INTERACTIONS AT THE SOLID-LIQUID INTERFACE AFFECTING THE MERCURY GEOCHEMICAL CYCLE

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ABSTRACT

The indiscriminate and unsustainable use of elemental mercury in garimpos has contributed for the dispersion of Hg through out the environment. Once released to the environment, complex chemical reactions at the inorganic and organic levels, might lead to the formation of methyl-mercury, the most toxic form of the metal, which is a high threat to humans. Speciation and complex formation are key processes in the reactivity and transport of Hg in surface, interstitial and ground waters. In this regard, parameters such as pH, Eh, concentration of inorganic ligands such as chloride and sulfide, as well as concentration of organic acids play an important role. The effect of organic acids in Hg chemistry is of particular interest due to its presence in dark river waters of tropical forests, where most of the garimpo activity take place. This paper highlights some physico-chemical reactions that affect the fate and cycling of Hg

INTRODUCTION

The unsustainable use of elemental mercury (Hg^o) for gold amalgamation, carried out by informal gold miners (garimpeiros), has contributed to the dispersion of mercury through out the environment. Once discharged to the atmospheric, aquatic and terrestrial compartments, Hg^o may undergo a series of transformations to methyl-mercury (CH_3Hg), the most toxic form of the metal, which is incorporated in living organisms and accumulates in the food chain. Methyl-mercury causes irreversible damage to the central nervous system of man [Cleary et al., 1994; Wood et al., 1978].

The complexity of mercury chemistry and biochemistry is related to its various possible species with different physico-chemical properties. In this respect, the speciation of mercury depends on biotic

and abiotic processes which are linked to the types of organisms and concentration of ligands in a particular system. Mercury interactions in the environment that affect its chemical behavior and bio-availability, include sorption at mineral surfaces and formation of complexes with organic materials.

With respect to interactions at the solid-liquid interface, it has been considered that, mercury dissolved in surface water, interstitial water and ground water, as well as adsorbed at the water soluble and exchangeable phases of minerals, are more mobile and more bio-available, while mercury adsorbed on Fe and Al oxides and at the residual phases are less mobile and less bio-available [Gambrel et al., 1980]. Thus, mercury speciation and the physical-chemistry of the system play important roles in its transport, fate and bio-availability.

Organic acids are important components of dark river waters in the tropics. Although the role of organic acids in mercury bio-availability is not very clear, it has been shown that the solubility of elemental mercury is enhanced in the presence of humic acid through a solubilization-complexation mechanism, and that the organo-mercury complex formed is relatively more mobile [Melamed et al., 1997].

This paper describes the importance of physico-chemical interactions in soils and natural water systems in the geochemical cycling of Hg.

UTILIZATION, DISCHARGE AND FATE OF MERCURY

Elemental mercury has been extensively used in rain forest areas, including the Brazilian garimpos. Calculations indicate that, in 1989, at least 160 tones of Hg^0 were used in Brazil only. The efficiency of Hg^0 to recover gold (Au) is related to the greate affinity of these two metals to amalgamate, forming complexes such as: $AuHg_2$, Au_2Hg and Au_3Hg.

Elemental mercury is sometimes introduced during the ore processing phase, or later, at the amalgamation step. In garimpos where gold occurs in alluvial deposits, Hg^o is introduced in sluice boxes, mounted on dredging barges or at the river borders. In this case, the fate of Hg^o is the water column and the river sediments. In garimpos, in which the gold is relatively free, occurring in quartz veins,

Hg^0 accumulates, at the end of the ore processing, in the tailings that are disposed at the soil surface, susceptible to leaching, erosion and volatilization or degassing.

In general, the processing phase is carried out in open circuit, without the use of an amalgamation drum for instance, and without any care to separate the tailings from the hydro-system. Approximately 20-25% of the mercury emitted to the environment comes from the amalgamation tailings.

At the last stage of gold recovery, the burning of the Au-Hg amalgam, usually in open circuit, without the use of retorts, promotes the emission of the Hg^o vapor to the atmosphere of approximately 75-80% of the total mercury input [Lacerda and Salomons, 1992]. The "bullion" (a porous mass of gold), taken by the garimpeiros to the dealer shops downtown, still contains 5% of Hg^o which are also transferred to the atmosphere due to an additional burning in open circuit. Elemental mercury has substantial vapor pressure ($2,46 \times 10^{-1}$ Pa at 25 ^oC) and Henry's constant (0,32 at 25 ^oC) which explain its high volatility [Iverfeldt and Lindqvist, 1986]. The relatively high first ionization potential of Hg^o (241 kcal mol^{-1}) justifies its presence in the atmosphere, mainly in the reduced form (Hg^0), despite the oxidizing potential of the atmospheric system.

Once in the atmosphere, the Hg^o vapor is oxidized to Hg(II) by reactions mediated by ozone (O_3), ultraviolet radiation and water vapor [Iverfeldt and Lindqvist, 1986], with formation of different forms of Hg(II) such as Hg^{2+} and Hg_2^{2+}, and $HgCl_2$.

During the raining season, Hg(II) is deposited in the aquatic environment and in soils. The Hg(II) in these compartments may be transformed, through either biotic or abiotic processes [Garvis and Ferguson, 1972; Rogers, 1977], to methyl-mercury (CH_3Hg^+). This species is considered the most harmful form of Hg, being very stable in acid pH and highly soluble in fats. Methyl-mercury can be highly incorporated by the aquatic biota and, consequently, accumulate in the food chain. At the top of the food chain, it is estimated that 90 % of incorporated mercury is in the methyl form [Huckabee et al., 1979].

Many pathways lead to Hg contamination, reflecting the complexity of Hg chemistry in the environment. Figure 1 shows the

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
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main pathways of concern of the mercury cycle and fate in soils, atmosphere and river waters. These pathways are:

- Direct input of Hg^0 into river waters

- Volatilization of Hg^0 following burning of Au-Hg amalgam

- Binding of volatilized Hg^0 to aerosol and transport

- Deposition of Hg^0 in soils and waters

- Oxidation of Hg^0 by ozone or radiation and deposition of Hg(II) in soils and waters

- Methylation of Hg(II) to methyl mercury

- Adsorption of Hg(II) to water suspended particulate matter and sedimentation

- Immobilization of Hg by anoxic layer sulfide

- Reduction of Hg(II) to Hg^0 mediated by radiation mediated by organic acids and volatilization at the water air interface.

- Solubilization of Hg^0 through organic acid induced dissolution-complexation

- Leaching and transport of Hg(II) through the soil matrix leading to groundwater contamination

- • Dimethylation of methyl mercury and volatilization at the water air interface

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
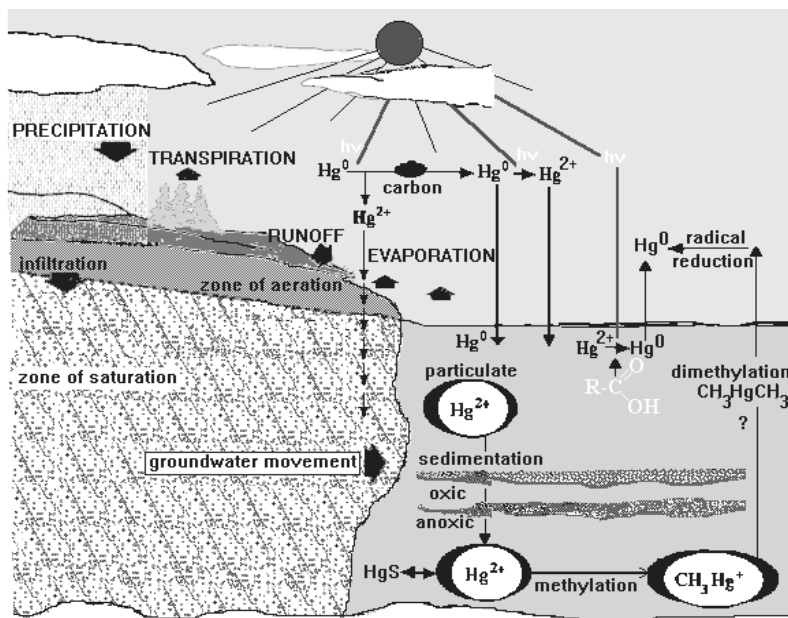Editors

Figure 1 - Pathways of the mercury geochemical cycle

EFFECT OF PHYSICO-CHEMICAL INTERACTIONS ON Hg SOLUBILITY, ADSORPTION AND METHYLATION

The complexity of Hg chemistry in the environment is related to the fact that the metal forms many soluble ionic complexes with various degrees of stability and the possibility of many oxidation states. Depending on the redox conditions of the system, the forms Hg^0 and Hg(II) may be present. Hg(II) is the stable form at redox potentials above 0.4 V.

The system pH also play a key role in different aspects of the chemistry and physical-chemistry of Hg. Due to its strong ability to form complexes, the ion Hg^{2+} is rarely found free under natural conditions. In acid solutions, $HgCl_2^0$ is the complex that usually occurs in soils

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

[MacNaughton and James, 1974]. Above pH 7, the complex $Hg(OH)_2^0$ is the stable form of Hg(II). One straight forward implication of system pH on Hg speciation is that this parameter affects the transport of Hg in soils. The effect of pH on mercury adsorption indicates that the metal behaves as other metals that form hydrolyzable cations. The increase in Hg(II) adsorption in an Oxisol is relatively high for a relatively small increase in pH [Melamed and Villas Bôas, 1998], producing a sigmoidal function usually referred as *adsorption edge* [Sposito, 1984], that reflects the competition of the cationic species with H^+ for the surface site.

The phenomenon of adsorption in soils is important in the geochemical cycle because it has a direct influence in mercury mobility and bio-availability. While specific adsorption may hinder metal bio-availability, the non-specific adsorption, corresponding to the exchangeable phase allows biotic and abiotic transformations. Ramamoorthy and Rust (1976) concluded that the retardation coefficient of Hg(II) decreases in the order: level of organic matter > CEC > surface area, reflecting a character of non-specific adsorption. On the other hand, Melamed et al. (2000) showed the specific adsorption character of Hg(II) in an Oxisol, for its high affinity with Fe oxides.

In addition to the redox potential and pH, the concentration of ions such as sulfide and chloride are parameters of importance in the chemical speciation of Hg in solution.

The concentration of Cl^- ions in solution has a great impact in the mobility of Hg(II) because the Cl^- ligand forms anionic complexes. These complexes have a much lower interaction at the soil/solution interface, and thus, are relatively more mobile. Adsorption and retention of Hg(II) in an Oxisol were shown to be enhanced in a $KClO_4$ system as compared to a KCl system [Melamed and Villas Bôas, 1998]. These findings are mainly relevant in estuarine environments, where the concentration of chloride ions are relatively high.

Another important property of Hg is to form strong complexes with the sulfide ion. In reduced conditions, the ionic form of Hg is stable in the presence of H_2S and HS^-. However, at higher redox potentials,

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

HgS precipitates, or in systems of high alkalinity, the ion HgS_2^{2-} is formed. In redox conditions normally found in surface soils, mercury is present as Hg(II). The presence of sulfide may cause a decrease in the conversion of Hg(II) to CH_3HgCl, as demonstrated with synthetic solutions of $HgCl_2$, Na_2S and methylcobalamin, a methylating agent. However, the presence of sulfide enhances the solubility of Hg^0, with the production of polysulfides in solution [Melamed and Villas Bôas, 2000].

Based on stability fields of Hg [Hem, 1970], one can estimate, for values of Eh and pH found in river waters, a maximum dissolved concentration of 25 **ppb**, even in spots saturated with Hg^0. However, the presence of organic acids, dissolved in soils and river waters of the tropics, may oxidize Hg^0, enhancing its solubility above the values forecasted for inorganic systems, by means of a dissolution-complexation mechanism [Veiga, 1994; Melamed et al., 1997].

The solubility of Hg^o in humic acid increases considerably with time. Experiments demonstrated that after 30 days of reaction the concentration of dissolved total Hg is, approximately, six times higher than its concentration after 1 day.

Organic acids are composed of a mix of substances resulted from the chemical and biological degradation of plants and animals mediated by the activity of microorganisms. They are predominantly aromatic, hydrophilic, chemically complex, and having a molecular weight that varies from hundreds to millions [Stevenson, 1982]. These substances since they vary in composition do not show specific physico-chemical characteristics such as defined boiling point, refraction index or elementary composition. They may be divided into three major fractions: humic acid, fulvic acid and humine. These three fractions are structurally very similar, differing in molecular weight and quantity of functional groups [Barros et al., 1994]. Humic acid is the main humic substance that can be found in rivers, soils and sediments. One major characteristic of humic substances in general is their high capacity of interaction with metallic ions, giving rise to stable complexes. This ability is due to the high percentage of functional groups having the oxygen element in their formula, as carboxyl, phenolic hydroxyl and carbonyl groups [Jordão et al., 1993; Varshal et al., 1999].

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

At the acidic range of the pH scale, the excess of H^+ ions competes with Hg(II) ions for active sites on the humic acid molecule. Another factor that may contribute to decrease the formation of organo-mercury is the precipitation of humic acids at low pH values [Jordão et al., 1993; Varshal et al., 1999]. As the pH rises, and the proton concentration diminishes, this competition decreases, and the formation of Hg(II) complexes with humic acid increases.

Considering the active sites present in the humic acid macromolecule, the carboxyl group is considered the most reactive, because it is able to dissociate, releasing H^+ ions into aqueous solution, as shown in the reaction:

$$R - C\overset{\displaystyle O}{\underset{\displaystyle OH}{}} \rightleftharpoons R - C\overset{\displaystyle O}{\underset{\displaystyle O^{\ominus}}{}} + H^{\oplus}$$
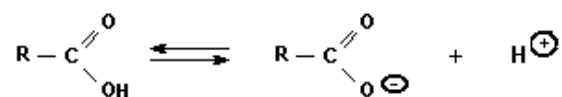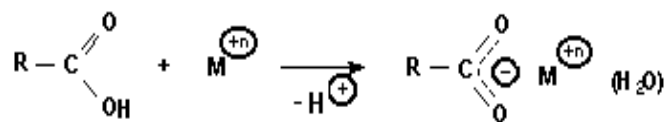
where R represents the organic chain.

The carboxylate ion, which resulted from carboxyl ionization, is stabilized by two resonant forms, identical and having the same energy, turning the equilibrium reaction to the direction of the dissociation of the acid:

$$R - C\overset{\displaystyle O^-}{\underset{\displaystyle O}{}} \longleftrightarrow R - C\overset{\displaystyle O}{\underset{\displaystyle O^-}{}}$$
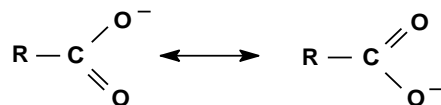
The high dissociation capacity of the -COOH group increases the chances of the formation of organo-mercury complexes to occur on this site, since a higher quantity of $-COO^-$ ions are available for the formation of complexes with a metal, as compared to the other acid sites of the humic acid molecule. The formation of the organo-mercury complex at the carboxylate site can be represented as follows:

$$R - C\overset{\displaystyle O}{\underset{\displaystyle OH}{}} + M^{\oplus n} \xrightarrow{-H^{\oplus}} R - C\overset{\displaystyle O}{\underset{\displaystyle O}{\ominus}} M^{\oplus n} \quad (H_2O)$$

where $M^{n+} = Hg^{2+}$, $HgCl_4^{2-}$, $HgCl_3^-$

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

The role of organic acids in mercury bio-availability is not very clear. However, in addition of enhancing the solubility of elemental mercury, the organo-mercury complex formed is relatively more mobile, which was attributed to the size of the molecule having a much lower interaction at the solid-liquid interface [Melamed et al., 1997]. The possibility of donation of methyl groups from the organic acid chain to promote mercury methylation is uncertain.

Although the sediment compartment is the most important mercury methylation site, studies conducted by Mauro et al. (1999) demonstrated the relevance of the roots of floating aquatic macrophytes, where high production of methyl-mercury occurs. The mechanism is attributed to the suitable environment, promoted by the large macrophyte stands and high temperatures, for optimum growth of sulfate reducing bacteria, which is considered the main Hg methylators [Compeau and Bartha, 1984]. These microorganisms are usually found where redox potentials are low, although they can also be found in oxic environments [Jorgensen and Bak, 1991].

Methylation by macrophytes increases from 10 to 35 ^{o}C. At pH values of 6 and 7, methylation was stimulated and a significant decrease was verified at pH 8. Increasing $KClO_4$ concentrations led to a significant decrease of the methylation rates, while for KCl and $CaCl_2$ solutions, only a slight decrease was observed.

Mercury adsorption kinetic studies [Melamed et al., 1997] demonstrated that the rate of adsorption of Hg(II) is much faster than the rate of adsorption of methyl-mercury and that methyl-mercury has a lower affinity for mineral surfaces as compared to Hg(II). Thus, the impact caused by methylation is two fold: it produces a compound that accumulates in living organisms, and because methyl-mercury has relatively lower affinity for mineral surfaces, it enhances the mobility and the dispersion of Hg throughout the environment.

CONCLUSIONS

The processing of gold in open circuit, widely practiced by garimpeiros, has been responsible for large quantities of elemental mercury discharged to the different environmental compartments. Many pathways lead to the formation of methyl-mercury, which accumulates and bio-magnifies in the food chain.

Roberto C. Villas Bôas , Christian Beinhoff , Alberto Rogério da Silva,
Editors

Adsorption in soils is important in the geochemical cycle because it has a direct influence in mercury mobility and bio-availability. In this regard, various physico-chemical parameters may interfere. In the absence of chloride, specific adsorption of Hg, in soils rich in Fe oxides, occurs and as such retention increases as the system pH is increased.

The presence of sulfide hinders the methylation process, however it enhances the solubility of elemental mercury.

The presence of organic acids dissolved in soils and dark river waters increases the solubility of Hg^o, resulting in the formation of a organo-mercury complex that has a relatively lower interaction with mineral surfaces.

Mercury methylation produces a compound that accumulates in living organisms and contributes for the dispersion of Hg throughout the environment, because methyl-mercury has a lower affinity for mineral surfaces.

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