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The effect of humic acid on mercury solubility and complexation†

R. Melamed,* F. E. Trigueiro and R. C. Villas Bôas
CETEM/CNPq — Center for Mineral Technology, Rua 4, Quadra D, Cidade Universitária, Ilha do Fundão, Rio de Janeiro, 21941-590

Utilization of mercury in gold mining in the tropics has contributed to large inputs of the metal into the aquatic environment. Although in this activity mercury is utilized in its elemental state, which is relatively immobile and inert, transformations to methylmercury occurring in natural systems lead to mercury contamination of aquatic organisms and the food chain. We investigated the effectiveness and mechanisms involved in the solubilization of mercury in the presence of humic acid, which is an important component of dark river waters in the tropics. Results showed that the solubility of elemental mercury was enhanced due to the presence of humic acid through a solubilization–complexation mechanism, which was attributed to the presence of acid sites on the humic acid molecule, mainly the carboxyl group. Calcium ions in solution prevent humic-acid-induced elemental mercury solubility. Although it was demonstrated that the mercury complex formed is more mobile in the presence of humic acid, preliminary results indicated that this mercury complex seem absorbed by fish. Copyright © 2000 John Wiley & Sons, Ltd.

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INTRODUCTION

For many years, informal gold-mining activity Brazil, (‘*garimpo*’) has contributed significantly to the dispersion of mercury in the environment by extensive use of elemental mercury [mercury(0)] in the process of gold extraction.

In ‘*garimpos*’, where gold occurs in alluvial deposits, mercury(0) is introduced via sluice boxes mounted on dredging barges or at the river edge. In this case, the ultimate fate of the mercury(0) is in the river sediment. Although the solubility of mercury(0) in water is very low,[1] the presence of dissolved organic acids in the water column of tropical rivers may alter its solubility, resulting in the formation of stable complexes which have a relatively lower interaction with mineral surface.[2]

In the final stages of gold recovery, burning of the gold–mercury amalgam, usually in open location, without the use of retorts, promotes emission of mercury(0) vapor to the atmosphere. Once in the atmosphere, mercury(0) vapor is oxidized to mercury(II) by reactions mediated by ozone (O_3), solar energy and water vapor,[3,4] and during the rainy season mercury(II) is deposited in the aquatic environment and in soils. The mercury(II) in these compartments may undergo methylation through either biotic or abiotic processes, giving methylmercury (CH_3Hg^+). This species is the most harmful form of mercury, being very stable at acid pH and highly soluble in fats. Methylmercury can be highly incorporated by aquatic biota, and consequently accumulates in the food chain. At the top of the food chain, it is estimated that 90% of incorporated mercury is in the methyl form.[5]

The general scenario in the Amazon river waters is, thus, the input of mercury as mercury(II) and mercury(0), in a system rich in dissolved organic acids.[6] Organic matter (e.g. humic substances) present in Amazon rivers is composed of a mixture of compounds resulting from chemical and biological degradation of plants and animals and from the activity of microorganisms. Humic substances are predominantly aromatic, hydrophilic and chemically complex materials, having molecular weights that vary from hundreds to millions.[7] They do not show specific physicochemical character-

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* Correspondence to: R. Melamed, CETEM/CNPq — Center for Mineral Technology, Rua 4, Quadra D, Cidade Universitária.

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istics, such as defined boiling points, refracting indices or elemental compositions. They may be divided into three major fractions (humic acid, fulvic acid and humine), which are structurally similar, differing in molecular weight and number of functional groups.[8] Humic acid is the main humic substance found in rivers, soils and sediments. The role of humic substances in water chemistry has received much attention due to their ability to form complexes with trace metals.[9] The aim of this work was to study the mechanisms of formation of mercuric complexes by humic acid, so the physical and chemical interactions of mercury with humic acid (HA) were studied. Moreover, the kinetics of solubilization of mercury(0) and the influence of pH on the mechanisms of solubilization and the complexation were also evaluated.

MATERIALS AND METHODS

Kinetic studies

Studies on the kinetics of the solubilization of mercury(0) in Aldrich humic acid (H1, 675-2 sodium salt, tech [1415-93-6] mp >300, merck index 10, 4649 MSC book 2, 1886 B) Chemicals were grade A reagents; HCl, KCl, $CaCl_2$ and $HgCl_2$ were used of (sodium salt) were conducted in test-tubes containing 0.2 g of metallic mercury in suspensions of humic acid at a concentration of 1.25 g l^{-1} dissolved in 0.01 M KCl. (ionic strength, The tubes were agitated for 10 min, five times daily, for a total period of 30 days. The experimental units were vacuum-filtered through a porous cellulose membrane 0.45 µm in diameter. The filtrate was analyzed for mercuric species.

Solubility of mercury(0) in humic acid

To evaluate the effect of HA in the solubility of metallic mercury, 0.2 g of mercury(0) was placed in contact with suspensions of 0, 0.25, 0.50 and 1.25 g l^{-1} HA in 0.01 M KCl, for a period of ten days. To study the effect of calcium, 0.2 g of mercury(0) was placed in contact with suspensions of 0.125 and 0.25 g l^{-1} HA with $CaCl_2$, also for a period of ten days.

Formation of mercury(II) complexes in humic acid

To study the interaction of mercury(II) with HA, solutions of 0.37, 0.74, 1.11, 1.48 and 1.85 mg l^{-1} $HgCl_2$ in 0.01 M KCl were reacted with 0.125 g l^{-1} HA humic acid, at different pH values, for a period of 15 days. Adjustment of the pH was made by the additions of 0.5–1.5 ml 0.1 M HCl.

Chemical analysis

Mercury was determined by atomic absorption spectroscopy with cold vapor generation and preconcentration in a gold lattice. The following nomenclature was used for the mercury species in solution.[10,11]

Hg^T	Total mercury (dissolved), determined after oxidation of mercury in bromine chloride (BrCl) solution and reduction with stannous chloride ($SnCl_2$);
Hg^A	Mercury species, including mercury(0) and inorganic complexes, determined after the reaction of the supernatant with $SnCl_2$;
Hg^X	Mercury in the form of soluble organic complexes, defined as the difference between Hg^T and Hg^A.

RESULTS AND DISCUSSION

Kinetics of mercury(0) dissolution

The kinetics of the solubilization and complexation of mercury(0) in HA is shown in Fig. 1. It was observed that the solubility of mercury in the presence of HA rose considerably with time. After 30 days, the concentration of dissolved or colloidal Hg^T was approximately six times higher than the concentration of Hg^T at the initial reaction time of 30 min, which indicated the high capacity of HA to dissolve the mercury(0). Hg^X concentration increased with time until it reached a maximum and constant value of 0.4 mg l^{-1}, after about 24 h of reaction.

Humic acid–pH interaction on the solubility of mercury(0)

Figure 2 shows the effect of HA on the solubility and complexation of mercury(0), at different pH values. Here we may note that the concentration of

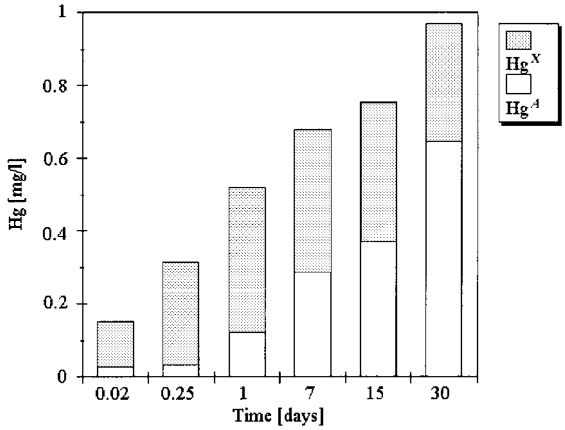

Figure 1 Kinetics of solubilization–complexation of mercury(0) HA.

HA also affects the formation of complexes. The higher the concentration of HA, the higher are the concentrations of Hg^X and of dissolved mercury(0).

Also, the addition of HA tended to raise the pH of the system. The addition of approximately 0.25 g l^{-1} of HA, for instance, elevated the pH of the system to around 7.3. The results shown in Fig. 2 demonstrate the importance of the system pH. For instance, at pH 2.5 and in the absence of HA, the concentration of dissolved mercury(0) in the system was six times higher than at pH 4.5. This shows that solubilization is higher at lower pH values. The results also indicate that pH affects the formation of mercuric complexes in the presence of HA. The formation of mercury complexes is proportionally higher as pH rises. In the system where 0.25 g l^{-1} humic acid was added, for instance, 35% of the dissolved mercury formed complexes at pH 2.5. As the pH rose, the complexation increased to nearly 43%.

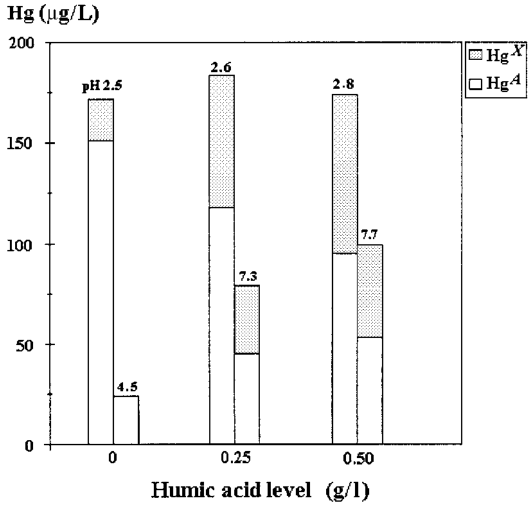

Figure 2 Effect of HA on the solubility of mercury(0) at different pH values.

Interaction of HA and mercury(II)

One major characteristic of humic substances in general is their high capacity to interact with metallic ions, giving rise to stable complexes. This ability is due to the high percentage of functional groups having oxygen in their formula, e.g. carboxyl, phenolic, hydroxyl and carbonyl groups.[12,13]

Figure 3 shows the interaction of HA with mercury(II) at different pH values.

The formation of complexes is higher as the pH rises. At acid pH values, the excess of H$^+$ ions compete with mercury(II) ions for active sites on HA. As the pH rises, and the proton concentration diminishes, this competition decreases, and the formation of mercury(II) complexes with HA increases. Another factor that may contribute to reduce the formation of complexes between Hg and HA is the possible precipitation of HA at low pH values.[12,13] These results are in agreement with those of others. Varshal *et al.*[13] also found that complex formation increases as the pH and concentration of humic acid rise.

Of the active sites present in the humic acid macromolecule, the carboxyl group was considered the most reactive[12] as it is able to dissociate rapidly.

The high dissociation capacity of the —COOH group increases the possibilities for formation of

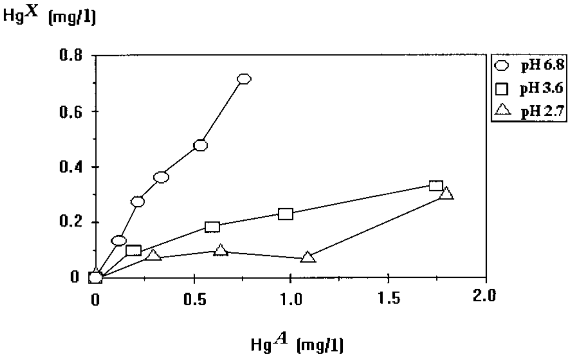

Figure 3 Complexation of mercury(II) in HA at different pH values.

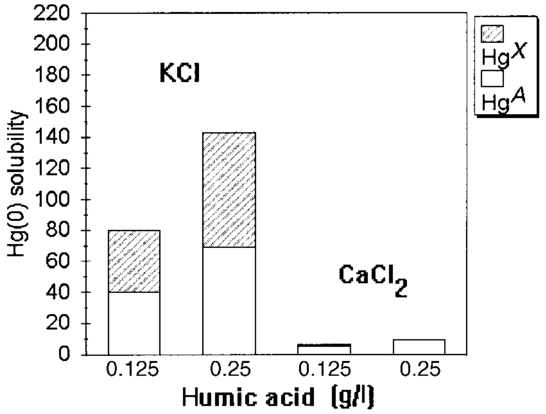

Figure 4 Effect of calcium–HA interaction on mercury(0) solubility.

mercury(II) complexes to occur on this site. IR studies[12] showed that the presence of metallic cations causes an intensification of the bands attributed to —COO$^-$ in comparison with the bands attributed to the carboxyl group in pure HA. This shows a higher ionization of the carboxyl group. A shift in the bands of the —COO$^-$ group was also observed when the HA–metal complex was formed.

Effect of calcium on HA induced solubility of mercury(O)

Introduction of calcium was successful as a method to reverse the high solubility of mercury-induced HA (Fig. 4). However, more data are needed to verify the effect of this amendment, and the possible development of this method in the presence of natural organic acids. The data in Fig. 4 shows that calcium prevents the dissolution of mercury(0), possibly precipitating HA rather than working in a competitive complexation mechanism, as reflected by the absence of HgX and also HgA.

CONCLUSIONS

The presence of organic acids dissolved in soils and sediments of rivers increases the solubility of mercury(0) by mechanisms involving solubilization and formation of complexes. The formation of mercuric complexes by HA may be attributed to the presence of acid sites in the acid macromolecule (mainly the carboxyl group) due to the high reactivity of carboxylate ion in complexing metals. The solubilization of mercury(0) is higher in acid environments, in the presence or absence of humic acid. Preliminary tests also show that the presence of calcium may counteract the solubility enhancement induced by HA.

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