

Article

## The Fate of $\text{Hg}^0$ in Natural Waters

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Vários aspectos da química aquática do mercúrio elementar ( $\text{Hg}^0$ ) são importantes para o entendimento do destino deste metal no ambiente, mas no entanto têm sido pouco estudados. Neste trabalho, observou-se que a dissolução reativa do mercúrio elementar é dependente da concentração do metal em solução, da velocidade de oxidação do metal, da concentração de material particulado, da natureza e concentração de outros íons e do pH. Quando  $1 \text{ g L}^{-1}$  de  $\text{Hg}^0$  foi usado em água destilada em um sistema aberto para a atmosfera, a concentração de mercúrio solúvel aumentou em função do tempo, obtendo-se  $5,4 \mu\text{g L}^{-1}$  de Hg total no estado estacionário. Deste total,  $3,2 \mu\text{g L}^{-1}$  foram devido às espécies  $\text{Hg}^{2+}$  formadas via oxidação. Em amostras de água de lago, os resultados mostraram uma inibição no processo de dissolução reativa e a concentração total do metal em água foi de  $3,1 \mu\text{g L}^{-1}$  no estado estacionário. Este efeito inibitório foi atribuído ao material particulado. Em água do mar, a concentração total de Hg solúvel aumentou em função do tempo, atingindo um valor de  $17,8 \mu\text{g L}^{-1}$  depois de 10 h. Em seguida, a concentração de Hg solúvel diminuiu, atingindo  $4,8 \mu\text{g L}^{-1}$ . Os experimentos realizados em diferentes valores de pH (4,0; 7,0 e 9,0), mostraram que a dissolução reativa do metal acontece em maior extensão em pH 4,0. Estudos de adsorção de ambas as espécies, íon mercúrico e mercúrio elementar, sobre o material particulado, mostraram uma dependência da área superficial, obtendo-se a seguinte ordem: 400 mesh > 200 mesh > sedimento *in natura*. As implicações destes resultados são discutidas, levando em consideração o cenário Amazônico.

Several aspects of the aquatic chemistry of elemental mercury ( $\text{Hg}^0$ ) are vital to the understanding of the fate of this metal in the environment, yet have scarcely been studied. Reactive dissolution of metallic mercury is shown to be dependent on the metal concentration in solution, the metal oxidation rate, particulate material concentration, nature and concentration of other ions, and pH. When using  $1 \text{ g L}^{-1}$  of  $\text{Hg}^0$  in distilled water open to the atmosphere, the concentration of soluble mercury increases as a function of time, reaching  $5.4 \mu\text{g L}^{-1}$  of total Hg in the steady state. From this,  $3.2 \mu\text{g L}^{-1}$  were due to  $\text{Hg}^{2+}$  formed via oxidation. In lake water, results showed an inhibition in the reactive dissolution process, and the total metal concentration in water was  $3.1 \mu\text{g L}^{-1}$  in the steady state. This inhibitory effect was attributed to particulate material. In seawater, the total concentration of soluble Hg increases as a function of time, reaching a peak of  $17.8 \mu\text{g L}^{-1}$  after 10 h. After this, the soluble concentration dropped, to  $4.8 \mu\text{g L}^{-1}$ . Experiments performed at different values of pH (4.0; 7.0 and 9.0), showed that the dissolution of the metal occurred to a higher extent at pH 4.0. Adsorption studies of both mercuric ions and elemental mercury species onto particulate material showed a dependence on the surface area, following the sequence 400 mesh > 200 mesh > sediment *in natura*. The implications of such findings are discussed, taking into consideration the Amazonian scenario.

**Keywords:** mercury, oxidation, adsorption, reactive dissolution

## Introduction

Predicting the real impact related to emissions of mercury into the environment still poses many problems, since some of the fundamental aspects of the aquatic chemistry of mercury have not yet been fully studied. Mercury species reaching the aquatic system are, in a broad sense, classified into inorganic ( $\text{Hg}^0$ ,  $\text{Hg}^{2+}$  and  $\text{Hg}_2^{2+}$ ) and organic ( $\text{CH}_3\text{Hg}^+$ ,  $(\text{CH}_3)_2\text{Hg}$ , etc.) forms<sup>1,2</sup>.

Organic mercurial compounds are considered to be the most toxic form of the metal. Due to their lipid solubility, these species can quickly enter the blood stream and damage the central nervous system<sup>3,4</sup>. Inorganic forms of mercury have much lower toxicity than the organic ones, with a decrease in toxicity from  $\text{Hg}_2^{2+} > \text{Hg}^{2+} > \text{Hg}^0$ . Recently, Jardim *et al.*<sup>5</sup>, showed that in microbial acute toxicity tests (up to 2 h), the inhibition in the respiration of *Escherichia coli* observed when stressed by  $5000 \text{ mg L}^{-1}$  of  $\text{Hg}^0$  was similar to the one caused by  $10 \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$ , showing the low toxicity of the elemental species compared to mercuric ions.

Worldwide, industrial and agricultural uses of mercury have dropped markedly in the last three decades. Presently, most countries are facing old inventory remediation actions rather than dealing with present inputs into the ecosystems. However, this is not the present scenario in Brazil where, due to the growing activity of gold extraction (*garimpos*) which use mercury to amalgamate gold, it has been calculated that about 1,500-3,000 tones of Hg have been released in the Amazon region in the last 15 years<sup>6</sup>.

Metallic mercury used in the *garimpos* can reach the aquatic system either by direct spills of liquid droplets, or by fugitive atmospheric emission during the roasting of the Au-Hg amalgam. The residence time of elemental mercury in the atmosphere depends on the concentration of oxidant species as well as the deposition rate of mercury vapors. Upon reaching the water bodies, independent of the emission source, the fate of mercury depends only on the physico-chemical and biological features of the water body<sup>2</sup>. The first and most important process concerning mercury speciation is the partitioning between solid and aqueous phase. In this case, mercuric ions should have more affinity for solids than the elemental form and adsorption can be considered as a key mechanism to ameliorate the metal ecotoxicology. Also, depending on the redox potential, dissolved  $\text{Hg}^0$  can be oxidized and later complexed with major inorganic ligands ( $\text{Cl}^-$ ,  $\text{OH}^-$ ,  $\text{S}^{2-}$ , etc.) and dissolved organic carbon<sup>4,7,8</sup>, thus increasing the metal solubility. Solar radiation is another important variable in the mercury aquatic chemistry, but this has scarcely been explored in the recent years, especially for tropical areas<sup>7,9,10</sup>. Other important processes related to the toxicity of mercury, not only to the biota, but mainly to humans, is methylation by enzymatic action of microorganisms<sup>4,11,12</sup>, favoring the accumulation of organic mercurial species in fatty tissues.

Despite the vast literature concerning both the toxicity and the chemistry of mercury in aqueous media, studies are centered on  $\text{Hg}^{2+}$  and organic mercurial species only. Since in the *garimpos* of Brazil mercury is almost solely used in the elemental form, very little is known about the fate of this species in tropical waters, specifically concerning the flux at air/water as well as, water/sediment interfaces, thus making difficult the risk assessment, as extrapolation from published data to the Brazilian scene has very limited validity.

In this work some fundamental aspects of the aquatic chemistry of elemental mercury was studied. These aspects involved the adsorption of both  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  onto particulate material in suspension, as well as the reactive dissolution of  $\text{Hg}^0$  in natural waters, followed by the extent of oxidation to  $\text{Hg}^{2+}$  with concomitant increase in the concentration of soluble mercury and the losses of  $\text{Hg}^0$  to the atmosphere. The experimental conditions were set in a manner that the results could be used as an adequate tool to support many ongoing studies on the impact of mercury in these regions.

## Experimental

The Environmental Chemistry Laboratory, where this research was carried out (Institute of Chemistry, State University of Campinas) works under Good Laboratory Practices (GLP). All glassware, including reaction vessels, was soaked in 10% nitric acid prior to use, followed by rinsing with distilled water.

### Mercury determination

Mercury was determined using a commercially available Cold Vapor Atomic Absorption (CVAAS) equipment adapted to FIA (Flow Injection Analysis) as described by Pasquini *et al.*<sup>13</sup>. Briefly, the system consists of the injection of the aqueous sample in a carrier containing a 5% solution (v/v) of  $\text{HNO}_3$ . The mixture receives the reductant (a 10% (w/v)  $\text{SnCl}_2$  solution) to promote the reduction of  $\text{Hg}^{2+}$  ions to the elemental form, which is then purged from the solution in a gas-liquid separation chamber. The metal vapor is carried to the detection cell after an optional (not used in this case) pre-concentration step consisting of a gold amalgamation column. Differentiation between total (reducible) mercury and  $\text{Hg}^0$  species was obtained when the sample was analyzed with and without using the reductant. The concentration of the  $\text{Hg}^{2+}$  species was obtained by difference. The limit of detection obtained using this method was  $0.1 \mu\text{g L}^{-1}$  of mercury at an analytical frequency of 50 samples  $\text{h}^{-1}$ . Detailed information about the whole analytical procedure is provided elsewhere<sup>13</sup>.

### Reactive dissolution of $\text{Hg}^0$ in natural waters

Dissolution of elemental mercury was carried out in seawater (collected at Ubatuba - SP, Brazil) as well as in

freshwater (UNICAMP lake, Campinas - SP, Brazil) using similar setups as described below. Experiments using distilled water were also performed for comparison. Solutions were contaminated with 1 g L<sup>-1</sup> of Hg<sup>0</sup> and the concentration of Hg<sup>0</sup> and Hg<sup>2+</sup> was monitored at pre-established time intervals. During the whole length of the experiment, solutions were magnetically stirred at a rate of approximately 120 rpm. A similar experiment was done using a 0.1 mol L<sup>-1</sup> solution of NaCl. Prior to the experiment, the following water parameters were monitored: temperature, pH, chloride concentration, particulate material and TOC (total organic carbon), and all experiments using natural waters were performed using unfiltered samples. Later on, experiments using 10 and 100 g L<sup>-1</sup> of metallic mercury and distilled water were done for comparison. Finally, the experimental set up and conditions identical to the ones used by Glew and Hames<sup>14</sup> to determine the solubility of Hg<sup>0</sup> were reproduced using 100 g L<sup>-1</sup> of elemental mercury.

#### *Adsorption of Hg<sup>2+</sup> and Hg<sup>0</sup> onto the particulate suspended material*

Particulate material was obtained from a sediment collected at the UNICAMP Lake. Larger particles in the wet sediment were separated by using a 1 mm Nylon sieve. After drying at room temperature, the sediment was further sieved in to 200 and 400 mesh fractions. Adsorption experiments were carried out at room temperature (23 ± 3 °C) using 2 L beakers under constant magnetic stirring, by adding 150 or 15 mg of particulate in 1500 mL to give a final concentration of 100 or 10 mg particulate L<sup>-1</sup>. Control was carried out in the absence of particulates. Suspensions were contaminated with either 10 µg L<sup>-1</sup> of Hg<sup>2+</sup> or 1 g L<sup>-1</sup> of Hg<sup>0</sup>. These experiments were carried out using 200 and 400 mesh sediments as well as the nonsieved (*in natura*) sediment. The total concentration of soluble mercury was experimentally determined in samples withdrawn at different time intervals and the process was later mathematically modeled.

#### *Reactive dissolution of Hg<sup>0</sup> as a function of pH*

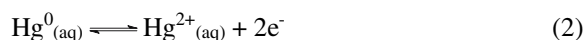
The dissolution of Hg<sup>0</sup> at different pH values (4.0, 7.0 and 9.0) was evaluated in the presence of 0.1 M NaNO<sub>3</sub>. The pH was set by using either NaOH or HNO<sub>3</sub> solutions at the beginning of the experiments.

## Results and Discussion

The first attempt to estimate the solubility of Hg<sup>0</sup> in water was done by Bonhoelfer and Reichardt<sup>15</sup>, where the authors showed the existence of the species Hg<sup>0</sup><sub>(aq)</sub> using the resonance line of mercury at 253.7 nm. Since then, the solubility of elemental mercury in water has been studied by many other researchers and, except for the fact that the concentration of Hg<sup>0</sup> has varied from 100 g L<sup>-1</sup><sup>14,16,17</sup> down to

22 g L<sup>-1</sup><sup>18</sup>, the common feature in all these studies is the absence of dissolved oxygen and presence of a reducing agent to avoid the formation of the Hg<sup>2+</sup> species in a closed system. As already pointed out, these experimental conditions, although necessary for the purpose, cannot be extrapolated to natural water conditions. One of the fewer papers that deals with the solubility of elemental mercury using experimental conditions more suitable to the ones found in natural waters was recently published by Magalhães and Tubino<sup>17</sup>, where they used air and CO<sub>2</sub> in the aqueous phase, but very high initial concentrations of elemental mercury.

The fate of mercury in natural waters involves three major steps, two of them occurring in the bulk solution and the other one at the water/atmosphere interface. The first step is the solubilization of mercury from the liquid phase to the aqueous phase, as in Eq. 1. The second step is the possible oxidation of the dissolved species, as presented in Eq. 2, depending on the redox conditions of the water body. The possibility of the direct oxidation of mercury droplets present in the water cannot be ruled out, although it should be very limited since it is an area-dependent process. Finally, Hg<sup>0</sup> species present in the aqueous phase will be at equilibrium with the overlying atmosphere, depending on the partial pressure of this species in the gas phase, according to Henry's law<sup>2</sup>.



In the oxidation of elemental mercury, there is a consensus in the literature that Hg<sub>2</sub><sup>2+</sup> are short-lived species in most natural waters, and their concentration should be negligible. However, with the recent development in mercury speciation techniques, this statement needs further study.

#### *Reactive dissolution of Hg<sup>0</sup> in natural waters*

Elemental mercury has been considered to be very unreactive in water bodies due to the low solubility of Hg<sup>0</sup>. Solubility of mercury obtained in laboratory studies shows values around 60 µg L<sup>-1</sup> at 25 °C<sup>14,16,18,19</sup>. Indeed, when trying to determine the solubility of elemental mercury in distilled water, using the same conditions as mentioned in the literature<sup>14</sup>, we obtained 61 µg L<sup>-1</sup>. However, in most impacted waters, even in the hot spots near the *garimpos* (Madeira River, Brazil), the highest concentration of total dissolved mercury found was 0.44 µg L<sup>-1</sup><sup>20</sup>, which indicates that either natural waters are far from the equilibrium, or that other processes are also important in mercury solubilization.

Figure 1 shows the increase in the soluble concentration of mercury ( $\text{Hg}^{2+}$  and  $\text{Hg}^0$ ) as a function of time in a freshwater sample (UNICAMP Lake). The results obtained using distilled water are also shown for comparison, and in both cases the initial concentration of  $\text{Hg}^0$  was  $1 \text{ g L}^{-1}$ . When using distilled water, the concentration of soluble mercury increases as a function of time, reaching the steady state after  $\sim 24 \text{ h}$  at  $5.4 \text{ } \mu\text{g L}^{-1}$ . Interestingly, the concentration of the starting mercury species ( $\text{Hg}^0$ ) reaches the steady state in a shorter time, around 5 h, at a concentration of  $1.7 \text{ } \mu\text{g L}^{-1}$ . For the lake water sample, soluble mercury concentrations are lower than the ones observed for distilled water, but the same trend was observed: while the elemental mercury reached  $0.6 \text{ } \mu\text{g L}^{-1}$ , soluble mercury was close to  $3.0 \text{ } \mu\text{g L}^{-1}$ .

In general, steady state concentrations for both  $\text{Hg}^{2+}$  and  $\text{Hg}^0$  species in the lake water sample were about half of the ones obtained for distilled water, indicating the presence of mechanisms that inhibit elemental mercury dissolution. Considering that this natural sample had  $\text{pH} = 7.1$ ,  $\text{TOC} = 5.8 \text{ mg C L}^{-1}$ , and Total Suspended Solids ( $\text{TSS} = 25 \text{ mg L}^{-1}$ ), this inhibitory effect was attributed to the particulate material, as will be shown later. Also, another important aspect observed in these experiments was the oxidation of  $\text{Hg}^0$  in both cases, a process that occurred to a large extent since the ratio  $\text{Hg}^{2+}/\text{Hg}^0$  varied between 3 and 5 for distilled water and lakewater samples respectively. This oxidation, very likely due to dissolved oxygen (since there are no other oxidizing agents in distilled water) shows that elemental mercury is not inert in oxygen-rich waters, thus increasing the solubility of the metal.

When this same experiment was carried out using elemental mercury at concentrations of 10 and  $100 \text{ g L}^{-1}$  in distilled water and in the absence of reducing agents (not shown), the total soluble concentration in the steady state was  $15.9$  and  $316 \text{ } \mu\text{g L}^{-1}$  respectively, reinforcing the idea that surface area at the interface liquid mercury/solution is a very important parameter controlling the reactive dissolution process.

Reactive dissolution of elemental mercury was also investigated in seawater to evaluate the possible effects of salinity (and chloride complexation) in comparison to freshwater samples. Sanemasa<sup>21</sup> showed that the dissolution of the metallic mercury in electrolytic solution depends on both the concentration and the nature of the anion present in solution. In general, the ionic strength effect on dissolution of a non-electrolyte is the result of phenomena like hydration, van der Waals interactions and internal pressure<sup>16,21,22</sup>.

In experiments using seawater ( $\text{pH} = 8.12$ ;  $\text{TOC} = 2.77 \text{ mg L}^{-1}$ ; salinity  $33.10 \text{ } \text{‰}$  and  $13 \text{ mg L}^{-1}$  of  $\text{TSS}$ ) a steady increase in the concentration of soluble mercury was observed, reaching a peak of  $17.8 \text{ } \mu\text{g L}^{-1}$  after 10 h. After

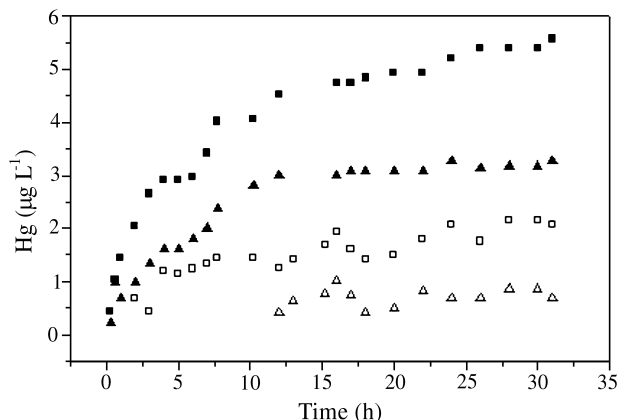


Figure 1. Reactive dissolution of metallic mercury ( $1 \text{ g L}^{-1}$ ) as a function of time in distilled water  $\square$  [ $\text{Hg}^0 + \text{Hg}^{2+}$ ] and  $\circ$  [ $\text{Hg}^0$ ] compared to freshwater (UNICAMP Lake)  $s$  [ $\text{Hg}^0 + \text{Hg}^{2+}$ ] and  $\Delta$  [ $\text{Hg}^0$ ] ( $26 \text{ } ^\circ\text{C}$ ).

this peak, the soluble concentration dropped, reaching the steady state value of  $4.8 \text{ } \mu\text{g L}^{-1}$  (Fig. 2). Interestingly, this same behavior was observed when the experiment was carried out using a  $0.1 \text{ M}$  solution of  $\text{NaCl}$  instead of seawater, except for the fact that the final concentration of soluble mercury species were higher, in this case, than the ones observed for seawater. In both cases, the transient peak in the concentration of soluble mercury was due to the mercuric species only. A possible explanation for this is the formation of stable chloride complexes ( $\text{HgCl}_4^{2-}$ ,  $\text{HgCl}_3^-$ ,  $\text{HgCl}^+$ ,  $\text{HgCl}_2$ , etc.), as already shown to occur<sup>17</sup>. Nonetheless, the increase, followed by a decrease in the concentration of  $\text{Hg}^{2+}$  species in these waters is yet to be explained.

Another important parameter related to dissolution in the aquatic chemistry of mercury is variation of  $\text{pH}$ . Cheng Yan *et al.*<sup>4</sup> studied the concentration of total mercury and methylmercury in the Adirondack lakes (northern New York State-USA), which are characterized by acidic water, low ionic strength and high concentration of dissolved organic carbon. The results obtained show that there is an in-

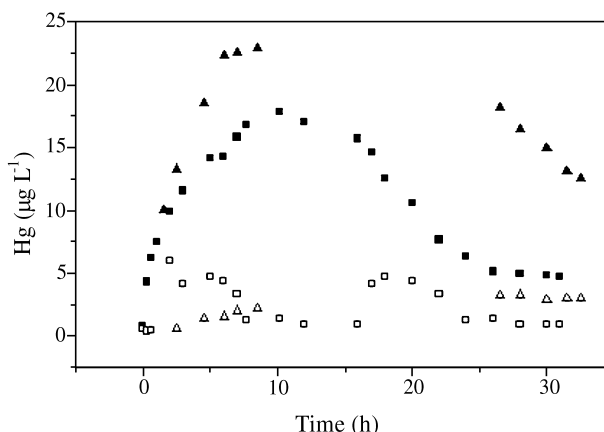


Figure 2. Reactive dissolution of metallic mercury in seawater and  $\text{NaCl}$  as a function of time.  $\square$  [ $\text{Hg}^0 + \text{Hg}^{2+}$ ] and  $\circ$  [ $\text{Hg}^0$ ] in seawater;  $s$  [ $\text{Hg}^0 + \text{Hg}^{2+}$ ] and  $\Delta$  [ $\text{Hg}^0$ ] in  $0.1 \text{ M NaCl}$  ( $26 \text{ } ^\circ\text{C}$ ).

crease in organomercuric species with a decrease in pH. In the present work, the reactive dissolution of metallic mercury was carried out at three different pH values (4.0, 7.0 and 9.0). As shown in Fig. 3, the total soluble concentration of mercury in the steady state is very similar for pH values of 7.0 and 9.0, reaching values around 3  $\mu\text{g L}^{-1}$ . In this case, the concentration of the species Hg<sup>0</sup> that contributes to the pool of all aqueous mercury accounts for 74% and 58%, respectively. However, when the same experiment is carried out at pH 4.0, the soluble concentration is much higher, reaching 20  $\mu\text{g L}^{-1}$ . From this figure, only 18% (3.6  $\mu\text{g L}^{-1}$ ) represents the Hg<sup>0</sup> species. The possible explanation for this behavior is the oxidation of metallic mercury in acidic pH, causing an increase in the soluble concentration of the metal. According to Amyot *et al.*<sup>7</sup>, this is expected in natural waters containing minute amounts of hydrogen peroxide, which act as an oxidizing agent in acidic pH, whereas under alkaline conditions the reduction of mercuric species is the dominant mechanism.

This observed trend is very important when one takes into consideration that in the Amazon region, the occurrence of rivers showing very acidic waters is common. In the Rio Negro basin, for instance, the average pH is 4.3 for the so-called black water rivers, which are very rich in dissolved organic carbon and poor in particulate material, conditions considered to be very suitable for increasing the ecotoxicology of mercury<sup>5</sup>.

#### Adsorption of Hg<sup>0</sup> and Hg<sup>2+</sup> species onto the suspended material

The role of particulate material in the reactive dissolution of Hg<sup>0</sup> as well as in the adsorption of soluble Hg<sup>2+</sup> species were also addressed in this study. This is a very important parameter in order to model to mimic the real scenario, since the *garimpo* activities also contribute to a massive increase in the amount of suspended solids in the *igarapés* (small rivers). This additional impact associated with the *garimpos* has been considered as being more criti-

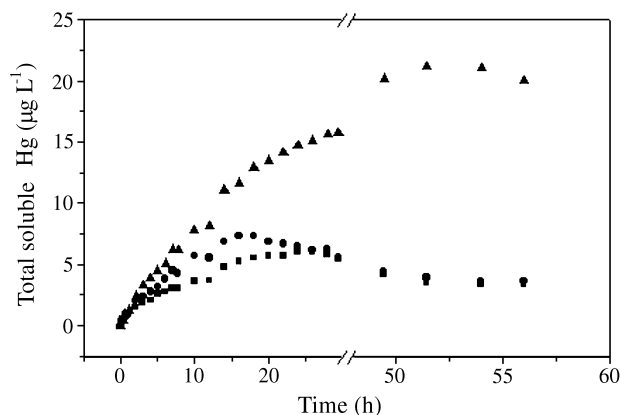


Figure 3. The influence of pH on the reactive dissolution of metallic mercury at pH values  $\square$  9.0;  $\circ$  7.0; and  $\triangle$  4.0.

cal on a short-time basis to the ecosystem than the use of mercury itself.

The effects of the particulate material (100  $\text{mg L}^{-1}$  of a 400 mesh material) on the reactive dissolution of metallic mercury is shown in Fig. 4. When in the presence of particulate material, the soluble concentration of mercury reaches about 1  $\mu\text{g L}^{-1}$ , whereas in the absence of adsorbent surfaces, the concentration is three times higher. These results are similar to the ones shown in Fig. 1, except for the fact that in this case the amount of particulate material is four times higher, but there is no organic material such as present in the lake water sample. Although the inhibitory effect of the particulate material on the reactive dissolution of mercury was determined, it was not possible to detect which species (Hg<sup>0</sup> or Hg<sup>2+</sup>) shows the higher affinity for the binding sites on the particulate material.

Figure 5 shows the affinity of mercuric species for different sizes of the particulate material. As expected, ad-

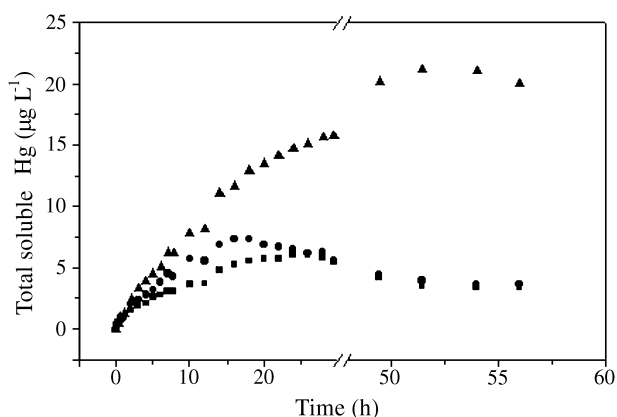


Figure 4. The influence of particulate material (400 mesh) on the reactive dissolution of metallic mercury. Values of  $[\text{Hg}] = [\text{Hg}^0 + \text{Hg}^{2+}]$   $\circ$  System without particulate material and  $\square$  in the presence of 100  $\text{mg L}^{-1}$ .

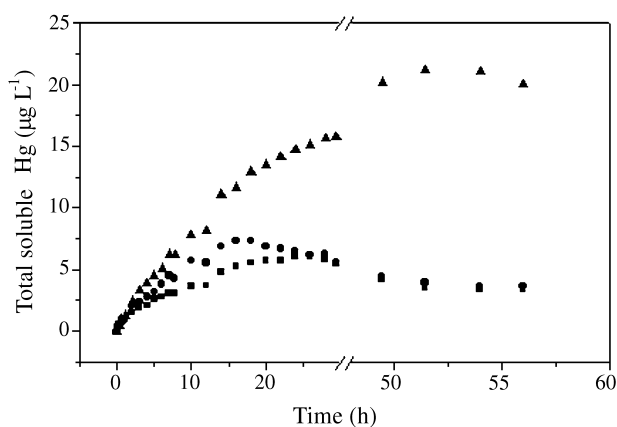


Figure 5. Adsorption of Hg<sup>2+</sup> using different amounts and particle sizes of suspended material as a function of time.  $[\text{Hg}^{2+}]_{\text{initial}} = 10 \mu\text{g L}^{-1}$ . Values of 100  $\text{mg L}^{-1}$  of particulate material  $\square$  400 mesh;  $\circ$  200 mesh;  $\triangle$  in natura are compared to the ones obtained for 10  $\text{mg L}^{-1}$  of particulate material  $\square$  400 mesh,  $\circ$  200 mesh and  $\triangle$  in natura. Model fittings for 100  $\text{mg L}^{-1}$  are also included for clarity.

**Table 1.** Values obtained for the constants  $a$  and  $b$  used in the mathematical modelling of mercury adsorption using  $100 \text{ mg L}^{-1}$  of particulate material and  $10 \text{ } \mu\text{g L}^{-1}$  of  $\text{Hg}^{2+}$

Particulate size	$a$	$b$	$a/b$
400 mesh	0.0244	0.1989	0.1227
200 mesh	0.0090	0.0765	0.1177
<i>in natura</i>	0.0078	0.0245	0.3298

sorption of  $\text{Hg}^{2+}$  ions follows the order of preference: 400 mesh > 200 mesh > sediment *in natura*, where the half-life values for mercuric ions in solution is approximately 5, 15 and 130 minutes respectively.

Modeling the disappearance of  $\text{Hg}^{2+}$  species in the aqueous phase due to adsorption onto the solid phase was carried out using the following mathematical equation:

$$\frac{dC}{dt} = a + bC \quad (1)$$

where  $C$  is  $\text{Hg}^{2+}$  concentration at a given time, and  $a$  and  $b$  are constants. In this particular case, Eq. 1 can be solved after integration:

$$C(t) = \left[ \frac{(a+b)}{b} \right] e^{bt} - \frac{a}{b} \quad (2)$$

where  $a/b$  is the mercury concentration in the aqueous phase in equilibrium with the solid phase. Values of  $a$  and  $b$ , obtained under the experimental conditions detailed in Fig. 5, are shown in Table 1.

## Conclusions

The use of mercury by the *garimpos* spread throughout the Amazon region has already been considered as a time bomb<sup>23</sup>, and very often compared to a new Minamata. However, this comparison stands within limited scientific information, especially when one takes into consideration the fact that the mercury being released in the Amazon is mostly metallic mercury, and not in organic forms as in Minamata.

Considering that the literature about the fate of elemental mercury in the aquatic system (and more specifically tropical waters) is nonexistent, evaluating the real impact of the release of mercury into this very unique ecosystem is still difficult. This paper brings some new insights about the fate of  $\text{Hg}^0$  in the aqueous system, indicating that the situation forecasted for the Amazon may not be as pessimistic (in a short time) as the one often explored. These results also show that metallic mercury is reactive in natural waters, undergoing reactive (oxidative) dissolution. This process, which alters the speciation of mercuric forms, leads to the production of a more toxic form, more suitable to methylation and a more mobile species than the one previously considered.

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