MC/4030-01-02 PROJECT SEQUENTIAL CHEMICAL SPECIATION OF MERCURY IN CONTAMINATED SITES OF MEXICO

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Content

EXECUTIVE SUMMARY

The aim of this project is to develop of an integrated and efficient and cost-effective methodology for identifying the mercury species distributed according to groups of solubility (water-soluble, weak acids, organic acids, and aqua-regia) to be applied to characteristic soils of Mexico which are contaminated with mining or industrial wastes.

According to the "Mexican mercury diagnosis" prepared by the Mexican National Institute of Ecology of SEMARNAT in 2000, it was estimated that the major industrial sectors which contribute to emissions of mercury to the environment are mining, secondary mercury production, chlor-alkali, thermoelectric sector, as well as the manufacture of fluorescent lamps. Among these, the most important states of the country according to mercury production are: Hidalgo, Queretaro, Guanajuato, Veracruz, Zacatecas, Nuevo Leon, Tamaulipas and Chihuahua.

Sites with mining background were selected for the states of Hidalgo (Pachuca and Zimapan), Guanajuato (Guanajuato), Queretaro (San Joaquin and Pinal de Amoles), Zacatecas (Osiris and La Zacatecana), Tamaulipas (San Carlos and San Nicolas) and Chihuahua (Avalos and San Gabriel) based on a review of the various mining districts existing in each state, according to the following criteria:

- Deposits of silver and gold exploitation in the colonial period through amalgamation
- Production data (exploitation of mineral)
- Population currently exposed at sites under study
- Previous studies

Sites with industrial background were selected for the states of Guanajuato (Salamanca), Nuevo Leon (Monterrey and Huajuco) and Veracruz (Tuxpan and Coatzacoalcos) based on a review of the various industrial reports.

A national meeting was held with assistants of the local government, academia and NGOs. The proposal of sites was showed and comments obtained according to local concerns and data generated by the states.

After the selection of sites was approved, based on the Mexican Standard NMX-AA-132-SCFI-2006, which sets out the different types of environmental sampling, it was decided to take surface soil samples (0 to 15 cm) due to the fact that this fraction can be ingested by children or adults with low standards of hygiene or when removed by the wind for further inhalation by the people in surrounding areas.

The methodology for sampling of contaminated soil was based on a systematic sampling procedure as reported by the *Guidance on Sampling and Analytical Methods for Use at Contaminated Sites*, Ontario, Canada 1996, according to which it is drawn a grid on the study area.

Once the sampling work was finished, analysis of the total concentration of mercury was developed. Additionally to mercury, it was decided to quantify the total concentration of lead and silver since these metals are associated with the presence of mercury in the waste of amalgamation of gold and silver.

The total mercury concentration was analyzed by Cold Vapor Atomic Absorption Spectrophotometry (CVAAS) with microwave digestion according to EPA SW 846 method 7471B. Laboratory analysis was carried out in triplicate samples in a PerkinElmer Atomic Absorption Spectrometer model 3110 with an ACE-90 autosampler and an ACE-60 burner. For calibration of the equipment, certified Aldrich-brand mercury standards were used. The technique used for the analysis was hydride-generation atomic absorption spectrophotometry with a detection limit for mercury of 0.31 mg/L. Laboratory material and reagents were used as specified in EPA SW 846 method 3050B.

The mercury speciation method developed in this study allows the identification of mercury species in contaminated soils using different extraction media, and identifying the following species: water soluble, elemental (amalgamated) mercury, exchangeable, strongly bounded (mineralized and Fe and Mn oxy-hydroxides), organic mercury, mercury sulfides and residual. From these, some represent a potential risk due to their toxicity and ability to mobilize in the environment and to be assimilated by organisms: water soluble, exchangeable and organic species.

Sequential chemical speciation of mercury was developed for samples with a total concentration higher than the reported limit of 23 mg/kg of mercury (NOM-147-SEMARNAT/SSA1-2004). Speciation was developed for the towns of Pachuca (Hidalgo), The results indicate that the highest concentration of mercury on these sites mostly corresponds to very stable chemical species with low mobility in air: mercury sulfide and elemental (in the form of amalgam). Soluble species were found in very low proportions with respect to the regulations for contaminated soils in the country.

From the results obtained, it is estimated that the potential risk is low, due to the high stability of the mercury species in the sites under study. However, this research is only a basis for carrying out bio-availability studies into the different species, and for evaluating mercury absorption by plants and crops in the agricultural lands of the towns of Osiris and La Zacatecana for the State of Zacatecas, Pachuca for the State of Hidalgo, Guanajuato for the State of Guanajuato and San Joaquin and Pinal de Amoles for the State of Queretaro. For this reason, a study is being conducted in order to evaluate the exposure routes and, with these results, to prepare an assessment of possible risks to vulnerable populations, so that adequate measures for mitigating present risks can be proposed to the corresponding authorities for their decision-making.

In the case of Queretaro, high concentrations of mercury, mainly in the elemental fraction, were found due to the presence of natural deposits. These species have low potential for mobility; however, additional studies should be developed to identify background concentrations in the area and identify sites that may pose potential risks.

With regard to industrial sites, concentration of mercury was found in smaller values than reported by official regulation in Mexico. These findings should be completed with studies in other compartments such as air and water to discard pollution in any of these.

In addition, the study considered the analysis of the total concentration of lead since it is associated with the silver ore, and mercury through its use in ancient mining processes. The results showed the presence of lead in high concentrations in many of the sites under study. For this reason, speciation of this metal might be developed, as well as a risk assessment.

It is recommended to contain contaminated soil that represent a potential source of risk through the use of ground cover, paving the streets, backyards and / or inside soil in houses located on mining wastes in order to avoid dispersion and exposure of population.

On the other hand, campaigns aimed at improving the hygienic habits of the residents of communities with high concentrations of mercury to avoid ingestion should be developed. Hand-Mouth mechanism among children should be controlled.

Results were presented in a Latin-American workshop where the method was showed to assistants from other countries with similar problems related to mercury contamination in order to share experiences and to evaluate the possibility of using the speciation method for hot-spots identification.

1.0 INTRODUCTION

1.1 Antecedents

Nriagu (1979) identified, through literature and existing models that the levels of mercury in the atmosphere have increased considerably since the start of the industrial age.

Additionally, mercury has been found in the various environment compartments and in food products (particularly in the different species of fish) in all regions of the world at levels that adversely affect humans and wildlife. Man's activity has increased cases of exposure through an improper disposal of waste mercury in soil, sediments and water bodies, the generation of large volumes of mining wastes and contaminated soils in industrial areas. This has led to the presence of mercury, even in the most remote regions where there are minimal emissions such as the Arctic, mainly due to atmospheric transcontinental transport.

Mercury is persistent and once released, remains in the atmosphere, where it circulates between air, water, sediment, soil and biota in its various forms. Current emissions are added to background levels of mercury in the world, which remain mobilized, deposited in the soil and water and mobilized again. The manner in which mercury is released varies depending on the types of sources that generate it and other factors.

The majority of air emissions are in the form of elemental mercury (gas), which is transported to other regions. The remaining emissions are produced in the form of inorganic mercury (such as mercuric chloride) or in the form of particles. These forms have a life span shorter in the atmosphere and can be deposited on land or water to distances between 100 and 1,000 miles from its original source (Gaona, 2004). Once deposited, mercury can change primarily by the action of microorganisms into methylmercury (Lovley, 2000), which has the ability to bioaccumulate and concentrate in food chains (biomagnification), especially in the aquatic food chain (fish and marine mammals).

Mercury and its compounds are highly toxic, especially to the developing nervous system. The level of toxicity in humans and other organisms varies depending on the chemical form, quantity, the route of exposure and vulnerability of the person exposed. Humans can be exposed to mercury from various sources including the consumption of fish, occupational and household uses, dental amalgams and mercury-containing foods. There are also some ecosystems and wildlife populations that are particularly vulnerable to mercury, including the major predators of aquatic food chains (such as birds and mammals that feed on fish), arctic ecosystems, wetlands, tropical ecosystems and soil microbial communities.

The mercury pollution has significant effects on the local, national, regional and global levels. These effects can be addressed through a package of measures in each of those levels, setting targets for reducing emissions. Numerous actions have been taken in Europe, North America and other countries getting a reduction at certain degree mercury releases. However, inventories are still incomplete in these regions and the rest of the world, due to the lack of specific field information to integrate a network of reliable data that would strengthen the existing dispersion models.

1.2 Chemistry of mercury

As part of their physical-chemical properties, mercury has an atomic number of 80, atomic weight of 200.59, melting temperature of -38.87ºC and a boiling temperature of 356.58ºC. Elemental mercury is a heavy metal with a silvery-white color, it is liquid under normal temperature and pressure. The vapor pressure of mercury is dependent on temperature, steaming rapidly under normal conditions. A 20 ºC its specific gravity is 13,456, air saturated at 20°C contains about 15 mg/m^3, 300 times greater than the allowed occupational permissible limit (0.05 mg/m^3) or 1000 times higher than the level of the allowable environmental exposure 0.015 mg/m^3 (Nriagu, 1979; WHO, 1978). Most of the mercury that is found in the atmosphere is elemental mercury in vapor form.

The mercury is extracted as mercury sulfide from cinnabar ore mine. Throughout history, deposits of cinnabar ore have been the source for commercial extraction of metallic mercury. The metal chemical form is refined from ore warming to temperatures exceeding 540 ºC. In this way, mercury is vaporized and, when the vapors are cooled, liquid mercury is formed. HgS decomposes between 363-562 ºC (EC, 2002).

Mercury has seven stable isotopes (196, 198, 199, 200, 201, 202, 204) and four unstable radioactive isotopes (194, 195, 197, 203). It can exist in three oxidation states: Hg^0 (metal), Hg^{2+} (mercurous) and Hg^{2+} (mercuric), having different properties between them. Mercuric and mercurous forms can form a large number of organic and inorganic compounds, but the mercurous forms are not stable under conventional environmental conditions, 12 hours light / dark, temperature of 22 ± 1ºC and 50% humidity (U.S. EPA, 1997).

Most of the mercury in the environment (excluding the amount present in the atmosphere) is in the form of inorganic and organomercuric compounds. The latter are defined by the presence of a covalent link C-H. Thus, mercury compounds most common in environmental conditions are: inorganic species of Hg^{2+}, $HgCl_2$, $Hg(OH)_2$ and HgS; and organic species of methyl mercury, methylmercury chloride (CH_3HgCl), and in smaller proportions methylmercury hydroxide (CH_3HgOH); and dimethyl and phenyl-mercury (Lee, 2000).

Mercury compounds tend to last in aqueous phase as coupled molecules, which is confirmed by reported solubility data. Most of the organomercuric compounds are not soluble and do not react with acids, or weak bases, due to low affinity of mercury to oxygen bonded to carbon. The CH_3HgOH is highly soluble due to the large capacity of the hydroxyl group to form hydrogen bridges. The inorganic mercury salts have a wide range of solubility. For example, the $HgCl_2$ has a high solubility in water, while HgS is practically insoluble, due to the high affinity of mercury for sulfur (Lee, 2000).

The mercury species have also been classified by Lindqvist et al. (1991) as shown in the following table:

Table 1. Classification of mercury species

Volatile species	Hg^0 y $(CH_3)_2Hg$
Reactive species	Hg^{2+}, HgX^+ , HgX_2 ,HgX^{3-} , y HgX_4^{2-} (where X=OH^-, Cl^- o Br^-), HgO in aerosol particles and Hg^{2+} complexed to organic matter
Non reactive species	CH_3Hg^+ , CH_3HgCl, CH_3HgOH , $Hg(CN)_2$, HgS & Hg^{2+} bonded S in humus.

Source: Lovley, 2000

1.3 Cycle of mercury

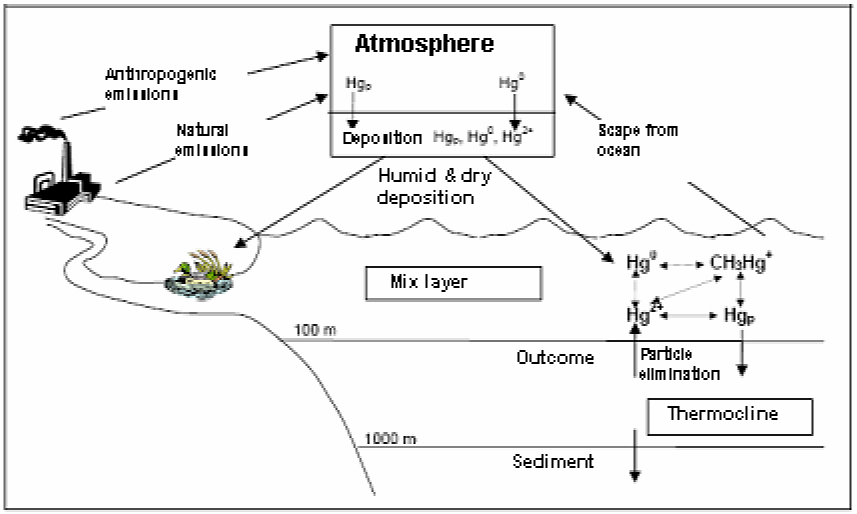
It is defined as a cycle of mercury to the continuous flow of this element in the atmosphere, soil and water, based on the behavior of Hg in the different compartments, in the involved chemical reactions, transport and their final destination. At any point on the planet, the amount of mercury is a function of:

- The global natural cycle.
- The global cycle altered by human activity.
- Regional cycles of mercury.
- Local cycles of mercury.

In spite of the recent advances for a general understanding about the cycle of global mercury and the impact of anthropogenic sources on it, it is very difficult to establish the flows at global, regional or scale of emissions and processes of mercury deposition.

It is important to understand that atmospheric deposition of mercury (flow of mercury from the atmosphere to land and ocean) can be local, global or hemispherical. Several major studies have supported the idea that, in addition to local sources such as industry, coal combustion and waste incineration, the general background concentration in the global atmosphere / hemispheric contribute significantly to the burden Mercury (U.S. EPA, 1997, EC 2001). Similarly, virtually any local source contributes to background levels. Also, ocean currents are means of mercury transport over long distances and oceans are important dynamic deposits of mercury in the global cycle (UNEP, 2002), as can be seen in schematic form in the following figure.

Figure 1. Dynamic interactions in the distribution mercury between environmental compartments (atmosphere-ocean)



Source: U.S. EPA, 1997, (based in Lamborg et al., 2002, according to adaptation of Mason et al., 1994).
Hg_p= particulate mercury. Mixed layer= Oceanic layer situated Ander the thermocline and where temperature difference is reduced with depth. Thermocline= Layer situated between the warm surface water and the colder water in the bottom.

Global mercury cycle

Nriagu found that ocean sediments may contain approximately 1017 grams of mercury, mainly as HgS, he also found that ocean water contains about 1013 grams of mercury, soil and sediment of freshwater 1013 g, biosphere 1011 g (mostly in soil biota), the atmosphere 108 grams and 107 grams freshwater. This balance excludes the mercury in underground mines and other deposits, estimating a total of 1057 mega tonnes.

A more recent proposal by Fitzgerald (1994) on the atmospheric reservoir is 25 Mmol (megamol) or about 5,000 tons. The estimate of Fitzgerald (1994) is 50 times higher than the estimate of Nriagu (1979), illustrating a great deal of uncertainty among the estimates made as a result of the models used and the knowledge about the cycle of mercury in the environment.

Similarly, to understand the cycle of mercury is necessary to provide data about the presence of anthropogenic mercury in the environment, however, due to the high mobility within the same cycle, this quantification is particularly difficult (Gaona, 2004).

The Group of Experts on the Atmospheric Mercury Processes (Expert Panel, 1994) concluded that the pre-industrial atmospheric concentrations are approximately one third of the current atmospheric concentration of mercury. The group found that anthropogenic emissions can now represent between 50 - 75% of the total annual entry into the global atmosphere (Expert Panel, 1994). The estimate of the group has been corroborated by Lindqvist et al, (1991), who estimated that 60 percent of the current atmospheric concentration is the result of anthropogenic emissions and Porcella (1994), who estimated that this fraction represents 50%. Horvat et al., (1993) assessed that the anthropogenic fraction constitutes between 40 and 50% of the total current.

This comprehensive range seems to agree with the observed increase in the inferences made via deposition rates (Swain et al., 1992). The current percentage of the total atmospheric mercury from anthropogenic origin may be much higher, close to the sources of mercury emissions.

The understanding of the relative contribution of mercury from anthropogenic sources is limited by the large uncertainty regarding the contribution of natural emissions and the amount of the original mercury re-emitted into the atmosphere from the soil, watersheds, and oceans. At the meeting of the Panel of Experts, it was reported that some studies indicate that of the approximately 200,000 tons of mercury emitted into the atmosphere since 1890, approximately 95% are found in terrestrial soils, about 3% in ocean waters and 2% in the atmosphere. It is also estimated that between 40 and 75% of atmospheric mercury is present as the source anthropogenic sources (Expert Panel, 1994).

Comparisons of measurements and contemporary and historical records (in the last 15-20 years), indicate that the total burden of atmospheric mercury has increased since the beginning of the industrial period by a factor of between two and five (Mason et al, 1994).

According to one estimation, about half of total anthropogenic emissions of mercury eventually enter the global atmospheric cycle (Mason et al., 1994), the remainder is removed by local or regional cycles. It is estimated that from 5 to 10% of primary emissions of Hg (II), are deposited within 100 km from the point of release and a fraction higher at regional level. The Hg (0), which is released may be removed from a local to regional to the extent that it is oxidized to Hg (II), part of Hg (0) can be directly taken by the foliage, most of Hg (0), which is not oxidized will be the subject of long range transport, due to the intractability of Hg (0) in the water. In general, emissions mainly of Hg (II), can be deposited on a local and regional level in the process of wet deposition at a rate that the Hg (II) soluble is removed. The dry deposition can be taken into account for the removal of Hg (II) aspirated. Assuming an emission rate constant, the quality of the mercury deposited at the regional and local levels can vary depending on the characteristics of the source (especially of the species of mercury emitted), weather and topography of the area and other factors (Expert Panel , 1994). For example, the rates of deposition in some places have been correlated with the wind trajectories and frequency of rainfall.

Despite these variations do not allow the spread of local and regional cycles, those cycles can be established for specific sites. For example, specific regional mercury cycles have been established for the region of Siberia (Sukhenko and Vasiliev, 1996) and for the drop zone winds of a chlorine-soda plant in German (Ebinghaus Kruger, 1996). Local and regional mercury cycles have been established for the high regions of the Great Lakes (Glass et al., 1991; Lamborg et al., 1995) and the Nordic countries.

1.4 Fate of mercury in soils

Once deposited in the soil, the Hg (II) species are subject to a wide range of chemical and biological reactions. Soil conditions (pH, temperature, humic acid content, etc.) are usually favorable for the formation of inorganic Hg (II) species such as $HgCl_2$, $Hg(OH)_2$ and complex inorganic Hg (II) anions bonded to organic molecules. However, it is not clear yet whether the mercury in sediments is in the form of $HgCl_2$ or $Hg(OH)_2$ when it is bonded to organic substances or in the least reactive forms of HgS or HgO (with a minor tendency to methylation that the other forms). Although some inorganic Hg (II) species are fairly soluble (and therefore mobile) they often form complexes with organic matter (especially humic and fulvic acids) and soil clays. This greatly limits the mobility of mercury in the soil, making it as a large reserve of anthropogenic mercury (Gaona, 2004; Meili, 1991).

Another species of mercury present in very small proportions in soils and sediments, but of great importance due to its toxicity and potential for bioaccumulation, is methylmercury. Its formation is mainly due to microbial processes (sulfur reductive bacteria) that act on compounds of Hg (II). The average methylmercury proportion in soil and sediment is usually about 1-3% of total mercury found. The other 97-99% of the total mercury in soil can be regarded largely as Hg (II). Methylmercury also has a great affinity for organic matter, limiting its mobility too (U.S. EPA, 1997).

Recently, the measurements of the exchange of emissions from air and soil may be similar in magnitude to atmospheric deposition, suggesting that the holding capacity of soil is less than thought. Similarly, the measurements of emissions in forest ecosystems indicate that they do not act as sites for efficient retention of atmospheric mercury (Lindberg, 1996).

The transformation of bacterial Hg compounds, either to species more toxic, bio-available or less toxic or intractable, are an important part of the biogeochemical cycle of mercury. Thus, microbial methylation of organic Hg increases the level of bioavailability methylmercury and, therefore, increases their transfer across different trophic level.

2.0 ANTROPOGENIC MERCURY EMISSION SOURCES

2.1 Natural and anthropogenic sources definitions

The releases of mercury in the environment can be grouped into four categories:

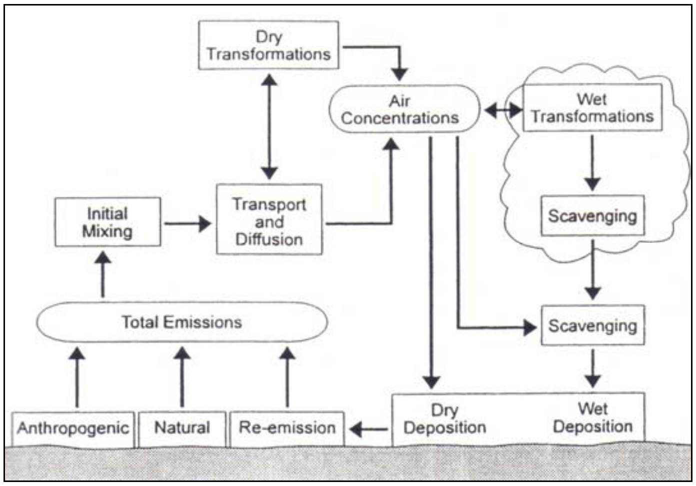
Natural source of mercury emissions, which considers the mobilization and the release of mercury emitted naturally from the earth's crust by volcanic activity or erosion of rocks, with the transfer of mercury into the atmosphere.

Anthropogenic source of mercury emissions, which considers the mobilization and the release of mercury emitted as a result of human activities, with the transfer of mercury into the atmosphere.

Mercury re-issued, which considers the transfer of mercury into the atmosphere through biological or geological processes from the surface of water or soil after an initial mobilization by any of the natural or anthropogenic sources (U.S. EPA, 1997b; Ebinghaus, et al., 1999).

Anthropogenic emissions of mercury include both point sources and diffuse sources. The first, representing nearly 98% of anthropogenic emissions and correspond to those associated with well-defined geographical locations. The second, lengthier and sometimes difficult to locate, those sources are usually small and many that cannot easily be associated with a specific geographic point (U.S. EPA, 1997b).

Figure 2. Natural and anthropogenic sources of mercury emissions



Source: Ebinghaus, 1999.

2.2 Diffuse anthropogenic sources

Diffuse anthropogenic sources comprise approximately 2.2% of anthropogenic emissions of mercury in the United States, according to the USEPA for the period 1994-1995.

The following are the major sources of mercury:

<u>Fluorescent lamps</u>

The electric lamps include mercury-containing lamps: fluorescent, mercury vapor, metal halide and sodium. Each year, more than half a trillion lamps containing mercury are produced. These lamps are used for both internal and external uses, including the lamps to generate heat, for lighting in rooms with high ceiling, for films, photographs, dental examinations, photochemistry, and lighting. When these electric lamps are broken during use or disposal, mercury contained in them is emitted into the atmosphere.

The useful life of a lamp of high intensity varies between 10,000 and 24,000 hours. The mercury lamps and metal halide contain a closed central quartz tube resistant to heat. This tube contains a small amount of mercury ranging from 20 mg in a 75-watt lamp up to 250 mg in a 1000-watt lamp. It is estimated that the industry of emissions of mercury from fluorescent lamps discarded in the U.S. is 0.18 tonnes / year (National Electrical Manufacturers Association, 1995).

Use in laboratories

Mercury is used in laboratories for tools, such as reactive as a catalyst. In 1994, it was estimated that 1.1 tons of mercury were emitted into the atmosphere for general use in laboratories in the U.S. This was used for an emission factor of 40 kg of mercury emitted for each mega-gram of mercury used in laboratories (Anderson, 1973). It is important to note that from 1990 to 1992, there was a decrease in the consumption of mercury in the laboratory.

Using in dental

The mercury used in dental industry, is mainly applied in amalgam fillings for teeth, although it can also be used in other dental equipment and supplies. In the US was issued in 1995 an estimated 0.7 tons of mercury in dental preparations and uses. The dental amalgam is prepared from an alloy of Ag (66.7-74.5%), Sn (25.3-27.0%), Cu (0.0-6.0%) and Zn (0.0-1.9%) mixed with elemental mercury (approximately 1: 1 in weight). The final result is a hard matrix, resistant to abrasion that adheres strongly to the tooth, it has a very low solubility and is impervious to saliva.

Landfills

Municipal solid waste (MSW), are deposited in landfills and consist primarily of non-hazardous household waste. These are sources of emissions of mercury into the air as a result of the elimination of waste such as lamps, batteries, thermometers, and so on. The mercury emitted by the MSW is recorded as a trace constituent of the anaerobic decomposition of waste. Emissions can be presented not only during the life of the landfill, but even if their activity has ended and the waste is covered by a layer of soil.

The EPA has estimated the average concentration of mercury in gases from the decomposition of MSW in 2.9×10^{-4} ppm (U.S. EPA, 1997b).

Other sources

A large number of mercury compounds are active fungicide and therefore have been used in paints and as hedges in deposits of seeds. This use is now banned in many countries, especially for compounds of methylmercury. Acetate, oleate or phenylmercuric dodecilsuccinate are still used in paints in some countries to prevent the growth of fungi and mold.

2.3 Point anthropogenic sources

Point sources of anthropogenic emissions of mercury can be classified into two groups: combustion sources and sources of production or manufacturing.

Combustion sources

Mercury exists naturally as a trace element in fossil fuels and can also be found in waste materials of very diverse origin. Given their high volatility and the temperatures reached during combustion, can be easily delivered along with combustion gases and trace contaminants.

Coal Fired

Coal-fired boilers are facilities for both generating electricity and heat. Thus, there are public and private installations that can be supplied with coal, oil, natural gas or a combination thereof. The main source of mercury from coal combustion occurs in boilers that operate at temperatures above 1100 ºC (2000 ºF), in which coal and oil are transformed into combustion gases.

Estimates in the US on mercury emissions from the boilers are approximately 52 tons per year, of which 51.6 tons were attributable to coal, 0.2 tons are attributed to the burning of oil and natural gas to 0.002 tons (U.S. EPA, 1997b).

In Mexico there are only three thermoelectric plants that use coal as fuel (Petacalco, Rio Escondido and Carbon II), being fueled primarily by natural gas and fuel oil, for which mercury emissions are considered of low significance (Acosta, 2001). One of the biggest thermoelectric plants powered by petroleum fuels is located in Tuxpan, Veracruz.

Combustion of solid waste

The thermal destruction of municipal solid waste (MSW) to reduce the volume of these is a common practice in various countries, coupled with alternative power generation. Many of these wastes are potential sources of mercury emissions, such as, batteries, fluorescent lamps and bulbs, paint waste, thermometers, thermostats, pigments, and so on (U. S. EPA, 1997b).

Burning of hospital waste

The main function of the burning of hospital waste is to destroy medical and biological waste, ensuring its inactivation, and reducing the volume and solid mass that must be provided in landfills.

The hospital waste incinerators are small units with a capacity of 1 ton/day to 60 tons per day of waste generated by facilities of medical, veterinary or research. Mercury emissions in the combustion of hospital waste occurs when there are medical materials contaminated with mercury, which vaporizes at temperatures of burning incinerator and is emitted in the waste gases.

The sources of mercury known in the medical waste include batteries, fluorescent lamps and high intensity lamps, thermometers, paper and film coatings for plastic pigments, antiseptics, diuretics, pigments of red infectious waste bags. Much of the mercury in hospital waste is believed to be produced as a mercuric chloride, owing to the large amount of chlorinated plastics used in disposable materials for medical use (U.S. EPA, 1997b).

Of the 27 incinerators of infectious biological waste approved in Mexico, only 24 are currently in operation. With very few exceptions, most began operations between 1997 and 1998. They have an operational capacity of 8 975 kg / hr and calculations performed with emission factors are an estimated release of mercury into the atmosphere of 0007 ton / year for facilities in operation (Acosta, 2001).

Burning of hazardous waste

The thermal destruction of hazardous waste is used primarily for the treatment of organic waste liquids.

In Mexico there are not garbage incinerators or non-hazardous waste. With regard to hazardous waste incinerators, the amount has changed frequently, but in 2000 there were 14 floors of incineration of hazardous waste operating with a total capacity of incineration of 103,000 tons / year with estimated emissions of 0.020 tons / year of mercury (Acosta, 2001).

Sources of production or manufacture

The sources of production or manufacture include both those that use mercury directly and those that produce mercury as a byproduct.

Mining production of mercury in Mexico

Mercury minerals are located mainly in the following states (especially in the northwest of the territory and central-east): Aguascalientes, Chihuahua, Coahuila, Durango, Guanajuato, Hidalgo, Mexico, Morelos, Nuevo Leon, Queretaro, San Luis Potosi, Sinaloa, Sonora, Tamaulipas, Tlaxcala and Zacatecas, having the main deposits in the states of San Luis Potosi, Zacatecas, Queretaro, Guanajuato and Guerrero (Statistical Yearbook of the Mexican Mining Industry, 2001).

There are records of the production of mercury in Mexico since 1891, and in recent years it has been shown the same downward trend that in global production. From 1920-1929 the production was minimal and reached its peak of 1,118 ton in 1942, in 1991 there were 340 tons of mercury, while in 1994 there were only 11 ton. Since 1995 there are no records of mining of mercury. (Statistical Yearbook of the Mexican Mining Industry, 2001)

Production of chlor-alkali

The production of chlor-alkali for many years was carried out through an electrochemical process using a cathode of mercury, with significant emissions of mercury. Although, at present most of chlor-alkali plants in the world operate with diaphragm cells (which do not require mercury and are more efficient), however, the process of cathode mercury is still used in some facilities. Each cell contains mercury about 3 tons of mercury, having up to 100 cells on each plant. Therefore, despite the strict controls, the chlor-alkali plants that use the process of cathode mercury are considered as important sources of mercury.

The chlorine-alkali process consists of two electrochemical cells. In this process, a stationary flow of brine is circulated among activated titanium anodes suspended in the brine from the top and a cathode of mercury placed on a steel base, which flows at the same time as the brine (U.S. EPA, 1984).

The three main sources of mercury air emissions in the process are: 1) flow-product of hydrogen, 2) the final box of air ventilation, and 3) ventilation room of the cells. (U. S. EPA, 1984).

Currently there are five chlor-alkali plants in Mexico operating at a total combined annual production of 447,000 tons of chlorine gas. From that, 147,000 tons of chlorine is produced using the technology of cathodes of mercury. Three of these plants still use the production process of chlorine with mercury cell. A mercury consumption of 5.76 (ton / year) is reported and it is estimated that emissions are generated by 4.90 tons / year (Acosta, 2001).

Cement Manufacturing

In cement production, the main sources of mercury are found in the stages of the oven preheat and precalcining by the use of fossil fuels. Emissions include particulate matter and other combustion products such as SO_2, NOx, and CO. It also generates carbon dioxide from the calcination of limestone having temperatures that reach its peak at about 2100ºF.

As a source of fuel, cement plants using natural gas to provide energy for the roasting and sporadically coal or oil. Other fuels are also used such as municipal solid waste, tires, petroleum coke, solvents and oils. Mercury emissions can be generated as a result of combustion of waste materials.

As the mercury is distilled to about 350ºC (660 °F), most of the mercury present in the raw materials can be delivered as a vapor in the cement kiln during the production of clinker (U.S. EPA, 1997b).

In Mexico there are 31 cement plants, twenty-eight of which are operated by three major cement groups: Cementos Apasco, Cementos Mexicanos and Cementos Cruz Azul. Of these, twenty-five plants are allowed to burn fuel "alternative", including hazardous waste, in amounts ranging from 5 to 30% of the total heat input required by the process. Several of the cement plants have taken advantage of this authorization, using liquid and solid waste as supplementary fuel. The total production of cement of the 17 plants in 1999 was 19,330,136 tons with a consumption of 989,320 m^3 of fuel oil, 4,930 m^3 of diesel and 221,160 tons of various types of alternative fuels. Based on emission factors, it is estimated a total mercury emissions from 0.0105 tons / year (Acosta, 2001).

Manufacture of pulp and paper

In the pulp and paper industry, wood pulp is produced from the original pulp through chemical processes, mechanical or a combination of both. When using chemical means, the reagents used in the process is recovered for reuse within the same process. Combustion sources used for the recovery of these reagents represent potential sources of mercury.

Mercury can be introduced in the production of wood pulp when the wood is treated with process water containing reactive mercury as a biocide. In 1999, six pulp and paper plants were operating in Mexico, with a total production of 544,100 tons per year of cellulose. Applying emission factors, it was estimated that 0.0240 tons/year of mercury are released into the atmosphere by industry of pulp and paper in the country (Acosta, 2001).

Mining Industry

World production of mercury from mining and smelting, according to a 1973 estimate is 10,000 tons per year, with an annual growth rate of 2%. The levels in local mineral water derived from mercury can also be high (more than 80 μg/L). Air pollution from industrial production is lower than the water pollution caused by mining tailings. The compound of mercury obtained by the process of mining is mercuric sulfide, mercury metal is refined from heating the mercury sulfide ore than 500 °C and condensing the vapors of mercury released (Mitra, 1986).

In relation to this area, some scientists have determined that the discharge of mercury into the environment from ores is higher than the 2000 ton/year. The discharge of mine tailings from cinnabar and other sulfuric-metal ores can contribute with substantial amounts not yet determined of mercury to water bodies. When refining sulfurous ores by heating the ore in ovens or retorts, a significant discharge of mercury into the air is generated (Mitra, 1986).

Other sources

It is known that oil may contain mercury, although there is uncertainty about the contribution that takes its combustion to air emissions. In the European Union is estimated that at the beginning of 1990 emissions from this source could be between 2.4 and 24 tons. (Mitra, 1986)

An additional source of mercury emissions into the atmosphere result of the processes associated with the non-ferrous metals, however, in either case the introduction of technologies applied to the flow of gases to eliminate mercury have significantly reduced such emissions, but at the same time have helped to generate solid waste containing mercury. (Mitra, 1986)

It is estimated that the major industrial sectors which contribute to emissions of mercury to the environment are mining, secondary production of mercury and production of chlorine-soda as shown in Table 2.

Table 2. Generation of mercury by industrial activities

Sector	**Mercury emission 1999 (ton/year)**
Thermoelectric plants	0.126
Carboelectric plants	0.786
Residential burning of wood	1.168
Mining	11.27
Secondary production of mercury	9.66
Copper foundries	1.543
Primary zinc and lead foundries	0.208
Siderurgic plants	0.086
Petroleum refining plants	0.68
Cement plants	0.0105
Limestone plants	0.003
Hazardous wastes incinerators	0.02
Biological wastes incinerators	0.007
Chlor-alkali plants	4.902
Cellulose and paper	0.024
Fluorescent plants	0.229
Thermometers	0.018
Dental amalgams	0.378

Source: Acosta, 2001b

Among these, it must be emphasized the contribution of the thermoelectric sector, as well as the manufacture of fluorescent lamps. This led to the inclusion within the study sites associated with these industrial activities.

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3.0 OBJECTIVE

The aim of this project is to develop a mercury sequential chemical speciation methodology with appropriate conditions for identifying: 1) water-soluble fraction, 2) elemental fraction, 3) interchangeable fraction, 4) strongly bound fraction, 5) organic fraction, 6) fraction as sulfides and 7) residual fraction, and to determine which of the mercury species present in mining and industrial soils in 9 contaminated sites of Mexico.

4.0 FIRST NATIONAL WORKSHOP

The first workshop for the development of the project "sequential chemical speciation of mercury contaminated sites in Mexico" took place on March 12, 2007 in Room 1 of the "Ignacio Chavez" Seminars Unit at the National Autonomous University of Mexico. It was attended by 33 representatives from different sectors.

Academia	10 assistants
Government	21 assistants
Non governmental organizations	2 assistants

Inside the workshop were presented a total of 5 papers that covered various topics on the contamination of soils contaminated by mercury, including analysis of various studies, risk assessment, toxicological aspects and measurement capability.

On the second part of the day, attendees focused on the plenary discussion which covered the following topics:

- Identification of priority sites in the area of contaminated soil at the study sites.
- Elements of collaboration in the project.
- Possible barriers to the development of the study.

At the end of the plenary discussion the findings and agreements were reviewed by all attendees to integrate the final report of the workshop.

4.1 Justification

The identification of species of mercury in soil contaminated by mining and industrial sites will let authorities to understand and predict the effects on the environment and provide the basis for determining appropriate mitigation actions.

The scientific information generated as a result of the study of speciation, will lay the groundwork for establishing the strategies for the identification of priority sites where restoration activities are required to reduce risks and to protect populations located in the contaminated areas or next to them.

4.2 General objective

Perform the sequence of chemical speciation of mercury contaminated sites in 10 mining and industrial sites of Mexico: Hidalgo, Zacatecas, Guanajuato, Queretaro, Chihuahua, Veracruz, Tamaulipas and Nuevo Leon.

4.3 Specific goals

- Develop the sequential chemical speciation of mercury contaminated sites in Mexico by mining activities (Pachuca, Zacatecas, Guanajuato, Queretaro, Chihuahua, Durango) and industrial (Coatzacoalcos, Monterrey, Tampico and Salamanca). The number of samples was determined according to the sampling methodology of contaminated sites developed by the Environmental Protection Agency of Canada.

- Validate the results of the speciation of mercury through a standard prepared sample.

- Establish the chemical species of mercury identified in the sites under study and identify the elements of risk to health and the environment for developing recommendations for risk management.

4.4 Presentations

During the workshop, a total of 5 presentations by representatives of government, researchers and members of NGOs.

Table 3. Presentations made during the workshop

March 12th, 2007

Nombre	Ponencia
PhD. Mario Yarto, *INE*	Applied research on toxic chemicals and environmental risks
PhD. Liliana Saldivar, *ALATOX*	Heavy metals and their toxicity
M. Sc. Gustavo Solórzano *INE-CENICA*	Advances in the North American Regional Action Plan for Mercury

Nombre	Ponencia
M. Sc. Manuel Macías, *Delegation of SEMARNAT in the State of Zacatecas*	Contamination of mercury: Success cases
PhD. Elvira Santos, *Chemistry School, UNAM*	Sequential chemical speciation of mercury in Mexico

4.5 Discussion

Once the presentations finished, attendees focused on the plenary discussion on the following topics:

- Identification of priority sites in the area of contaminated soil at the study sites.
- Elements of collaboration in the project.
- Possible barriers to the development of the study.

4.6 Agreements

It was established that links for the development of the project would be through the delegations of SEMARNAT in each state and the National Institute of Ecology.

The areas that were considered for the development of the study of sequential chemical speciation of mercury are:

- mining sites with a history of the colonial era
- sites with a history of industrial use of mercury as part of the process
- sites adjacent to the priority areas where an affectation is suspected

The coordination of the project will send to each state delegation a proposal of sites for approval and to ensure access to the areas of sampling.

5.0 METHODOLOGY

According to the "Mexican mercury diagnosis" prepared by the Mexican National Institute of Ecology of SEMARNAT in 2000, it was estimated that the major industrial sectors which contribute to emissions of mercury to the environment are mining, secondary mercury production, chlor-alkali, thermoelectric sector, as well as the manufacture of fluorescent lamps as shown in Table 4.

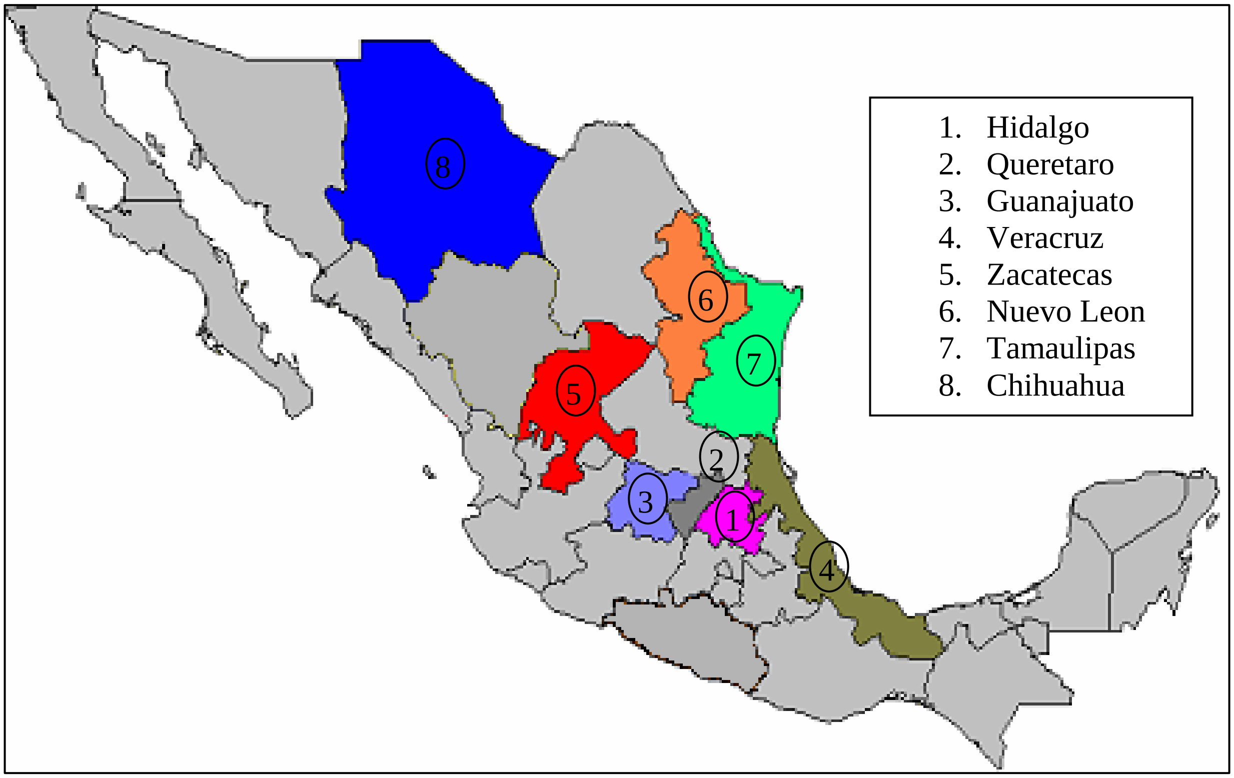
Table 4. Generation of mercury by industrial activities

Sector	Emission of mercury 1999 (ton/año)
Thermoelectric	0.126
Carboelectric	0.786
Residential wood burning	1.168
Mining	11.27
Mercury secondary production	9.66
Copper foundry	1.543
Lead and zinc foundry	0.208
Siderurgic	0.086
Petroleum processing	0.68
Cement plants	0.0105
Lime plants	0.003
Hazardous wastes incinerators	0.02
Biologic wastes incinerators	0.007
Chlor-alkali plants	4.902
Cellulose and paper plants	0.024
Fluorescent lamps	0.229
Thermometers	0.018
Dental amalgams	0.378

Source: Acosta, 2001

Among these, the most important states of the country according to mercury production are shown in figure 3.

Figure 3. States considered for mercury speciation in Mexico



The methodology was established in the following stages:

5.1 Geographic location of the study sites with a mining background.

Sites with mining background were selected for the states of Hidalgo, Guanajuato, Queretaro, Zacatecas, Tamaulipas and Chihuahua was based on a review of the various mining districts existing in each state, according to the following criteria:

- Deposits of silver and gold exploitation in the colonial period through amalgamation
- Production data (exploitation of mineral)
- Population currently exposed at sites under study
- Previous studies

Literature and official reports of the Council of Mineral Resources (COREMI) were reviewed and processed data are shown in Tables 5 to Table 9.

Table 5. Mining regions in the state of Hidalgo and selection of study sites

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
Pachuca-Actopan	Pachuca	267,751	Metallic (Pb, Zn, Ag, Au)	Colony (1528)	300 000
Pachuca-Atotonilco-Actopan	NA	NA	Non metallic	NA	NA
Nicolás Flores – Jacala	Molango	NA	Metallic (Mn)	NA	NA
Zimapán	Zimapán	11,466	Metallic (Pb, Zn, Ag)	Colony (1632)	246 825
Tulancingo	NA	NA	Non metallic	NA	NA
Agua blanca	NA	NA	Non metallic	NA	NA
Zacualtipan	NA	NA	Non metallic	NA	NA
Huasteca	NA	NA	Non metallic	NA	NA
Pacula	NA	NA	Non metallic	NA	NA
San Nicolás	NA	NA	Non metallic	NA	NA
Zimapán	NA	NA	Non metallic	NA	NA
Cardonal	NA	NA	Non metallic	NA	NA
Huichapan-Tecozautla	NA	NA	Non metallic	NA	NA
Tepatepec-San Miguel Acambay	NA	NA	Non metallic	NA	NA
Tula	NA	NA	Non metallic	NA	NA

Source: COREMI, 1991; INEGI, 2005
NA: Not reported.

As seen in table 5, the cities of Pachuca and Zimapan in the State of Hidalgo have mercury sources and were considered for the study.

Table 6. Mining regions in the state of Guanajuato and selection of study sites

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
Guanajuato-Sierra de León	Guanajuato	70,798	Metallic (Ag, Au)	Colony (1548)	1 058 500
	Guanajuato	70,798	Non-metallic	NA	NA
	Sierra de León (Duarte/Alfaro)	5,875/1,381	Metallic (Au, Pb, Zn, Ag, Cu)	Colonia (1548)	NA (Started 1940)
	Sierra de León (Duarte/Alfaro)	5,875/1,381	Non-metallic	NA	NA
	Providencia	NA	Metallic (Au, Pb, Ag, Cu)	1890	NA
El Realito	El Realito		Non-metallic	NA	NA
San José Iturbide	San José Iturbide	NA	Non-metallic	NA	NA
Comonfort	Comonfort	NA	Non-metallic	NA	NA

Source: COREMI, 1991; INEGI, 2005
NA: Not reported.

As seen in table 6, the city of Guanajuato in the State of Guanajuato has mercury sources and was considered for the study.

Table 7. Mining regions in the state of Querétaro and selection of study sites

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
Pinal de Amoles	Ánimas	Pinal De Amoles	Metallic (Pb, Zn, Ag, Au)	Colony (1557)	600000
	Río Blanco	Camargo / Río Blanco	Metallic (Pb, Zn, Ag, Au)	Colony (1557)	4500
	El Soyatal	NA	Metallic (Sb)	NA	NA
	Plazuela-Bucareli	NA / Minera	Metallic	Cinnabar	50

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
		La Tranca	(Hg)		
San Joaquín	Maconi	NA	Metallic (Pb, Zn, Ag, Cu)	NaA	300000
	Santo Entierro / Nepomuceno	S Joaq./ S Crist/ S Gracia	Metallic (Pb, Zn, Ag, Cu)	Colony	ND
	Calabacillas	S Joaq./ S Crist/ S Gracia	Metallic (Hg)	Cinnabar	200
Cadereyta	Marmolero Vizarrón	NA	Non-metallic	NA	NA
	Coahuila	NA	Metallic (Sb, Ag)	NA	NA
Bernal	San Martín	NA / Minera Luismin	Metallic (Ag, Au)	Colony (1760)	300000
	Caleras San Antonio	NA	Non-metallic	NA	NA
Colón	Opalo Tequisquiapan	NA	Non-metallic	NA	NA
	Ezequiel Montes	NA	Non-metallic	NA	NA
Querétaro	San Pedrito	Rancho San Pedrito	Metallic (Ag, Au)	Colony (1870)	NA
	La Cañada	NA	Non-metallic	NA	NA
Amealco	Sillar	NA	Non-metallic	NA	NA

Source: COREMI, 1991; INEGI, 2005
NA: Not reported.

As seen in table 7, the zones of Pinal de Amoles and San Joaquin in the State of Queretaro have mercury sources and were considered for the study.

Table 8. Mining regions in the state of Chihuahua and selection of study sites

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
Parral	Parral	Hidalgo de Parral, Talamantes, Villegas	Metallic (Pb, Zn, Ag, Au, Cu)	Mining	300000
	Santa Bárbara	Santa Bárbara, San Fco. Del Oro	Metallic (Pb, Zn, Ag, Au, Cu)	Mining	4500
	Talamantes	NA	Metallic (Mn)	None	NA
	Los azules	NA	Metallic (Pb, Zn, Ag, Au)	None	NA
	San Juan Cordero	NA	Metálico (Pb, Zn, Ag, Au, Cu)	None	NA
	Almoloya	Ojo de Almoloya	Metálico (Pb, Zn, Ag, Au, Cu)	Mining	1000000
Jiménez	Los Reyes	San Martín de los Reyes	Metálico (Pb, Ag, Cu)	None	3833
	Corralitos	NA	Non-metallic	None	NA
	Las adargas	NA	Metallic (Pb, Zn, U)	None	NA
Camargo	Naica	Minera Peñoles	Metallic (Pb, Zn, Ag, Au, Cu)	Mining	62000/month current
	Savonaroia	Mina Margarita, Reina y Enjambre	Metallic (Pb, Zn, Ag, Cu)	None	15000/historic estimation
	La Gavilana	NA	Metallic (Ag, Mn)	None	Couple of hundreds
La Perla	La Perla	NA	Metallic (Fe)	None	NA
	La Negra	NA	Metallic (Fe)	None	NA
Chihuahua	Santa Eulalia	Santa Eulalia / Sn Antonio / Fco. Portillo / Chihuahua	Metallic (Pb, Zn, Ag, Sn)	Mining	26100

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
		/ Aqules Serdán / San Guillermo			
	Peña Blanca	NA	Metallic (U)	None	NA
	Terrazas	NA	Metallic (Cu)	None	NA
	Minillas	NA	Metallic (Pb, Zn, Ag, Au)	NA	NA
	La Descubridora	NA	Metallic (Pb, Ag, Au)	None	NA
Plomosas	Plomosas	NA	Metallic (Pb, Zn)	None	NA
	Placer de Guadalupe	ND	Metallic (Au, U)	NA	NA
	Las Vigas	NA	Metallic (Cu)	None	NA
	Cuchillo Parado	NA	Metallic (Pb, Ag, Cu)	None	NA
	El Roque y la Amargosa	NA	Metallic (Ba)	None	NA
San Carlos	San Carlos	NA	Metallic (Pb, Zn, Ag, Au, Cu)	None	NA
	Presón-Leones	NA	Metallic (Pb, Zn, Ag, Au, Cu)	None	NA
	Dos Marías	NA	Metallic (Pb, Zn)	None	NA
Los Arados	Los Arados	NA	Metallic (Pb, Zn, Ag, Au, Cu)	None	NA
	La Mojina	NA	Metallic (Mn)	None	NA
	Terrenates	NA	Metallic (Mn)	None	NA
Juárez	Los Lamentos	NA	Metallic (Pb, Ag)	None	NA
	Dunas de Samalayuca	NA	Metallic (Si, Fe, K)	None	NA
	Salinas de Samalayuca	NA	No metàlico	None	NA
	Salinas de La Unión-Lucero	NA	No metàlico	None	NA
	La Gloria-	NA	Metallic	None	5000/estimado

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
	Mosqueteros		(Pb, Zn, Ag, Au, Cu)		hist
	La Alcaparra	NA	Metallic (Pb, Ag)	None	NA
	San Ignacio	NA	Metallic (Pb, Zn, Ag, Cu)	None	NA
Casas Grandes	San Pedro Corralitos	NA	Metallic (Pb)	None	NA
	El Sabinal	NA	Metallic (Ag)	None	NA
	Bismark	NA	Metallic (Pb, Zn, Ag, Cu)	None	NA
	5 de Mayo	NA	Metallic (Pb, Zn, Ag, Au)	None	NA
	La Fortuna	NA	Metallic (Pb, Zn)	None	NA
Cuauhtemoc	Cusihuiriachi	None	Metallic (Pb, Zn, Ag, Au, Cu)	Mining	1100/historic estimation
	Calera	NA	Metallic (Pb, Zn, Ag)	None	NA
	Namiquipa	NA	Metallic (Pb, Zn, Ag, Au)	None	NA
	Milpillas	NA	Metallic (Pb)	None	NA
Dolores	Dolores	NA	Metallic (Ag, Au)	None	NA
	Huizopa	NA	Metallic (Ag, Au, Cu)	None	NA
	Guaynopa	NA	Metallic (Ag, Au, Cu)	None	NA
Ocampo	Ocampo	None	Metallic (Ag, Au)	Mining	450000/historic estimation
	Pilas-Moris	El Pilar	Metallic (Ag, Au, Pb)	Mining	NA
	Pinos Altos	Pinos Altos	Metallic (Ag, Au)	Mining	NA
	Candameña	ND	Metallic (Ag, Au)	None	100000/ historic estimation
	Concheño	NA	Metallic	None	NA

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
			(Ag, Au)		
	Uruachi	Uruachi / Tascate / Gosogachi	Metallic (Ag, Au)	None	750000/ historic estimation
	Maguarichi	Maguarichi	Metallic (Pb, Zn, Ag, Cu)	Mining	300000/ historic estimation
Témoris	Temoris	Témoris / Llanos de Uruapa	Metallic (Ag, Au)	Mining	NA
	Guazapares	Guazapares / Batosegachi	Metallic (Pb, Zn, Ag, Cu)	Mining	400000/ historic estimation
	Chinipas	Chinipas / El Zapote	Metallic (Pb, Zn, Ag, Cu)	Mining	NA
Batopilas	Batopilas	Batopilas / La Bufa / Yoquivo	Metallic (Pb, Zn, Ag nativa, Cu)	None	NA
	Urique	Urique	Metallic (Pb, Zn, Ag, Au)	None	2891/en 1929
	Piedras Verdes	La Florida / El Gallo	Metallic (Pb, Zn, Ag, Au, Cu)	None	14400
	Reforma	None	Metallic (Pb, Zn, Ag, Au, Cu)	None	NA
	Lluvia de Oro	None	Metallic (Ag, Au)	None	NA
Guadalupe y Calvo	Guadalupe y Calvo	Guadalupe y Calvo	Metallic (Ag, Au)	Mining	600000/ historic estimation
	Potrero de Bohorquez	NA	Metallic (Tu)	None	NA
	Morelos	Morelos / Santa Ana / La Canastilla	Metallic (Ag native, Au)	Mining	NA

Source: COREMI, 1991; INEGI, 2005
NA: Not reported.

As seen in table 8, the zones of Chihuahua and San Guillermo in the State of Chihuahua have mercury sources and were considered for the study.

Table 9. Mining regions in the state of Tamaulipas and selection of study sites

Region	District	Population involved	Metal Sources	Mercury Sources	Production (Tons/year)
Miquihuana	Miquihuana	3,390	Metallic (Ag, Pb, Zn)	(1849)	NA
El Novillo	Cañon del novillo	3,024,238	Non-metallic (Serpentine)	NA	NA
Sierra de Tamaulipas	El picacho	NA	Metallic (Rare earths, Au, Cu)	NA	NA
	El cabrito	40,946	Metallic (Rare earths, Au, Cu)	NA	NA
Jiménez	NA	NA	Metallic (Rare earths, Au, Cu)	NA	NA
San Carlos – Cruillas	San Nicolás	1,044	Metallic (Ag, Pb, Zn)	Mining (1748)	NA
	Moctezuma	9,261	Metallic (Ag, Pb, Zn)	Mining (1766)	NA
Cuenca terciaria del Golfo	NA	NA	Non-metallic (Carbon, silicon, travertine)	NA	NA
Llera	Llera	17,317	Metallic (Pb, Zn, Barite)	Colony (1747)	NA

Source: SGM, 2007; INEGI, 2005
NA: Not reported.

As seen in table 9, the towns of San Carlos and San Nicolas in the State of Tamaulipas have mercury sources and were considered for the study.

In the case of the state of Zacatecas, the delimitation of the study area was made based on the work of Pearson, 2003, to conduct sampling of soil, in an area of 16 km^2 in the community of "Osiris" and 16 km^2 in the community of "La Zacatecana" which, according to previously conducted studies showed high levels of contamination by Hg (Iskander, 1994; Martinez-Lopez, 1997, Acosta, 2001).

5.2 Geographic location of the study sites with an industrial background.

State of Veracruz

In the southern part of the State of Veracruz is located one of the most important Petrochemical areas of Mexico, consisting of eight facilities: the Cangrejera Petrochemical Complex, the Cosoleacaque Petrochemical Complex, the Morelos Petrochemical Complex, the Pajaritos Petrochemical Complex, The Petrochemical Complex Escolin and Petrochemical Unit Camargo (PEMEX, 2008).

These are dedicated to the development, marketing and distribution of products, such as acetaldehyde, ammonia, benzene, ethylene, ethylene oxide, glycols, ortoxileno, paraxylene, propylene, toluene, xylenes, acetronitrile, hydrocyanic acid, acrylonitrile, low and high-density polyethylene, methanol and vinyl chloride, to meet the demand of the domestic market and international market share. Its core business processes are not basic petrochemical derivatives of the first processing of natural gas, methane, ethane, propane and gasoline from Petroleos Mexicanos (PEMEX, 2008).

Cangrejera Petrochemical Complex

The Cangrejera Petrochemical Complex is located southeast of the city of Coatzacoalcos, about 5 kilometers from the center Shipper and the Pajaritos Maritime Terminal, which are the centers of national distribution and export of the products it develops. Its operation began in 1980 and is the largest facility of its kind in Latin America, with plants whose production capacity is located at the height of the best and biggest in the world.

Currently operates 16 plants in use, which are aimed at a stream of ethylene derivatives and other aromatics, giving as the main products of low density polyethylene, styrene, ethylene oxide, benzene, toluene among others, which are used to obtain final products such as paints, detergents, cosmetics, telephones, bags, toys, pharmaceuticals, tapes, etc.

Petrochemical complex Cosoleacaque

The Cosoleacaque Petrochemical Complex is located on Cosoleacaque, Veracruz, on the Isthmus of Tehuantepec. It began operations in the year 1971. The main objective of this work center is to develop market and distribute non-basic petrochemical products, mainly for the country's agricultural sector.

The products that are derived from plants are the ammonia and carbon dioxide which are used as raw materials in other industries, such as explosives, synthetic fibers and solvents, among others, as well as a by-product, carbon dioxide is generated for Industries such as fertilizers and chemical refreshments.

Morelos Petrochemical Complex

The Morelos Petrochemical Complex is located at the east of the city of Coatzacoalcos, about 7 kilometers of road Coatzacoalcos - Villahermosa. It began operations in the year 1988.

Currently operates with 9 processing plants which produce petrochemical products derived from ethylene and propylene oxide as major products of ethylene glycols, high-density polyethylene, acrylonitrile among others, which constitute raw material by the processing industry and processing of synthetic fibers , plastic containers, creams, pipes, solvents, paints, enamels, among others.

Pajaritos Petrochemical Complex

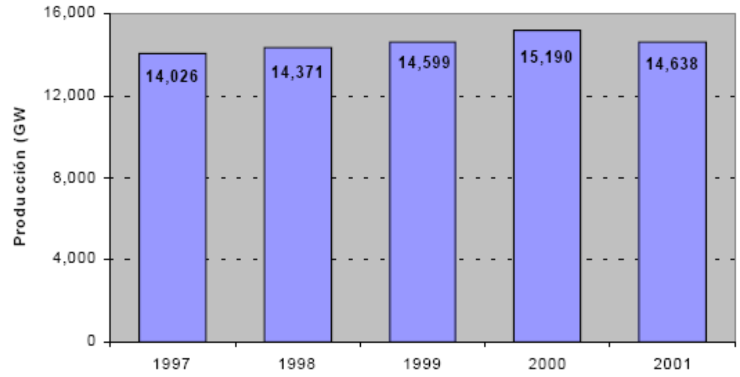
The Pajaritos Petrochemical Complex is located approximately 7 km from the city of Coatzacoalcos Veracruz., A pioneer in the petrochemical industry in Mexico starting operations in 1967.

This plant distributes and sells petrochemical products derived from ethylene and chlorine to maximize its economic value, satisfying market demand through the application of polyethylene. It is the only company in Mexico that produces vinyl chloride monomer with coverage of 35% of national demand, in addition to other products of family olefins such as ethylene oxide and ethylene, as well as muriatic acid.

On the other hand, another important industrial sector is chlor-alkali, which are the main consumers of mercury in Mexico. Currently there are three chlor-alkali plants operating in the country using the mercury cell technology, which together produce 147,000 tons of chlorine annually. It is estimated that on average each cell of these plants contains 2,287 kg of mercury, bringing the total inventory of mercury in these plants is approximately 275 tons with an annual consumption of 5.7 tons per year. Among these is the company IQUISA in Coatzacoalcos, Veracruz, which was built in 1967 (Acosta, 2001).

Given the large amount of Pemex facilities and the presence of two of the leading companies of chlorine-soda, the city of Coatzacoalcos was selected as one of the sites of the study.

On the other hand, the city of Tuxpan was included as a study site because of the location of the thermoelectric plant Adolfo Lopez Mateos of the Federal Electricity Commission, which has the largest capacity of its kind in the country with 6 steam generating units with a total installed capacity of 2100 MW in 2000 produced around 15,000 GWh and consumed more than 3.7 million cubic meters of fuel oil. The following figure shows the production of electrical energy of this complex within the period of 1997-2001 (INE, 2003).



Source: INE, 2003

The importance of this facility is that previous studies have been identified that pollutants from power plants in Mexico, are a potential risk to the health of the population, due to the release of gases from the waste product of the enormous consumption heavy oil with high sulfur content and with an unknown content of mercury. The plant annually consumes about 3.7 million m3 of fuel oil released into the atmosphere and 257,000 tons / year of SO2, 22,000 tons / year of NOx and 17,000 tons / year of PM10 (INE, 2003).

State of Guanajuato

The city of Salamanca in the state of Guanajuato was included in the study due to the lack of information on the mercury content in the oil processed by the refinery Ing. Antonio M. Amor (RIAMA), which began operations in 1950 with the operation of the first production units, comprising a primary distillation plant, with capacity to process 25,000 barrels per day of gasoline (PEMEX, 2008).

Currently, the refinery Salamanca is made up of 53 processing plants which produce 42 finished products. It began operations in 1950 and has had several phases of growth in 1955, 1962, 1970-74, 1979, until the last one in 1992-96. Additionally, the process is starting to increase production of high-octane gasoline through the construction of six new processing plants (of a gasoline reformer with a capacity of 22,400 barrels of gasoline with hydrodesulphurizer unit with a capacity of 25,000 barrels per day, a butane isomerization unit with capacity of 3100 barrels per day, an alkylation plant with a capacity of 5,000 barrels per day, a plant with capacity of MTB 30,000 tons per year and a plant TAME 80000 tons per year) (PEMEX, 2008).

On the other hand, in Salamanca is located a chlor-alkali plant with mercury cell, MONROSE MEXICANA, which started operations before 1968 in Salamanca, Guanajuato. The chlorine produced by this plant was used for the production of organochlorine pesticides such as DDT, BHC, toxaphene and others. This plant was acquired by the governmental company FERTIMEX and sold to VELPOL in 1992, which in turn sold it to TEKCHEM, its current owner. It is not known the date on which this plant suspended its production of chlorine, although this has probably happened around 1976 to reduce the use of DDT in Mexico (Acosta, 2001).

State of Nuevo Leon

The study included the city of Monterrey in the state of Nuevo Leon, due to the existence of the business of chlorine-soda CYDSA in Monterrey, Nuevo Leon (Acosta, 2001), as well as the company General Electric, which is one of the three companies located in the country that manufacture of fluorescent lamps, which has an estimated production of 8700000 lamps with an annual average mercury content of 20 to 25 mg per unit and of which between 95-97 % Is earmarked for the domestic market.

5.3 Selection and distribution of sampling sites.

Based on the Mexican Standard NMX-AA-132-SCFI-2006, which sets out the different types of environmental sampling, it was decided to take surface soil samples due to the fact that this fraction can be ingested by children or adults with low standards of hygiene or when removed by the wind for further inhalation by the people in surrounding areas.

The characteristics of the sampling procedure are as follows:

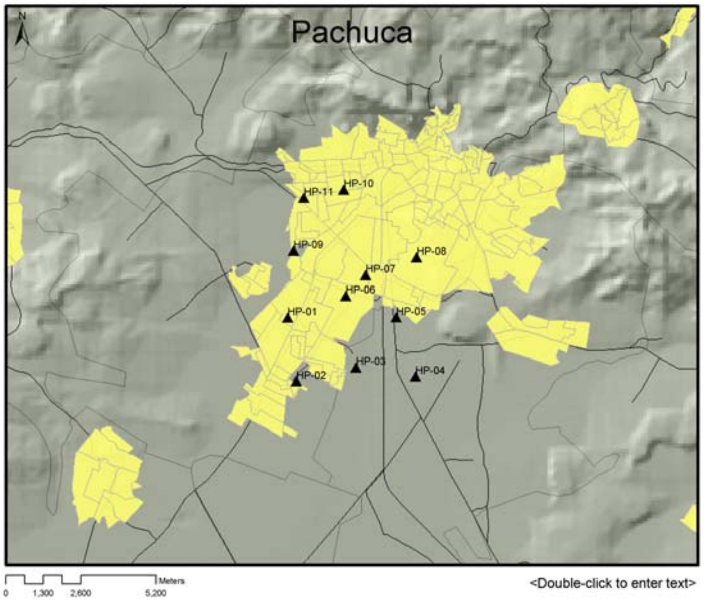
- Sampling surface (0 cm to 15 cm deep).
- Type of samples: Simple, in each sampling site.
- Minimum number of sampling points
- Distribution of sampling points, based on an expert opinion and systematic sampling in accordance with NMX-AA-132-SCFI-2006.

The methodology for sampling of contaminated soil was based on a systematic sampling procedure as reported by the *Guidance on Sampling and Analytical Methods for Use at Contaminated Sites*, Ontario, Canada 1996, according to which it is drawn a grid on the study area.

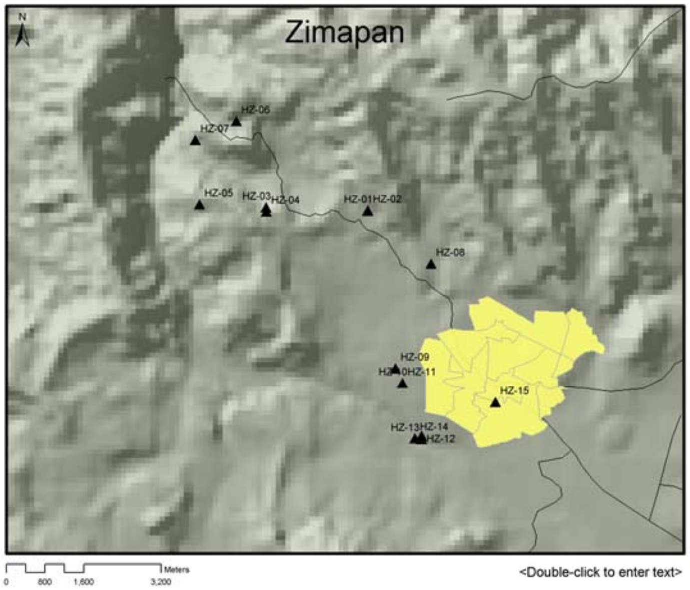
States of Hidalgo, Guanajuato, Queretaro, Nuevo Leon, Chihuahua, Tamaulipas and Veracruz

For the states of Hidalgo, Guanajuato, Queretaro, Nuevo Leon, Chihuahua, Tamaulipas and Veracruz are no reports of previous studies found concentrations of mercury, thus decided to conduct an exploratory sampling by the state with a minimum of 20 samples per state, in an area no larger than 12 km^2, for reasons of cost and to prevent the spread was too big and generate the first data from the area under study. By agreement with the federal and local environmental authorities, it was decided to select two sites potentially contaminated by states. The sites selected for sampling were mapped using the Arc Gis 8.3 and are shown in Figures 4 to 10.

Figure 4. Sampling sites in the state of Hidalgo

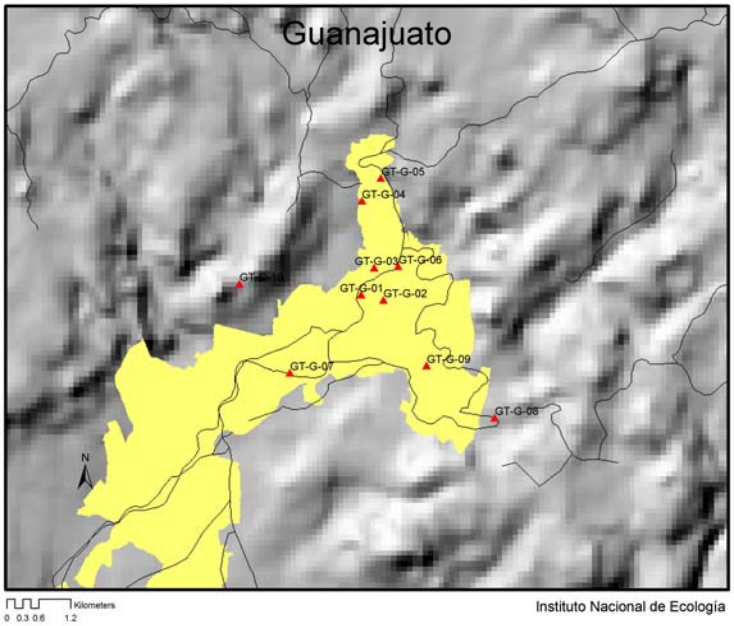


Pachuca, Hidalgo



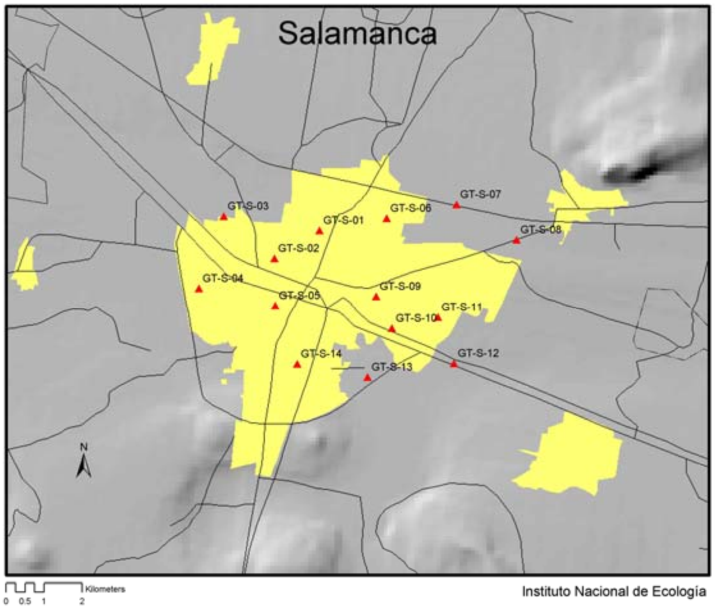
Zimapan, Hidalgo

Figure 5. Sampling sites in the state of Guanajuato



Instituto Nacional de Ecología

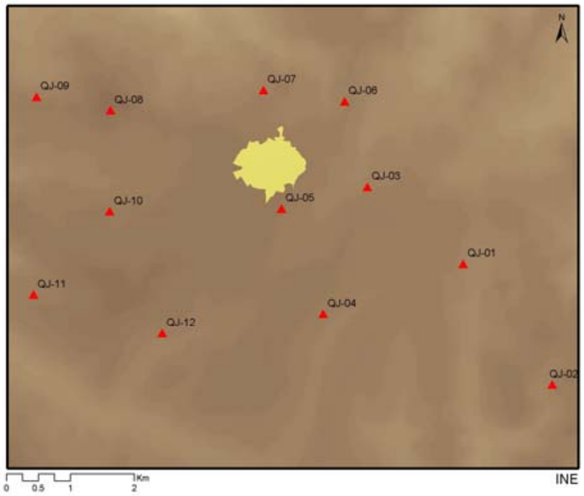
Guanajuato, Guanajuato



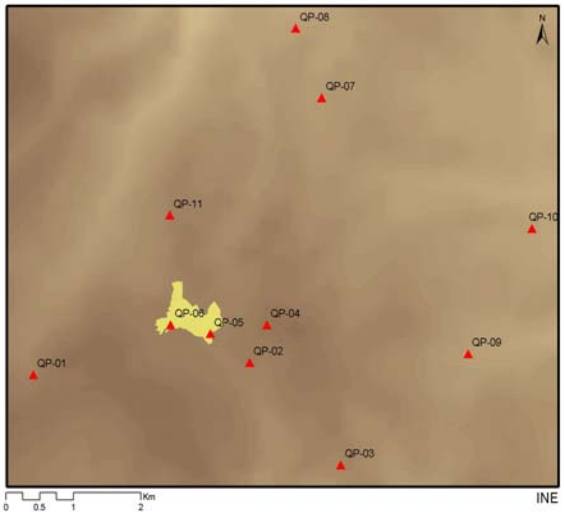
Instituto Nacional de Ecología

Salamanca, Guanajuato

Figure 6. Sampling sites in the state of Queretaro



San Joaquin, Queretaro



Pinal de Amoles, Queretaro

Figure 7. Sampling sites in the state of Nuevo Leon

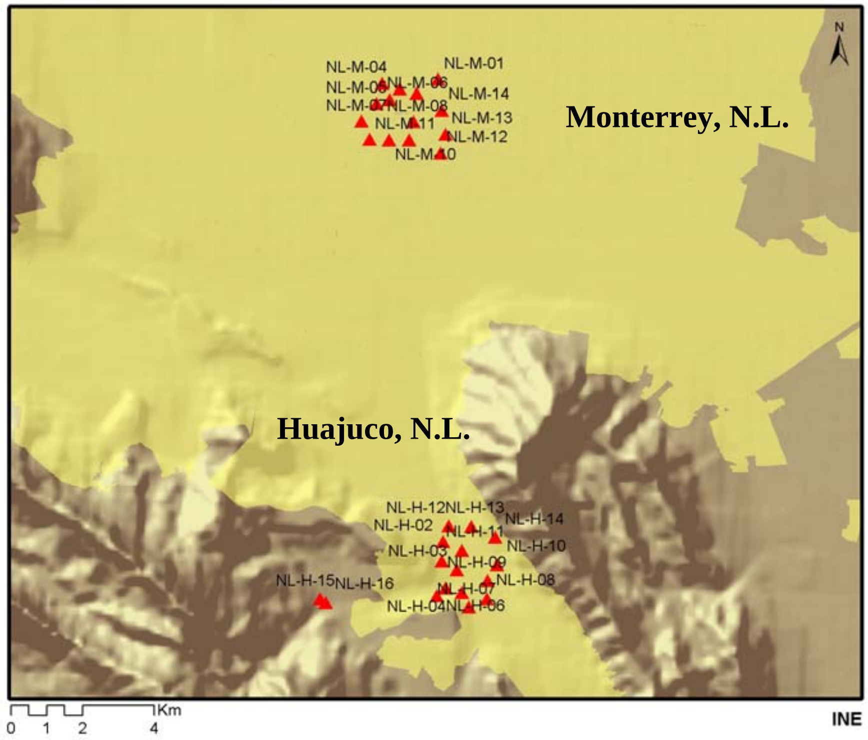


Figure 8. Sampling sites in the state of Chihuahua

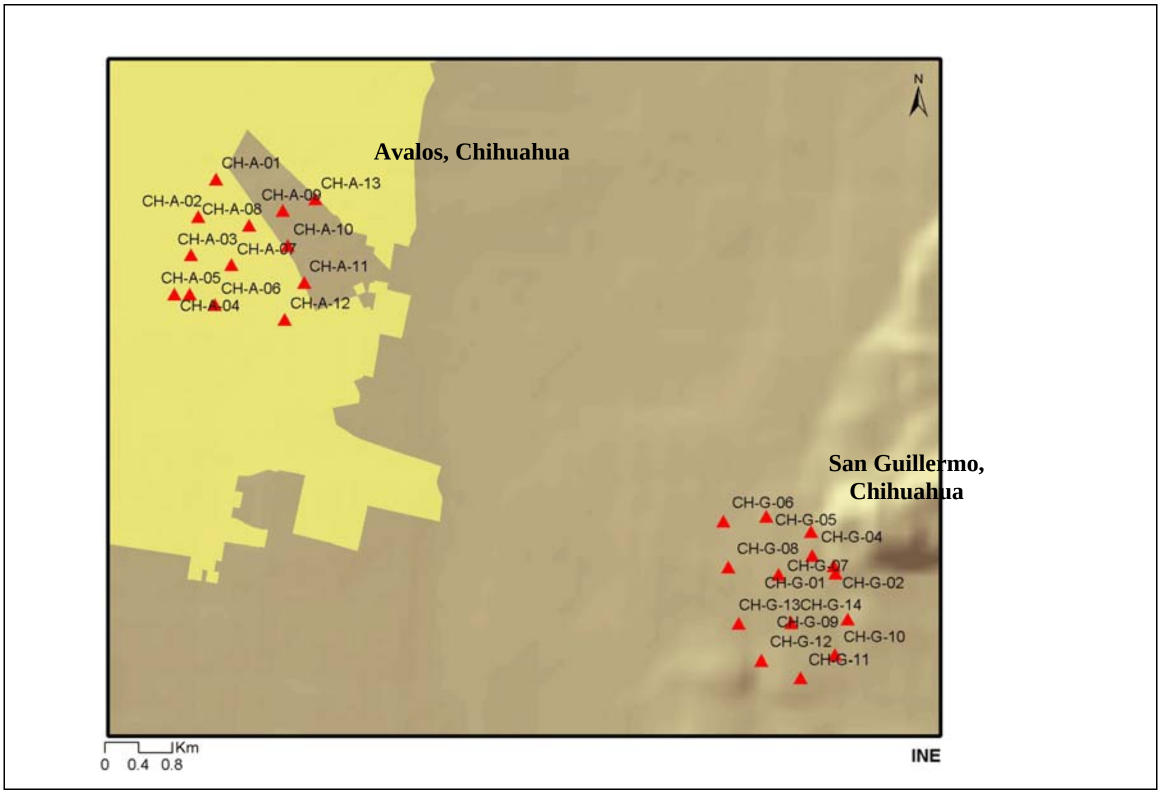
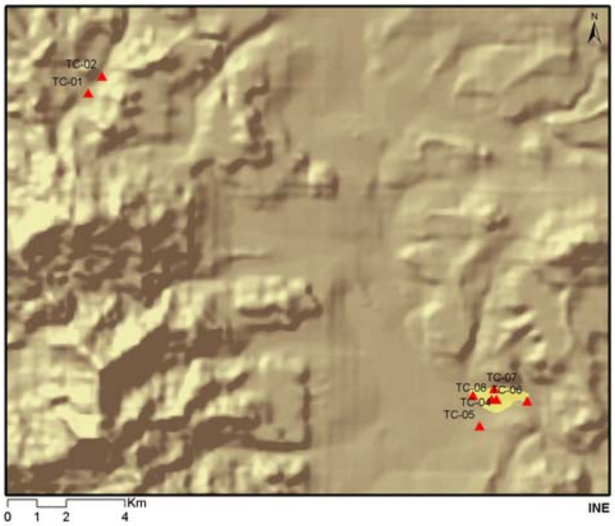
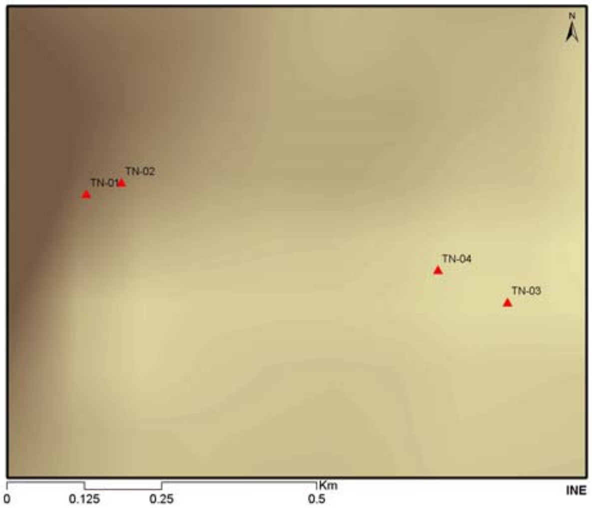


Figure 9. Sampling sites in the state of Tamaulipas

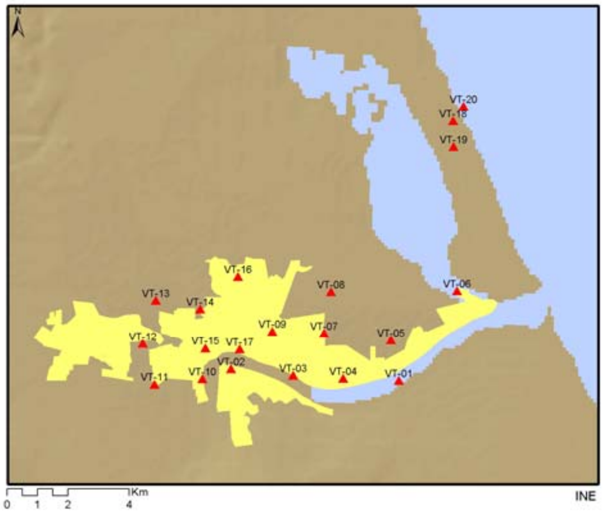


San Carlos, Tamaulipas

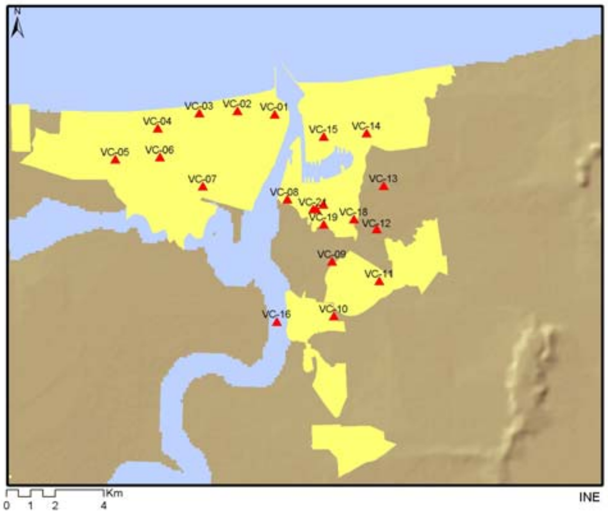


San Nicolas, Tamaulipas

Figure 10. Sampling sites in the state of Veracruz



Tuxpan, Veracruz



Coatzacoalcos, Veracruz

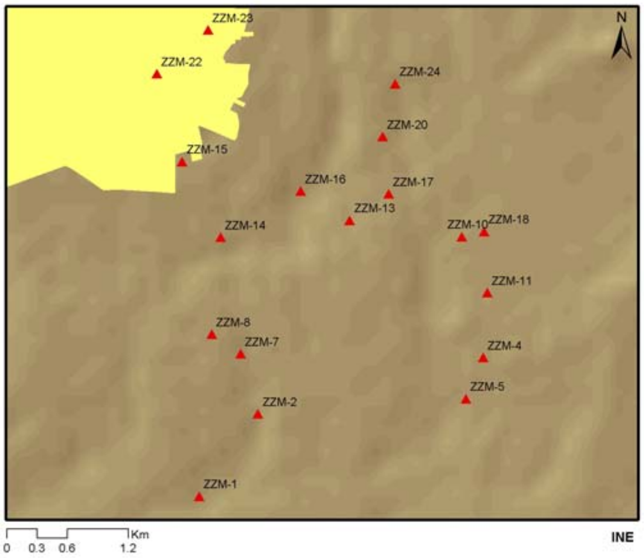
State of Zacatecas

In the case of the state of Zacatecas, the delimitation of the selected area was made with basis on the work of Pearson, 2003 considering an area of 16 km^2 in the community of "Osiris" and 16 km^2 in the community of La Zacatecas, "which, according to previously conducted studies showed high levels of contamination by Hg (Iskander et al, 1994; Martinez-Lopez, 1997, Acosta, 2001).

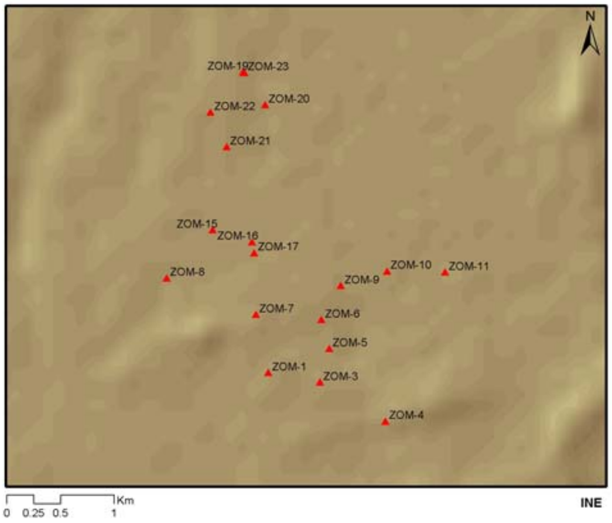
The number of samples, n, was calculated using a statistic inference according to McBean (1998), with the formula: n = [Zα2 * p * (1-p)] / d2. In this design, a 95% confidence interval was established (1-α) and a Zα of 1.96 was calculated. Previous studies in the state of Zacatecas (Santos et al, 2006; Iskander et al, 1994; Pearson, 2003; Ogura et al, 2003) indicate that 1% of the samples analyzed showed mercury concentrations above the recommended limit of 23 mgkg-1 for agricultural soil (NOM-147-SEMARNAT/SSA1-2004), which corresponds to a proportion value p of 0.01; further, taking these same studies as a basis, a precision value d of 4% was established. Thus, the number of samples, n = 22.81, was calculated.

Based on the calculation of the number of samples, a decision was made to make a systematic, judicious sampling in which two 2 X 2 km grids were established within the towns of Osiris and La Zacatecana, respectively, covering a total area of 8 km2, in order to have a regular pattern for the sampling area. Sampling was made in each grid, situating points at each 500-m interval. Precise positioning and adjustment was developed, so that 23 samples were taken for the town of Osiris (OM-1 to OM-23) and 24 for the town of La Zacatecana (ZM-1 to ZM-24), as indicated in Figure 11.

Figure 11. Sampling sites in the state of Zacatecas



Osiris, Zacatecas



La Zacatecana, Zacatecas

5.5 Analysis of total concentration of heavy metals (mercury, lead and silver) by atomic absorption spectrometry.

Once the sampling work was finished, analysis of the total concentration of mercury was developed. Additionally to mercury, it was decided to quantify the total concentration of lead and silver since these metals are associated with the presence of mercury in the waste of amalgamation of gold and silver.

The samples were dried at ambient temperature for 48 hrs and passed through a mesh sieve for a particle size of 2 mm. The total mercury concentration was analyzed by Cold Vapor Atomic Absorption Spectrophotometry (CVAAS). Microwave digestion was carried out with the addition of 3 mL of concentrated HNO_3 and 10 mL of de-ionized water (Type 3 II) with 0.5 g of the sample. The mixture was heated at 121 °C and at a pressure of 0.98 atm for 15 minutes and then cooled to ambient temperature. It was then diluted to a volume of 25 mL with de-ionized water; 10 mL of concentrated H_2SO_4 was added before performing the analysis. Next, a few drops of a saturated solution of $KMnO_4$ were added, and then 6 mL of a sodium chloride-hydroxylamine sulfate solution were added in order to reduce the excess permanganate, according to EPA SW 846 method 7471B (Environmental Protection Agency, 2008). The results were expressed as the average of the triplicate analysis of the samples, in milligrams of mercury per kg of dry soil. A value of 23 mg Hg/kg was taken as the reference allowable concentration in agricultural soil as established in NOM-147-SEMARNAT/SSA1-2004.

Laboratory analysis was carried out in triplicate samples in a PerkinElmer Atomic Absorption Spectrometer model 3110 with an ACE-90 autosampler and an ACE-60 burner. For calibration of the equipment, certified Aldrich-brand mercury standards were used. The technique used for the analysis was hydride-generation atomic absorption spectrophotometry with a detection limit for mercury of 0.31 mg/L. Laboratory material and reagents were used as specified in EPA SW 846 method 3050B/7471B (Environmental Protection Agency, 2008; Taverniers et al, 2004).

The proposed speciation method was tested using a prepared soil sample with standard concentration of the different species of mercury considered in the method. The reference material was developed in cooperation with Mexican Center of Metrology (CENAM).

5.6 Evaluation of the extraction efficiency for the mercury chemical speciation methods reported in literature

Chemical speciation methods for identifying mercury species have several years of application in research, mainly in developed countries. The main difference in these methods can be summarized in the number of species included and the reproducibility of these in different matrixes.

After this, the work during this stage was divided into two parts:

a) Review of the mercury chemical speciation methods described in the literature.
b) Valuation of the efficiency of methods on prepared samples.

The strategy followed for conducting the experiment began with a review of the speciation methods reported in the literature (Bloom et al, 2003; Ebinghaus et al, 1999; Biester and Scholz, 1997; Di Giulio and Ryan, 1987; Tessier et al, 1979; Wallschläger et al, 1998). We then proceeded to select those that could be applied and reproduced with the available infrastructure in a standard laboratory, and the performance level of each extraction method was observed by means of tests with Aldrich-brand analytical reactive grade mercury salts (HgS, $HgSO_4$, HgO, $HgCl_2$) in a prepared soil matrix. Each test carried out was done in triplicate.

The results of the efficiency evaluation are shown in the results section.

5.7 Sequential chemical speciation of mercury in contaminated soils of Mexico

Based on the results obtained with the prepared samples, an integrated methodology was established in order to identify a greater number of fractions taking the results obtained with the Ebinghaus (1999) and Bloom et al (2003) methods as the basis, with some adjustments in the extraction stages, chemicals used and reaction time so that the efficiency could be increased during the experiment and the sample losses considerably minimized.

The integrated methodology for sequential chemical speciation (Figure 12) was applied to the contaminated soil samples that showed a total mercury concentration above the limit recommended by the regulations.

In the first part of the method, Extraction of **water-soluble species (F1)**, 50 mL of de-ionized water was added to the original sample and shaken for 120 minutes. The mixture was centrifuged for 20 minutes at 3000 RPM, decanted, and the mercury concentration in the supernatant was analyzed by Cold Vapor Atomic Absorption Spectrophotometry (CVAAS). The sediment was then set aside for the next stage (F2).

Elemental Mercury (F2): the sediment from stage F1 was heated to 180 °C in a muffle to separate out the metallic mercury; to prevent contamination, the recipient was covered with a watch glass containing activated charcoal to captures mercury vapor; then the quantity of mercury remaining in the residual solid was measured by CVAAS after acid digestion; to obtain the value of elemental mercury (F2), the concentration extracted in stage F1 and the concentration of mercury in the residue from this stage was subtracted from the total mercury concentration. The residue was set aside for the next stage (F3).

Extraction of exchangeable species (F3): 50 mL of magnesium chloride solution was added to the second fraction of sediment from stage F1 and shaken at ambient temperature for 2 hours. The sample was centrifuged for 20 minutes at 3000 RPM and then the supernatant was decanted to measure the quantity of mercury by CVAAS. The sediment is set aside for the following stage (F4).

Extraction of strongly bound species (F4): 50 mL of hydrochloric acid was added to the sediment from stage F3 and shaken for 2 hours at ambient temperature. Then the sample was centrifuged for 20 minutes at 3000 RPM and the supernatant was decanted to measure the quantity of mercury by CVAAS. The sediment was set aside for the next stage (F5).

Extraction of organic mercury (F5): 25 mL of 0.2 M sodium hydroxide was added to the sediment from stage F4, and the mixture was shaken at ambient temperature for 2 hours. Then 25 mL of a 4% (v/v) solution of glacial acetic acid was added, and the mixture was shaken at ambient temperature for 2 hours. The sample was centrifuged for 20 minutes at 3000 RPM, and the supernatant was decanted to measure the quantity of mercury by CVAAS. The sediment was set aside for the next stage (F6).

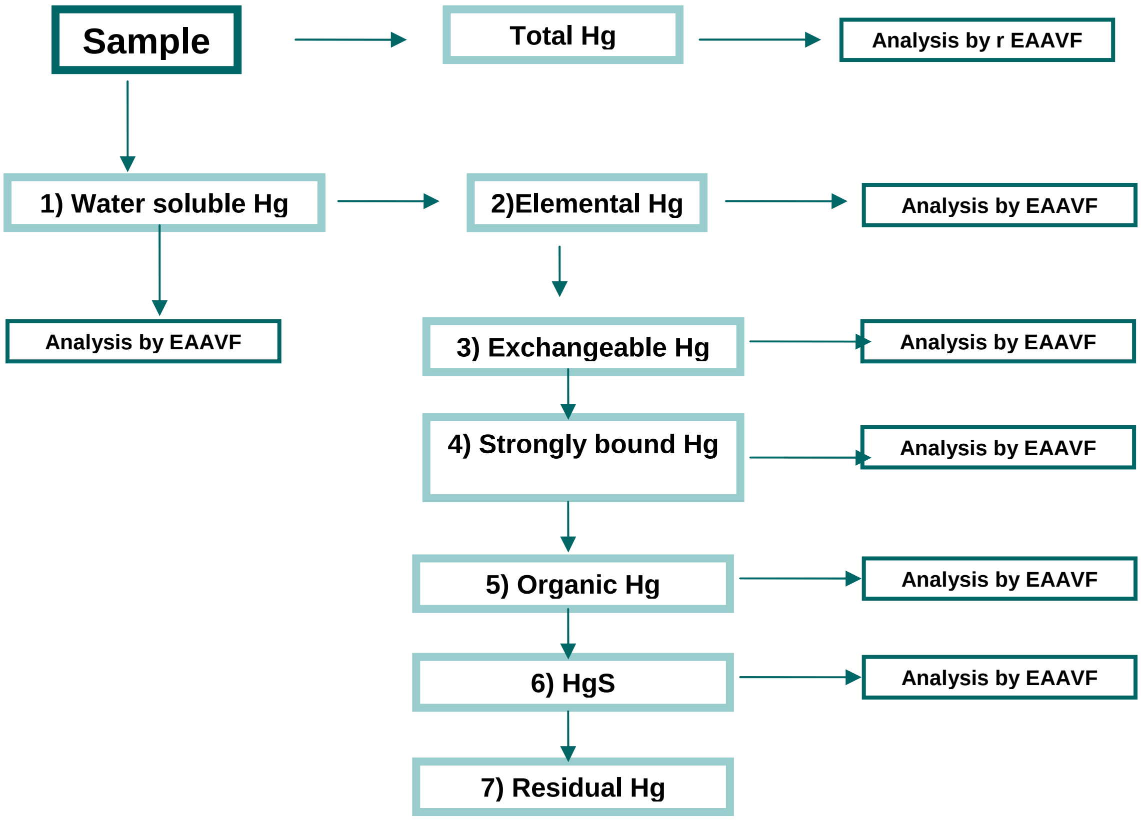
Extraction of the sulphide fraction (F6): 25 mL of a saturated solution of sodium sulphide was added to the sediment from stage F5, and the mixture was shaken at ambient temperature for 24 hrs. Then the sample was centrifuged for 20 minutes at 3000 RPM. The supernatant was separated and set aside. 25 mL of de-ionized water was added to the solid, and the sample was centrifuged for another 20 minutes at 3000 RPM. The supernatant was decanted and mixed with the supernatant obtained previously. The sediment was set aside for the next stage (F7).

The quantity corresponding to the mercury sulphide fraction (F6) was obtained subtracting F1, F2, F3, F4, F5 and F7 fractions from the total mercury concentration, difference is HgS.

Extraction of residual mercury (F7): digestion with 5 mL of HNO_3 conc. and 15 of acid hydrochloric concentrate was carried out on the sediment from stage F6, heating it at 85°C for 45 minutes. Next, it was centrifuged for 20 minutes at 3000 RPM and the supernatant was decanted, increasing it to a volume of 50 mL using hydrochloric acid 3 N, and the analysis of the quantity extracted by CVAAS was then performed.

According to the literature (Ebinghaus et al, 1999; Kim et al, 2003), the mercury species found in the seven speciation stages are as follows: F1) Water soluble species: $HgCl_2$, F2) Elemental species: Amalgamated Hg, F3) Exchangeable species: $HgSO_4$ & HgO, F4) Strongly bounded species: Hg bounded to Fe & Mn, F5) Organic species: Organic Hg, F6) HgS, and F7) Residual: HgSe & residual.

Figure 12. Integrated method of mercury sequential chemical speciation



EAAVF: Cold Vapor Atomic Absorption Spectrometry

Once developed the modified chemical speciation method, it was used for those samples that exceeded the limit set by the standard NOM-147-SEMARNAT/SSA1-2004. The results of the implementation of the methodology are in the results section.

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Laboratory analysis was carried out in triplicate samples in a PerkinElmer Atomic Absorption Spectrometer model 3110 with an ACE-90 autosampler and an ACE-60 burner. For calibration of the equipment, certified Aldrich-brand mercury standards were used. The technique used for the analysis was hydride-generation atomic absorption spectrophotometry with a detection limit for mercury of 0.31 mg/L. Laboratory material and reagents were used as specified in EPA SW 846 method 3050B/7471B (Environmental Protection Agency, 2008; Taverniers et al, 2004).

The proposed speciation method was tested using a prepared soil sample with standard concentration of the different species of mercury considered in the method. The reference material was developed in cooperation with Mexican Center of Metrology (CENAM).

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Wallschläger, D., Desai, M. Spengler, M., Wilken, R., 1998. Mercury speciation in floodplain soils and sediments along a contaminated river transect. J. Environ. Qual. 27, 1034-1044.

6.0 RESULTS AND DISCUSSION

6.1 Analysis of total concentration of heavy metals (mercury, lead and silver) by atomic absorption spectrometry.

The following section shows the results of the analysis of the total concentration of mercury, lead and silver for each sample site selected in 8 states of Mexico (Tables 9 to 16 and Figures 13 to 36).

State of Hidalgo

Table 9 shows the location of sampling points in Pachuca and Zimapan, as well as the total concentration of mercury, lead and silver.

Table 9. Total concentration of Hg, Pb and Ag in samples of Pachuca (HP) and Zimapan (HZ) in the state of Hidalgo

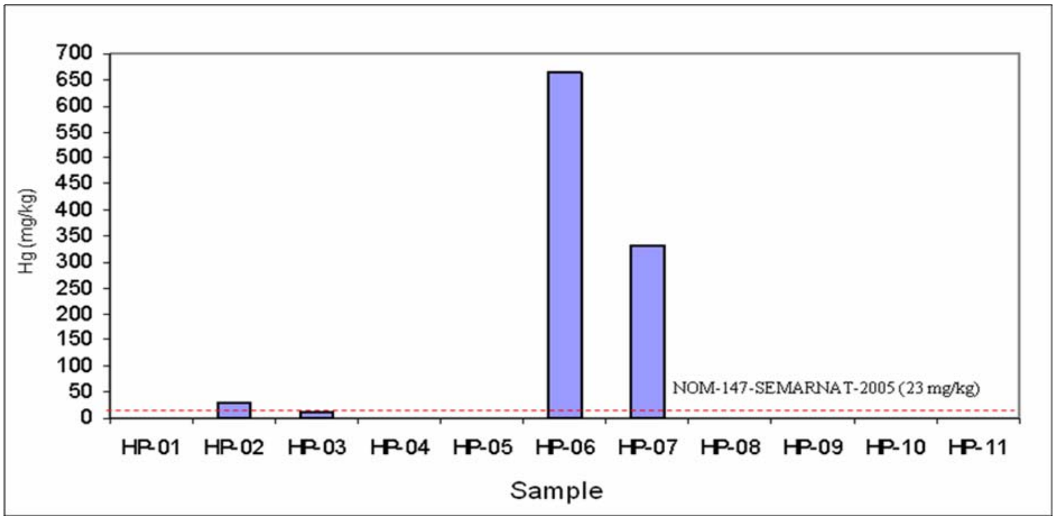
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
HP-01	N- 20°¨04,33.5’ WO- 98° 46,47.3’ A 2362 m	1.5	29.83	2.46	HZ-01	N- 20° 46,10.0’ WO- 99° 24,31.8’ A 1872 m	1.16	587.45	3.93
HP-02	N- 20° 03´21.3’ WO- 98° 46,37.1’ A 2354 m	28.25	53.79	4.61	HZ-02	N- 20° 46,10.3’ WO- 99° 24,31.6’ A 1866 m	1.58	587.45	3.71
HP-03	N- 20° 03, 6.9’ WO- 98° 45,25.8’ A 2370 m	11.67	76.97	8.25	HZ-03	N- 20° 46,12.1’ WO- 99° 25,44.4’ A 1910 m	0.23	510.18	21.74
HP-04	N- 20° 03,26.6’ WO -98° 44,14.8’ A 2358m	0.74	21.33	1.09	HZ-04	N- 20° 46,09.3’ WO- 99° 25,44.3’ A 1925 m	1.32	5223.95	44.91
HP-05	N- 20° 04,33.6’ WO- 98° 44,37.6’ A 2359 m	0.33	2982.98	8.25	HZ-05	N- 20° 46,14.0’ WO- 99° 26,32.1’ A 1811 m	1.11	4837.58	29.4
HP-06	N- 20° 04,57.9’ WO- 98° 45,38.0’ A 2360 m	664.62	1437.48	44.73	HZ-06	N- 20° 47,10.3’ WO- 99° 26,05.9’ A 1782 m	0.19	ND	4.16
HP-07	N- 20° 05,21.5’ WO- 98° 45,14.0’ A 2367 m	336.58	3751.98	20.76	HZ-07	N- 20° 46,57.4’ WO- 99° 26,35.2’ A 1781 m	0.18	213.85	14.37
HP-08	N- 20° 05,41.4’ WO- 98° 44,13.2’	0.69	68.97	18.82	HZ-08	N- 20° 45,34.3’ WO- 99° 23,46.2’	0.13	62.29	5.91

	A 2402 m					A 1770 m			
HP-09	N- 20° 05,49.1’ WO- 98° 46,40.3’ A 2372 m	0.29	108.75	7.23	HZ-09	N- 20° 44,23.8’ WO- 99° 24,11.5’ A 1758 m	0.43	643.11	14.69
HP-10	N- 20° 06,58.1’ WO- 98° 45,40.0’ A 2393 m	1.48	17.18	0.72	HZ-10	N- 20° 44,13.9’ WO- 99° 24,06.6’ A 1752 m	0.18	2442.05	20.99
HP-11	N- 20° 06,48.8’ WO- 98° 46,27.9’ A 2391 m	0.05	18.18	9.61	HZ-11	N- 20° 44,13.9’ WO- 99° 24,06.5’ A 1748 m	0.08	2055.68	20.81
					HZ-12	N- 20° 43,38.4’ WO- 99° 23.52.7’ A 1678 m	0.58	ND	ND
					HZ-13	N- 20° 43,36.2’ WO- 99° 23,52.7’ A 1669 m	0.53	ND	ND
					HZ-14	N- 20° 43,36.7’ WO- 99° 23,57.6’ A 1669 m	1.11	2751.15	20.24
					HZ-15	N- 20° 44,01.1’ WO- 99° 23,0’ A 1738 m	0.43	2210.23	19.31

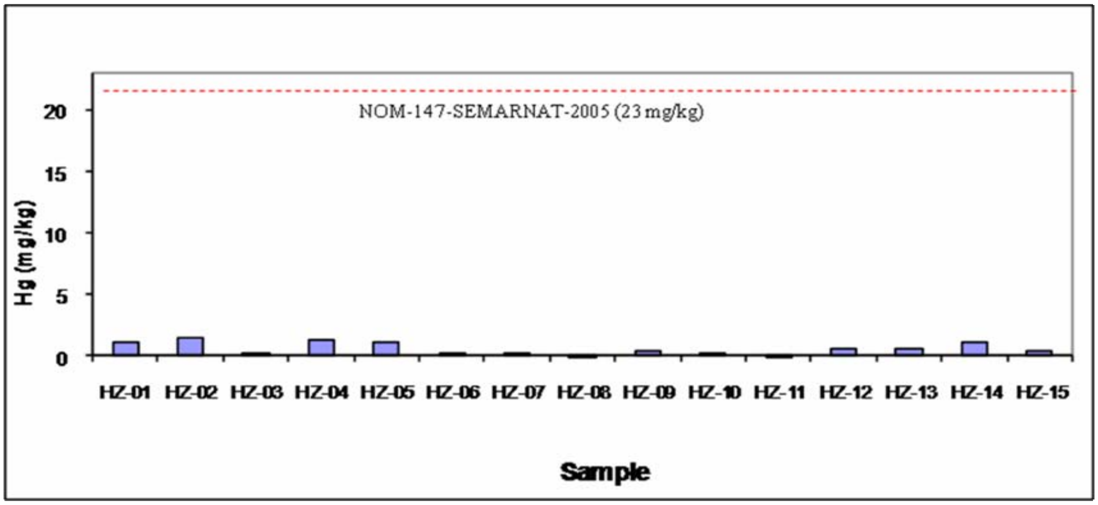
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

Samples HP-02, HP-06 and HP-07 from the town of Pachuca have a total concentration of mercury higher than the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury). For this reason these samples were selected to be speciated with the proposed method. On the other hand, none of the samples collected in Zimapan exceeded the limit specified by the existing legislation (Figure 13).

Figure 13. Total concentration of mercury in the towns of Pachuca and Zimapan in the state of Hidalgo



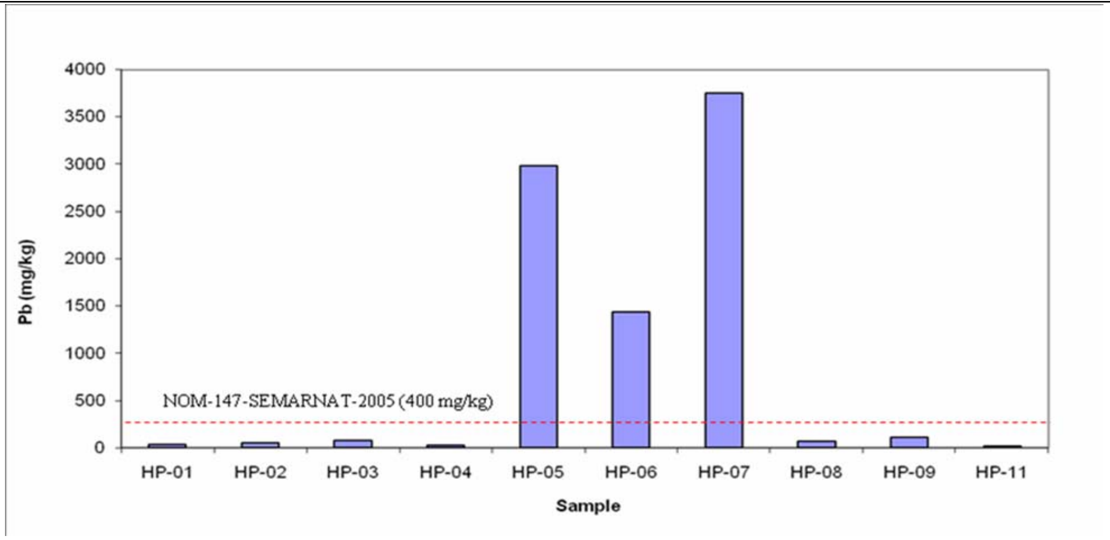
Pachuca, Hidalgo



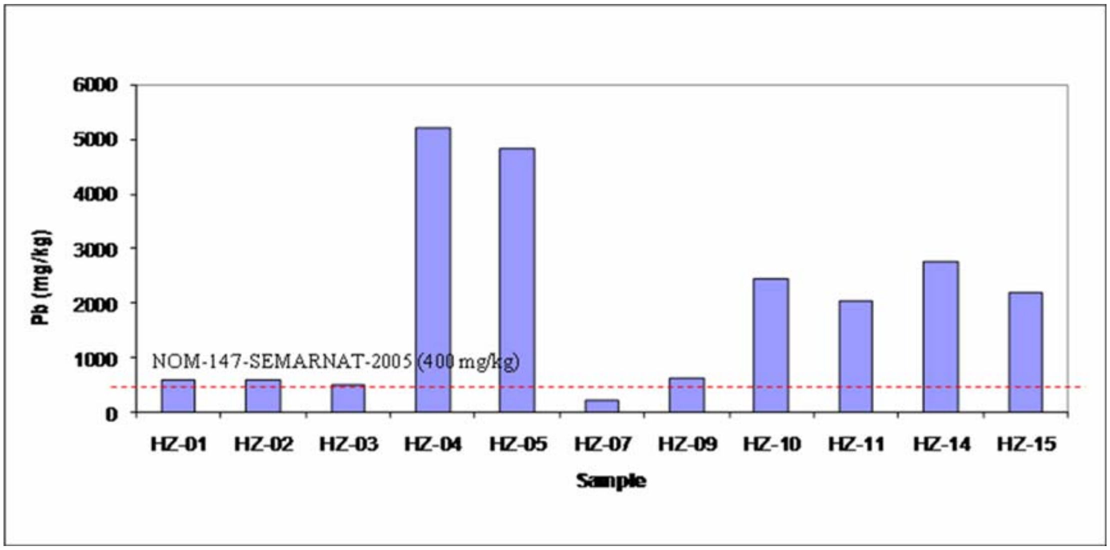
Zimapan, Hidalgo

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by a wide margin (samples HP-05, HP-06, HP-07, HZ-01, HZ-02, HZ-03, HZ-04, HZ-05, HZ-07, HZ-09, HZ-10, HZ-11, HZ-14 and HZ-15), reaching values up to 5200 mg/kg as shown in Figure 14. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 15.

Figure 14. Total concentration of lead in the towns of Pachuca and Zimapan in the state of Hidalgo

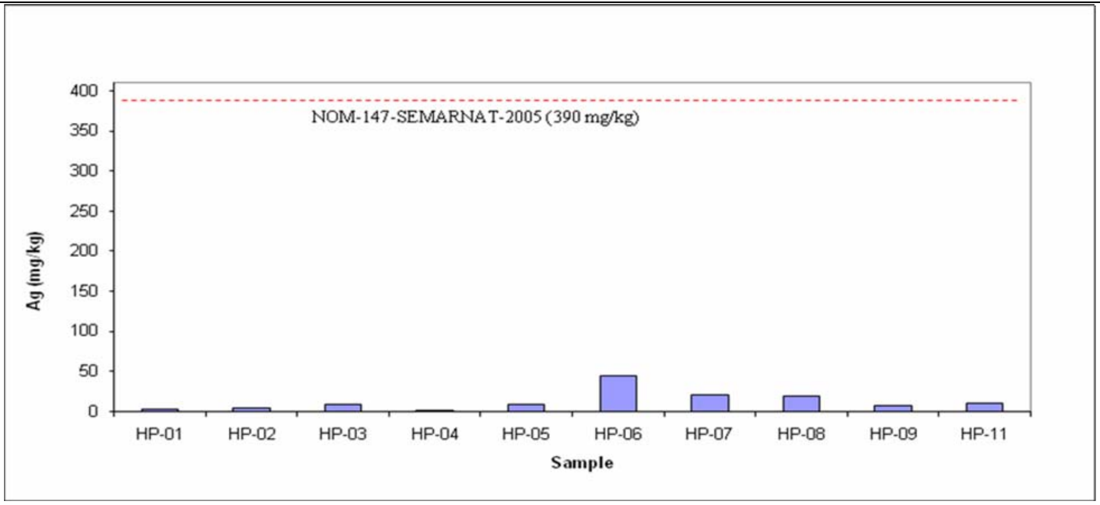


Pachuca, Hidalgo

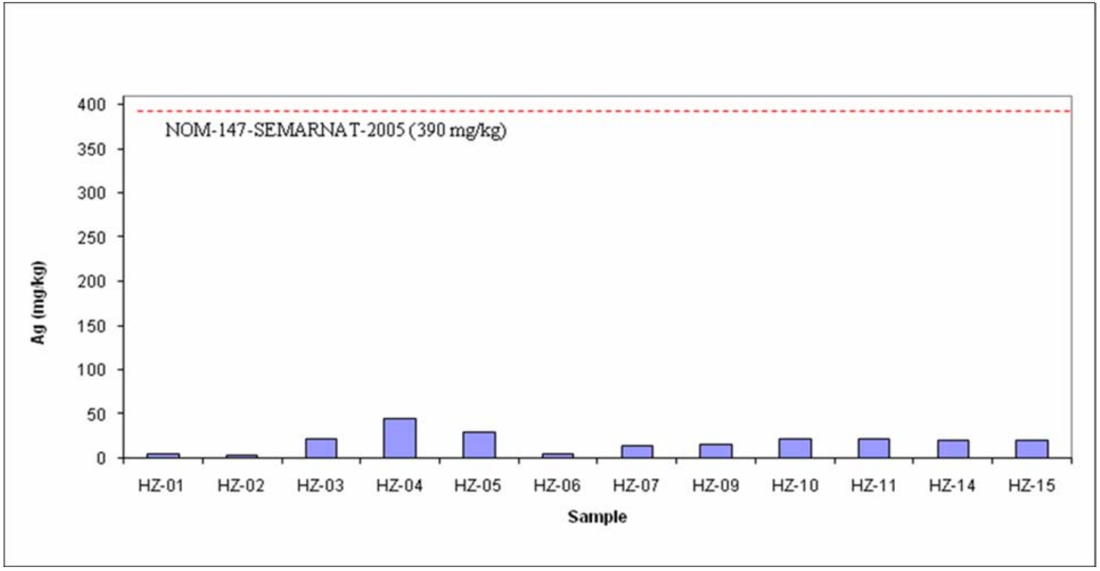


Zimapan, Hidalgo

Figura 15. Total concentration of silver in the towns of Pachuca and Zimapan in the state of Hidalgo



Pachuca, Hidalgo



Zimapan, Hidalgo

State of Guanajuato

Table 10 shows the location of sampling points in Guanajuato and Salamanca, as well as the total concentration of mercury, lead and silver.

Table 10. Total concentration of Hg, Pb and Ag in samples of Guanajuato (GG) and Salamanca (GS) in the state of Guanajuato

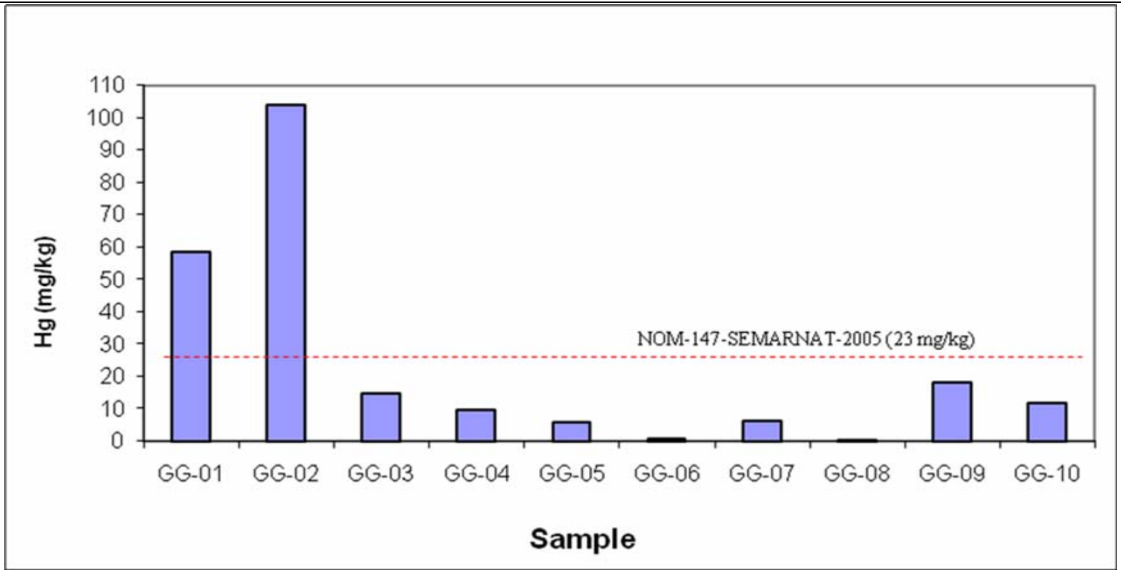
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
GG-01	-	58.60	51.73	7.53	GS-01	N- 20° 35,10.5' WO- 101° 11,30.0' A 17.3 m	1.72	27.7	20.96
GG-02	N- 21° 01,21.1' WO- 101° 15,25.8' A 22.28 m	103.92	286.99	16.79	GS-02	N- 20° 34,46.0' WO- 101° 12,10.8' A 17.11 m	3.42	50.16	22.34
GG-03	N- 21° 01,40.9' WO- 101° 15,32.1' A 25.28 m	14.9	49.82	7.83	GS-03	N- 20° 35,21.4' WO- 101° 12,57.2' A 17.18 m	1.1	44.42	15.34
GG-04	N- 21° 02,21.9' WO- 101° 1540.8' A 22.02 m	9.49	105.11	66.1	GS-04	N- 20° 34,19.5' WO- 101° 13,19.0' A 17.10 m	11.1	50.54	17.04
GG-05	N- 21° 02,36.1' WO- 101° 15,28.6' A 22.14 m	5.79	122.34	6.66	GS-05	N- 20° 34,05.4' WO- 101° 12,09.5' A 17.08 m	0.66	47.14	36.38
GG-06	N- 21° 01,42.0' WO. 101° 15,16.4' A 20.67 m	0.71	23.4	12.87	GS-06	N- 20° 35,21.5' WO- 101° 10,29.2' A 17.15 m	1.11	105.4	34.72
GG-07	N- 21° 00,35.4' WO- 101° 16,26.3' A 19.82 m	6.41	22.07	2.48	GS-07	N- 20° 35,34.1' WO- 101° 09,25.8' A 17.16 m	0.21	59.57	37.93
GG-08	N- 21° 00,09.5' WO- 101° 14,11.9' A 21.08 m	0.25	27.27	1.61	GS-08	N- 20° 35,04.7' WO- 101° 08,30.8' A 17.25 m	0.42	56.94	55.51
GG-09	N- 21° 00,41.0' WO- 101° 14,56.9' A 20.23 m	18.04	36.35	4.73	GS-09	N- 20° 34, 14.5' WO- 101° 10,37.8' A 17.13 m	0.3	31.76	42.40
GG-10	N- 21° 01,29.8' WO- 101° 17,00.2' A 19.74 m	11.72	28.54	3.66	GS-10	N- 20° 33,47.3' WO- 101° 10,23.0' A 17.17 m	4.26	30.57	26.62
					GS-11	N- 20° 33,57.3' WO- 101° 09,41.4' A 17.13 m	0.58	33.66	28.63
					GS-12	N- 20° 33,17.8' WO- 101° 09,26.2' A 17.12 m	0.57	23.11	27.72

	GS-13	N- 20° 33,05.2’ WO- 101° 10,44.5’ A 17.17 m	0.61	24.79	27.32
	GS-14	N- 20° 33,15.7’ WO- 101° 11,48.8’ A 17.23 m	1.27	17.92	27.24

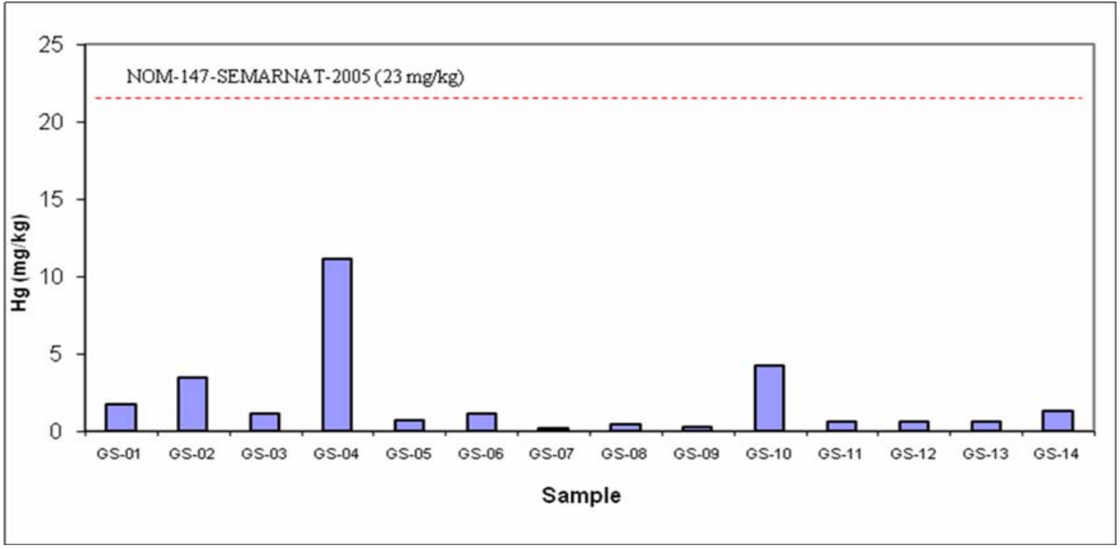
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

Samples -01 and GG-02 from the town of Guanajuato have a total concentration of mercury higher than the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury). For this reason these samples were selected to be speciated with the proposed method. On the other hand, none of the samples collected in Salamanca exceeded the limit specified by the existing legislation (Figure 16).

Figure 16. Total concentration of mercury in the towns of Guanajuato and Salamanca in the state of Guanajuato



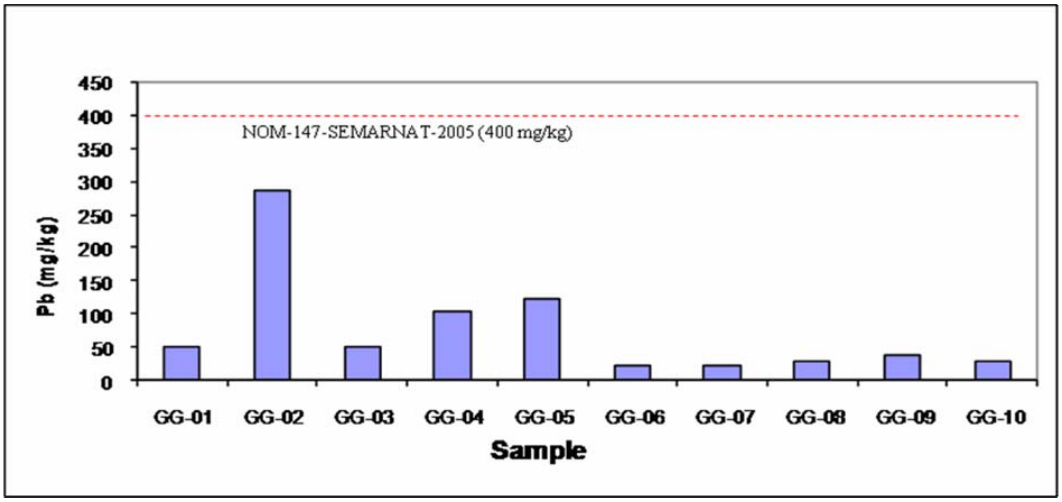
Guanajuato, Guanajuato



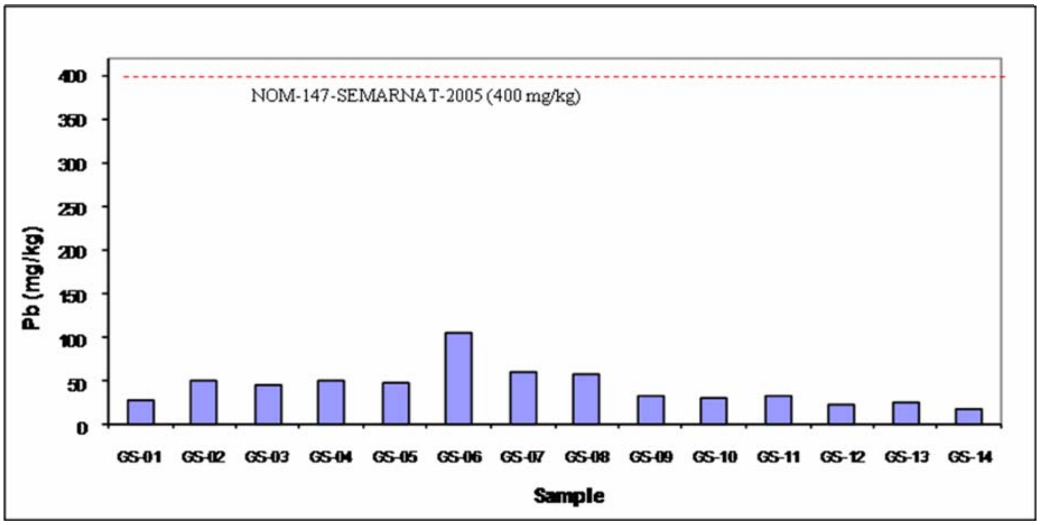
Salamanca, Guanajuato

In the case of lead and silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg and 390 mg/kg) was not exceeded as shown in Figures 17 and 18.

Figure 17. Total concentration of lead in the towns of Guanajuato and Salamanca in the state of Guanajuato

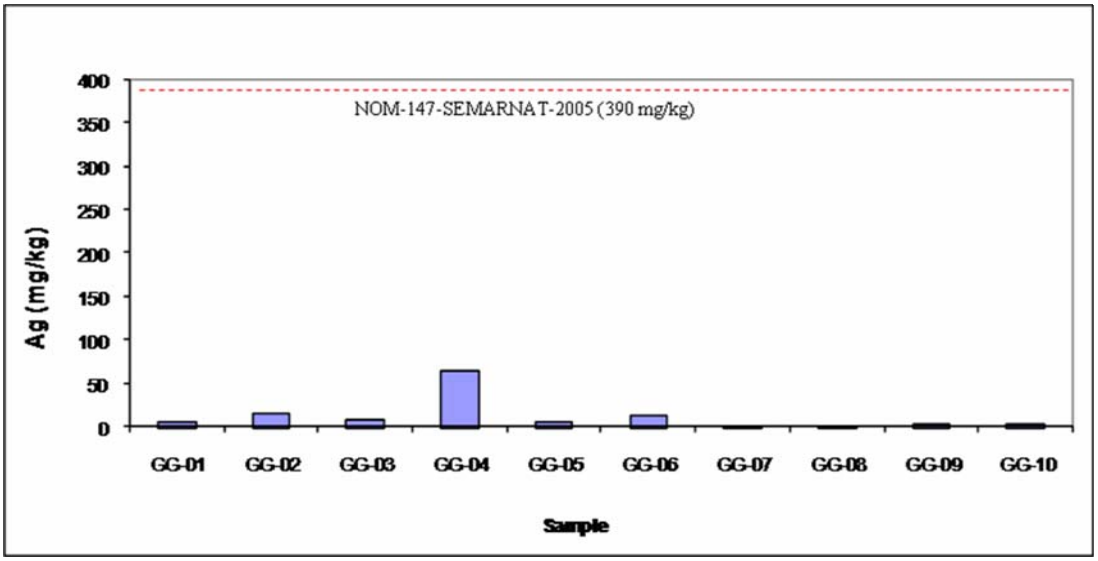


Guanajuato, Guanajuato

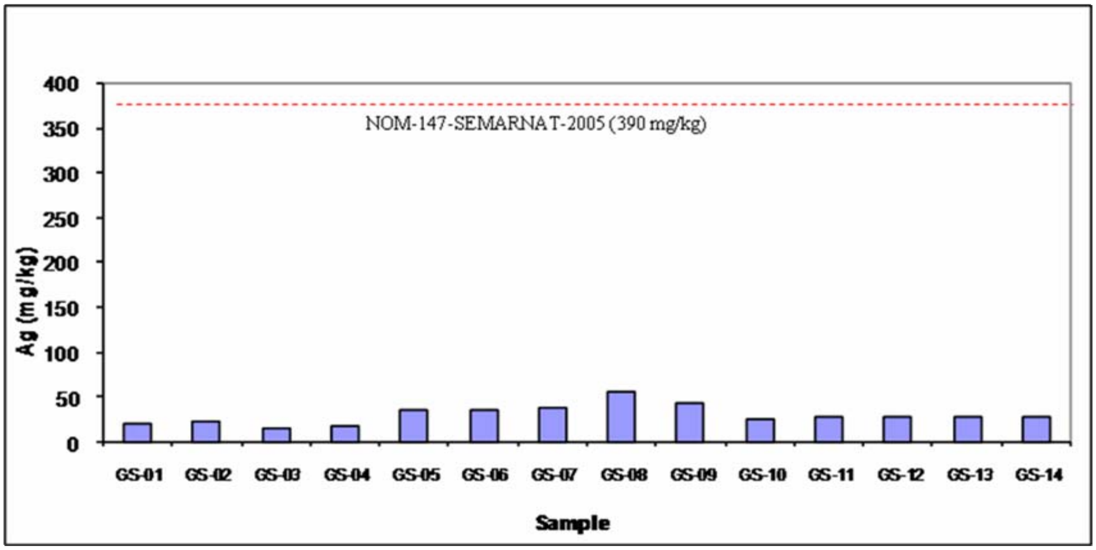


Salamanca, Guanajuato

Figure 18. Total concentration of silver in the towns of Guanajuato and Salamanca in the state of Guanajuato



Guanajuato, Guanajuato



Salamanca, Guanajuato

State of Queretaro

Table 11 shows the location of sampling points in San Joaquin and Pinal de Amoles, as well as the total concentration of mercury, lead and silver.

Table 11. Total concentration of Hg, Pb and Ag in samples of San Joaquin (QJ) and Pinal de Amoles (QP) in the state of Queretaro

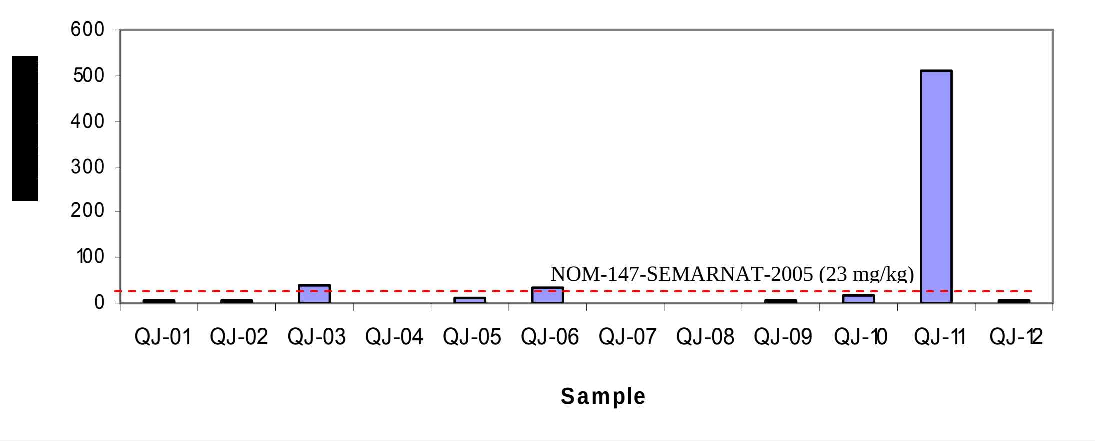
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
QJ-01	N 20°53’59.0’’ W 99°32’16.0’’ A 2300 m	4.08	20.8	0.91	QP-01	N 21°07’38.7’’ W 99°38’53.7’’ A 2429 m	261.5	52.06	4.16
QJ-02	N 20°52’57.1’’ W 99°31’27.4’’ A 2367 m	8.21	26.25	1.83	QP-02	N 21°07’44.6’’ W 99°37’02.4’’ A 2328 m	0.43	113.64	22.99
QJ-03	N 20°54’37.8’’ W 99°33’08.1’’ A 2425 m	36.81	35.34	0.58	QP-03	N 21°06’58.7’’ W 99°36’15.4’’ A 2264 m	1.22	81.32	1.95
QJ-04	N 20°53’33.1’’ W 99°33’31.8’’ A 2383 m	1.54	33.46	1.08	QP-04	N 21°08’01.5’’ W 99°36’53.7’’ A 2500 m	3.7	40.76	4.39
QJ-05	N 20°54’26.5’’ W 99°33’54.7’’ A 2435 m	11.67	21.97	0.83	QP-05	N 21°07’57.4’’ W 99°37’22.7’’ A 2301 m	1.95	949.04	65.38
QJ-06	N 20°55’21.7’’ W 99°33’20.7’’ A 2373 m	32.45	51.41	1.01	QP-06	N 21°08’01.3’’ W 99°37’43.1’’ A 2347 m	1.58	57.67	2.81
QJ-07	N 20°55’27.3’’ W 99°34’04.8’’ A 2379 m	2.18	23.18	0.59	QP-07	N 21°09’43.7’’ W 99°36’25.8’’ A 1994 m	436.2	54.54	2.19
QJ-08	N 20°55’16.7’’ W 99°35’27.7’’ A 2474 m	1.17	805.38	8.98	QP-08	N 21°10’14.7’’ W 99°36’39.4’’ A 2028 m	1198.71	72.75	2.63
QJ-09	N 20°55’23.5’’ W 99°36’07.9’’ A 2413 m	6.8	217.15	1.97	QP-09	N 21°07’48.9’’ W 99°35’10.1’’ A 1886 m	0.74	247.82	3.75
QJ-10	N 20°54’24.8’’ W 99°35’27.9’’ A m	14.3	30.7	0.76	QP-10	N 21°08’45.3’’ W 99°34’37.4’’ A 1828 m	1.69	29.67	2.13
QJ-11	N 20°53’42.4’’ W 99°36’09.1’’ A 2482 m	508.83	130.85	1.54	QP-11	N 21°08’50.6’’ W 99°37’43.8’’ A 2303 m	0.48	65.57	2.5

QJ-12	N 20°53’22.9’’ W 99°34’59.1’’ A 2360 m	7.82	33.49	0.72

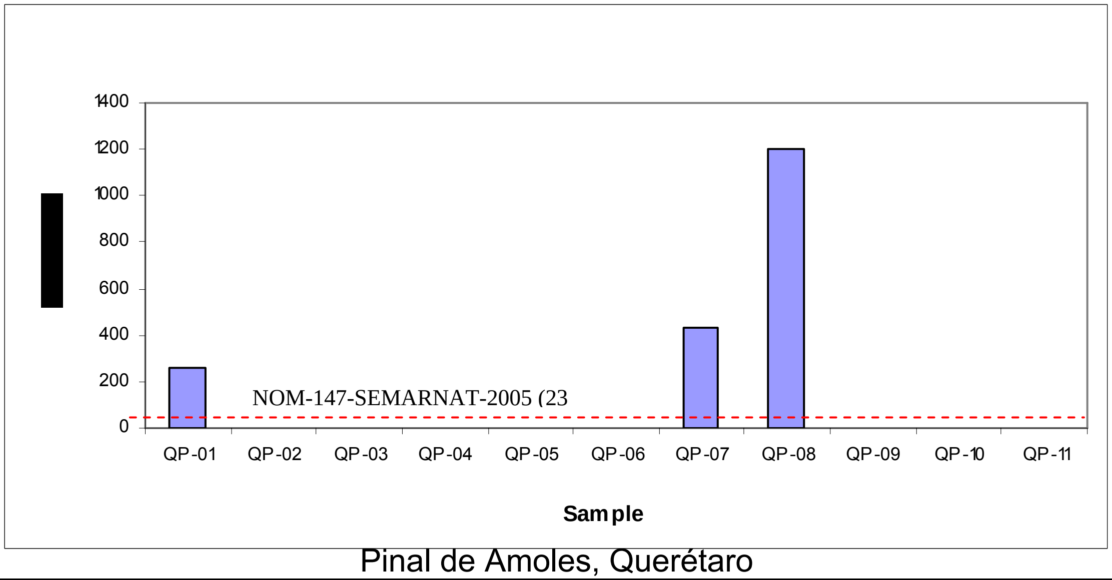
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

Samples QP-01, QP-07 and QP-08 from the town of Pinal de Amoles have a total concentration of mercury higher than the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury). Besides, samples QJ-03, QJ-06 and QJ-11 from the town of San Joaquin also exceeded the limit specified by the existing legislation. For this reason these samples were selected to be speciated with the proposed method (Figure 19).

Figure 19. Total concentration of mercury in the towns of San Joaquin and Pinal de Amoles in the state of Queretaro



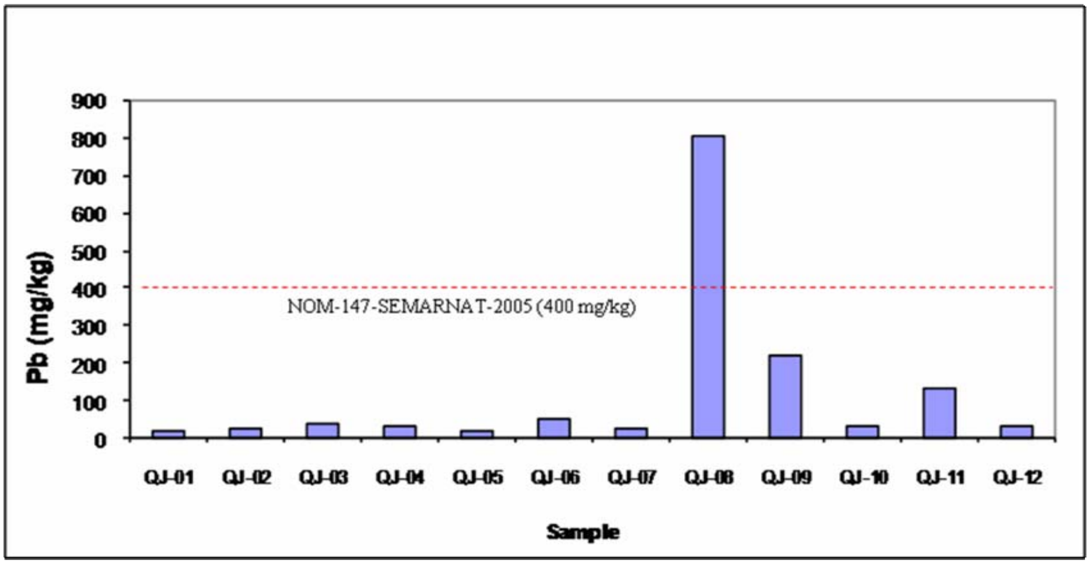
San Joaquín, Querétaro



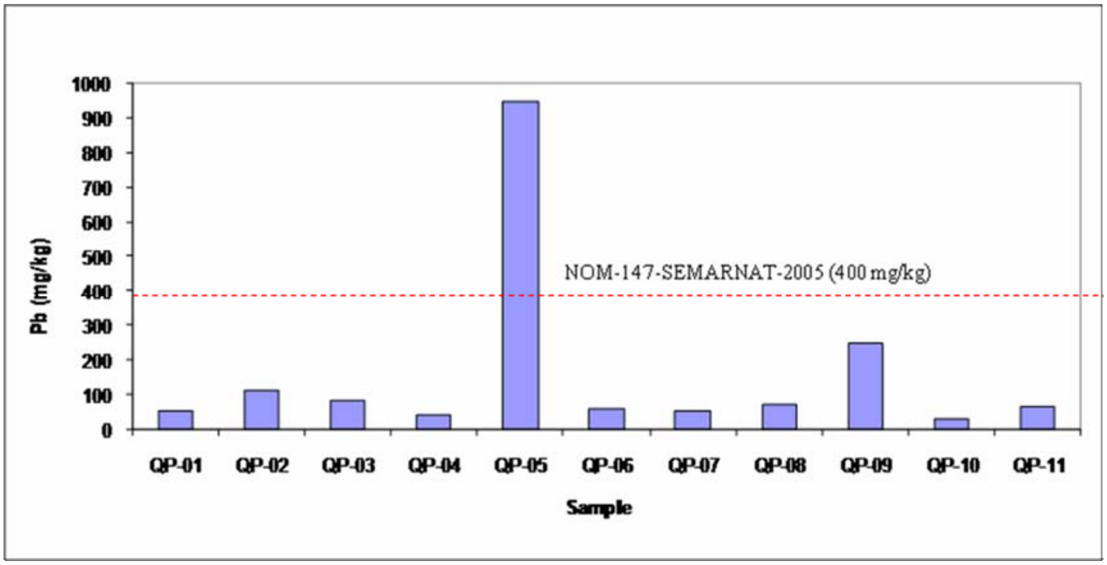
Pinal de Amoles, Querétaro

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by sample QJ-08. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was exceeded by sample QP-05. Results are shown in Figures 20 and 21.

Figure 20. Total concentration of lead in the towns of San Joaquin and Pinal de Amoles in the state of Queretaro

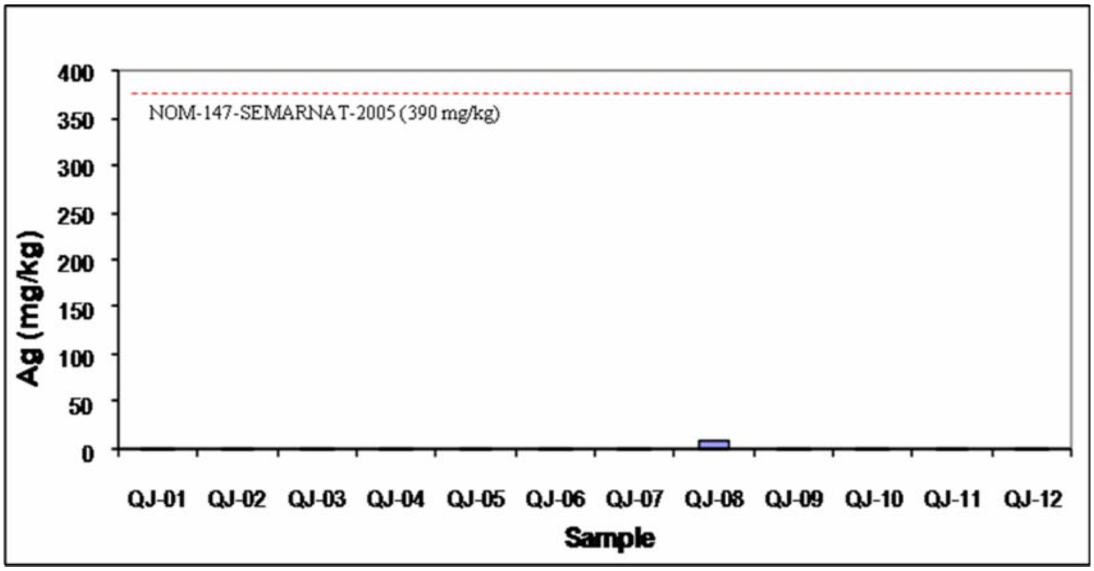


San Joaquín, Queretaro

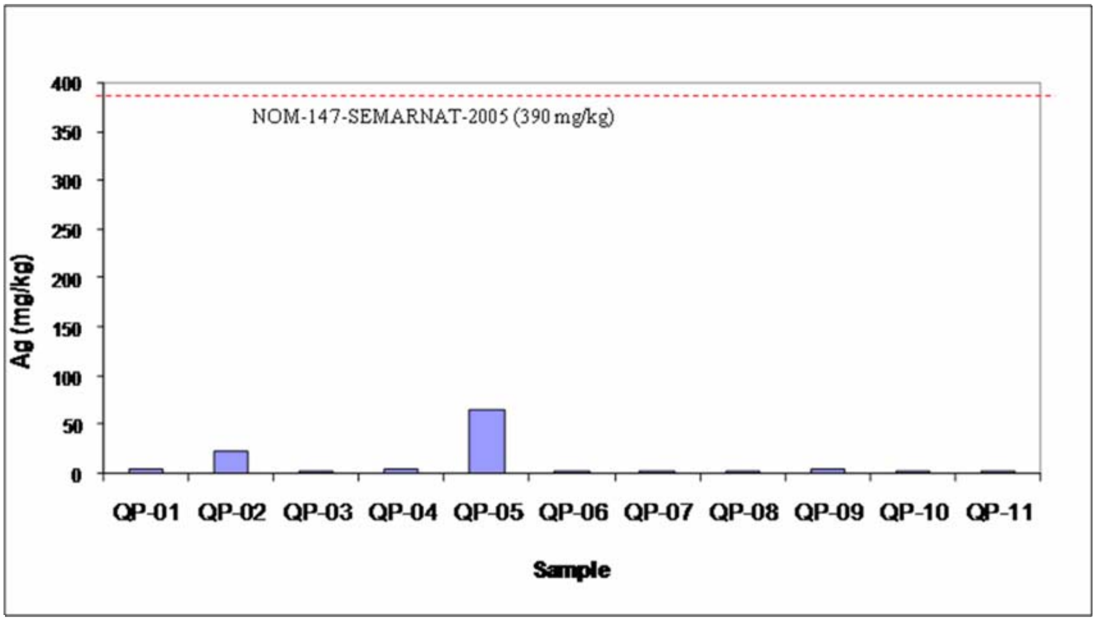


Pinal de Amoles, Queretaro

Figure 21. Total concentration of silver in the towns of San Joaquin and Pinal de Amoles in the state of Queretaro



San Joaquín, Querétaro



Pinal de Amoles, Querétaro

State of Nuevo Leon

Table 12 shows the location of sampling points in Monterrey and Huajuco, as well as the total concentration of mercury, lead and silver.

Table 12. Total concentration of Hg, Pb and Ag in samples of Monterrey (NL-M) and Huajuco (NL-H) in the state of Nuevo Leon

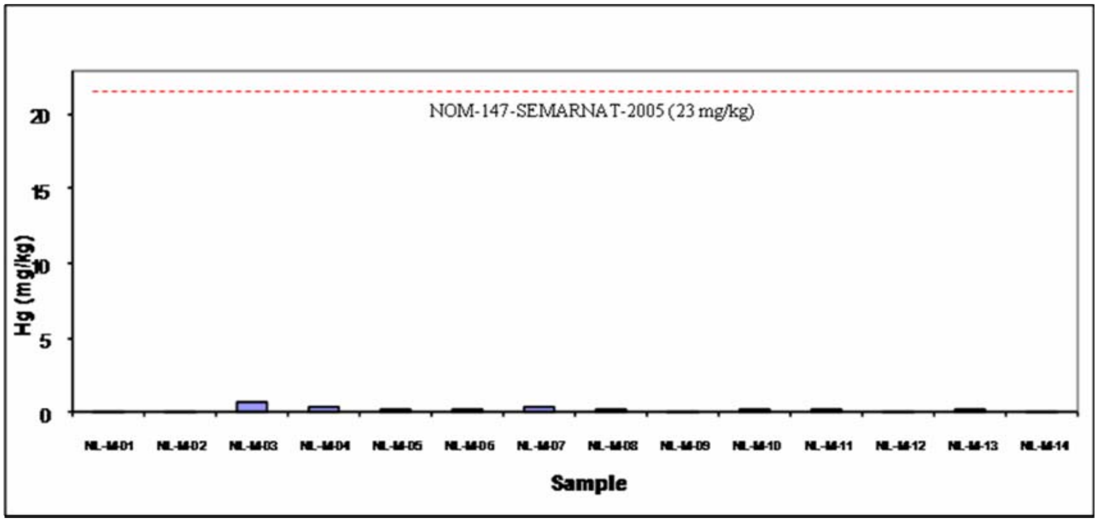
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
NL-M-01	N 25° 42' 59.0'' W 100° 16' 10.0'' A 507 m	0.11	32.14	3.64	NL-H-01	N 25° 35' 41.0'' W 100° 16' 01.4'' A 611 m	0.09	34.16	1.33
NL-M-02	N 25° 42' 46.2'' W 100° 16' 31.4'' A 508 m	0.09	273.62	5.95	NL-H -02	N 25° 35' 58.3'' W 100° 16' 00.5'' A 581 m	0.1	59.84	2.69
NL-M-03	N 25° 42' 50.4'' W 100° 16' 48.1'' A 499 m	0.74	1786.71	10.41	NL-H -03	N 25° 35' 33.1'' W 100° 15' 46.4'' A 577 m	0.22	1525.02	10.81
NL-M-04	N 25° 42' 54.8'' W 100° 17' 05.8'' A 516 m	0.46	38.98	3.77	NL-H -04	N 25° 35' 16.3'' W 100° 15' 57.5'' A 597 m	0.04	26.32	2.01
NL-M-05	N 25° 42' 36.8'' W 100° 17' 11.5'' A 512 m	0.18	98.7	4.16	NL-H -05	N 25° 35' 12.6'' W 100° 15' 40.7'' A 600 m	0.04	21.39	1.34
NL-M-06	N 25° 42' 40.5'' W 100° 16' 58.4'' A 496 m	0.29	309.46	4.04	NL-H -06	N 25° 35' 09.1'' W 100° 16' 06.1'' A 612 m	0.07	24.54	1.6
NL-M-07	N 25° 42' 20.6'' W 100° 17' 26.3'' A 518 m	0.45	331.22	6.21	NL-H -07	N 25° 34' 59.4'' W 100° 15' 33.9'' A 616 m	0.07	28.22	1.74
NL-M-08	N 25° 42' 20.5'' W 100° 16' 34.0'' A 514 m	0.26	309.12	3.36	NL-H -08	N 25° 35' 07.1'' W 100° 15' 15.7'' A 602 m	0.15	95.65	2.42

NL-M-09	N 25° 42’ 03.9’’ W 100° 16’ 38.4’’ A 494 m	0.07	32.19	4.32	NL-H -09	N 25° 35’ 23.5’’ W 100° 15’ 15.0’’ A 592 m	0.12	53.9	6.08
NL-M-10	N 25° 42’ 03.8’’ W 100° 16’ 58.6’’ A 519 m	0.26	250.96	6.07	NL-H -10	N 25° 35’ 38.1’’ W 100° 15’ 05.6’’ A 583 m	0.07	36.42	5.12
NL-M-11	N 25° 42’ 04.1’’ W 100° 17’ 18.2’’ A 522 m	0.27	294.69	17.72	NL-H-11	N 25° 35’ 50.9’’ W 100° 15’ 41.3’’ A 580 m	0.06	41.05	4.45
NL-M-12	N 25° 41’ 52.4’’ W 100° 16’ 06.4’’ A 503 m	0.15	483.63	5.79	NL-H -12	N 25° 36’ 12.9’’ W 100° 15’ 54.9’’ A 569 m	0.16	55.11	3.9
NL-M-13	N 25° 42’ 09.7’’ W 100° 16’ 01.8’’ A 497 m	0.18	42.11	9.89	NL-H -13	N 25° 36’ 12.8’’ W 100° 15’ 32.0’’ A 554 m	0.22	676.23	5.26
NL-M-14	N 25° 42’ 31.3’’ W 100° 16’ 05.5’’ A 508 m	0.07	27.4	3.77	NL-H -14	N 25° 36’ 03.0’’ W 100° 15’ 07.8’’ A 635 m	0.23	48.33	4.32
					NL-H -15 (16)	N 25° 35’ 05.3’’ W 100° 18’ 03.6’’ A 698 m	0.05	5.34	4.32
					NL-H -16 (17)	N 25° 35’ 02.3’’ W 100° 17’ 57.7’’ A 684 m		2466.57	18.73

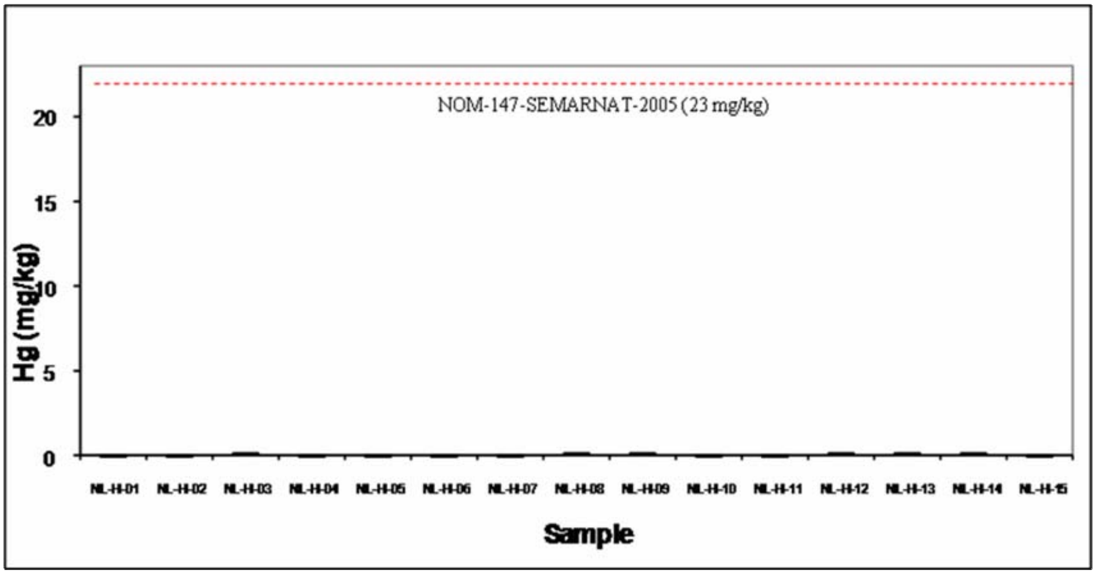
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

In case of mercury, no samples exceeded limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury) as shown in Figure 22.

Figure 22. Total concentration of mercury in the towns of Monterrey and Huajuco in the state of Nuevo Leon



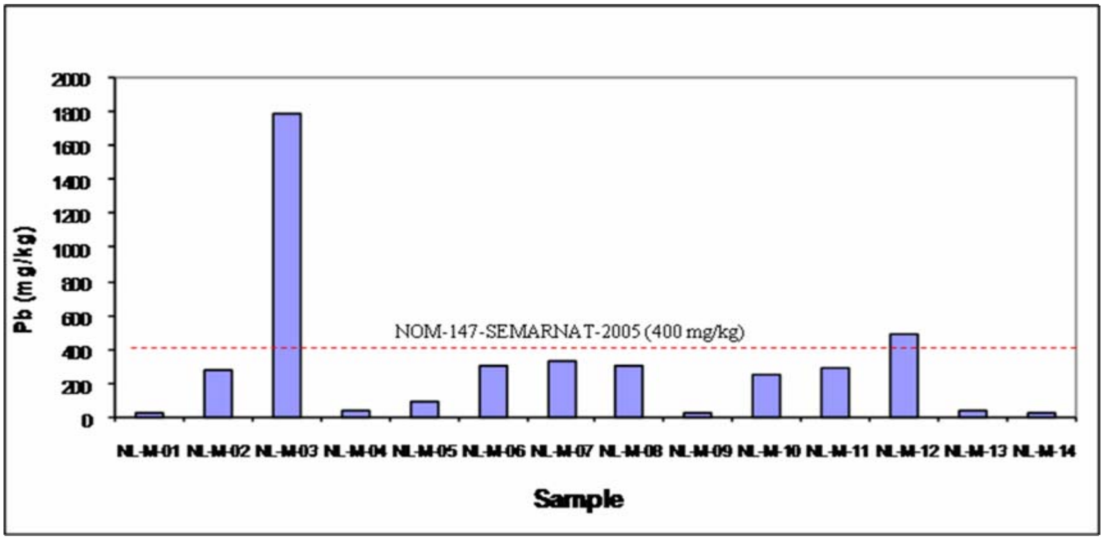
Monterrey, Nuevo Leon



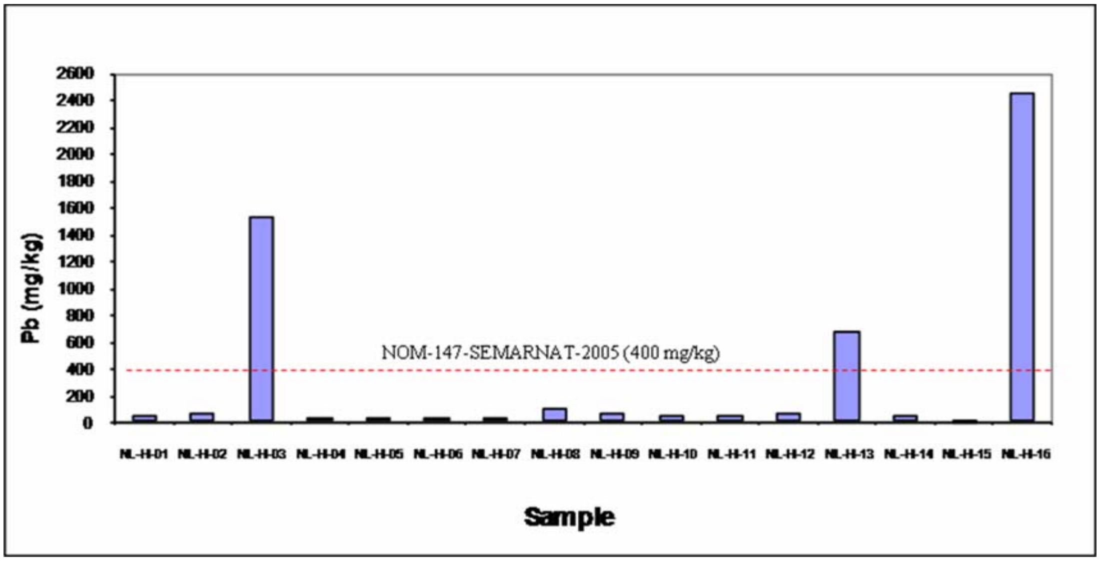
Huajuco, Nuevo Leon

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by samples NL-M-03, NL-M-12, NL-H-03, NL-H-13 and NL-H-16 as shown in Figure 23. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 24.

Figure 23. Total concentration of lead in the towns of Monterrey and Huajuco in the state of Nuevo Leon

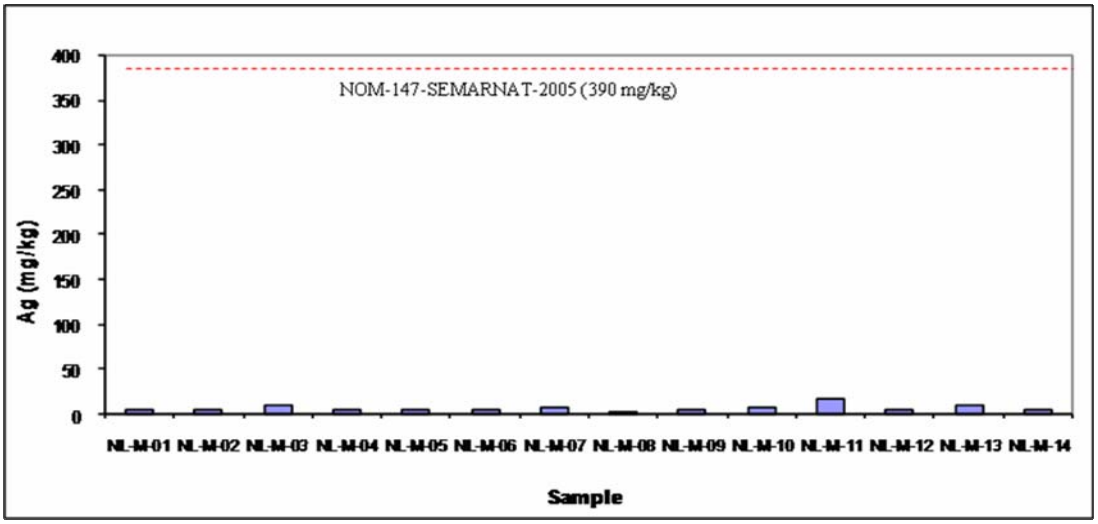


Monterrey, Nuevo Leon

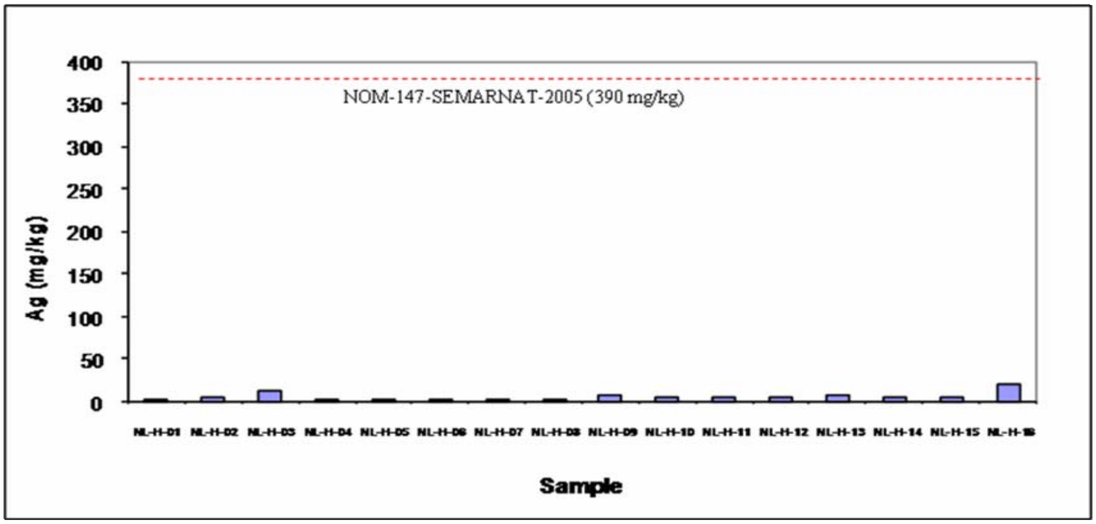


Huajuco, Nuevo Leon

Figure 24. Total concentration of silver in the towns of Monterrey and Huajuco in the state of Nuevo Leon



Monterrey, Nuevo Leon



Huajuco, Nuevo Leon

State of Chihuahua

Table 13 shows the location of sampling points in San Guillermo and Avalos, as well as the total concentration of mercury, lead and silver.

Table 13. Total concentration of Hg, Pb and Ag in samples of San Guillermo (CH-G) and Avalos (CH-A) in the state of Chihuahua

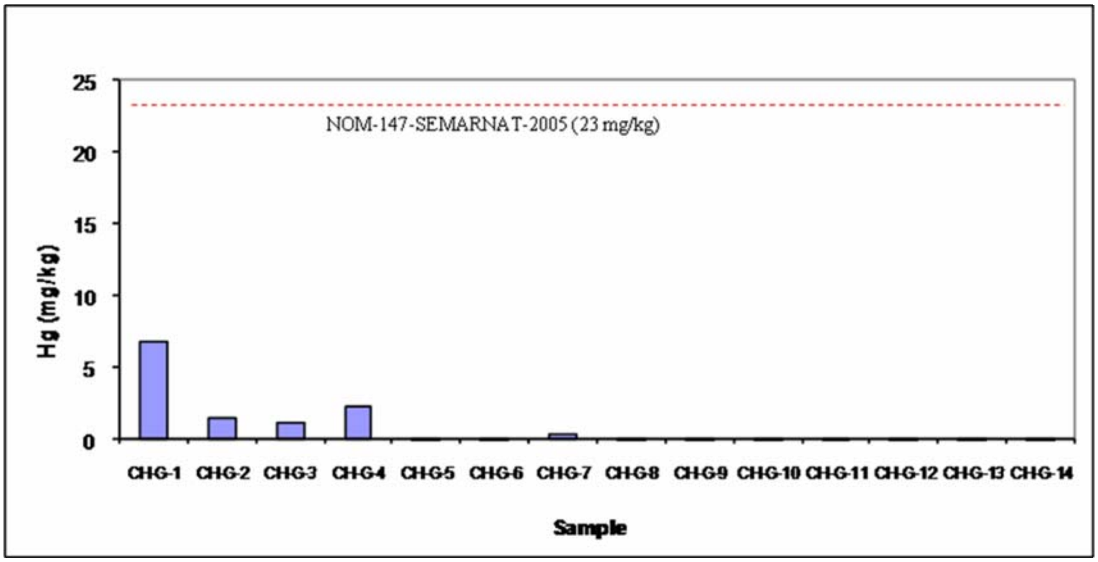
Sample*	**Latitude, longitude & altitude**	**Hg**	**Pb**	**Ag**	**Sample***	**Latitude, longitude & altitude**	**Hg**	**Pb**	**Ag**
			(mg/kg)					**(mg/kg)**	
CH– G –O1	N 28°35'16.6'' W 105°55'42.6'' A 1556 m	6.74	426.13	52.8	CH– A –O1	N 28°37'33.3'' W 106°00'21.6'' A 1432 m	0.041	6170.93	9.1
CH– G –O2	N 28°35'19.5'' W 105°55'43.7'' A 1570 m	1.47	3370.51	32.85	CH– A –O2	N 28°37'18.5'' W 106°00'28.4'' A 1491 m	3.269	4505.95	35.22
CH– G –O3	N 28°35'32.2'' W 105°55'54.4'' A 1548 m	1.19	3257.36	19.62	CH– A –O3	N 28°37'03.8'' W 106°00'30.5'' A 1455 m	3.167	7833.2	25.62
CH– G –O4	N 28°35'23.1'' W 105°55'53.2'' A 1544 m	2.32	3719.97	34.67	CH– A –O4	N 28°36'48.4'' W 106°00'36.8'' A 1444 m	0.376	368.88	2.6
CH– G –O5	N 28°35'37.0'' W 105°56'14.1'' A 1521 m	0.07	303.84	2.87	CH– A –O5	N 28°36'48.8'' W 106°00'30.1'' A 1444 m	0.7	4675.94	11.73
CH– G –O6	N 28°35'34.2'' W 105°56'32.6'' A 1509 m	0.07	255.3	2.45	CH– A –O6	N 28°36'45.4'' W 106°00'18.8'' A 1447 m	0.43	43.82	0.97
CH– G –O7	N 28°35'14.9'' W 105°56'07.4'' A 1533 m	0.4	8336.63	18.19	CH– A –O7	N 28°37'01.0'' W 106°00'12.7'' A 1437 m	2.07	7996.03	17.63
CH– G –O8	N 28°35'16.7'' W 105°56'29.5'' A 1519 m	0.07	113.78	2.29	CH– A –O8	N 28°37'16.5'' W 106°00'06.1'' A 1437 m	0.75	7202.85	11.98
CH– G –O9	N 28°34'59.4'' W 105°55'36.2'' A 1555 m	0.06	701.34	4.82	CH– A –O9	N 28°37'22.7'' W 105°59'51.8'' A 1433 m	2.54	8555	13.45
CH– G –10	N 28°34'45.4'' W 105°55'40.9'' A 1556 m	0.05	106.5	3.87	CH– A –10	N 28°37'09.6'' W 105°59'48.7'' A 1429 m	0.36	7134.64	16
CH– G –11	N 28°34'35.9'' W 105°55'55.3'' A 1544 m	0.08	305.88	2.42	CH– A –11	N 28°36'55.9'' W 105°59'40.6'' A 1431 m	1.51	9951.62	23.64

CH– G –12	N 28°34’41.8’’ W 105°56’12.6’’ A 1528 m	0.04	63.5	4.61	CH– A –12	N 28°36’41.4’’ W 105°59’48.3’’ A 1437 m	2.5	113.93	N.D.
CH– G –13	N 28°34’55.4’’ W 105°56’23.4’’ A 1524 m	0.06	95.37	2.43	CH– A –13	N 28°37’27.9’’ W 105°59’38.0’’ A 1421 m	1.4	590.29	3.13
CH– G –14	N 28°34’56.6’’ W 105°56’00.6’’ A 1543 m	0.07	304.17	2.13					

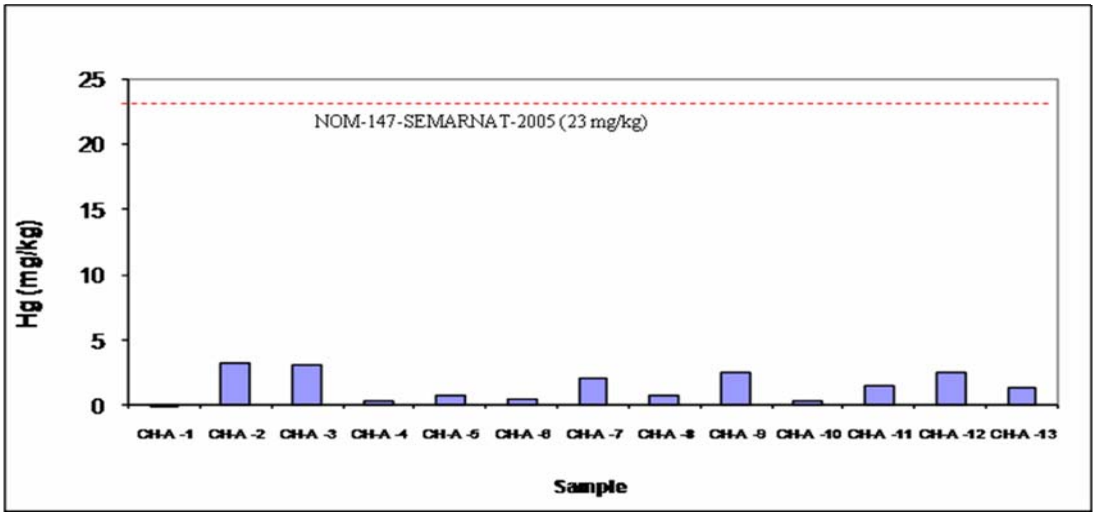
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

In case of mercury, no samples exceeded the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury) as shown in Figure 25.

Figure 25. Total concentration of mercury in the towns of San Guillermo and Avalos in the state of Chihuahua



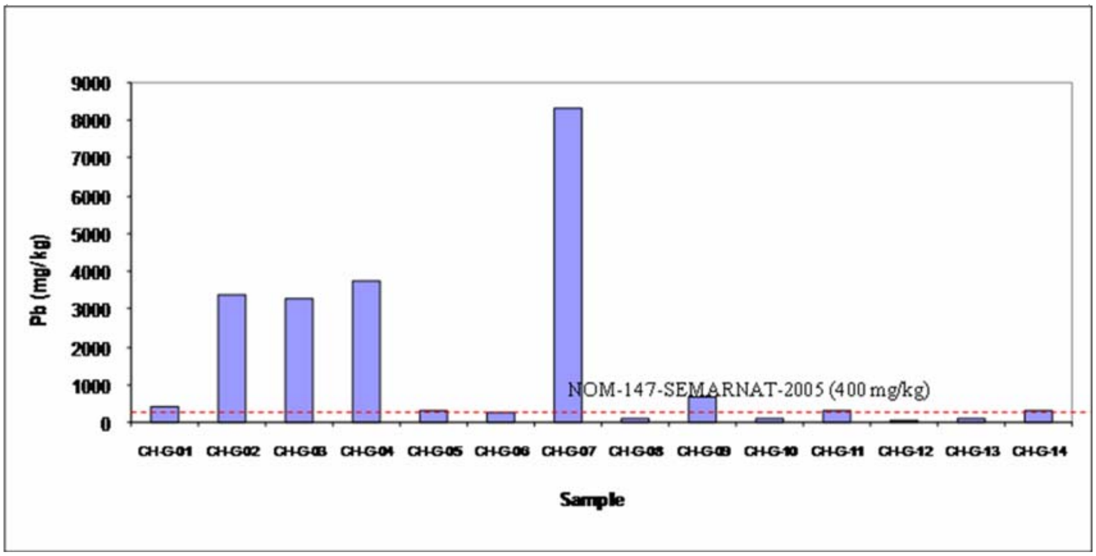
San Guillermo, Chihuahua



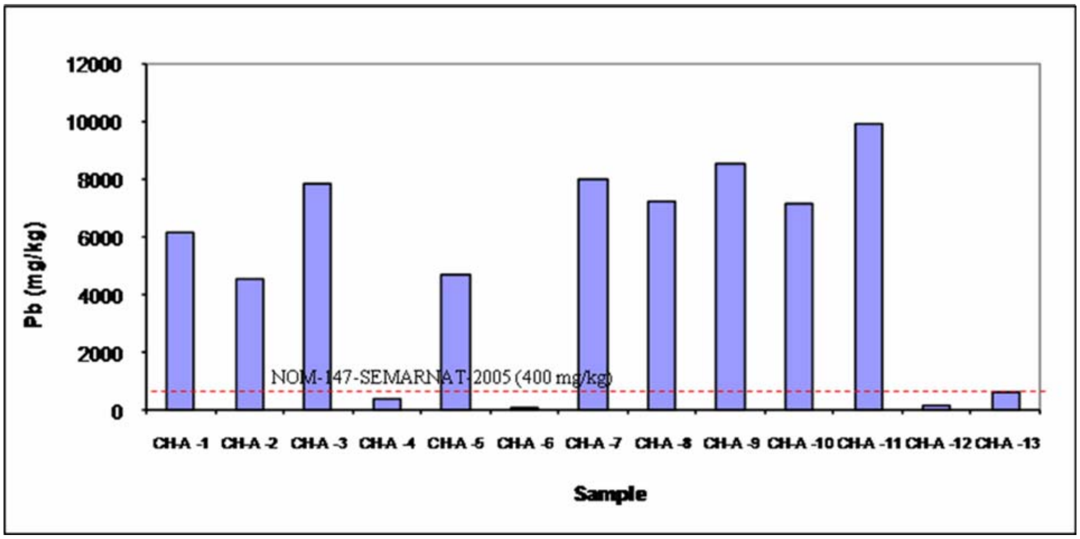
Avalos, Chihuahua

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by samples CH-G-02, CH-G-03, CH-G-04, CH-G-07, CH-G-09, CH-A-01, CH-A-02, CH-A-03, CH-A-05, CH-A-07, CH-A-08, CH-A-09, CH-A-10, CH-A-11 and CH-A-13 as shown in Figure 26. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 27.

Figure 26. Total concentration of lead in the towns of San Guillermo and Avalos in the state of Chihuahua

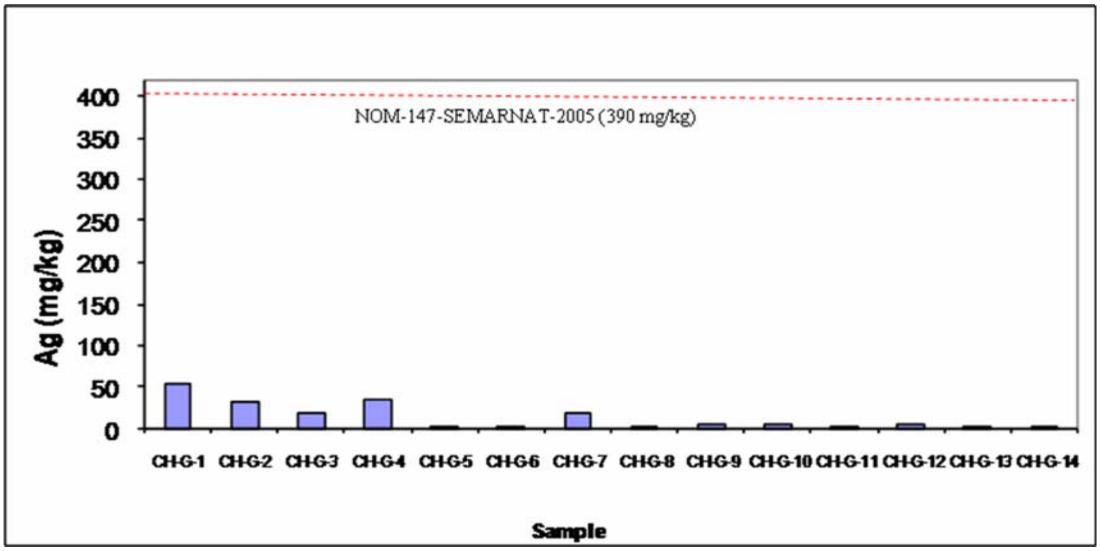


San Guillermo, Chihuahua

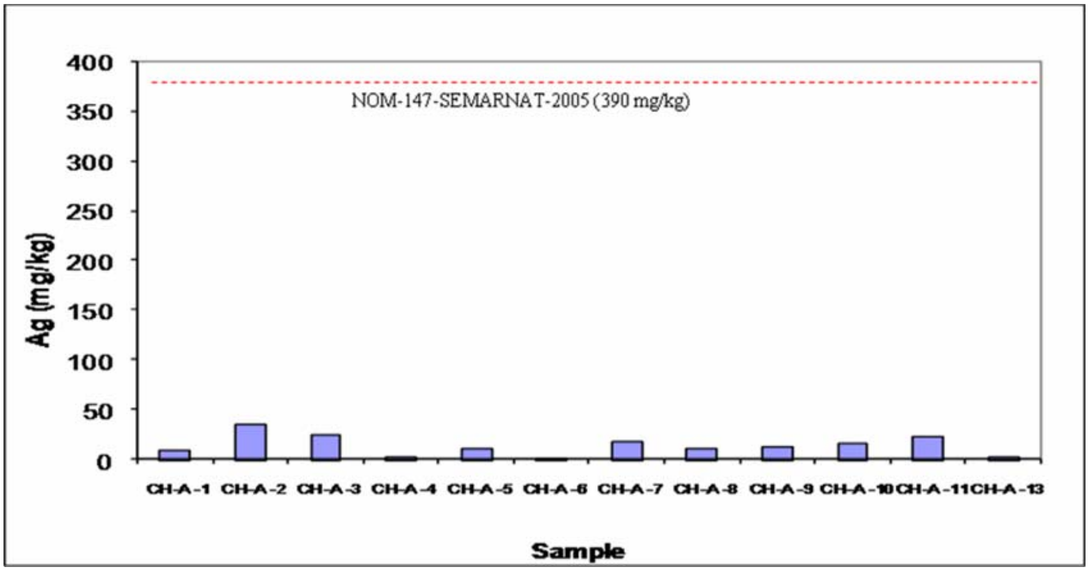


Avalos, Chihuahua

Figure 27. Total concentration of silver in the towns of San Guillermo and Avalos in the state of Chihuahua



San Guillermo, Chihuahua



Avalos, Chihuahua

State of Tamaulipas

Table 14 shows the location of sampling points in San Carlos and San Nicolas, as well as the total concentration of mercury, lead and silver.

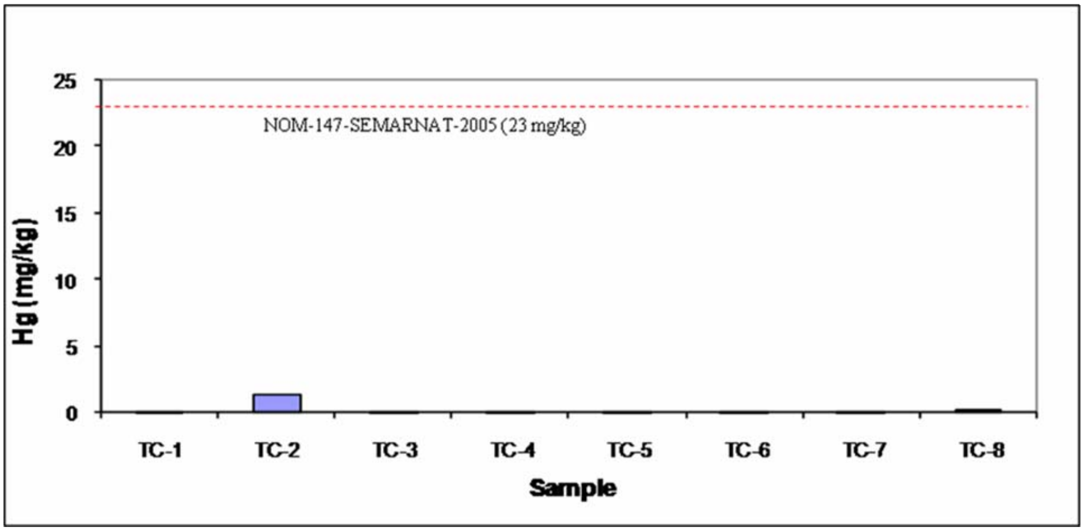
Table 14. Total concentration of Hg, Pb and Ag in samples of San Carlos (TC) and San Nicolas (TN) in the state of Tamaulipas

Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
TC – 01	N 24°40’37.6’’ W 99°04’46.5’’ A 682	0.07	125.72	2.94	TN – 01	N 24°44’06.5’’ W 98°53’48.5’’ A 601	2.53	7327.1	220.81
TC – 02	N 24°40’56.6’’ W 99°04’30.1’’ A 669	1.38	12.11	27.2	TN – 02	N 24°44’07.1’’ W 98°53’46.5’’ A 587	1.55	7391.7	150.83
TC – 03	N 24°35’01.5’’ W 98°56’59.4’’ A 446	0.01	3.75	1.05	TN – 03	N 24°44’00.8’’ W 98°53’24.3’’ A 602	2.95	8436.33	151.48
TC – 04	N 24°34’57.0’’ W 98°56’31.3’’ A 439	0.05	58.55	1.97	TN – 04	N 24°44’02.5’’ W 98°53’28.3’’ A 608	1.84	6250.47	189.4
TC – 05	N 24°34’27.4’’ W 98°56’51.7’’ A 462	0.03	9.94	3.6					
TC – 06	N 24°34’55.3’’ W 98°55’54.0’’ A 438	0.02	26.91	1.6					
TC – 07	N 24°35’08.8’’ W 98°56’34.0’’ A 478	0.06	37.73	1.85					
TC – 08	N 24°34’57.4’’ W 98°56’37.1’’ A 453	0.22	190.75	4.85					

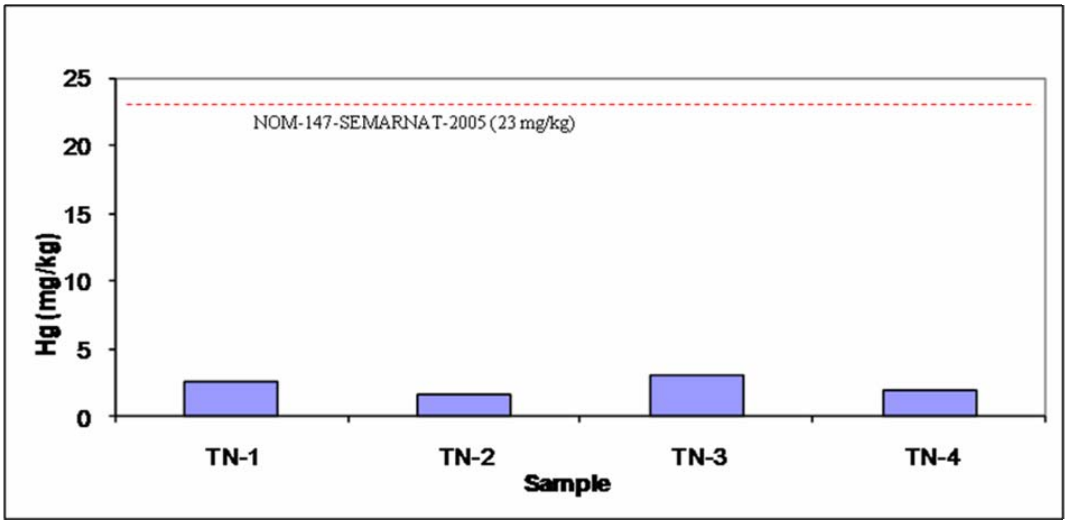
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

In case of mercury, no samples exceeded the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury) as shown in Figure 28.

Figure 28. Total concentration of mercury in the towns of San Carlos and San Nicolas in the state of Tamaulipas



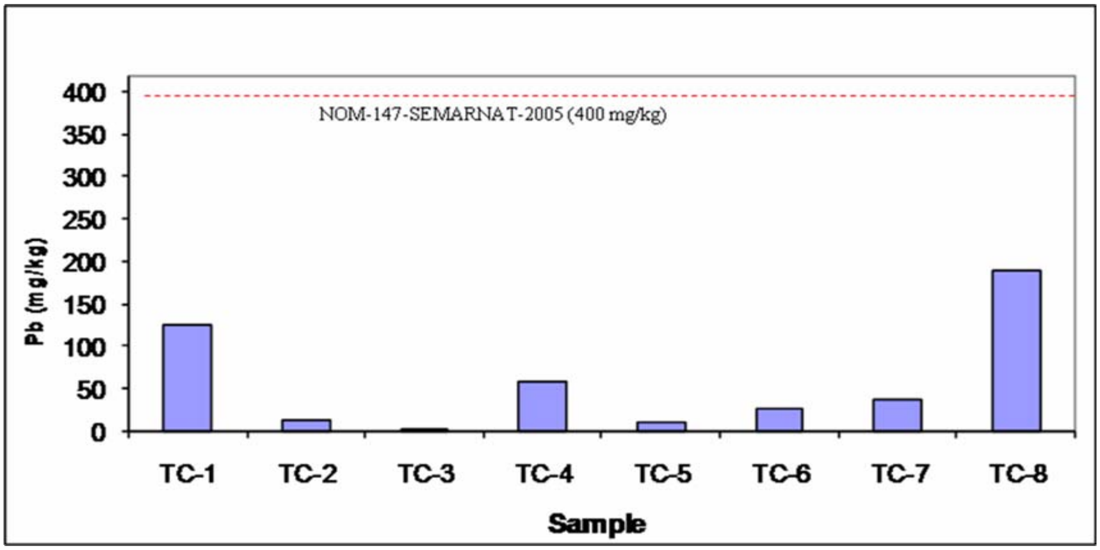
San Carlos, Tamaulipas



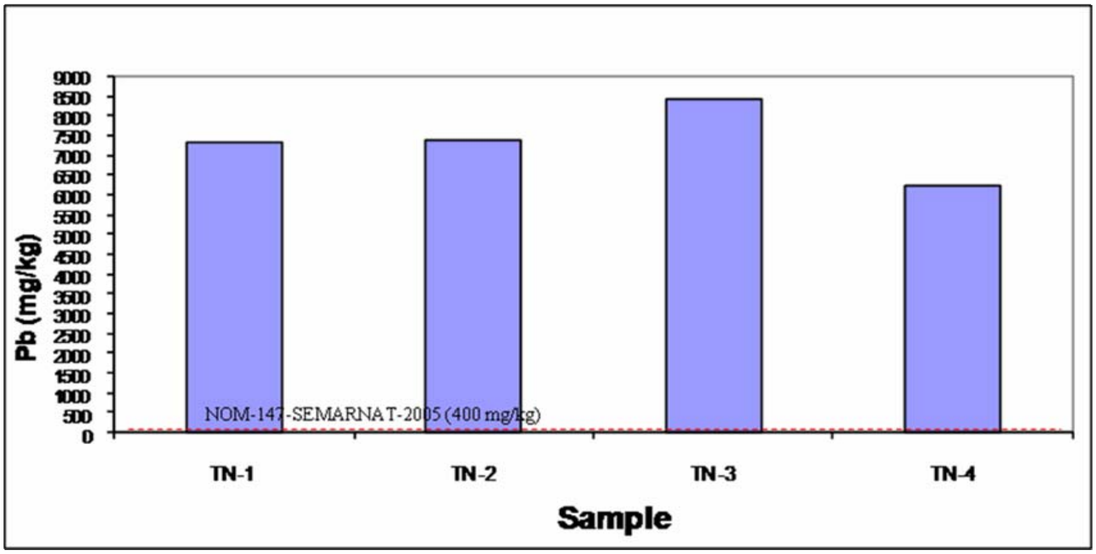
San Nicolas, Tamaulipas

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by samples TN-01, TN-02, TN-03 and TN-04 as shown in Figure 29. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 30.

Figure 29. Total concentration of lead in the towns of San Carlos and San Nicolas in the state of Tamaulipas

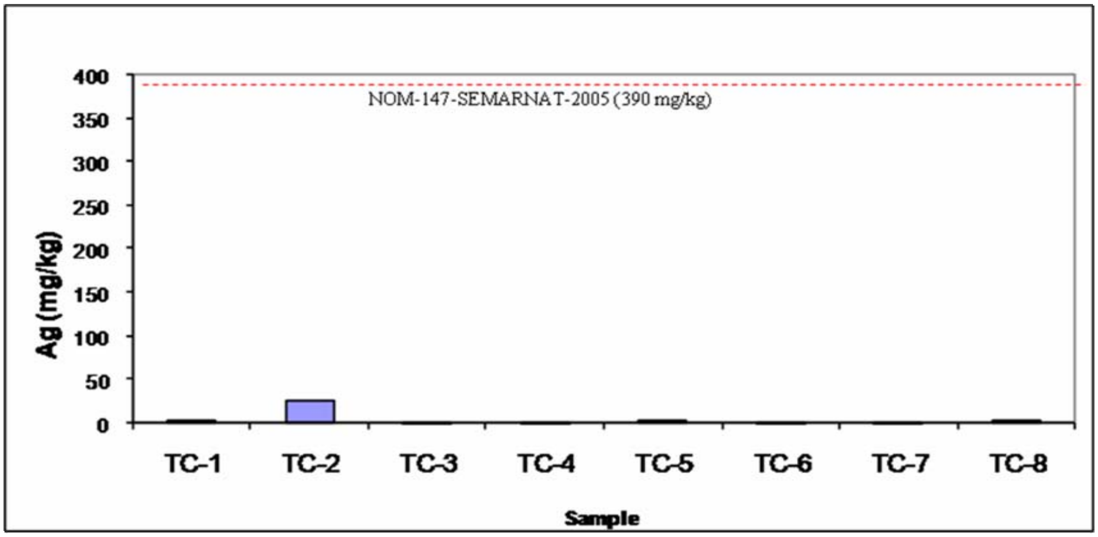


San Carlos, Tamaulipas

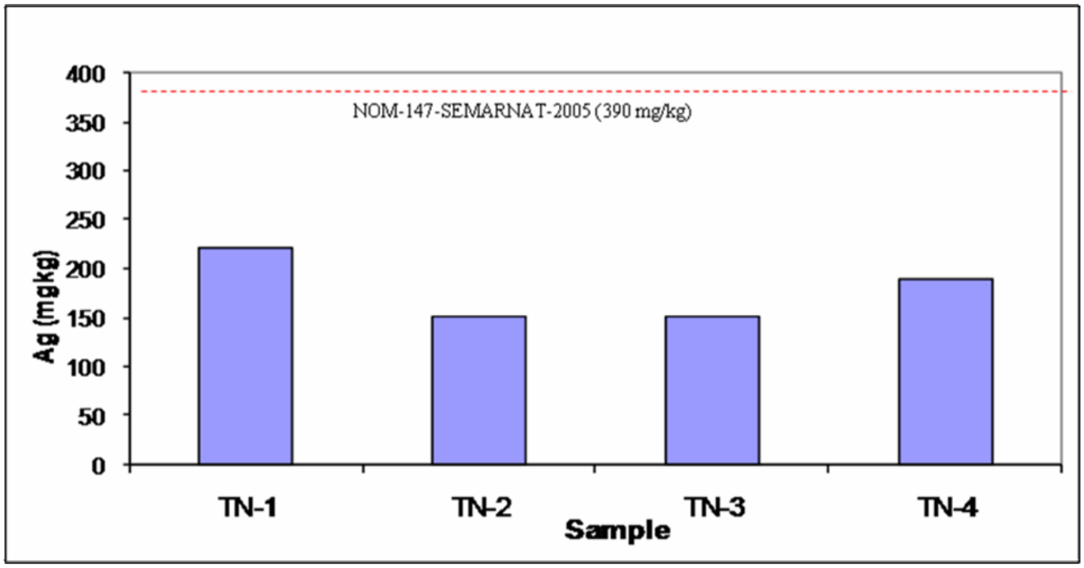


San Nicolas, Tamaulipas

Figure 30. Total concentration of silver in the towns of San Carlos and San Nicolas in the state of Tamaulipas



San Carlos, Tamaulipas



San Nicolas, Tamaulipas

State of Veracruz

Table 15 shows the location of sampling points in Coatzacoalcos and Tuxpan, as well as the total concentration of mercury, lead and silver.

Table 15. Total concentration of Hg, Pb and Ag in samples of Coatzacoalcos (VC) and Tuxpan (VT) in the state of Veracruz

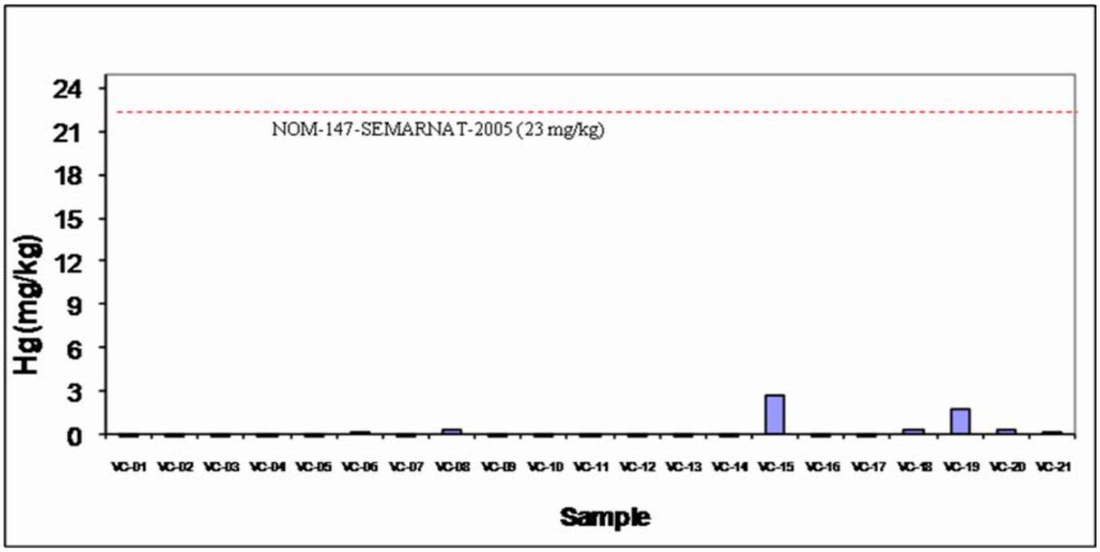
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
VC-01	N 18°08’50.8’’ W 94°24’59.0’’ A 16 m	0.112	16.24	0.8	VT-01	N 20°56’37.1’’ W 97°21’23.5’’ A -2 m	0.08	41.94	1.81
VC-02	N 18°08’56.5’’ W 94°25’51.1’’ A 0 m	0.059	46.46	0.384	VT-02	N 20°56’51.6’’ W 97°24’33.5’’ A 13 m	0.06	6.82	0.67
VC-03	N 18°08’54.6’’ W 94°26’44.1’’ A - 6 m	0.059	14.15	0.435	VT-03	N 20°56’43.9’’ W 97°23’23.0’’ A -6 m	0.15	74.99	1.81
VC-04	N 18°08’35.5’’ W 94°27’43.0’’ A 6 m	0.085	22.78	0.436	VT-04	N 20°56’40.0’’ W 97°22’26.6’’ A 0 m	0.17	19.69	1.7
VC-05	N 18°07’55.5’’ W 94°28’43.0’’ A 1 m	0.047	11.33	0.333	VT-05	N 20°57’21.0’’ W 97°21’31.6’’ A -3 m	0.13	21.96	1.65
VC-06	N 18°07’57.1’’ W 94°27’40.7’’ A - 4 m	0.169	7.66	0.437	VT-06	N 20°58’13.1’’ W 97°20’16.0’’ A 0 m	0.1	18.84	1.65
VC-07	N 18°07’16.5’’ W 94°26’42.0’’ A - 2 m	0.059	62.47	0.488	VT-07	N 20°57’29.2’’ W 97°22’47.8’’ A -7 m	0.06	24.19	2.59
VC-08	N 18°06’56.3’’ W 94°24’44.5’’ A - 5 m	0.288	28.44	0.383	VT-08	N 20°58’13.5’’ W 97°22’39.3’’ A 13 m	0.05	13.95	1.14
VC-09	N 18°05’31.9’’ W 94°23’44.0’’ A 1 m	0.094	12.1	0.331	VT-09	N 20°57’31.7’’ W 97°23’46.2’’ A 2 m	0.04	21.05	2.43
VC-10	N 18°04’17.9’’ W 94°23’44.0’’ A 4 m	0.081	12.12	0.435	VT-10	N 20°56’41.3’’ W 97°25’06.6’’ A 4 m	0.14	24.66	1.92
VC-11	N 18°05’03.6’’ W 94°22’39.0’’ A 12 m	0.065	17.46	0.384	VT-11	N 20°56’35.9’’ W 97°26’00.9’’ A 20 m	0.16	26.37	2.85

VC-12	N 18°06’12.7’’ W 94°22’40.7’’ A 0 m	0.1	42.78	0.54	VT-12	N 20°57’20.0’’ W 97°26’13.7’’ A 26 m	0.25	24.14	2.95
VC-13	N 18°07’11.2’’ W 94°22’29.7’’ A 20 m	0.086	35.9	0.593	VT-13	N 20°58’06.1’’ W 97°25’58.1’’ A 37 m	0.15	34.36	2.64
VC-14	N 18°08’22.2’’ W 94°22’51.6’’ A 3 m	0.066	39.94	0.436	VT-14	N 20°57’56.3’’ W 97°25’08.1’’ A 7 m	0.11	34.02	2.23
VC-15	N 18°08’19.2’’ W 94°23’51.4’’ A 3 m	2.702	8.06	0.437	VT-15	N 20°57’14.3’’ W 97°25’02.4’’ A 8 m	0.09	246.48	3.2
VC-16	N 18°04’12.6’’ W 94°25’03.3’’ A 1 m	0.05	110.38	0.538	VT-16	N 20°58’30.6’’ W 97°24’24.9’’ A 22 m	0.05	23.22	2.84
VC-17	N 18°06’47.8’’ W 94°23’54.6’’ A 2 m	0.126	32.23	0.645	VT-17	N 20°57’12.9’’ W 97°24’23.8’’ A 6 m	0.19	28.64	2.64
VC-18	N 18°06’26.9’’ W 94°23’12.2’’ A 15 m	0.295	118.08	0.538	VT-18	N 21°01’14.5’’ W 97°20’18.4’’ A 13 m	0.02	9.48	1.6
VC-19	N 18°06’21.1’’ W 94°23’54.5’’ A - 1 m	1.825	11.32	0.488	VT-19	N 21°00’46.4’’ W 97°20’18.2’’ A 12 m	0.06	12.18	1.97
VC-20	N 18°06’41.6’’ W 94°24’04.6’’ A 0 m	0.339	12.98	1.061	VT-20	N 21°01’29.4’’ W 97°20’06.5’’ A 30 m	0.17	30.36	2.64
VC-21	N 18°06’41.8’’ W 94°24’08.7’’ A 6 m	0.161	16.63	0.539					

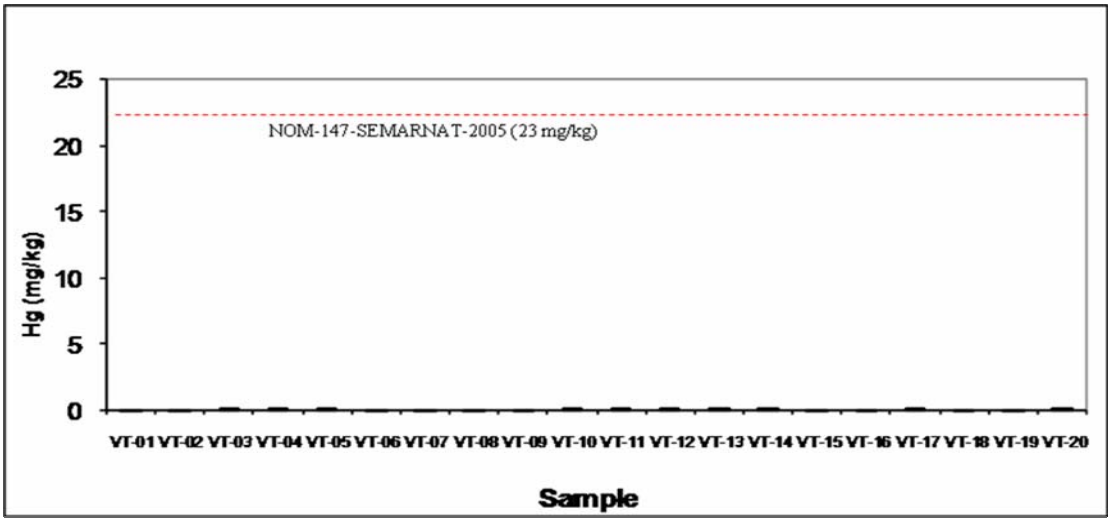
**Mean concentration of triplicate samples*
ND: Concentration under detection limit

In case of mercury, no samples exceeded the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury) as shown in Figure 31.

Figure 31. Total concentration of mercury in the towns of Coatzacoalcos and Tuxpan in the state of Veracruz



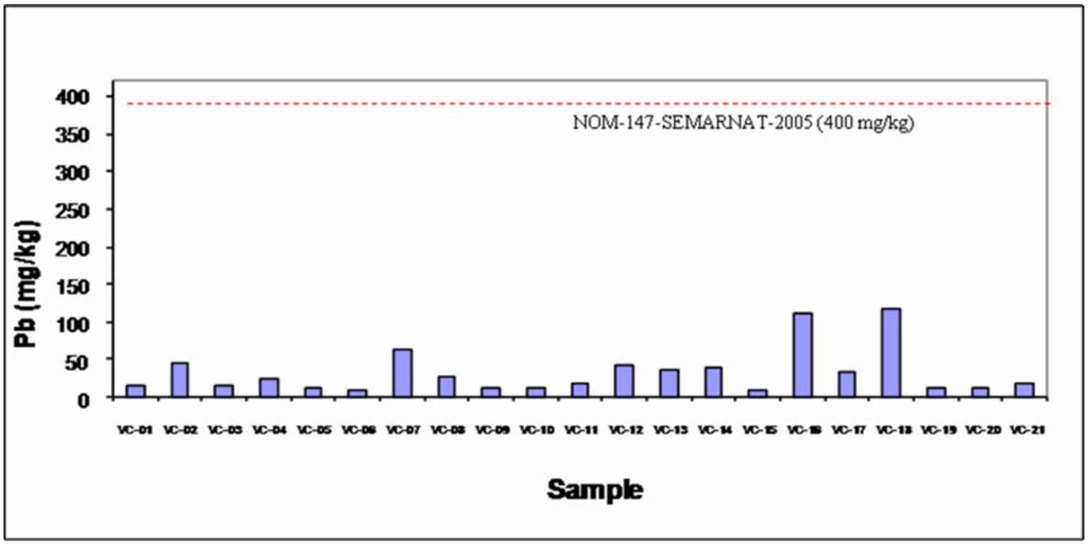
Coatzacoalcos, Veracruz



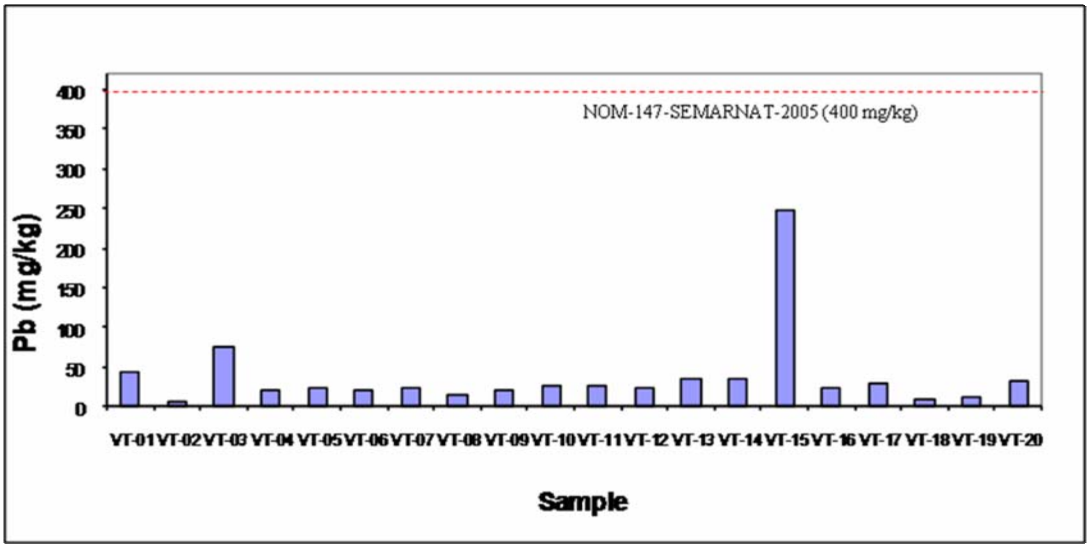
Tuxpan, Veracruz

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was not exceeded as shown in Figure 32. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 33.

Figure 32. Total concentration of lead in the towns of Coatzacoalcos and Tuxpan in the state of Veracruz

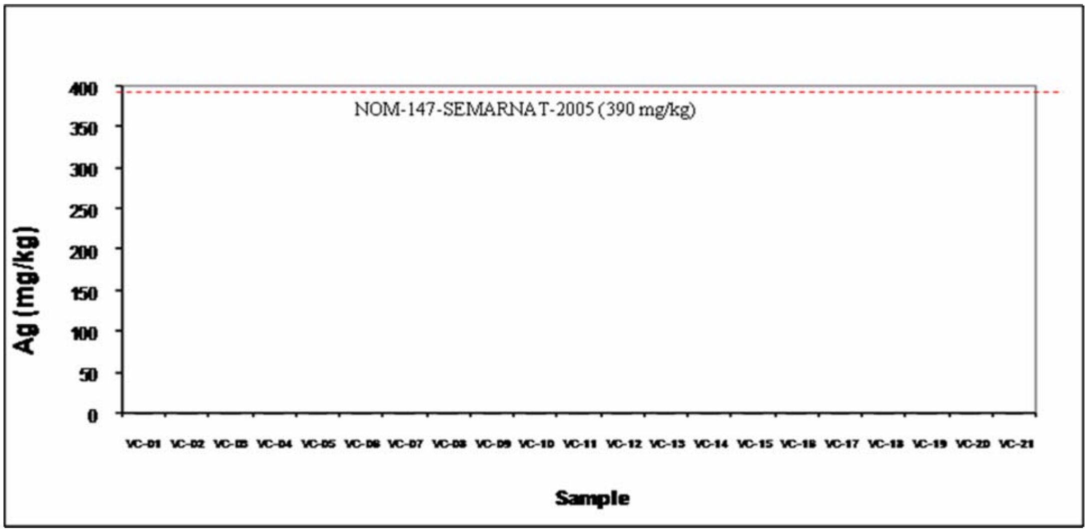


Coatzacoalcos, Veracruz

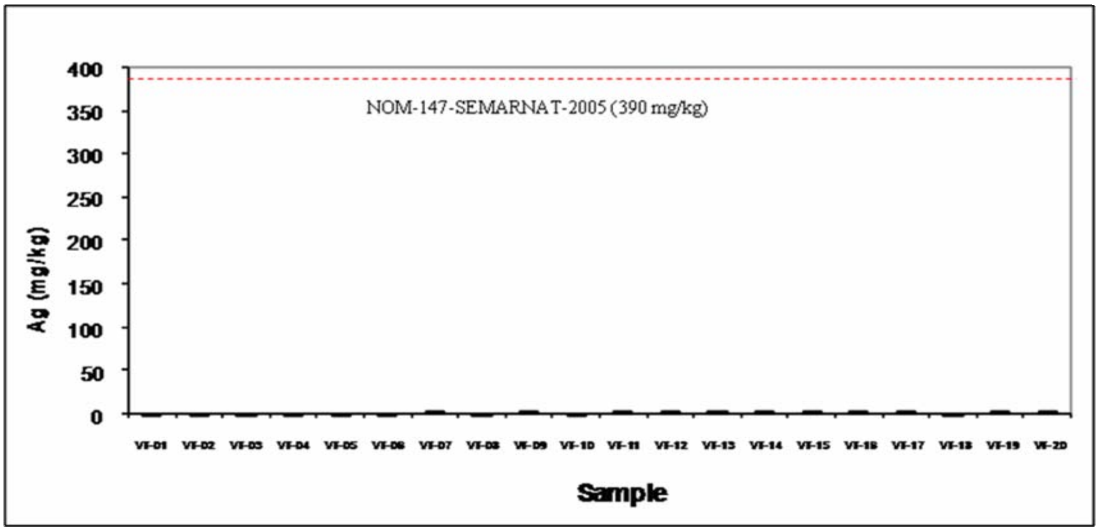


Tuxpan, Veracruz

Figure 33. Total concentration of silver in the towns of Coatzacoalcos and Tuxpan in the state of Veracruz



Coatzacoalcos, Veracruz



Tuxpan, Veracruz

State of Zacatecas

Table 16 shows the location of sampling points in Osiris and La Zacatecana, as well as the total concentration of mercury, lead and silver.

Table 16. Total concentration of Hg, Pb and Ag in samples of Osiris (OM) and La Zacatecana (ZM) in the state of Zacatecas

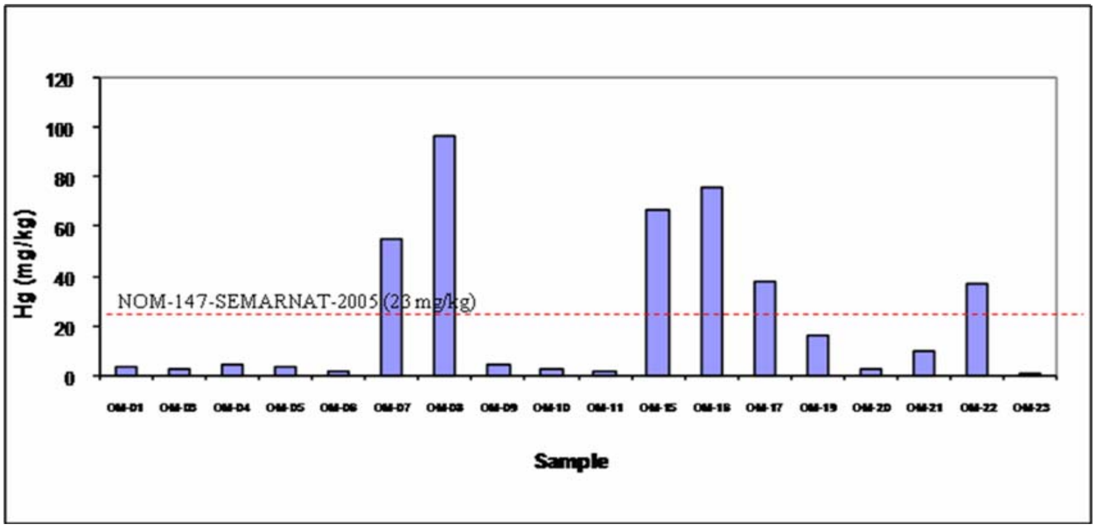
Sample*	Latitude, longitude & altitude	Hg	Pb	Ag	Sample*	Latitude, longitude & altitude	Hg	Pb	Ag
			(mg/kg)					(mg/kg)	
OM-01	N- 22° 44.684´ W- 102° 27.075’ A 2208 m	3.26	92.37	8.75	ZM-01	N- 22° 42 533 W- 102° 29 859 A 2265 m	0.34	14.59	17.43
OM-03	N- 22° 44.630’ W- 102° 26.796’ A 2197 m	2.38	98.86	2.58	ZM-02	N- 22 °42 969 W- 102 °29 510 A 2245 m	0.38	33.41	17.69
OM-04	N- 22° 44.425’ W- 102 26.444’ A 2199 m	4.31	152.98	8.59	ZM-04	N- 22° 43 250 O- 102° 28 203 A 2221 m	2.8	30.83	17.97
OM-05	N- 22° 44.800’ W- 102° 26.742’ A 2202 m	3.85	246.75	8.83	ZM-05	N- 22° 43 030 W- 102° 28 307 A 2230 m	0.8	73.85	20.84
OM-06	N- 22° 44.948’ W- 102° 26.782’ A 2202 m	1.72	133.57	7.75	ZM-07	N- 22° 43 292 W- 102° 29 604 A 2245 m	0.12	59.89	19.88
OM-07	N- 22° 44.981´ W- 102° 27.138’ A 2194 m	55.43	412.78	7.06	ZM-08	N- 22° 43 399 W- 102° 29 770 A 2249 m	0.06	101.86	21.27
OM-08	N- 22° 45.174´ W- 102° 27.620’ A 2202 m	96.56	2006.68	1.51	ZM-10	N- 22° 43 899 W- 102° 28 316 A 2223 m	9.66	204.04	21.36
OM-09	N- 22° 45.120’ W- 102° 26.673’ A 2195 m	4.41	177.58	1.32	ZM-11	N- 22° 43 596 W- 102° 28 173 A 2216 m	5.35	130.93	22.97
OM-10	N- 22° 45.190’ W- 102° 26.421’ A 2195 m	2.29	154.79	1.53	ZM-13	N- 22° 43 997 W- 102° 28 961 A 2230 m	0.31	70.22	19.3
OM-11	N- 22° 45.180´ W- 102° 26.105´ A 2191 m	1.98			ZM-14	N- 22° 43 918 W- 102° 29 709 A 2246 m	1.45	316.4	24.72
OM-15	N- 22° 45.416’ W- 102° 27.365’ A 2197 m	67.12	938.42	15.45	ZM-15	N- 22° 44 326 W- 102° 29 924 A 2253 m	0.16	226.27	24.1
OM-16	N- 22° 45.351’ W- 102° 27.152’ A 2190 m	76.14	1538.1	8.52	ZM-16	N- 22° 44 157 W-102° 29 241 A 2240 m	1.73	331.11	23.87

OM-17	N- 22° 45.296' W- 102° 27.140' A 2210 m	37.83	517.62	9.69	ZM-17	N- 22° 44 134 W- 102° 28 733 A 2224 m	0.96	280.18	24.29
OM-19	N- 22° 46.219' W- 102° 27.184' A 2197 m	16.19			ZM-18	N- 22° 43 925 W- 102° 28 187 A 2242 m	26.16	495.17	24.13
OM-20	N- 22° 46.050' W- 102° 27.068' A 2190 m	2.67	268.59	3.63	ZM-20	N- 22° 44 442 W-102° 28 764 A 2226 m	47.95	3330.54	24.89
OM-21	N- 22° 45.840' W- 102° 27.280' A 2194 m	10.34	280.83	5.47	ZM-22	N- 22° 44 799 W-102° 30 061 A 2257 m	17.69		17.43
OM-22	N- 22° 46.017' W- 102° 27.364' A 2199 m	37.15	2877.09	4.54	ZM-23	N- 22° 45 030 W-102° 29 761 A 2223 m		275.14	17.69
OM-23	N- 22° 46.216' W- 102°27.177' A 2199 m	1.17	237.42	7.49	ZM-24	N- 22° 44 724 W-102° 28 685 A 2255 m	19.82	14.59	17.97

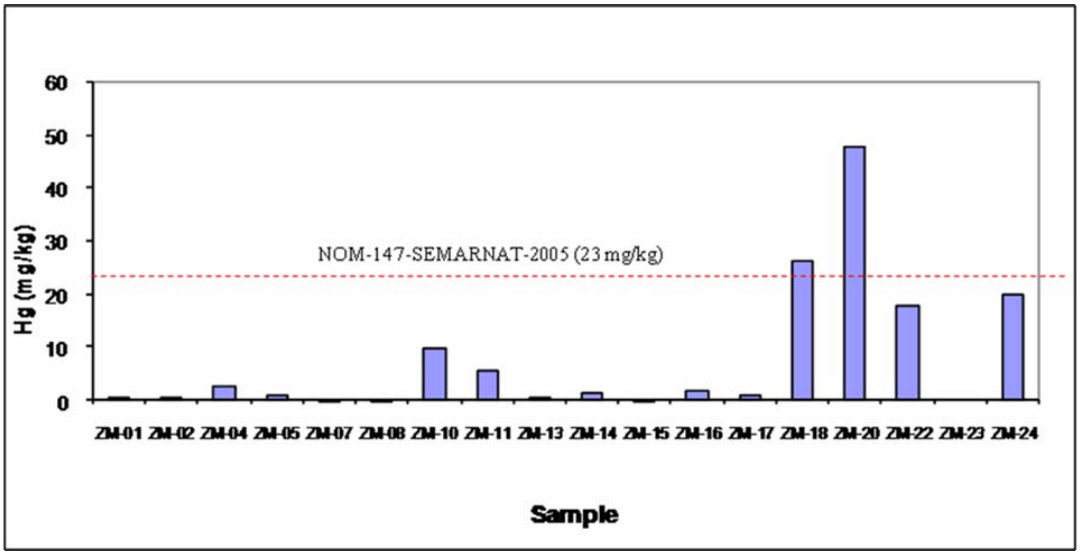
**Mean concentration of triplicate samples*
Missing data had a concentration under detection limit

Samples QP OM-7, OM-8, OM-15, OM-16, OM-17 and OM-22 from the town of Osiris have a total concentration of mercury higher than the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (23 mg/kg of mercury). Besides, samples ZM-18 and ZM-20 from the town of La Zacatecana also exceeded the limit specified by the existing legislation. For this reason these samples were selected to be speciated with the proposed method (Figure 34).

Figure 34. Total concentration of mercury in the towns of Osiris and La Zacatecana in the state of Zacatecas



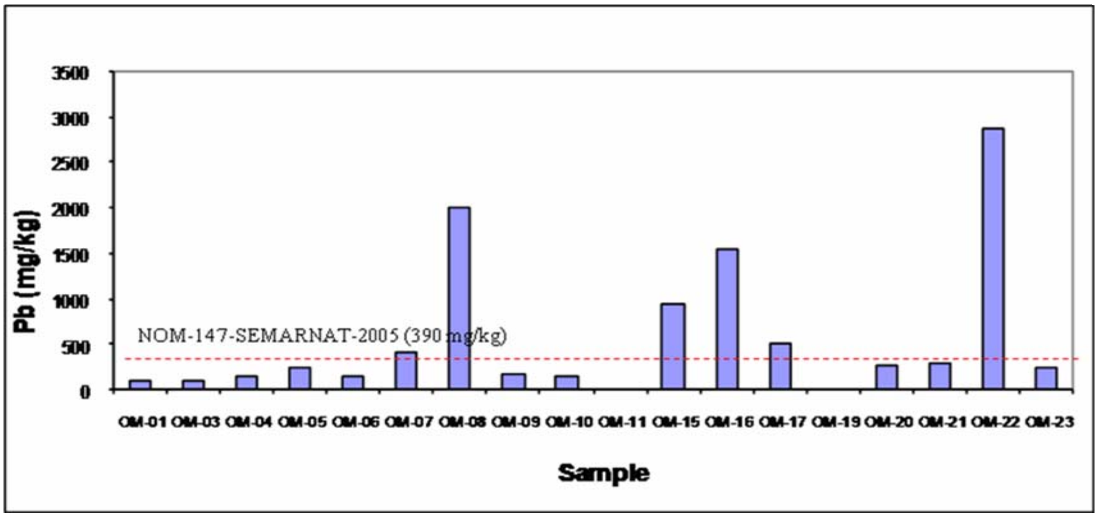
Osiris, Zacatecas



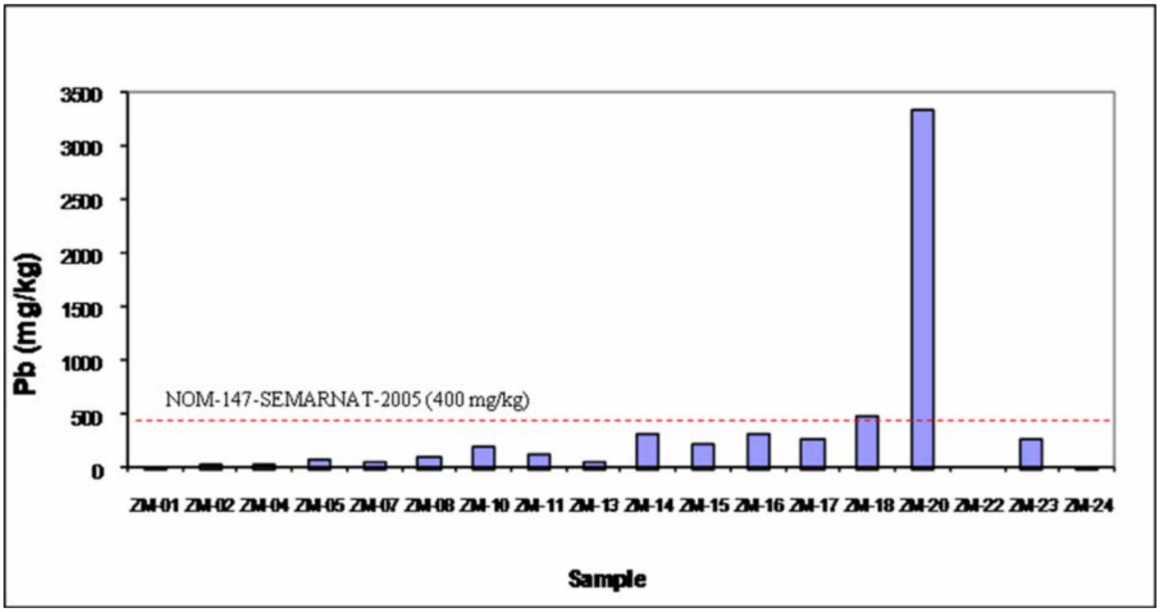
La Zacatecana, Zacatecas

In the case of lead, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (400 mg/kg) was exceeded by samples OM-06, OM-07, OM-11, OM-16, OM-17, OM-22, ZM-18 and ZM-20 as shown in Figure 35. In the case of silver, the limit specified by the NOM-147-SEMARNAT/SSA1-2004 (390 mg/kg) was not exceeded as shown in Figure 36.

Figure 35. Total concentration of lead in the towns of Osiris and La Zacatecana in the state of Zacatecas

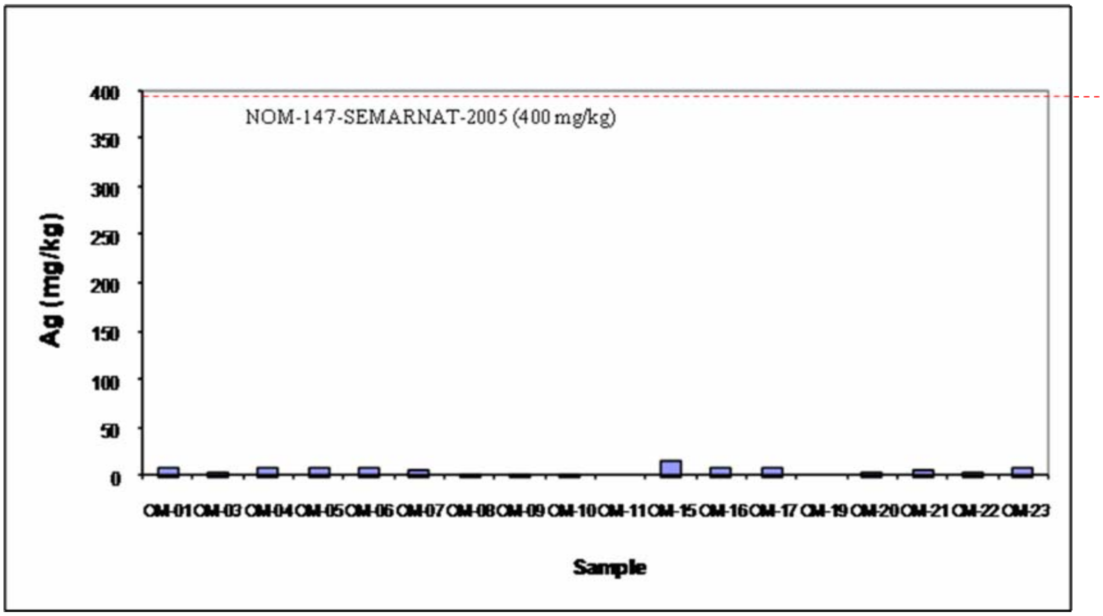


Osiris, Zacatecas

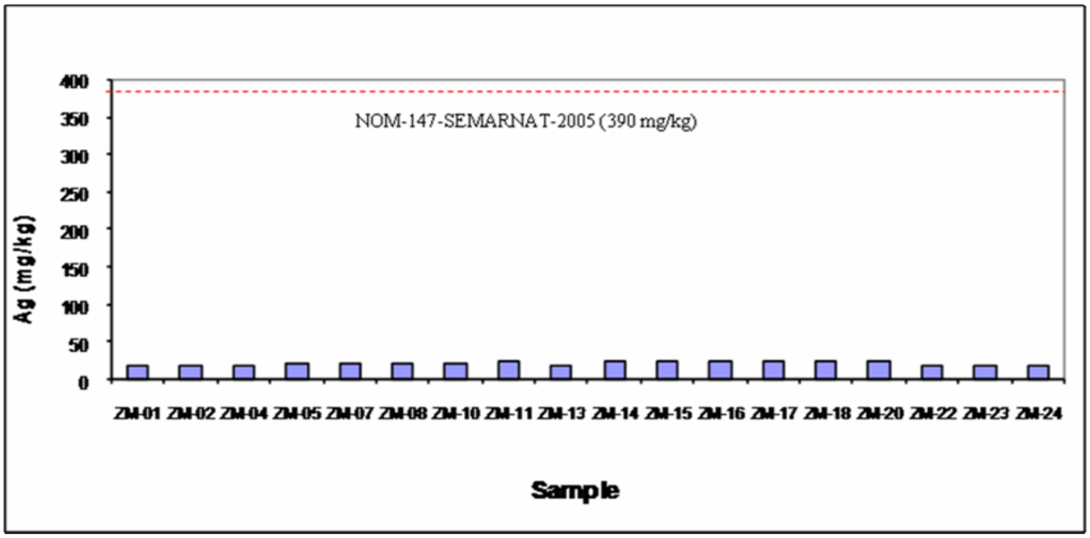


La Zacatecana, Zacatecas

Figure 36. Total concentration of silver in the towns of Osiris and La Zacatecana in the state of Zacatecas



Osiris, Zacatecas



La Zacatecana, Zacatecas

6.2 Evaluation of the extraction efficiency for the proposed mercury chemical speciation method

At this stage, tests were developed for evaluating the performance of the developed method with different salts of mercury.

Since one of the stages consists in a severe warming of the sample (180 °C for 48 hours), the effect of warming on the standard of mercury salts was evaluated, with the aim of verifying the specificity of this test for extracting the elemental mercury fraction and the extent of overlapping of other species.

Figure 37 shows the experimental results of the mercury speciation tests.

Figure 37. Loss of mercury by heating of different salts at 180 °C for 48 hours

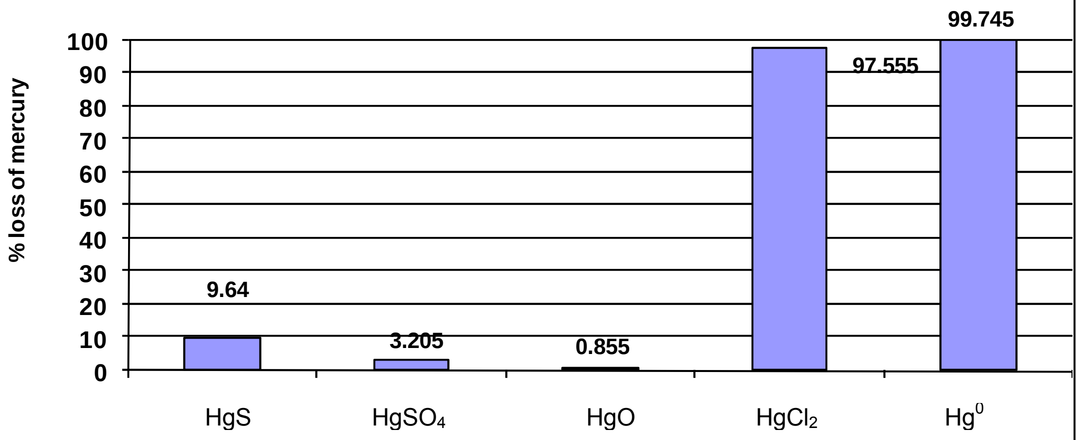


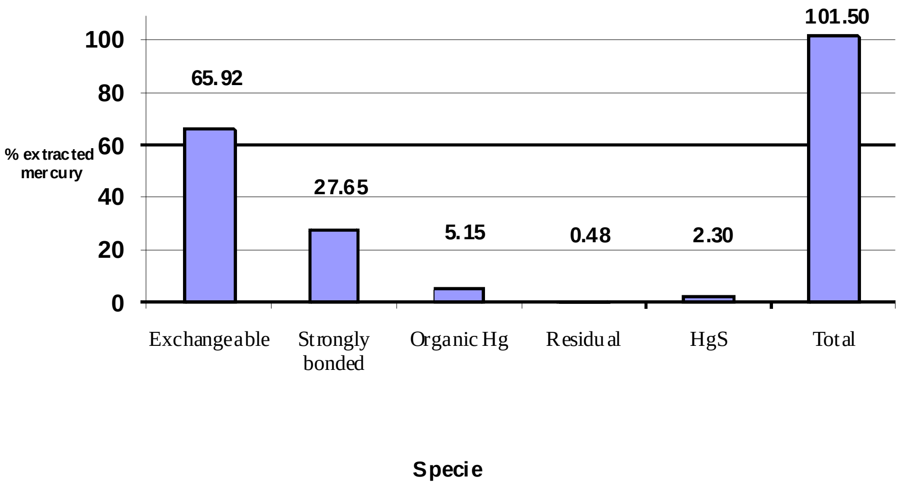
Figure 37 shows that after heating the samples to the previously described conditions, elemental mercury (Hg°) and mercuric chloride ($HgCl_2$) were almost completely lost through evaporation. Mercuric sulfide (HgS) suffers a loss of 10%, and mercuric sulfate ($HgSO_4$) and mercuric oxide (HgO) have the lowest percentage of loss. In this way, the order of decreasing loss by volatilization of different samples would be as follows:

$$Hg° > HgCl_2 > HgS > HgSO_4 > HgO$$

It is important to note that the phase 2 of the method, in which the sample is heated to 180°C to volatilize the Hg°, also would lead to the volatilization of the $HgCl_2$ specie if present in the sample. To attribute the presence of mercury in that fraction only to the metallic specie would represent an error. It is important to consider this parameter before starting the speciation on a contaminated sample since $HgCl_2$ solubility (74 mg/mL of water) has a higher mobility in the event of a leaching that might contaminate groundwater; on the other hand, elemental mercury is less soluble in water (5.6X10-5 mg / ml of water). For this reason, it was considered a water extraction as first stage, with the aim of separating the soluble species and thereafter to proceed with the warming stage.

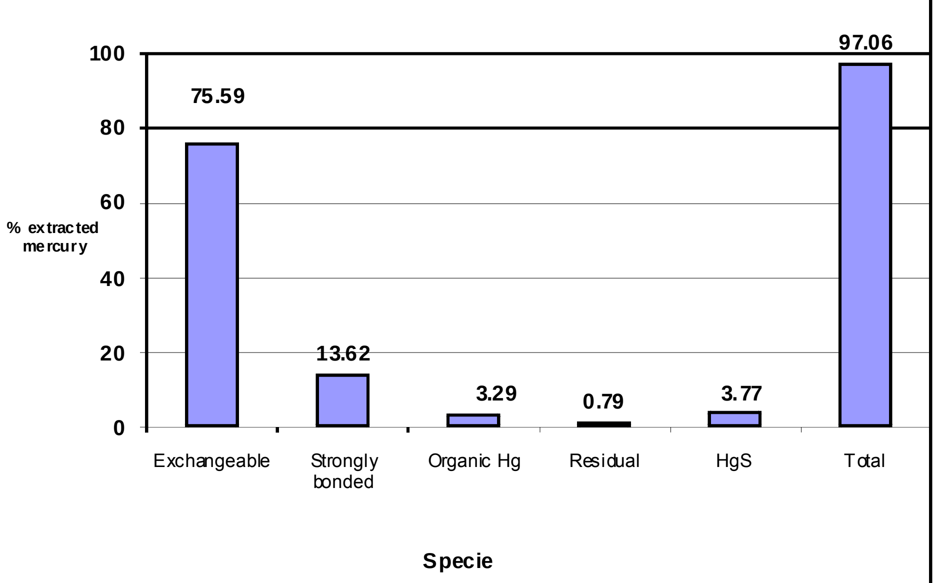
With these results, the method was adjusted by testing HgO, $HgSO_4$ y HgS to the proposed method. Figures 38 to 40 show the mean results for each of the mercury salts.

Figure 38. Mercury recovery (%) using HgO



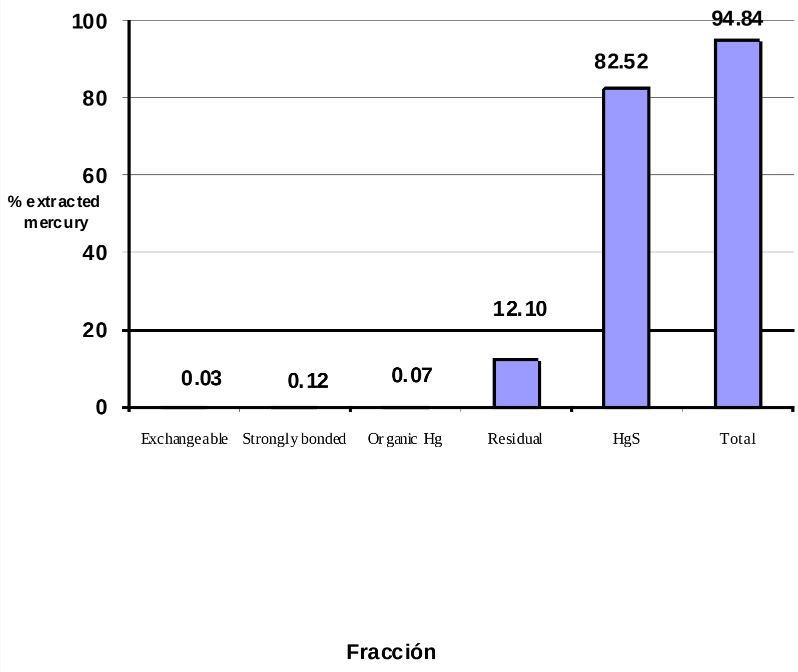
As seen in Figure 38, HgO is distributed in two fractions: a) exchangeable species mainly and in minor proportion b) strongly bonded species.

Figure 39. Mercury recovered (%) using $HgSO_4$



As seen in Figure 39, $HgSO_4$ shows a similar behavior to HgO appearing in major proportion in the exchangeable fraction and in lower proportion in the strongly bonded fraction. From this, it can be concluded that $HgSO_4$ is 10% more specific for the exchangeable species conditions.

Figure 40. Mercury recovered (%) using HgS



As seen in Figure 40, HgS extraction performance is higher (82.52%) in individual species, having a 12% in the residual stage.

6.3 Sequential chemical speciation of mercury in contaminated soils of Mexico

In the following section results from the sequential chemical speciation of mercury in samples with a total concentration higher than the reported limit of 23 mg/kg of mercury (NOM-147-SEMARNAT/SSA1-2004) according to the States of Zacatecas, Hidalgo, Guanajuato and Querétaro.

State of Zacatecas

The results of the sequential chemical speciation for samples of contaminated soil from the towns of Osiris and La Zacatecana in the state of Zacatecas that showed a total mercury concentration above the limit recommended by the regulations indicate that the predominant fraction corresponds to a) Elemental mercury and b) strongly bonded, followed by the fraction c) of mercury species such as sulfides and residual, as indicated in Table 17. On the other hand, fractions such as: water soluble and organic can be found in lower concentrations than specified in the NOM-147-SEMARNAT/SSA1-2004.

Table 17. Sequential chemical speciation of mercury in samples from the towns of Osiris (OM) and La Zacatecana (ZM) in the State of Zacatecas (mg/kg)

Sample*	Water soluble species	Hg^0 (elemental or amalgamated)	Exchangeable species	Strongly bonded	Organic species	Sulfides	Residual	Total
OM-07	0.64	16.42	9.89	12.17	0.61	13.27	2.43	55.43
DS	0.09	1.57	1.24	1.60	0.33	1.18	0.12	
OM-08	3.29	38.74	2.79	0.45	6.16	40.70	4.43	96.56
DS	0.84	3.76	0.08	0.05	0.34	4.90	0.49	
OM-15	1.11	25.88	3.21	0.74	0.22	33.02	2.94	67.12
DS	1.15	0.22	0.78	0.05	0.06	1.11	0.11	
OM-16	3.53	53.41	1.15	2.10	0.11	11.11	4.73	76.14
DS	0.63	1.96	0.35	0.19	0.02	1.49	0.15	
OM-17	0.39	23.22	1.10	1.87	0.12	8.51	2.62	37.83
DS	0.16	0.35	0.81	0.03	0.41	0.06	0.06	
OM-22	0.61	14.29	2.52	4.46	0.05	10.33	4.89	37.15

DS	0.86	1.13	0.35	0.11	0.01	0.78	0.40	
ZM-18	2.33	12.36	0.05	0.16	0.03	7.60	3.63	26.16
DS	0.40	0.12	0.01	0.01	0.01	0.21	0.10	
ZM-20	1.64	35.16	1.31	1.04	0.04	5.28	3.48	47.95
DS	1.26	0.33	0.05	0.03	0.01	1.10	0.05	

**Samples with a total mercury concentration higher than recommended by NOM-147-SEMARNAT/SSA1-2004*
Samples are expressed as a mean of triplicate analysis
DS = Standard deviation

With the results obtained from the sequential chemical speciation method developed for this study, it can be seen that the "elemental mercury" and "mercury sulfide" species are the predominant in analyzed samples (OM-07, OM-08, OM-15 , OM-16, OM-17, OM-22, ZM-18 and ZM-20) from the towns of Osiris (OM) and La Zacatecana (ZM) in the state of Zacatecas.

The "mercury sulfide" specie is presented in concentrations from 5.28 to 40.70 mg/kg, this represents that the mercury contained in the soil analyzed has a low availability and high stability in the environment due to its reduced solubility in different compartments and due to the fact that it is not susceptible to be methylated in anaerobic media; however, it might be methylated in aerobic conditions that allow the release of the mercuric ion (Hg^{2+}) in a soluble form and through the oxidation of sulfide to sulfates and sulfites.

The "elemental fraction" in the soils under study was found in concentrations up to 53.41 mg/kg, which exceeded the maximum limit allowed in the NOM-147-SEMARNAT/SSA1-2004; however, this specie is very stable. The probable origin of this mercury is related to its use in the extraction of precious metals in the Spanish colony. Mercury can be found not only as metallic mercury but also in the form of amalgam formed by the combination with some constituents of the soil. This last factor can give stability to mercury at these sites, due to reduced availability to the microorganisms that methylate it and since it requires very high temperatures to be released from the amalgam (the method used in this study suggests 180 ºC).

The water soluble mercury species were found in the samples up to 8.9% (OM-07, OM-08, OM-15, OM-16, OM-17, OM-22, ZM-18 and ZM-20). This result was higher than results for other states, however, it remains below what is reported in the NOM-147-SEMARNAT/SSA1-2004. In these sites, tailings reprocessing activities are being carried out. The potential risk of these mercury species lies in a possible leaching into the groundwater and reaching a mercury concentration higher than 0.001 ppm which is the maximum level in drinking water allowed by the Ministry of Health. On the other hand, these mercury species may be subject to a methylation process since mercury is already oxidized, which can increase the levels of aryl or alkyl-mercury species in the soil and might increase the risk bioaccumulation in organisms. To evaluate if this mercury species in this soils represent a potential risk, it should be referred to the Mexican standard NOM-147-SEMARNAT/SSA1-2004 which establishes maximum concentrations in contaminated soils for toxic metals and the requirements to implement remediation techniques.

On the other hand, organometallic species such as methylmercury are in percentages below 6% of the total mercury present in soils. This can be attributed to the reduced amount of organic matter.

To evaluate the possible application of specific remediation techniques for soils contaminated with mining waste is required to conduct a broader study with the methods of speciation.

State of Hidalgo

The results of the sequential chemical speciation for samples of contaminated soil from the town of Pachuca in the state of Hidalgo that showed a total mercury concentration above the limit recommended by the regulations indicate that the predominant fraction corresponds to a) Elemental mercury, mostly represent more than 50% of the total mercury content and b) mercury species such as sulfides and residual, as indicated in Table 18. On the other hand, fractions such as: water soluble and organic can be found in lower concentrations than specified in the NOM-147-SEMARNAT/SSA1-2004.

Table 18. Sequential chemical speciation of mercury in samples from the town of Pachuca (HP) in the State of Hidalgo (mg/kg)

Sample *	Water soluble species	Hg^0 (elemental or amalgamated)	Exchangeable species	Strongly bonded	Organic species	Sulfides	Residual	Total
HP-02	0.11	18.14	3.68	4.12	1.11	1.10		28.25
DS	0.16	3.18	1.43	0.27	0.06	0.07		
HP-06	0.01	368.10	9.15	3.47	0.28	283.60		664.62
DS	0.01	38.90	0.90	1.64	0.07	33.70		
HP-07	0.003	316.81	2.90	3.25	0.22	13.40		336.58
DS	0.01	34.61	0.85	0.39	0.10	1.29		

**Samples with a total mercury concentration higher than recommended by NOM-147-SEMARNAT/SSA1-2004*
Samples are expressed as a mean of triplicate analysis
DS = Standard deviation

With the results obtained from the sequential chemical speciation method developed for this study, it can be seen that the "elemental mercury" and "mercury sulfide" species are the predominant in analyzed samples (HP-02, HP-06 and HP-07) from the town of Pachuca (HP) in the state of Hidalgo.

The "mercury sulfide" specie is presented in concentrations from 1.10 to 283.6 mg/kg, this represents that the mercury contained in the soil analyzed has a low availability and high stability in the environment due to its reduced solubility in different compartments and due to the fact that it is not susceptible to be methylated in anaerobic media; however, it might be methylated in aerobic conditions that allow the release of the mercuric ion (Hg^{2+}) in a soluble form and through the oxidation of sulfide to sulfates and sulfites.

The "elemental fraction" in the soils under study was found in concentrations up to 368.1 mg/kg, which exceeded the maximum limit allowed in the NOM-147-SEMARNAT/SSA1-2004; however, this specie is very stable. The probable origin of this mercury is related to its use in the extraction of precious metals in the Spanish colony. Mercury can be found not only as metallic mercury but also in the form of amalgam formed by the combination with some constituents of the soil. This last factor can give stability to mercury at these sites, due to reduced availability to the microorganisms that methylate it and since it requires very high temperatures to be released from the amalgam (the method used in this study suggests 180 ºC).

The water soluble mercury species were found in the samples up to 0.38% (HP-02, HP-06 and HP-07). This result was expected since these wastes have been exposed to climate conditions for many years such as rain, natural flows. The potential risk of these mercury species lies in a possible leaching into the groundwater and reaching a mercury concentration higher than 0.001 ppm which is the maximum level in drinking water allowed by the Ministry of Health. On the other hand, these mercury species may be subject to a methylation process since mercury is already oxidized, which can increase the levels of aryl or alkyl-mercury species in the soil and might increase the risk bioaccumulation in organisms. To evaluate if this mercury species in this soils represent a potential risk, it should be referred to the Mexican standard NOM-147-SEMARNAT/SSA1-2004 which establishes maximum concentrations in contaminated soils for toxic metals and the requirements to implement remediation techniques.

On the other hand, organometallic species such as methylmercury are in percentages below 4% of the total mercury present in soils. This can be attributed to the reduced amount of organic matter.

To evaluate the possible application of specific remediation techniques for soils contaminated with mining waste is required to conduct a broader study with the methods of speciation.

State of Guanajuato

Just like in the previous case, the results of the sequential chemical speciation for samples of contaminated soil from the town of Guanajuato in the state of Guanajuato that showed a total mercury concentration above the limit recommended by the regulations indicate that the predominant fraction corresponds to a) Elemental mercury, mostly represent close to 50% of the total mercury content and b) mercury species such as sulfides and residual, as indicated in Table 19. On the other hand, fractions such as: water soluble and organic can be found in lower concentrations than specified in the NOM-147-SEMARNAT/SSA1-2004.

Table 19. Sequential chemical speciation of mercury in samples from the town of Guanajuato (GG) in the State of Guanajuato (mg/kg)

Sample*	Water soluble species	Hg^0 (elemental or amalgamated)	Exchangeable species	Strongly bonded	Organic species	Sulfides	Residual	Total
GG-01	0.105	51.77	0.14	0.065	0.065	4.445	2.01	58.6
DS	0.007	0.156	0.028	0.021	0.035	0.52	0.28	
GG-02	0.14	46.81	0.535	0.17	0.04	50,165	6.06	103.92
DS	0.0001	3.903	0.092	0.042	0.014	2,482	1.485	

**Samples with a total mercury concentration higher than recommended by NOM-147-SEMARNAT/SSA1-2004*
Samples are expressed as a mean of triplicate analysis
DS = Standard deviation

With the results obtained from the sequential chemical speciation method developed for this study, it can be seen that the "elemental mercury" and "mercury sulfide" species are the predominant in analyzed samples (GG-01 and GG-02) from the town of Guanajuato (GG) in the state of Guanajuato.

The "mercury sulfide" specie is presented in concentrations from 4.45 to 50.17 mg/kg, this represents that the mercury contained in the soil analyzed has a low availability and high stability in the environment due to its reduced solubility in different compartments and due to the fact that it is not susceptible to be methylated in anaerobic media; however, it might be methylated in aerobic conditions that allow the release of the mercuric ion (Hg^{2+}) in a soluble form and through the oxidation of sulfide to sulfates and sulfites.

The "elemental fraction" in the soils under study was found in concentrations up to 51.77 mg/kg, which exceeded the maximum limit allowed in the NOM-147-SEMARNAT/SSA1-2004; however, this specie is very stable. The probable origin of this mercury is related to its use in the extraction of precious metals in the Spanish colony. Mercury can be found not only as metallic mercury but also in the form of amalgam formed by the combination with some constituents of the soil. This last factor can give stability to mercury at these sites, due to reduced availability to the microorganisms that methylate it and since it requires very high temperatures to be released from the amalgam (the method used in this study suggests 180 ºC).

The water soluble mercury species were found in the samples up to 0.18% (GG-01 and GG-02). This result was expected since these wastes have been exposed to climate conditions for many years such as rain, natural flows. The potential risk of these mercury species lies in a possible leaching into the groundwater and reaching a mercury concentration higher than 0.001 ppm which is the maximum level in drinking water allowed by the Ministry of Health. On the other hand, these mercury species may be subject to a methylation process since mercury is already oxidized, which can increase the levels of aryl or alkyl-mercury species in the soil and might increase the risk bioaccumulation in organisms. To evaluate if this mercury species in this soils represent a potential risk, it should be referred to the Mexican standard NOM-147-SEMARNAT/SSA1-2004 which establishes maximum concentrations in contaminated soils for toxic metals and the requirements to implement remediation techniques.

On the other hand, organometallic species such as methylmercury are in percentages below 0.1% of the total mercury present in soils. This can be attributed to the reduced amount of organic matter.

To evaluate the possible application of specific remediation techniques for soils contaminated with mining waste is required to conduct a broader study with the methods of speciation.

State of Queretaro

Just like in the previous case, the results of the sequential chemical speciation for samples of contaminated soil from the towns of San Joaquin (QJ) and Pinal de Amoles (QP) in the state of Queretaro that showed a total mercury concentration above the limit recommended by the regulations indicate that the predominant fraction corresponds to a) Elemental mercury, mostly represent close to 50% of the total mercury content and b) mercury species such as sulfides and residual, as indicated in Table 20. On the other hand, fractions such as: water soluble and organic can be found in lower concentrations than specified in the NOM-147-SEMARNAT/SSA1-2004.

Table 20. Sequential chemical speciation of mercury in samples from the towns of San Joaquin (QJ) and Pinal de Amoles (QP) in the State of Queretaro (mg/kg)

Sample *	Water soluble species	Hg^0 (elemental or amalgamated)	Exchangeable species	Strongly bonded	Organic species	Sulfides	Residual	Total
QJ-03	0.02	22.74	N.D	0.41	N.D.	11.97	1.66	36.81
DS	0.006	8.50	-	0.02	-		0.29	4.85
QJ-06	N.D.	15.79	N.D.	0.04	N.D.	13.48	3.14	32.45
DS	-	1.77	-	0.01	-		0.46	2.94
QJ-11	0.03	433.69	0.11	4.27	0.95	7.54	62.24	508.83
DS	0.006	65.30	0.03	0.36	0.12		6.17	9.97
QP-01	0.0016	190.29	1.73	7.07	0.06	49.17	13.17	261.5
DS	0.007	11.86	0.38	0.93	0.003		2.60	45.03
QP-07	0.16	402.78	4.62	2.66	2.14	1.02	28	436.2
DS	0.04	19.76	4.33	0.40	0.56		9.12	18.60
QP-08	0.02	1019.25	0.23	2.66	0.11	86.82	89.62	1198.71
DS	0.006	36.94	0.01	0.40	0.04		15.55	10.77

**Samples with a total mercury concentration higher than recommended by NOM-147-SEMARNAT/SSA1-2004*
Samples are expressed as a mean of triplicate analysis
DS = Standard deviation

With the results obtained from the sequential chemical speciation method developed for this study, it can be seen that the "elemental mercury" and "mercury sulfide" species are the predominant in analyzed samples (QJ-03, QJ-06, QJ-11, QP-01, QP-07 and QP-08) from the towns of San Joaquin (QJ) and Pinal de Amoles (QP) in the state of Queretaro.

The "mercury sulfide" specie is presented in concentrations from 1.02 to 86.82 mg/kg, this represents that the mercury contained in the soil analyzed has a low availability and high stability in the environment due to its reduced solubility in different compartments and due to the fact that it is not susceptible to be methylated in anaerobic media; however, it might be methylated in aerobic conditions that allow the release of the mercuric ion (Hg^{2+}) in a soluble form and through the oxidation of sulfide to sulfates and sulfites.

The "elemental fraction" in the soils under study was found in concentrations up to 1019.25 mg/kg, which exceeded the maximum limit allowed in the NOM-147-SEMARNAT/SSA1-2004; this specie is very stable but since the concentration is extremely high, **more studies are required**. The probable origin of this mercury comes from natural metallic mercury (native). There is reduced availability to the microorganisms that methylate it; however, elemental mercury is very volatile and might be transported to other compartments such atmosphere where it can be absorber through the respiratory system.

The water soluble mercury species were found in the samples up to 0.05% (QJ-03, QJ-06, QJ-11, QP-01, QP-07 and QP-08). This result was expected since these wastes have been exposed to climate conditions for many years such as rain, natural flows. The potential risk of these mercury species lie in a possible leaching into the groundwater and reaching a mercury concentration higher than 0.001 ppm which is the maximum level in drinking water allowed by the Ministry of Health. On the other hand, these mercury species may be subject to a methylation process since mercury is already oxidized, which can increase the levels of aryl or alkyl-mercury species in the soil and might increase the risk bioaccumulation in organisms. To evaluate if this mercury species in this soils represent a potential risk, it should be referred to the Mexican standard NOM-147-SEMARNAT/SSA1-2004 which establishes maximum concentrations in contaminated soils for toxic metals and the requirements to implement remediation techniques.

On the other hand, organometallic species such as methylmercury are in percentages below 0.49% of the total mercury present in soils. This can be attributed to the reduced amount of organic matter.

To evaluate the possible application of specific remediation techniques for soils contaminated with mining waste is required to conduct a broader study with the methods of speciation.

7.0 LATINAMERICAN WORKSHOP

The latinamerican workshop for the development of the project "sequential chemical speciation of mercury contaminated sites in Mexico" took place on December 11th and 12th, 2008 in Room 1 of the "Ignacio Chavez" Seminars Unit at the National Autonomous University of Mexico. It was attended by 55 representatives from different sectors.

Academia	12 assistants
Government	30 assistants
Non-governmental organizations	4 assistants
Representatives from Latin America (Brazil, Bolivia, Colombia, Ecuador & Peru)	5 assistants
International assistants	4 assistants

Inside the workshop there were presentations of the different countries of the region as seen in the agenda.

7.1 Agenda

Day 1

8:30 to 9:00 Registration
9:00 to 9:10 Opening of the Workshop (words from INE)

9:10 to 9:30 Introduction Ministry of Foreign Affairs

9:30 to 9:40 Presentation of the participants at the workshop

9:40 to 10:00 Presentation: Applied research on toxic substances and environmental risks

10:00 to 10:30 Presentation: Advances in the Regional Action Plan on Mercury, CEC

10:30 to 11:00 Presentation on EPA actions on mercury

11:30 to 14:00 Presentation of results of the project "chemical speciation Sequential mercury contaminated sites in Mexico"

14:00 to 15:30 Lunch

15:30 to 16:00 Presentation: Other related activities of research on mercury in Mexico

16:00 to 16:30 Presentation: Health problems related to mercury in Mexico

16:30 to 17:00 Presentation: Gold and silver artisanal mining with mercury

17:00 to 17:30 Presentation: XSAFS method for speciation of heavy metals

Day 2

9:00 - 9:30 Presentation: Contaminated sites and its remediation in Mexico

9:30 - 10:00 Presentation: Status of mercury contamination in Brazil

10:00 - 10:30 Presentation: Status of mercury contamination in Peru

10:30 - 11:00 Presentation: Status of mercury contamination in Colombia

11:30 - 12:00 Presentation chlor-alkali industry in Mexico (Mexichem)

12:00 - 12:30 Presentation lamps and the mercury content

12:30 to 14:30 Plenary discussion on future applications of the methodology in other countries of the Latin-America region

14:30 to 16:00 Lunch

16:00 - 16:30 Summary of the plenary discussion

16:30 Closure

7.2 Agreements

It was concluded that there are similarities of the mercury contamination problem in Latin-America.

Countries showed interest in using the proposed mercury speciation method, but asked for more pilot studies with samples from the region

Since mercury is about to get in an international agreement, more support has to be given from UNEP for this kind of projects.

8.0 CONCLUSIONS

8.1 Conclusions

The mercury speciation method developed in this study allows the identification of mercury species in contaminated soils using different extraction media, and identifying the following species: water soluble, elemental (amalgamated) mercury, exchangeable, strongly bounded (mineralized and Fe and Mn oxy-hydroxides), organic mercury, mercury sulfides and residual. From these, some represent a potential risk due to their toxicity and ability to mobilize in the environment and to be assimilated by organisms: water soluble, exchangeable and organic species.

The importance of this study is related to the development of an integrated and efficient and cost-effective methodology for identifying the mercury species distributed according to groups of solubility (water-soluble, weak acids, organic acids, and aqua-regia) to be applied to characteristic soils of Mexico which are contaminated with mining or industrial wastes. The results indicate that the highest concentration of mercury on these sites mostly corresponds to very stable chemical species with low mobility in air: mercury sulfide and elemental (in the form of amalgam).

Soluble species were found in very low proportions with respect to the regulations for contaminated soils in the country (NOM-147-SEMARNAT/SSA1-2004).

From the results obtained, it is estimated that the potential risk is low, due to the high stability of the mercury species in the sites under study. However, this research is only a basis for carrying out bio-availability studies into the different species, and for evaluating mercury absorption by plants and crops in the agricultural lands of the towns of Osiris and La Zacatecana for the State of Zacatecas, Pachuca for the State of Hidalgo, Guanajuato for the State of Guanajuato and San Joaquin and Pinal de Amoles for the State of Queretaro. For this reason, a study is being conducted in order to evaluate the exposure routes and, with these results, to prepare an assessment of possible risks to vulnerable populations, so that adequate measures for mitigating present risks can be proposed to the corresponding authorities for their decision-making.

In the case of Queretaro, high concentrations of mercury, mainly in the elemental fraction, were found due to the presence of natural deposits. These species have low potential for mobility; however, additional studies should be developed to identify background concentrations in the area and identify sites that may pose potential risks.

With regard to industrial sites, concentration of mercury was found in smaller values than reported by official regulation in Mexico (NOM-147-SEMARNAT/SSA1-2004). These findings should be completed with studies in other compartments such as air and water to discard pollution in any of these.

In addition, the study considered the analysis of the total concentration of lead since it is associated with the silver ore, and mercury through its use in ancient mining processes. The results showed the presence of lead in high concentrations in many of the sites under study. For this reason, speciation of this metal might be developed, as well as a risk assessment.

8.2 Recommendations

Developing campaigns aimed at improving the hygienic habits of the residents of communities with high concentrations of mercury to avoid ingestion.

Observe and control the Hand-Mouth mechanism among children.

Consider the development of risk communication about the findings in environmental samples.

It is recommended to contain contaminated soil that represent a potential source of risk through the use of ground cover, paving the streets, backyards and / or inside soil in houses located on mining wastes in order to avoid dispersion and exposure of population.

8.3 Acknowledgment

- Delegations of SEMARNAT in the States of: Chihuahua, Guanajuato, Hidalgo, Nuevo Leon, Queretaro, Tamaulipas, Veracruz and Zacatecas.
- State and Municipal governments in the sites considered for this study.
- Directorate of Research on Air Quality of the National Institute of Ecology.