and 10 ml of de-ionized water (Type II) for 0.5 gm of sample. The mixture was heated to 121 °C and 15 lb of pressure for 15 minutes and cooled, then diluted to a volume of 25 ml with de-ionized water; 10 ml of concentrated H_2SO_4 were added before analysis. After this, a lead analysis was carried out by FLAAS. In the case of mercury, a few drops of saturated $KMnO_4$ solution were added to the previous mixture, and 6 ml of sodium chloride - hydroxylamine sulfate solution were added to reduce the excess permanganate, in accordance with the analytical method: EPA SW 846: 7471A. For arsenic analysis, the same methodology was used for microwave digestion up to the addition of H_2SO_4; then 5 ml of concentrated HCl were added as the final step, in accordance with the analytical method: EPA SW 846: 3050B/6010B [21]. Results represent the mean of three replicate analyses, expressed as milligrams of contaminant per kilogram of dry soil. Recommended concentrations for agricultural land use, established by the Federal Office for Environmental Protection (PROFEPA) in 2001 as 20 mg/kg for arsenic and mercury and 100 mg/kg for lead, were used in this study as reference.

Laboratory quality assurance and quality control

Laboratory analysis was developed by triplicate in a 3110 Perkin Elmer Atomic Absorption Spectrometer with a AS-90 self-sampler and a AS-60 burner. Aldrich certified standards were used for arsenic, mercury and lead. Mercury and arsenic analysis were developed by Hydride Generation Atomic Absorption Spectrophotometry with a detection limit of 0.095 mg/L for arsenic and 0.468 mg/L for mercury. In case or lead, analysis was developed by Flame Atomic Absorption Spectrophotometry with a detection limit of 0.19 mg/L. Labware and reagents were used in accordance with the analytical method: EPA SW 846: 3050B/6010B [21].

On the other hand, a duplicate of the samples were analyzed by the Commission of Environmental Cooperation in a certified laboratory in Ontario, using the same analytical protocols and equivalent equipment. The Spearman rank correlation test was used to compare the results of both laboratories showing a significant relationship for all contaminants (correlation values: As = 0.8821, Hg = 0.7106, Pb = 0.9683) [16].

IDW interpolation method

An Inverse Distance Weighted (IDW) Interpolation algorithm (ARC GIS 8.3, 2003) was used to establish iso-concentration

zones with data obtained from soil-sample analysis (G-1 to G-26) because of the high variability of the data obtained. The grid cell values were estimated by averaging the values of the sample data points in the vicinity of each cell and assuming that each sample point has a local influence that diminishes with distance (the points closer to the processing cell are more heavily weighted than those farther away). A power of two was established to emphasize on the nearest points and give more detail to the resulting surface (make it less smooth).

Correlation of data

The results of the concentration of arsenic, lead and mercury in the soil were compared by testing the level of correlation using the Spearman rank correlation test (where n=26 and $p<0.05$) in order to identify a common source of contamination for them [16].

Results and Discussion

This study identified arsenic, lead and mercury contamination in agricultural soil in the Guadalupe County in the state of Zacatecas. As result of the disperssion modelation developed, the main source of heavy metal contamination is related to old mining activities carried on in the surrounding area of *Osiris* and *La Zacatecana*, as seen in Figure 1.

Manzanares [8] analyzed lead and mercury in blood of people at *La Zacatecana*, finding normal levels in the sampled peopled. This could be explained by assuming that contaminants might have been stabilized, probably due to weather conditions, into a more stable chemical form or by interaction with other elements and chemical species in the soil as seen in previous research in other parts of the world [22-24]. In spite of that, there are two exposition routes of high relevance in the site: the respiratory intake of particles and dust as well as deposition in crops for cattle feeding.

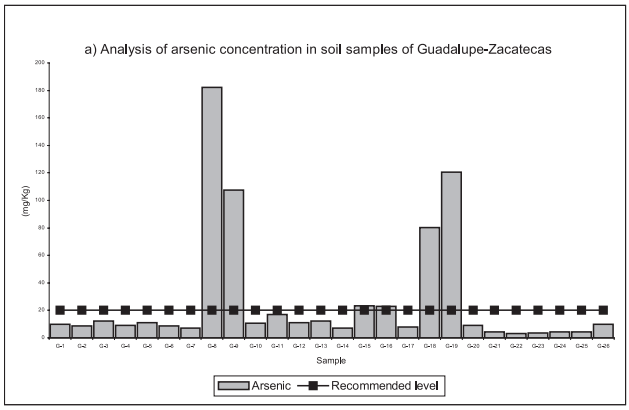
Analysis of arsenic, lead and mercury concentration in soil samples is reported in Table 2 and Figure 2.

According to the recommended concentrations for agricultural land use, the highest concentration of arsenic, lead and mercury in soil was found in samples identified as G-8; G-9; G-18 & G-19. However, samples identified as G-15 and G-16 only showed higher concentration of arsenic than recommended by Mexican authorities (PROFEPA Interim Criteria). Concentration of the contaminants in soil exceeded recommended levels by 15% to 812% for arsenic, 333% to 768% for lead, and 82% to 892% for mercury. Rankings were signifi-

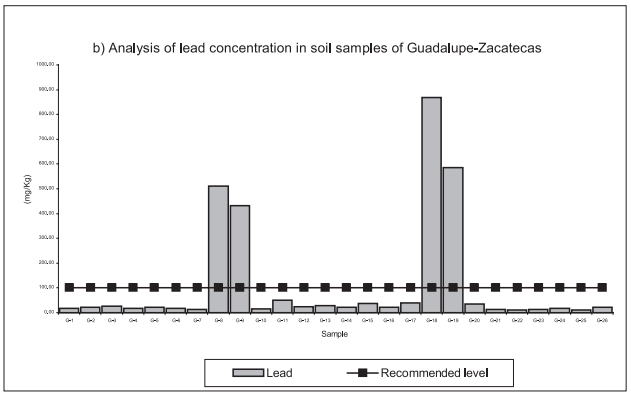
Table 2. Analysis for arsenic, lead and mercury in soil samples collected in Zacatecas.

Sample*	pH	Arsenic (mg/Kg)	Mercury (mg/Kg)	Lead (mg/Kg)
G-1	7.35	9.82 ± 0.15	0.25 ± 0.01	17.29 ± 0.20
G-2	7.41	8.64 ± 0.07	0.70 ± 0.05	22.51 ± 0.46
G-3	6.87	12.21 ± 0.38	0.76 ± 0.03	27.22 ± 1.20
G-4	7.14	9.28 ± 0.55	0.25 ± 0.01	17.34 ± 0.33
G-5	7.87	11.00 ± 0.27	0.31 ± 0.09	22.13 ± 0.51
G-6	8.26	8.62 ± 0.42	0.86 ± 0.02	18.41 ± 0.20
G-7	6.91	7.00 ± 0.09	0.59 ± 0.06	14.04 ± 0.05
G-8	7.62	182.41 ± 7.87	36.41 ± 0.53	511.97 ± 16.44
G-9	7.45	107.65 ± 15.36	32.11 ± 1.08	432.90 ± 4.92
G-10	6.66	10.49 ± 0.64	0.20 ± 0.01	15.58 ± 0.07
G-11	7.34	17.08 ± 0.78	3.41 ± 0.08	51.17 ± 1.12
G-12	6.84	11.22 ± 0.61	0.64 ± 0.08	23.78 ± 3.09
G-13	7.36	12.25 ± 0.34	0.49 ± 0.03	29.44 ± 1.07
G-14	7.31	7.24 ± 0.65	0.54 ± 0.10	21.77 ± 2.90
G-15	7.10	23.26 ± 2.57	0.74 ± 0.03	36.72 ± 4.66
G-16	7.72	23.03 ± 0.95	0.75 ± 0.03	21.61 ± 0.32
G-17	6.84	7.79 ± 0.22	0.86 ± 0.03	38.94 ± 15.60
G-18	7.71	80.32 ± 9.07	198.35 ± 8.28	868.13 ± 22.17
G-19	7.51	120.73 ± 4.89	90.78 ± 8.14	586.23 ± 22.17
G-20	7.02	8.97 ± 0.07	1.77 ± 0.11	34.59 ± 0.62
G-21	6.99	4.20 ± 0.08	0.07 ± 0.01	14.00 ± 038
G-22	6.57	3.30 ± 0.05	0.08 ± 0.01	11.00 ± 0.59
G-23	7.90	3.60 ± 0.03	0.09 ± 0.01	14.00 ± 0.41
G-24	6.94	4.30 ± 0.07	0.14 ± 0.02	17.00 ± 0.34
G-25	6.88	4.20 ± 0.07	0.05 ± 0.01	10.00 ± 0.56
G-26	7.99	10.00 ± 0.21	0.57 ± 0.09	23.00 ± 0.33

* Results shown as an average for three analysis of each sample



Analyses expressed as mean of three repetitions



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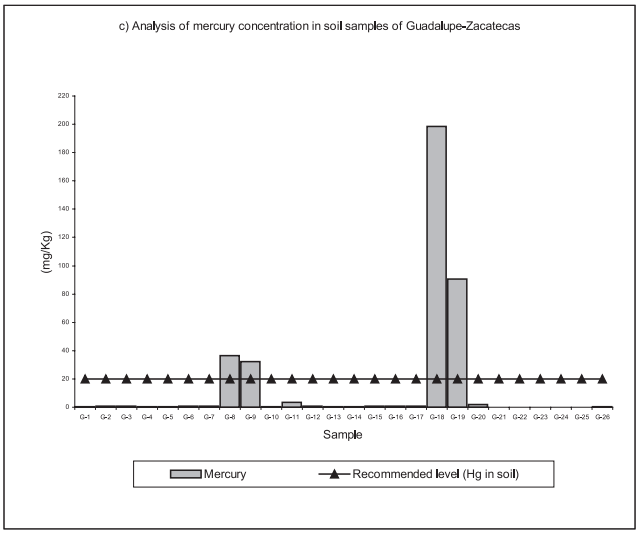


Analyses expressed as mean of three repetitions

Fig. 2. Analysis of concentration of arsenic, lead and mercury in soil samples of Guadalupe, Zacatecas

cantly correlated for arsenic, lead and mercury concentrations in the soil by using the Spearman rank correlation test as shown in Figure 2.

A significant relationship was detected for all contaminants in the soil, suggesting a common source of contamination (correlation values: As-Pb = 0.79, As-Hg = 0.68, Pb-Hg = 0.86), which confirms the theory that old mining activities are the main source of contamination in the site. It is important to emphasize that two abandoned tailing-reprocessing plants (activity developed since 1920) for silver extraction were identified in the area where high concentration of contaminants was found (within a range of less than 500 meters from the hot spots).

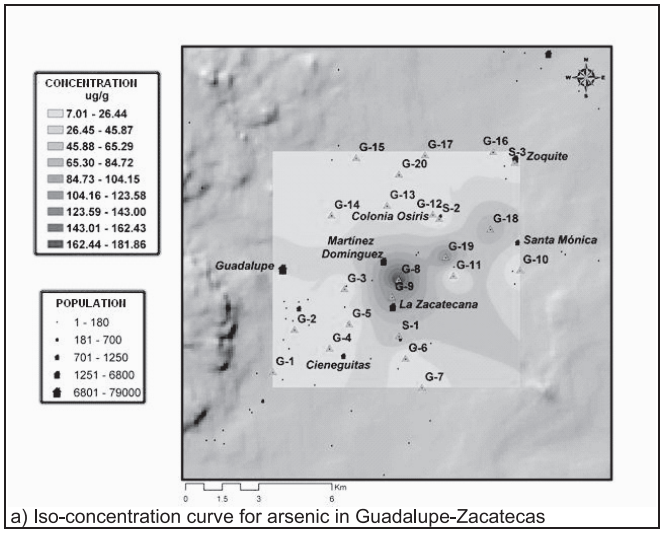
La Zacatecana and *Osiris*, which had the highest concentration of heavy metals in soil and mercury in crops, have intense farming activities for cattle feed, thus contaminated soil deposited in the crops might be ingested by cattle. These activities in the area increase the risk since dust particles might be ingested by hand-mouth mechanism or inhaled by the population, particularly children, which represent an important exposition route. More research has to be developed on crops uptake since few samples were taken and considering that scientific literature reports that the presence of other elements or chemical compounds in the soil such as P, Zn, Cu, organic matter, or $CaCO_3$ might influence the values of the plant/soil transfer coefficients of heavy metal ions to crops by synergistic effects or even by soil tillage [22-24].

Results from IDW interpolation model are shown in Figure 3. According to the interpolation method, *La Zacatecana, Martínez Domínguez, La Purísima* and *El Vivero* populations showed higher risk of arsenic, lead and mercury contamination in the soil. Crops farming activities are carried on in vicinity of these towns and have a potential risk for mercury deposition by dust. The two sites with highest concentrations of arsenic, lead and mercury are located at an altitude of 2167 m and 2192 m above sea level, which is below the medium altitude of the study area (2223 m above sea level). This confirms the influence of the flooding pattern in dispersion of contaminants as identified in previous research [6].

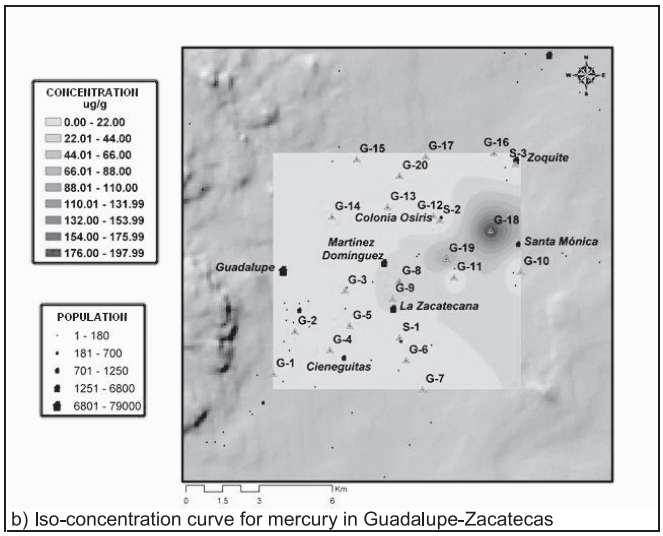
Conclusions

The importance of this research study is to have a scientific evaluation of heavy metal contamination in a mining impacted zone of the Guadalupe County in Zacatecas, Mexico, including arsenic, lead and mercury in soil samples. Considering the intense agricultural practices in the area, a risk assessment related to contaminants uptake in crops used for human and cattle consumption might be developed. The results indicate that the highest concentration of contaminants in soil is found in the northern part of *El Pedernalillo* basin and in the vicinity of the towns of *El Vivero* and *La Purísima,* which agrees with previous results obtained in *El Pedernalillo* basin [6].

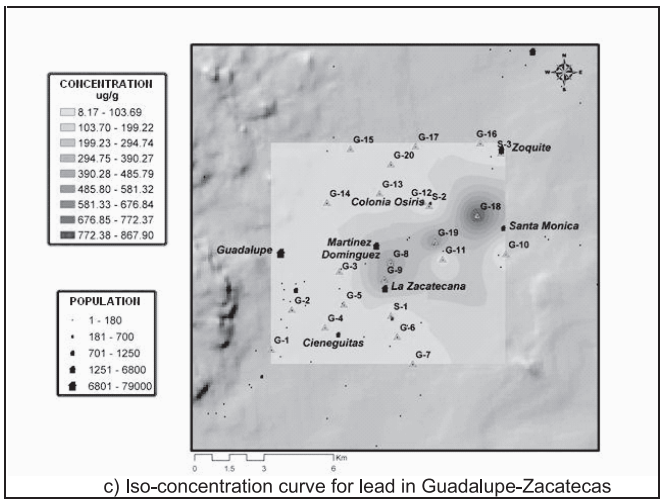
A significant correlation of concentration of arsenic, lead and mercury in soil was found which let us to consider the idea of a common source of the contaminants (old mining activities). It is important to say that the scope of this study is not to identify the contribution of the different sources of tailing contamination in the area. Mining activities (using cianuration) are still being developed in different areas of the State of Zacatecas. Tailing reprocessing activities are also still being developed.



a) Iso-concentration curve for arsenic in Guadalupe-Zacatecas



b) Iso-concentration curve for mercury in Guadalupe-Zacatecas



c) Iso-concentration curve for lead in Guadalupe-Zacatecas

Fig. 3. Iso-concentration curves for arsenic, lead and mercury in Guadalupe-Zacatecas as modeled by the Inverse Distance Weighted interpolation model using samples G-1 to G-20.

Considering the concentration levels found for arsenic, lead and mercury in soils of two areas of the Guadalupe County, mitigation activities might include covering of contaminated areas where dust is generated with native plants, since respiratory/ingestion process is the most important source of access to the body. In a second stage of this study, speciation of chemicals in soil is being developed to evaluate the available fraction in *La Zacatecana* and *Osiris*. Determination of lixiviation rates under different conditions in reprocessed tailings might be developed. Additionally, future studies should also include sampling stages throughout different seasons of the year to identify the influence of weather conditions in soil and crop concentration of contaminants. Interaction of these factors should be considered in order to develop an environmental risk assessment by considering the resulting effects to air, soil, water and biota.

Acknowledgments

The authors would like to thank the State Office of SEMARNAT in Zacatecas, the Government of Guadalupe County and the SMOC Task Force of the Commission for Environmental Cooperation of North America for the technical support provided throughout sampling activities.

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