
Characterization and Remediation of Soils and Sediments Polluted with Mercury: Occurrence, Transformations, Environmental Considerations and San Joaquin's Sierra Gorda Case

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1. Introduction

Soil as important part of the ecosystems which must be protected in the environment context, and it is necessary be studied the possible overall impact of measures for protection, with a very special attention from mining activities. The soil resource occupies a fundamental part of the ecosystems; when a soil is degraded, the others components of the ecosystems are degraded too.

The fate of the heavy metal in soils depends upon many soil processes that are governed by several soils properties of which soil pH and redox potential are known to be the most important parameters. Thus, the solubility of trace elements is often shown as a function of pH affected by amount and kind of organic matter. Trace elements are known to be accumulated in surface soils as a result of contamination from point sources as mining activities. An appreciable amount of the soils has been made unusable because of pollution. Highly contaminated soils belong to a high healthy risk to human being and their environmentally harmful effects. That is why soil should be correctly understood and underestimated long range lethal effects that can have irreversible consequences. The improvement of soils damaged and contaminated by pollutants need of the particular soils, requires a full understanding of soil properties and of the deteriorating factors.

Mercury is one of the most toxic elements to human health and ecosystem; because of all mercury species are toxic. A wide variety of mercury species exist in the environment and its

various chemical forms can differ in bioavailability, transport, persistence, and toxicity. Still, every mercury species is toxic with methyl mercury being the most toxic species. The World Health Organization (WHO) recommends a maximum methyl mercury intake of $1.6 \mu\text{g Kg}^{-1}$ per week, while the Environmental Protection Agency (EPA) lists a maximum recommended intake of $0.1 \mu\text{g Kg}^{-1}$ of body weight per day for adults. Due to high bioaccumulation, mercury is found on many levels of the food chain (Hinton and Veiga, 2001; Bengtsson, 2008). Any form of mercury in the environment may evolve into a more toxic species (methyl mercury) under biogeochemical transformation processes (Figure 1). Due to these processes and the high mobility of mercury species, a good understanding of how mercury species transform and accurate monitoring are essential for assessing the risk of mercury in the environment.

The impact of mercury depends strongly on its chemical species; understanding mercury transformations and the impact of its various chemical forms are vital to preventing harmful effects on humans and the environment. Nevertheless, the physicochemical characteristics of mercury are either useful or necessary for many industrial and agricultural applications, and mercury may be scattered over large area, depending on the source (Leopold et al, 2010).

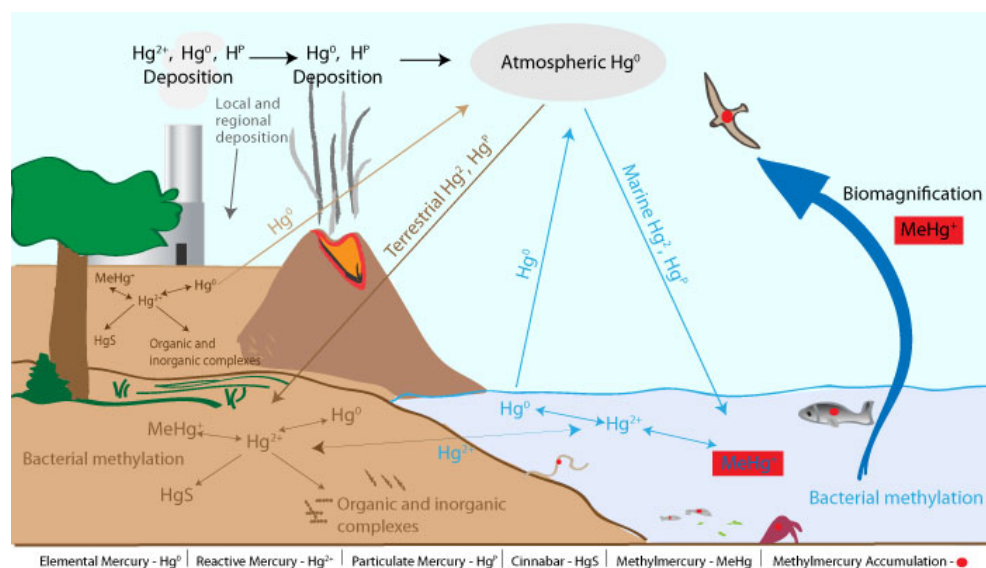


Figure 1. Biogeochemical transformation processes of mercury (Leopold et al, 2010).

Mercury concentrations in ground water indicate that the highest concentration of mercury in groundwater comes from the soil and from aquifers. While simulating mercury predictions can often be difficult, mercury can be estimated in experiments conducted in batch mode or in columns. The percentage of Hg that can potentially leach from the soil was previously estimated in batch experiments. Distribution analyses of species in leachate confirmed the

presence of inorganic species (Hg^{2+} and Hg^0) ranging from 90 – 100 % (Bollen, 2008; Harvey, 2002).

The most commonly used techniques for the remediation of mercury contaminated soils have been classified as either excavation techniques or containment techniques, and are grouped as follows (Hinton and Veiga, 2001): (a) *ex situ* treatments: physical separation, thermal treatments, hydrometallurgical treatments; (b) *In situ* recuperation: vapor extraction coupled with evaporation (soil), permeable reactive barriers; (c) *In situ* leaching and extraction: electrokinetic separation, interceptor systems, phytoremediation, passive remediation; (d) *containment*: pump and treat impermeable barriers, sealed surfaces and drainage, stabilization and solidification, sediment covering.

2. Physicochemical properties of mercury

Mercury (Hg) is a chemical element with an atomic number of 80. Mercury is a silver plated heavy metal, liquid and odorless at normal conditions. It easily alloys with many other metals like gold or silver producing amalgams, is insoluble in water and soluble in nitric acid. The main source of Hg is cinnabar or mercury sulfide (HgS), a stable compound and insoluble usually recovered as a byproduct of ore processing. Mercury in this form is found in the earth's crust average concentrations of 0.5 ppm (Hinton and Veiga, 2001).

Mercury is one of the most toxic elements to human health and ecosystem. At temperatures above 40 °C mercury produces toxic and corrosive fumes. It is harmful by inhalation, ingestion and contact, is a very irritating to skin, eyes and respiratory tract, even to nervous system, its gaseous form is absorbed by lung tissues (Hinton and Veiga, 2001, Bengtsson, 2008).

A wide variety of mercury species exist in the environment and its various chemical forms can differ in bioavailability, transport, persistence, and toxicity. Still, every mercury species is toxic with methyl mercury being the most toxic species. This element can exist in the environment as elemental (Hg^0), oxidized inorganic (Hg^{2+} -mercuric, Hg_2^{2+} -mercurous) or oxidized organic (methyl/ethyl mercury) forms. Mercuric and mercurous forms are more stable under oxidizing conditions. In moderately reducing conditions, the organic or inorganic mercury can be reduced to its elemental form and be converted to forms leased by biotic or abiotic processes: these are the most toxic forms of mercury, as well as being soluble and volatile. Hg (II) forms strong soluble complexes with a variety of organic and inorganic ligands oxidized in aqueous systems. Hg sorption in soil, sediment and humic materials is an important mechanism for the removal of mercury from solutions, another mechanism, a high pH is their co-precipitation sulfide (HgS) (Leopold et al, 2010).

Any form of mercury in the environment may evolve into a more toxic species (methyl mercury) under biogeochemical transformation processes. Due to these processes and the high mobility of mercury species, a good understanding of how mercury species transform and accurate monitoring are essential for assessing the risk of mercury in the environment. The impact of mercury depends strongly on its chemical species; understanding mercury trans-

formations and the impact of its various chemical forms are vital to preventing harmful effects on humans and the environment. Nevertheless, physicochemical characteristics of mercury are either useful or necessary for many industrial and agricultural applications, and mercury may be scattered over large area, depending on the source (Leopold et al, 2010; Nick, 2012).

The metal mercury (Hg^0) is mainly used to produce chlorine gas and caustic soda, and is part of some types of alkaline batteries, fluorescent lamps, electrical contacts, and instruments such as pressure gauges and thermometers, among others. Hg salts are used in antiseptic ointments and creams and skin lightening. Among the activities that generate the most pollution by Hg, is the burning of coal and chlor-alkali plants: other important sources are mining and metallurgy and the burning of municipal solid waste, which may contain instruments such as pressure gauges, thermometers, alkaline batteries and fluorescent lamps. The mercury released into the air tends to settle and adhere to soil organic matter (Hinton and Veiga, 2001; Nick, 2012).

Natural and anthropogenic mercury emissions are mainly in the form of elemental mercury (Hg^0), which makes up about 99 % of total atmospheric mercury. However, biogeochemical transformations can oxidize it, forming Hg^+ and Hg^{2+} . Most inorganic Hg compounds are water soluble in small doses, and can be found in soil and sediments. In contrast, the presence of inorganic forms of Hg^{2+} bonded to organic and/or inorganic species ($[\text{HgCl}_x]^{2-x}$; $[\text{Hg}^{\text{II}}\text{-DOC}]$; $[\text{HgS}]$) depends on the local chemical environment. The life time of these compounds in air is very short (on the scale of minutes) and they are rapidly removed by deposition processes because of high water solubility and surface activity. Figure 2 shows the main mercury species in the atmosphere, hydrosphere and sediment (Leopold et al, 2010; Nik, 2012; Slowey et al, 2005; Wartel et al, 1999; Shi et al, 2005).

Over 90 % of surface water mercury is from atmospheric deposition. Hg^{2+} usually undergoes a biomethylation process that forms methylmercury (MeHg , CH_3Hg^+) and dimethyl mercury (DMeHg , $(\text{CH}_3)_2\text{Hg}$), though these reactions can be reversed using microorganisms and/or photolytic decomposition. All these species are highly mobile.

Three main forms of mercury are found in natural waters: elemental mercury (Hg^0), inorganic Hg^{2+} (Hg^{2+} and its complexes) and organic mercury (MeHg , MeHg complexes and DMeHg). With solubility (at 25°C) of 0.08 mg L⁻¹, Hg^0 can be found at all depths. Inorganic mercury (Hg^{2+}) and MeHg forms complexes with other dissolved compounds in fresh water, but for the most part, only forms complexes with chlorine in sea water. DMeHg is found in the deep sea. (Wartel et al, 1999, Shi et al, 2005, Slowey et al, 2005).

3. Edaphology properties of soil related with mercury

Soil is a collection of natural bodies on the Earth' surface, in places that most of them have been modified by man in its quality and containing living matter and supporting or capable of supporting plants. Soil grades at its lower margin to hard rock or to earthy materials virtually devoid of roots, animals or marks of other biologic activity.

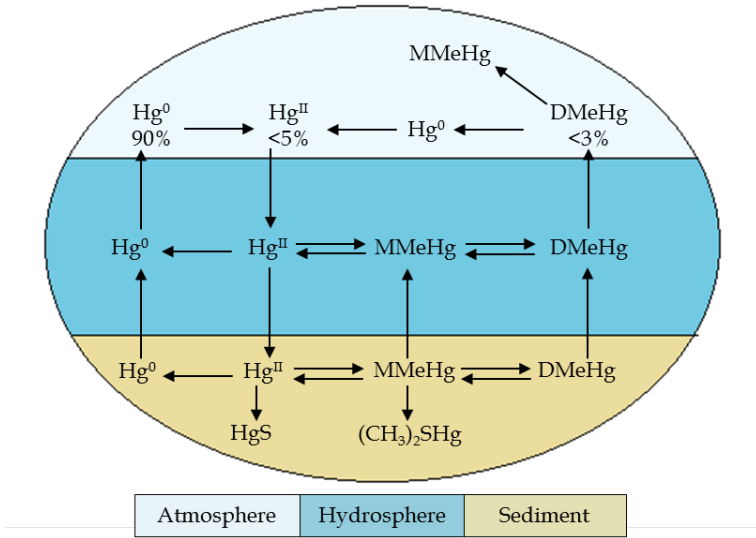


Figure 2. Distribution of mercury species in atmosphere, hydrosphere and sediment (Leopold et al, 2010).

In general, physical, chemical and biological soil characteristics are highly correlated parameters that are necessary to understand. The specific elemental composition of each particular soil reflects, to a degree modified over time by weathering and the chemical composition of the parent material from which the soil is formed. For instance, the extractability of the different elements depends on the soil properties.

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An appreciable amount of the soils has been made unusable because of pollution. Highly contaminated soils belong to a high healthy risk to human being and their environmentally harmful effects. That is why soil should be correctly understood and underestimated long range lethal effects that can have irreversible consequences. The improvement of soils damaged and contaminated by pollutants need of the particular soils, requires a full understanding of soil properties and of the deteriorating factors.

Mercury is a microelement: its Clark value in the Earth's crust is $56 \mu\text{g Kg}^{-1}$ (Fügedi et al, 2011). It is characterized by a dual geochemical behavior: it is liable to extreme concentration

and to dispersion, the latter resulting in an approximately entirely even concentration. It is found either as a native metal (near to 80 % in hydrothermal and vapors) or in cinnabar, corderoite, livingstonite and other minerals. Cinnabar (HgS) is the most common ore. Mercury ores usually occur in very young orogenic belts where rock of high density on upper mantle is forced to the crust of the Earth (Ozerova, 1996).

Given that mercury is enriched by an extremely wide variety of geological processes (Fergusson, 1990) from the formation of hydrocarbon to hydrothermal mineral occurrences, it can be regarded as an universal geochemical indicator of young geological effects; its dispersion halos are more extensive than that of any other element (Fügedi et al, 2011).

Historically there were two main registered Mercury mines: Almaden (Spain) and Idrija (Slovenia) in Europe. Later new occurrences were found in California and worldwide. It was used in gold separation. In Mexico we know mercury mines from the Pre-Hispanic era (Scharek et al., 2010) and a usage in cultic fests (Figure 3). In 2005, China was the top producer of mercury with almost two-thirds global share followed by Kyrgyzstan. Several other countries are believed to have unrecorded production of mercury from copper electro winning processes and by recovery from effluents.



Figure 3. Typical cinnabar occurrences in a limestone system (Formation Las Trancas, San Joaquin, Querétaro, Mexico, photo by P. Scharek)

4. Mobilization and loadings the mobilized mercury

The mobilization of the different mercury forms can due to by evaporation and dissolution. Here we do not deal with the erosion which able to mobilize all form of mercury if it has attached to the solid particle, however in case of soils and fly as particles in the flue gas this particle associated mobilization mechanism can play important role in the mercury transport.

4.1. Evaporation

The evaporation governed by the vapor pressure depends on the volatility of the compound and the temperature. Concerning the volatility of the different mercury compounds evaporation at ambient temperature can be significant in case of elemental and the organic mercury cases, however the volatilization of the other mercury forms (the inorganic mercury compounds) can become considerable if the temperature reaches a couple hundred degree centigrade. All of the mercury compounds have relatively low boiling points (Table 1), some of them decompose before melting, others can sublimate. Based on these data it is obvious the vaporization can play important role of the mercury compound transport and mobilization.

Hg	Melting T, °C		Boiling T, °C	
	-38.9		356.5	
HgS (cinnabar, α)	580 sublimate			
HgS (metacinnabar, β)	446 sublimate			
Hg ₂ O	100 decompose			
HgO	500 decompose			
Hg SO ₄	450 decompose			
Hg ₂ Cl ₂	302		384	
HgCl ₂	277		304	
HgBr ₂	237		322	
HgI ₂	259		354	
CH ₃ HgCl	-		92	
(CH ₃) ₂ Hg	-43		94	

Table 1. Melting and boiling points of the mercury and mercury compounds

The partial pressure of the elemental mercury (Hg⁰) reach 1 Pa at 42 °C and enhances exponentially till the boiling point (T_b = 356.5 °C). At 20 °C the Hg vapor pressure is 0.18 Pa the Hg concentration in the air saturated with the mercury is 7.64 10⁻⁸ mol dm⁻³ = 15.3 µg m⁻³. Due to this high volatility the elemental mercury evaporate if stored and processed an open container. Elemental mercury can escape from solution if the oxidized mercury is able to reduce. The

analytical data will be inaccurate if the sample is not preserved agents the elemental mercury formation.

Concerning the global mercury contamination till the middle of the past century evaporation of elemental mercury used to extract silver and gold was the main source of the mercury emission, (Nriahu, 1994). All the once produced and recently available elemental mercury stock (in the past five century one million tons was produced from cinnabar and from other ores) if in used either evaporation or after transformation can contribute to the mercury contamination worldwide (Hylander and Meili, 2003). This is the reason why the elemental mercury use is banned. Recently one of the most significant sources of mercury emission by evaporation is the coal firing. During the coal burning the mercury associated with pyrite and be organically bonded to the coal minerals are released in the combustion flame as elemental mercury, which is partially oxidized to Hg(II) in homogeneous and heterogeneous catalytic reaction governed by the chlorine and the ash content of the combustion gases (Sondreal et al, 2004).

Generally accepted view is that the evaporated oxidized forms of mercury contaminate the environment locally, close to the emission source. However they can transform to elemental mercury and depend on this transformation rate it can become part of the global mercury cycle.

The transformation of the oxidized to reduce the reduced to oxidized forms can happen both in gas and aquatic environment according to the circumstances. There is similar transformation between the inorganic and organic forms.

Different species of macro algae from the dissolved mercury can produce different methylated mercury compounds in the ocean. Because of these methylated mercury compounds have high volatility and at the dimethylated form has low solubility in ocean water they are easily emitted into the atmosphere and can contribute significantly to the global atmospheric mercury (Pongratz and Heuman, 1998). Beside this different bacteria (e.g. sulfate reducing) and in case of abiotic route the tin- alkyls and the humic acids also can transform the dissolved mercury (II) to methyl mercury form (Weber, 1993). A quite detailed set of possible transformation in gas and aquatic media and the Henry constants which inform about the dissolved compound volatility are collected by Shon et al, 2005.

During heating mercury compounds can transform directly or via oxides to elemental mercury. Beside the elemental mercury only the halogenides and the sulfides since last have a tendency to sublime can occur in evaporated forms. The sulfides at presence of oxygen at 600 °C transform to Hg and SO₂, however in presence of Fe and CaO the HgS also will decompose to Hg and Fe- or Ca- sulfides. Using the temperature programmed evaporation technique based on the volatility difference of mercury compounds the compound forms can be distinguished and can use for mercury speciation in solids (Lopez-Anton et al, 2010, 2011).

In a high temperature process since the mercury compounds decompose the original speciation of mercury does not preserve a new speciation can be formed which is determined by the gas composition. In the high temperature gases high portion of mercury exists in elemental and just a small portion in oxidized form. This is the reason why these technologies such as coal fired energy production, the cement kiln, the incineration has difficulty in the mercury capture.

Focusing to the soil, the heating comes from sunlight can mobilize only the weakly sorbed elemental and organic mercury but the fire on the soil surface, for example the forest fire can evaporate the less volatile mercury forms as well. This case the contamination level of the fired soil decreases but, due to the transport, at other places the contamination becomes higher (Caldwel et al, 2000).

The volatilization can be the cause of contamination but can use for decontamination as well. Based on the volatilization of mercury compounds, mercury removal process was established from coal cleaning by mild pyrolysis (Wang et al., 2000) and for the soil cleaning by thermal treatment. In case of coals the speciation of mercury determines the maximum efficiency of the mercury removal. The efficiency of the process generally remains below 100 %, (bituminous coal case at 500 °C it was approx. 75 %). Since the efficiency remains below 100 % the rest of mercury still remain in the process and pass to the flue gas after the coal burning. The speciation of the mercury in the contaminated soil also has influence on the efficiency of the thermal remediation, see more details later.

Concerning that the different mercury forms exhibit different volatility the actual distribution of the mercury species in a medium the rate of the transformation process which able to modify it together govern the mercury mobilization by evaporation.

It is well known, if elemental mercury forms in the water this elemental mercury can easily escape to the gas phase. It is quite intensive if gas bubbling through the water or the water surface is disturbed (Okouchi and Saaski, 1984). Sunlight induced H₂O₂ formation in alkaline condition can result reduction of the oxidized mercury forms to elemental mercury. This can explains that the Hg concentration above the lake water surface can be higher day time than night. The fulvic and humic compounds are able to complex the mercury (II) ion in aquatic media but these compounds can take part in the mercury alkylations, further at a suitable pH can work as a reducing agent. The redox potential at 0 pH for Hg (II) reduction is 0.85 V (Allard and Arsenie, 1991).

This type of mercury transformation between oxidized and reduced forms together with the alkylation will generate not only a modification between the concentrations of the mercury species in the aquatic phase but will modify the mercury transport between the phases. The mercury transformation processes are important in the technological processes used for the mercury removal since can effect they efficiency (Somoano et al., 2007).

4.2. Dissolution

The mobilization by dissolution can arrange two groups: (a) dissolutions ways exist in the nature (b) dissolution way can be applied in the laboratory and in the remediation technology to determine the loading forms or remove the mercury from the contaminated media.

4.2.1. Dissolutions ways exist in the nature

The solubility of elemental mercury and the ore of mercury can find in the nature (cinnabar etc.) are very low in water. This low solubility result low mercury concentration level in aquatic

phase and restricts the transport between phases by dissolution. However the oxidation both cases enhances these mercury forms solubility. The elemental mercury can be oxidized by ozone, halogens, some components of acid rains, or by oxy-acids in laboratory (HNO_3 and the hot H_2SO_4) resulting a soluble form. The ozone in air if does not consumed by the other more reactive air contaminants can oxidize Hg to Hg(II) (Iverfeld and Linquist, 1986; Shonet et al, 2005).

In aquatic media oxidation can occur at acidic conditions if the sunlight produces oxidative radicals OH, or peroxides. This process can play role in the trap of the physically dissolved elemental mercury in water, and also can hinder the transformation of the oxidized mercury forms towards the reduced elemental mercury direction. The oxidative transformation of elemental mercury is essential in case of many mercury capture process since the oxidized forms of mercury has higher tendency to sorb and dissolve, therefore different oxidation procedures are available and applied in the demercuration technologies (Ko et al, 2008; Lakatos et al, 2009; Sondreal et al, 2004).

However the mercury in the natural minerals is in the oxidized forms these minerals luckily due to the very low solubility can be considered not a mobile occurrence of the mercury. The environmental risk improves if the natural processes can transform the minerals a more soluble form. One of the most significant ore transformations which effect the mercury mobilization is the sulfide ore oxidation in the air. The oxidations of sulfides to sulfate a considerable enhancement ensue in mercury solubility (Holley et al, 2007). This process, the oxidation of the tailings, can accused for the mercury contamination all around the abandoned mercury ore mines.

Compound	Solubility in Water c, ppm
Hg	0.049*
HgS (cinnabar, α)	0.01
HgS (metacinnabar, β)	-
HgSO ₄	-
Hg(NO ₃) ₂	soluble
Hg ₂ O	51
HgO	51
Hg ₂ Cl ₂	10
HgCl ₂	66 000*
HgBr ₂	5 100
HgI ₂	51
CH ₃ HgCl	5 780
(CH ₃) ₂ Hg	-

*Solubility from paper of Ko et al, 2008.

Table 2. Solubility of different mercury compounds.

Among the mercury compounds (Table 2) the mercury-chloride and nitrates are those which have the highest solubility in water. The simple cationic form of Hg(II) is not the common form in the aquatic media, it exist only in acidic solutions, at less acidic condition the dissolved mercury appears as HgOH^+ , HgOHCl , $\text{Hg}(\text{OH})_2$ and HgCl_2 molecules and complex anions HgCl_4^{2-} at high chloride concentration. It means that the sea water contains the oxidized mercury mainly in this chlor- complex form. Beside the chlor- complex the mercury -fulvo and -humic complexes also exists in aquatic environment. The speciation in the solution, the molecular forms govern the mercury loadings and play important role at the way and efficiency of the removal.

4.2.2. Dissolution for leaching mercury from different medium

Beside the thermal way and the application of the species sensitive analytical methods for mercury analysis (XPS, EXAFS etc.) the sequential extraction is often applied technique to specify the mercury chemical form and associations in solids. The thermal methods and the species sensitive elemental analysis can distinguish the elemental Hg, the HgS forms and the organically bonded mercury forms which generally exist in the soil. However these techniques do not allow doing any estimation about mobility and bioavailability of mercury. To get the loading specific information in soil for mercury, beside the classical Tessier six step extraction used generally, different modified procedure are available for Hg which able to distinguish better the mercury forms than the Tessier method can do (Orecchio and Polizzotto, 2013; Han et al,2006). For example it can determine mercury bounded to amorphous iron oxides (by NH_4 oxalate-oxalic acid extraction), mercury bonded to crystalline iron oxides (by $\text{NH}_2\text{OH}\cdot\text{HCl}$ - 25 % acetic acid extraction), non-cinnabar mercury (elemental mercury, organic bounded, humine bounded (by 4 M HNO_3 extraction), cinnabar mercury (by extracted with saturated Na_2S , Han et al, 2006). The advantage of this protocol is the ability of the separation of humic and sulfide bounded mercury which important in the soil case. Two set of sequential extraction regime can compared at Table 3 and 4.

Mobilization of mercury can occur through complex formation, ligand exchange reactions with chloride and sulfur-containing ligands which leading to enhanced Hg solubility in soil solutions. The sulfur containing ligands: tiosulfates ($\text{S}_2\text{O}_3^{2-}$), thiocyanites (SCN^-) can mobilize the mercury efficiently and could improve the phytoextraction efficiency (Moreno et al, 2004).

Removal mercury by phytoextraction from soils and others soil like materials eg. waste water plants biosolids often need additives which improve the solubility of the mercury. These mobilizations agents are used in accelerate phytoextraction. One type is the chelating agents: citrate, oxalate, malate, succinate, tartarate, salicilate, acetate, and amino-poly-carboxylic acids: EDTA (Lomonte et al, 2011). Since the EDTA is persistent compound, recently the biodegradable ethylendiamine-disuccinate (EDDS) or nitrilotriacetic acid (NTA) suggested as alternative chelator instead of EDTA (Evangelu et al, 2007).

Specific compounds used the mercury extraction from tissues: they can pay role in case of poisoning for detoxification : EDTA was tested for detoxification by Aposhian (Aposhian et al,1995), 2,3- dimercapto- 1- propansulfonate was used to extract mercury from tissues of rats exposed to different mercury compounds (Buchet and Lauwerys, 1989). The EDTA was not

Mobilization Protocol	Determination of Association of Mercury to Soil Component
Loading form of mercury	Extraction procedure
Water soluble mercury	NH ₄ -acetate
Exchangable mercury	(1 M NH ₄ -acetate pH 7 set with NH ₄ OH: solid:liquid 1:25, 30 min 25 °C)
Carbonate bounded mercury	Hydroxylamine – HCl
Easily reducible oxides bounded mercury (Mn-oxides)	(0.1 M NH ₂ OH.HCl +0.01 M HCl solid:liquid 1:25, 30 min 25 °C)
Elemental and organic bounded mercury	H ₂ O ₂ (3 mL 0.1 M HNO ₃ +5 mL 30 % H ₂ O ₂ 80 °C 2 h; 2 mL H ₂ O ₂ 80 °C 1 h; 50 mL 1M NH ₄ ⁺ acetate)
Amorphous iron- oxide bounded mercury	NH ₄ -oxalate –oxalic acid (0.2 M oxalate buffer 1:1, pH 3.25 solid:liquid 1:25)
Crystalline iron oxide bounded mercury	Hydroxilamine – HCl- acetic acid (hot) (0.04 M NH ₂ OH.HCl in 25 % acetic acid 97-100 °C 3 h solid:liquid 1:25)
Non cinnabar bounded mercury (Hg, organically bounded, humin bounded) TOT (non cinnabar mercury)	4 M HNO ₃ (4 M HNO ₃ 80 °C 16 h solid:liquid 1:25)
Cinnabar bounded mercury	Na ₂ S (4 mL saturated Na ₂ S 12 h repeated twice)

Table 3. Mobilization protocol for determination of association of mercury to soil component (Han et al, 2006).

Mobilization Protocol	Determination of Association of Mercury to Soil Component
Loading form of mercury	Extraction procedure
Water soluble mercury	H ₂ O 100°C, 1h stirred, solid:liquid 1:8
Exchangable mercury	Na-acetate (1M Na-acetate, 1 h stirred, solid:liquid 1:8)
Carbonate bounded mercury	Na-acetate –acetic acid pH 5 (1M Na-acetate –acetic acid pH 5, 4 h stirred, solid:liquid 1:8)
Fe, Mn-oxide bounded mercury	Hydroxylamin HCl - acetic acid 0,04 M NH ₂ OH•HCl in 25 % Acetic acid, 96 °C, 6 h, Solid:liquid 1:8
Elemental and organic bounded mercury	Mineralisation by HNO ₃ -H ₂ O ₂ (a)heated previously 180 °C - organic bounded - microwave digestion in cc HNO ₃ -H ₂ O ₂ mixture; (b) no heat - elemental + organic bounded - microwave digestion in cc HNO ₃ -H ₂ O ₂ mixture)
Sulfid bounded mercury	Aqua regia (HCl:HNO ₃ 3:1)

Table 4. Mobilization protocol for determination of association of mercury to soil component (Orecchio and Polizzotto, 2013).

found the best for mercury removal in human application since does not the best chelator for Hg and has side effects, however there are two other compounds which suggested to keep in stock in any poison control center as mercury chelator DMPS (2,3-dimercapto-1-propane sulfonic acid, (unithiol)) and DMSA (meso-2,3 dimercapto succinic acid, succimer, Guzzi et al, 2010).

4.3. Loadings of mercury

The mercury contaminations are in the environment can exist different phases: as vapor in the air (Hg, and compounds, particle associated), dissolved in aquatic media (Hg^{2+} , $\text{Hg}(\text{OH})_2$, HgCl_2 , HgCl_4^{2-} , different complexes, particle associated) and solid as precipitates or minerals and in associated forms bonded to different manner to the component of different solids (soil, fly ash, waste water sludge, etc). In the previous section it was demonstrated that how the associations can be identified.

The loadings of mercury to solid can be considered as positive or negative phenomenon. It can restrict the dispersion of the contamination one side it is positive, the negative this way it can preserve the contamination. Since the loadings depends on the character of the collector and the speciation of the mercury, difficult to establish general rules for this process. However it can state that the elemental mercury has low sorption ability, the cationic sorbs better than the anionic forms on clays, and negatively charged carbon surfaces (coals, activated carbons, humic materials) the loading is more effective to that surfaces which have contain sulfides. It was interesting findings after the cinnabar oxidation a part of liberated mercury could load to the cinnabar surface this way it can be not just the source but the collector of mercury ions. Unfortunately the most toxic forms (alkyls) have the highest ability for bioaccumulation.

The nature works against the mercury contamination. Except the alkylation it transforms the mercury toward the most stable less soluble form. Near the chlor-alkali plant the total mercury sometimes reach the four order of magnitude higher level, than the background concentration, luckily it found a non-volatile and non-soluble associations since transforms to sulfides (Bernaus et al, 2006).

The history of mercury contamination is recorded by loadings. The dept profile of mercury concentration on peat can provide a clear picture how the mercury contamination changed during the mankind history (Barraclough et al, 2002).

The loadings play important role in the environmental technologies used for decrease the mercury emission or clean the contaminated medium. Sulfur and halogen containing carbons, oxidative inorganic sorbents (Lakatos et al, 2009) were developed for elemental mercury removal from flue gas. Beside a range of, classical, functionalized sorbents, sulphur containing carbon nanotubes widen the collection one can chose among for eliminate the mercury contamination in aquatic media (Pillay et al, 2013).

The coals especially the low rank and the oxidized coals are very good mercury ion collectors. Due to this feature we must face that the coal-firing are the main source of the anthropogenic mercury contamination nowadays. However this material offers us an application for cure a slice of the mercury problem: remove the mercury from aquatic media. It can use in batch mode

or dynamic systems as the reactive barrier material, by the high mercury capture coal are able to retard or remove the aquatic mercury contamination (Lakatos et al,1999).

5. Remediation of polluted soil with mercury

The most commonly used techniques for the remediation of mercury contaminated soils have been classified as either excavation techniques or containment techniques, and are grouped as follows (Hinton and Veiga, 2001): excavation and *ex-situ* treatments, containment and *in situ* chemical treatment (Figure 4).

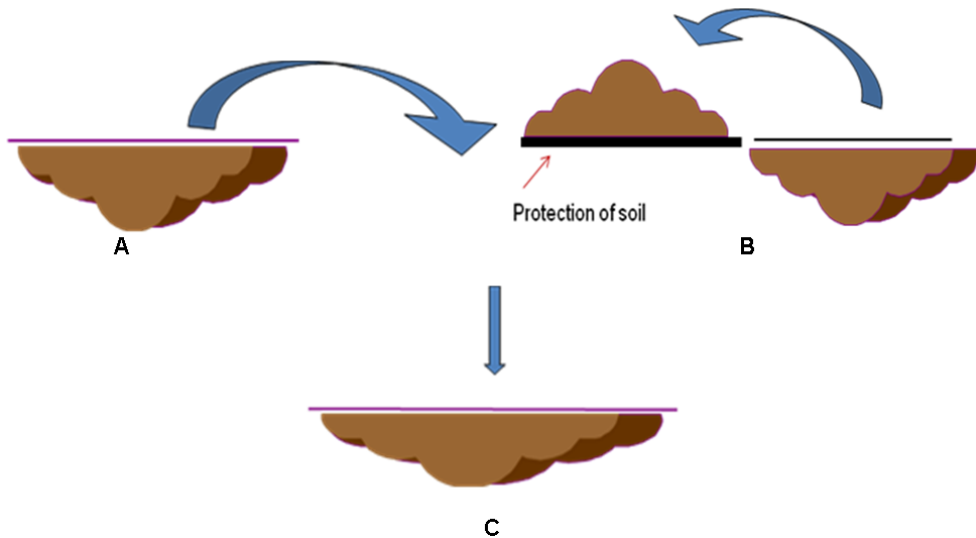


Figure 4. Representation of the techniques for the remediation of mercury contaminated soils: (A) excavation and *ex-situ* treatments, (B) containment and (C) *in situ* chemical treatment.

5.1. Excavation and *ex situ* treatments

They will be treated off-site soil contaminated when removing soil or contaminated soil-like materials to a place outside the place in which they are located, for submission to authorized treatment fixtures. (Hinton and Veiga, 2001):

1. *Physical separation.* Mercury has affinity for the smallest particles of soil.
2. *Thermal treatment.* The volatility of mercury increases with increasing temperature; therefore, a heat treatment technique of excavated soil is a potentially effective technique for the removal of mercury in soils.

3. *Hydrometallurgical treatment.* Chemical extraction of mercury in contaminated soils can be induced by four mechanisms: desorption of adsorbed species, oxidation of metallic mercury, use of strong complexing agents, and dissolution of Hg precipitate. The efficiency and mechanism employed decrease with respect to time due to recomplexation, readsorption and removal of the soluble fraction. Two of the two most promising hydrometallurgical techniques are electrokinetics and electroleaching / methods of leaching.
4. *In situ recuperation.* *In situ* techniques have not been studied as much as *ex situ* techniques due to surface heterogeneity and longer treatment times. However, *in situ* techniques may be promising due to better cost-effectiveness and practicality.
5. *Vapor extraction coupled with evaporation.* Vacuums are used in unsaturated zone to remove volatile and semi-volatile contaminants.
6. *Permeable reactive barriers.* Dissolved compounds react with compounds found on the walls and then precipitate out. This technique has been employed for the treatment of sites contaminated with organic compounds and metals. These barriers are placed perpendicularly to the flow of contaminants.
7. *In situ leaching and extraction.* Used together with pumps in treatment, this method uses chemicals injections to improve the solubility of mercury in groundwater.
8. *Electrokinetic separation.* This process involves the generation of an electric field by applying a potential difference or current into a soil matrix. Metals such as mercury migrate towards electrodes placed in the soil where they accumulate and can be removed at a lower cost by excavating the affected area.
9. *Interceptor systems.* Interceptor systems such as ditches and drains are simple and effective for the recovery of mercury as free product, but these treatments are limited by site topography and stratigraphy.
10. *Phytoremediation.* Some plants have the ability to assimilate and concentrate metals in soil. The recovery of these metals occurs after collecting and incinerating the plants.
11. *Passive remediation of the wetlands.* Using wetlands to immobilize mercury is a controversial topic as some wetlands contain microorganisms that can convert mercury into even more toxic species.

5.2. Containment

In the containment treatment the soils are treated on one side of the contaminated site, where the processing is performed on an area adjacent to the contaminated site or an area within the contaminated site upon removal of soil or soil-like materials. In this classification are (Hinton and Veiga, 2001):

1. *Pump and treat.* With certain contaminants or systems, pollution removal is not possible and it is necessary to protect hydraulic content. When the contaminant mass remains in the subsurface, pump and treat systems can prevent site contamination.
2. *Impermeable barriers (sealed surfaces and drainage).* Mud barriers are slightly permeable barriers made of bentonite or cement-bentonite mixtures. Generally, these barriers are between 0.5 and 2 m thick and have a maximum depth of 50 m. There are other types of barriers that are constructed by injection molding or by vibratory forces. On the other hand, surface seals and drainage are used to controlling filtration and limit pollutant movement towards groundwater.
3. *Stabilization and solidification.* Stabilization and solidification techniques use both *in situ* or *ex situ* conditions by mixing impacted sites. Stabilization attaches contaminants to the soil structure, which usually decreases soil permeability. Moreover, solidification improves the physical characteristics of materials such as mudor sediments; they can be excavated and transported more easily.
4. *Sediment covering.* *In situ* covering involves placing an insulating layer over the contaminated material.

5.3. *In situ* chemical treatment

Another option is the *in situ* chemical treatment option, which is the name of all treatments that involve the injection of a chemical reagent into an aquifer source upstream of the contaminated site. This chemical agent reacts with the contaminant, transforming it into an innocuous form; eventually, it can pump through a given volume of water which can later be recycled for injection. The following actions must be considered:

1. Increase the output rate of the ground water through the contaminated zone by increasing the hydraulic gradient through injection and extraction.
2. Transform the contaminant using chemical reaction within the aquifer.

5.4. Electroremediation of polluted soil with mercury

Electroremediation has been successfully applied in a variety of soil restoration studies, this methodology having the advantage of exhibiting simultaneous chemical, hydraulic and electrical gradients. Indeed, for efficient mercury removal from a saturated soil with electroremediation, application of either an electric field or direct current through two electrodes (anode and cathode) is required. These are usually inserted in wells containing a supporting electrolyte made from inert salts, leading to improved electric field conductive properties (Rajeshwar et al, 1994; Huang et al, 2001; Acar and Alshawabkeh, 1993).

Furthermore, since electroremediation is a physicochemical technique based on ion transport, it is an excellent tool for the removal of inorganic species, such as Hg^{+2} (Rajeshwar et al, 1994;

Bustos, 2013). The main advantages of electroremediation, as compared with other soil treatment procedures, are (Huang et al, 2001; Acar and Alshawabkeh, 1993; Ibañez et al, 1998; Segall and Bruell, 1992; Cabrera – Guzmán et al, 1990): (1) electroosmotic flow is not dependent on either pore or particle size, (2) hydraulic gradient is enhanced by electromigration, (3) treatment can be applied *in situ*, (4) it can be applied to low permeability soils, (5) there is minimal disruption of normal activities at the site, (6) the required investment is usually lower than that for other conventional treatments, and (7) it can be applied in conjunction with techniques such as pumping, vacuum extraction or bioremediation.

The processes taking place during electroremediation can be classified into two main categories: (a) processes occurring as a consequence of the applied electric potential. These processes include electromigration (ion transport), electroosmosis (mass transport), and electrophoresis (charged particle transport); (b) processes occurring in the absence of an electric potential. This includes concentration induced processes like diffusion, sorption, complexation, precipitation and acid - base reactions (Reed et al, 1995; Bustos, 2013).

Specifically, for mercury polluted soil electroremediation, the use of complexing agents like ethylenediaminetetraacetic acid (EDTA), KI, and NaCl under a constant potential gradient has been reported (Reddy et al, 2003). Based on the above precedents, the electroremediation was developed aided by extracting agents for mercury removal from San Joaquin's Sierra Gorda soil samples (Figure 5, Robles et al, 2012).

Electroremediation of mercury polluted soil, facilitated by the use of complexing agents, proved to be an attractive alternative treatment for the removal of mercury from polluted soil in mining areas located at Sierra Gorda in Queretaro, Mexico (Figure 5A and 5B). Implementation of this remediation protocol is expected to improve the living conditions and general health of the population in the Mine "El Rincón" in San Joaquin (Figure 5C). Experimental observations suggest that it is possible to remove up to 75 % of metal contaminants in mercury polluted soil samples by wetting them with 0.1 M EDTA, placing them in an experimental cell equipped with Ti electrodes, and then applying a 5 V electric field for 6 hours (Figure 5D, Robles et al, 2012). When we followed the electrochemical removal of mercury in a batch reactor (Figure 6A), it was removed around 87 % of Hg²⁺ in a time of 9 hours close to the anode side by the presence of EDTA (Figure 6B). The pH remains nearly constant at 4 and conductivity showed values close to 10 mS cm⁻¹ by the ionic species.

The efficient removal of mercury contaminants observed under these conditions is attributed to electromigration of the coordination complexes that form between the terminal hydroxyl groups in EDTA and divalent mercury (Hg²⁺), which is probably strengthened by supramolecular interactions between unshared electrons at EDTA's tertiary amino nitrogens and Hg²⁺. These interactions are particularly effective with the presence of potassium ions. This observation is supported by molecular modeling of several possible interactions in the proposed complex using the Density Functional Theory method (B3LYP LANL2DZ, Robles et al, 2012, Figure 7).

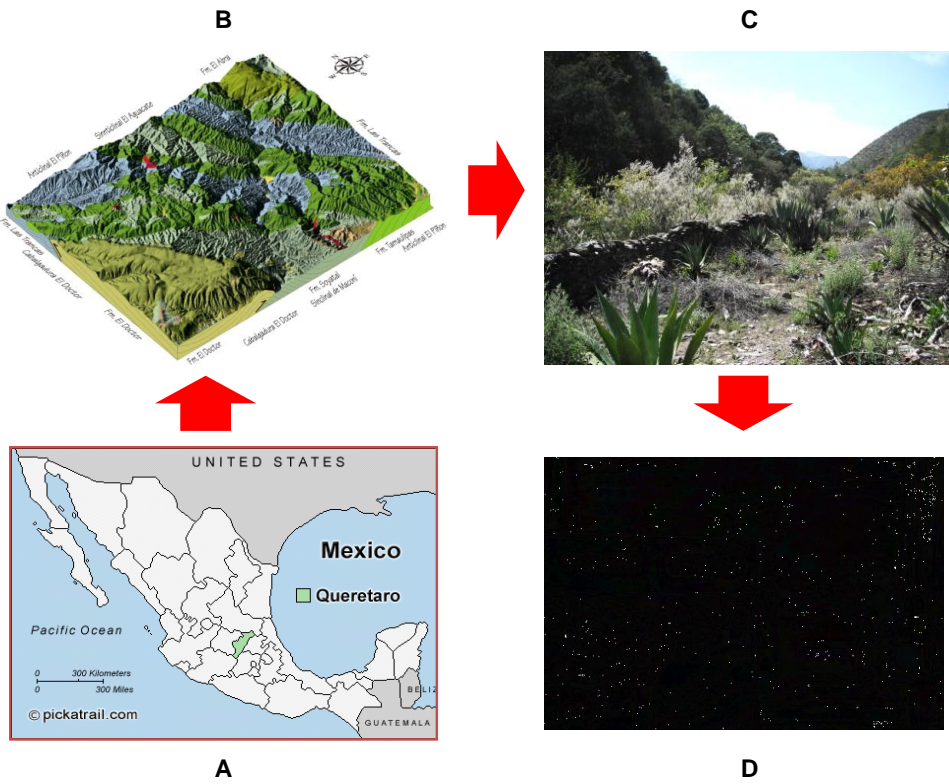


Figure 5. Localization of Queretaro in Mexico (A) with satellite image from San Joaquin's Sierra Gorda, Queretaro (B) where there is the Mine "El Rincón" (C) with high concentration of Hg^{2+} , which was removed with electroremediation process in continues flow in presence of EDTA (D).

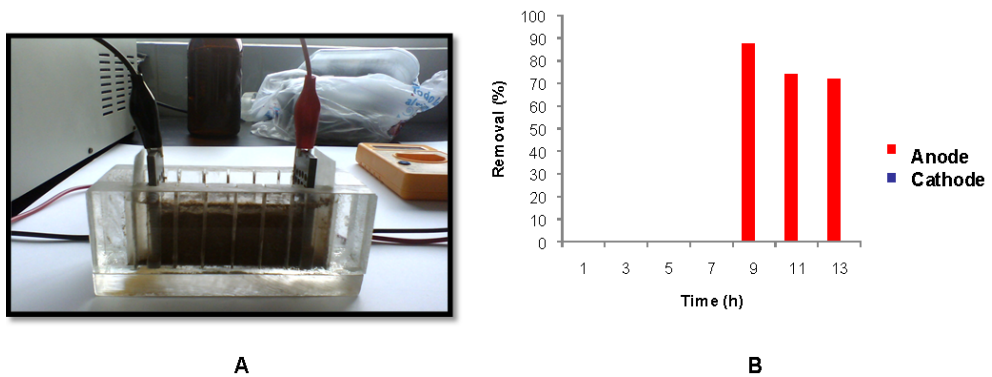


Figure 6. Electroremediation process in batch reactor assisted by EDTA (A), and its corresponding removal percentage of Hg^{2+} followed during 13 h of treatment, close to anode and cathode.

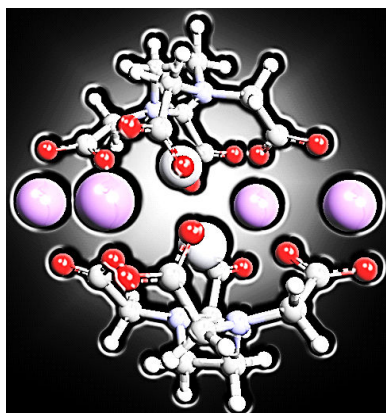


Figure 7. Optimized conformation and molecular structure of the proposed $2 \text{Hg}^{+2} / 2 \text{EDTA} / 4 \text{Na}^+$ complexes (B3LYP LANL2DZ, Robles et al, 2012).

6. Conclusions

Mercury is a non-essential metal that can bioaccumulated in living organisms, causing toxic effects of various kinds. Therefore, it is vital to understand how this metal is transmitted through the environment and the changes that occur due to contact with living organisms, or environmental conditions such as high temperatures or strong winds. A study of the reactions that form organic or inorganic compounds, which are even more toxic, is also necessary to limit mercury toxicity. This research gives a brief overview of the techniques commonly used for treatment of sediment and soil contaminated with mercury, mobilization and loadings the mobilized mercury across different matrixes of environment, in specially electroremediation of mercury polluted soil, facilitated by the use of complexing agents as EDTA, proved to be an attractive alternative treatment for the removal of mercury from polluted soil in mining areas.

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