

CCA-1192

YU ISSN 0011-1643

UDC 456.49

Original Scientific Paper

## Model Studies of the Solubility of Inorganic Mercury in the Polluted Coastal Marine Environment

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Received March 27, 1979

In order to determine the possible solubility of inorganic mercury in the polluted coastal marine environment, both experimental and model studies have been performed. Dissolution of  $\text{HgS(s)}$  in bicarbonate solutions of various concentrations and pH values showed increasing solubility of mercury with the pH and  $[\text{CO}_3^{2-}]$  increase. Approximately constant value of  $40 \mu\text{g dm}^{-3}$  was obtained when  $\text{HgS(s)}$  was dissolved in various dilutions of sea water with  $\text{NaHCO}_3$  of  $10^{-3} \text{ mol dm}^{-3}$ . The model calculation shows that mercury in the presence of oxygen can be released from the sediments as elemental mercury,  $\text{Hg}^0(\text{aq})$ , which is in equilibrium with volatile  $\text{Hg}^0(\text{g})$ . The rate at which oxidation proceeds is still unknown. Recent studies show that the solubility of inorganic and organic salts of mercury (II) are much higher than solubility of elemental mercury.

From the experimental results and from the model calculation, one can predict continuous leaching of soluble mercury from polluted sediments long after polluting industries will be closed all over the world.

### INTRODUCTION

The effluents from chlor-alkali plants on the coast of Yugoslavia, Thailand, Norway, Finland, Canada and some other countries, where environmental legislation was relatively ineffective till recently, still contain high levels of mercury. Serious danger threatens for a repetition of previous pollution experiences from »Minamata disease« as in 1950 is possible.

The amounts of mercury released into sea water at different places, after many years of operation of numerous chlor-alkali plants in various countries, have recently been summarized by Skei<sup>1</sup>. Mercury data of effluents from chlor-alkali plant in Yugoslavia have not yet been published. It is possible to estimate roughly, that after 30 years of operation, at least 40 tons of mercury have been »lost« in the shallow bay (X) of the Adriatic Sea. To emphasize the importance of the local problem, a series of review articles have been published.<sup>2</sup>

It is still assumed by many industrial chemists that metallic mercury and inorganic salts of mercury will simply sink to the sea bottom and remain

there. Namely, from precise equilibrium constants of mercury sulphide system<sup>3</sup>, Stumm and Brauner<sup>4</sup> have calculated the solubility of HgS in sea water, which equals  $10^{-10}$  mol dm<sup>-3</sup>, for anaerobic conditions, where sulphide ion remains stable ( $pO_2 < 10^{-68}$  atm). The chemical equilibrium model of Los Angeles sewage developed by Morel, Westal, O'Melia and Morgan<sup>5</sup>, has shown that most metals tend to be solubilized upon disposal into the ocean, due to oxidation and dilution of the sewage.

Experimentally found values of mercury in seawater<sup>6</sup> range from  $1.5 \times 10^{-10}$  to  $1 \times 10^{-8}$  mol dm<sup>-3</sup>.

The maximum value is two orders of magnitude higher than the one calculated for solubility determined by solubility of HgS.

The aim of this paper is to throw more light on the factors that control the concentration of mercury in seawater of different salinity, and to emphasize that the solution of any local mercury problem should not be postponed.

Mercury in the zero oxidation state in solution was studied less extensively than mercurous and mercuric salts and their alkylation products. The solubility of metallic mercury in water was determined by Stock<sup>7</sup> i. e. 25 µg/dm<sup>3</sup> at 25 °C. In spring water it was found by Glew and Hames<sup>8</sup> to be 60 µg/dm<sup>3</sup>. In this work, model experiments have been performed to determine the highest possible mercury concentration in seawater of different salinity in the case of mercury being released into seawater by waste waters. Speciation of mercury (II) is calculated dependant on pε, using the equilibrium constants taken from literature<sup>9</sup>. The formation of organic complexes of mercury in natural waters<sup>10,11</sup> can in addition enhance mercury ion release from the sediments.

#### EXPERIMENTAL

##### Chemicals

Black HgS was precipitated with H<sub>2</sub>S from HgCl<sub>2</sub> acid solution, which was 0.3 mol dm<sup>-3</sup> in HCl, as described a previously text<sup>12</sup>. Stock solutions 0.1 mol dm<sup>-3</sup> of NaHCO<sub>3</sub>, Na<sub>2</sub>HPO<sub>4</sub>, and Na<sub>2</sub>SO<sub>4</sub> were prepared by dissolving Merck p. a. chemicals in bidistilled water. Natural sea-water (Banjole, Adria, Yugoslavia, S = 37.3‰) was diluted with 10<sup>-3</sup> mol dm<sup>-3</sup> NaHCO<sub>3</sub> to obtain various salinities. Samples were prepared in plastic bottles. HgS was dissolved in carbonate solutions or diluted sea-water for a month at 25 °C. Samples were filtered using 0.45 µm Milipore filter.

##### Instrumentation

Dissolved mercury was determined by atomic absorption method, using JARELL ASH atomic absorption spectrophotometer. pH was determined by pH meter 26, RADIOMETER with the electrode GK2322C, using calibration by buffers.

#### RESULTS AND DISCUSSION

##### A. Solubility Measurements

Figure 1. shows solubility of black HgS in bicarbonate solutions of various concentrations and pH values. Concentration of soluble mercury is plotted vs. log [CO<sub>3</sub><sup>2-</sup>]/mol dm<sup>-3</sup>. pH value for each point is presented in the diagram. The concentration of free carbonate, [CO<sub>3</sub><sup>2-</sup>], was calculated for each solution using the equation

$$[CO_3^{2-}] = [C]_{TOT} / (1 + 9.31 \times 10^9 [H^+] + 2.19 \times 10^{16} [H^+]^2) \quad (1)$$

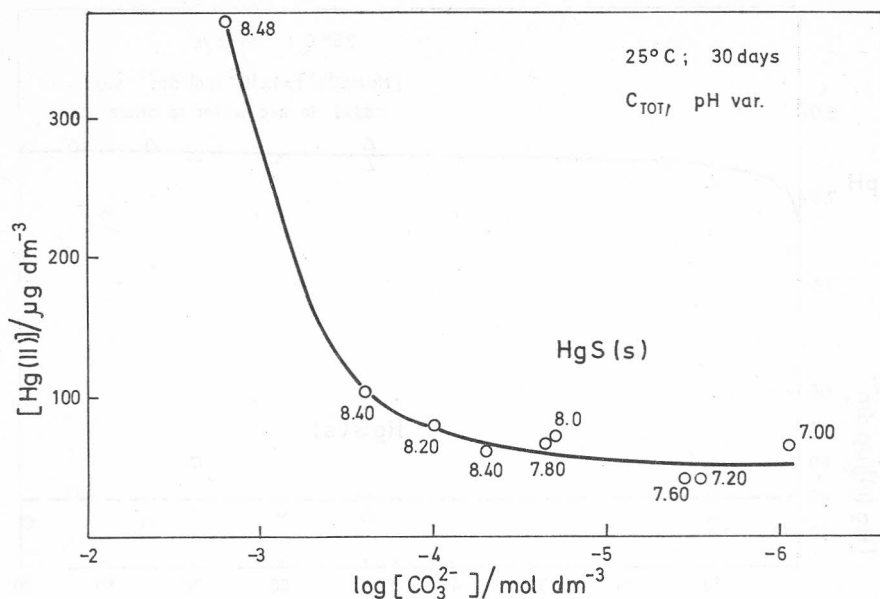


Figure 1. Solubility of black HgS in bicarbonate solutions, presented as  $[\text{Hg(II)}]_{\text{sol}}$  vs.  $\log [\text{CO}_3^{2-}]$ . pH values are plotted for each point (25 °C, 30 days).

with acidity constants  $\text{p}K_1 = -10.33$ ,  $\text{p}K_{1,2} = -6.35$ ,  $I \rightarrow 0$ , from the existing literature<sup>9</sup>.

It was observed that solubility of HgS increased either as a result of pH or  $[\text{CO}_3^{2-}]$  increase.

To study the effect of small amounts of phosphate and sulphate on the dissolution of mercury in carbonate solutions,  $2 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{HPO}_4$  in one series and  $2 \times 10^{-4} \text{ mol dm}^{-3}$  of  $\text{Na}_2\text{SO}_4$  in other series of carbonate solutions were added with the concentration of  $[\text{CO}_3^{2-}]$  in the range  $5 \times 10^{-7}$  to  $1 \times 10^{-4} \text{ mol dm}^{-3}$ . They are interesting for natural waters. In the case of phosphate ion no change of mercury solubility was found, while in the presence of sulphate, solubility of mercury increased to approximately  $110 \mu\text{g dm}^{-3}$ . A similar effect was observed by Dickson and Tunell<sup>13</sup> for ground waters. They found that high bicarbonate concentrations increased the solubility of some metal sulphides. Also, that the traces of chloride, bromide and iodide together with bicarbonate ions enhanced the degree to which mercury can concentrate.

Figure 2 shows solubility of black HgS in various dilutions of sea water. To maintain approximately constant concentration of total carbonate, characteristic for natural waters,  $10^{-3} \text{ mol dm}^{-3}$   $\text{NaHCO}_3$  solution was used to prepare diluted sea water samples. Solubility data are plotted as  $[\text{Hg(II)}]_{\text{soluble}}$  vs. percentage of sea water diluted. An approximately constant value of  $40 \mu\text{g dm}^{-3}$  was obtained, independent of salinity.

### B. Model Calculation

Computer calculation of Anfält, Dyrssen, Ivanova and Jagner<sup>14</sup> shows that  $\text{HgCl}_4^{2-}$  is the predominant species in sea water. This model is valid for

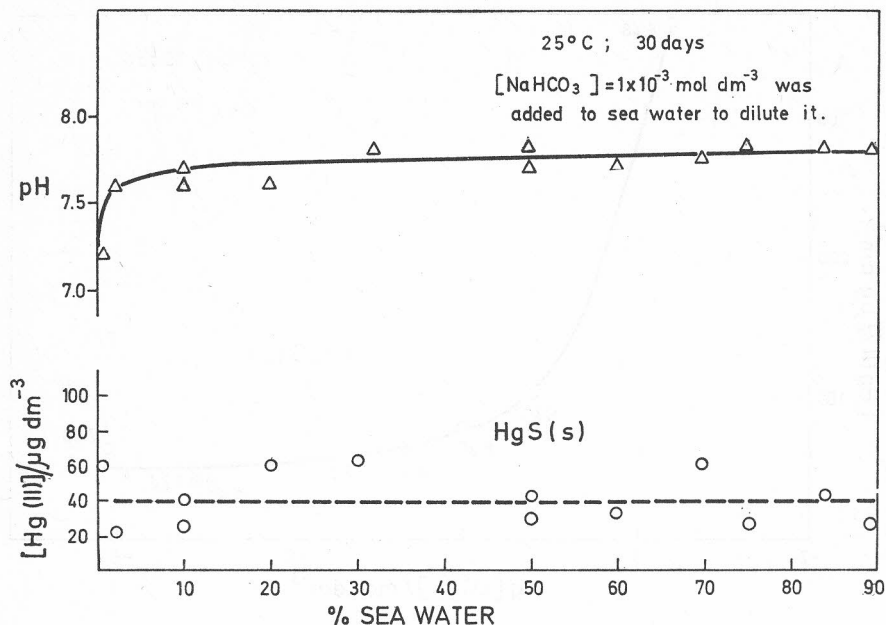
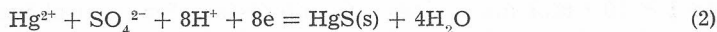


Figure 2. Solubility of black HgS in various dilutions of sea water (Solution  $0.1 \text{ mol dm}^{-3} \text{ NaHCO}_3$  was used to prepare various dilutions).  $[\text{Hg (II)}]_{\text{sol}}$  is plotted vs. % sea water (25 °C, 30 days).

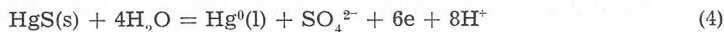
the surface layer of sea water in contact with the atmosphere. Both existing models for mercury speciation<sup>4,14</sup> are valid for extreme cases. O'Brien and Birkner<sup>15</sup> have measured kinetics of oxygenation of reduced sulphur species in aquatic solution. The oxidation process must be considered in a more complete model calculation as suggested by Stumm<sup>16</sup>. From the available constants<sup>9</sup> for the reactions



with  $\log K_{S_1} = -70.0$ , and



with  $\log K_2 = -28.8$ , it is possible to calculate the equilibrium constant for the reaction



The obtained value is  $\log K_o = -41.2$ .

Using this constant and the characteristic values for sea water for  $\text{pH} = 8.0$  and  $[\text{SO}_4^{2-}] = 10^{-2} \text{ mol dm}^{-3}$ , it is possible to calculate  $p_\epsilon$  value for the coexistence of HgS(s) and Hg(l) in sea water. The obtained value is  $p_\epsilon = -4.13$ , where  $p_\epsilon = -\log \{e\}$  according to a definition. To obtain the distribution of soluble mercury in dependence of  $p_\epsilon$ , the following system of equations has been solved with  $p_\epsilon$  as a parameter:

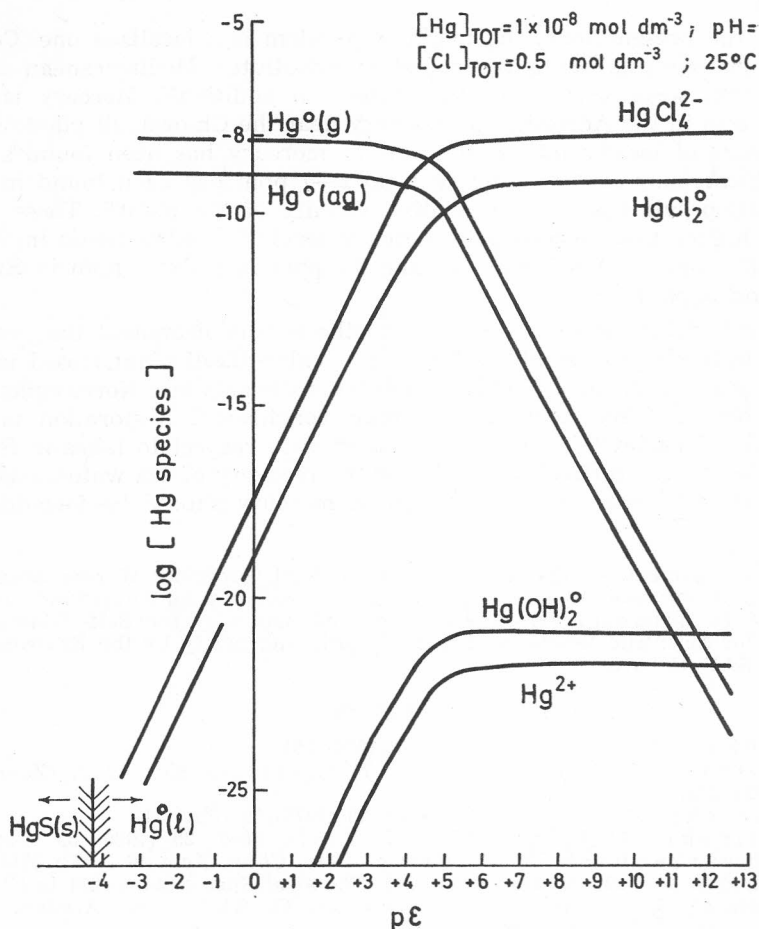
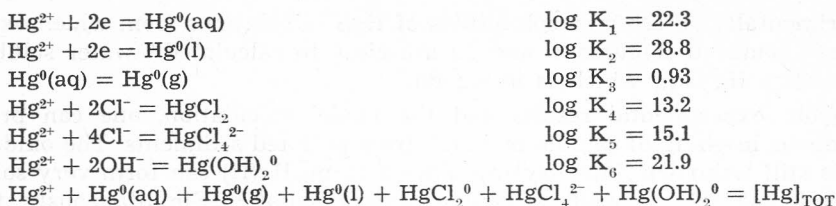


Figure 3. Calculated distribution of soluble mercury in sea water in dependence on  $p\varepsilon$  (assumed:  $[\text{Hg}]_{\text{TOT}} = 1 \times 10^{-8} \text{ mol dm}^{-3}$ ,  $[\text{Cl}]_{\text{TOT}} = 0.5 \text{ mol dm}^{-3}$  and  $\text{pH} = 8.0$ ).

Figure 3 shows the distribution of soluble mercury, calculated for assumed  $[\text{Hg}]_{\text{TOT}} = 1 \times 10^{-8}$ ,  $[\text{Cl}]_{\text{TOT}} = 0.5$ , and  $\text{pH} = 8.0$ . Water in solubility equilibrium with atmosphere has a well defined  $p\varepsilon$  (For  $p\text{O}_2 = 0.21 \text{ atm}$ ,  $E_{\text{H}} = 800 \text{ mV}$ , at  $\text{pH} = 7.0$  and  $25^\circ\text{C}$ )<sup>17</sup>. Calculation presented in Figure 3 shows that  $\text{HgCl}_4^{2-}$  and  $\text{HgCl}_2^0$  complexes predominate at  $p\varepsilon > 5$ . For  $-4 < p\varepsilon < 5$ , mercury predominates in zero oxidation state, as soluble  $\text{Hg}^0(\text{aq})$  and volatile  $\text{Hg}^0(\text{g})$ .

Experimentally determined solubilities of HgS in solutions from which oxygen was not removed (Figures 1. and 2.) are close to calculated<sup>16</sup> water solubility of mercury Hg<sup>0</sup>(aq), which is 60  $\mu\text{g dm}^{-3}$ .

From experimental results and the model calculation, one can predict continuous leaching of soluble mercury from polluted sediments. The oxidation rate is still unknown. Mercury in oxidized form, Hg(II) can form very soluble inorganic salts<sup>18,19</sup>, as well as soluble organic salts<sup>20,21</sup>. Simultaneously, there exists very low adsorbability of mercury chloro complexes<sup>22</sup> and of methyl mercury<sup>23</sup>.

Up to the present time, the mercury problem is a localized one. Concentration of mercury is being controlled in unpolluted Mediterranean surface waters<sup>24</sup>, with some vertical profile studies in addition<sup>25</sup>. Mercury is being controlled also in the Adriatic, but not very near the Chloralkali plant. Additional evidence of locally increased levels of mercury has been found<sup>26</sup>. Especially high mercury content ranging from 2—7 ppm has been found in shells *Mytilus galloprovincialis* in the relative vicinity of the plant<sup>27</sup>. These values are much higher than permissible mercury levels in edible tissue in various countries (0.5 ppm in USA, and Canada; 0.7 ppm in Italy; 1 ppm in Sweden, Finland and Japan).

Turner and Lindberg<sup>28</sup> have found in the real environment that mercury continues to leach from solid wastes from a chlor-alkali plant closed in 1972, after 20 years of operation. Skei has analyzed sediments in a Norwegian semi-enclosed bay, and has come to a similar conclusion<sup>1</sup>. Restoration methods suggested by Jernelov<sup>29</sup> have been discussed with respect to lakes in Sweden and seem to be very difficult to apply for the recovery of sea water sediments. Waters with sediments overburdened with mercury should be forbidden for fishing.

*Acknowledgement.* — The authors wish to thank Professor Werner Stumm for valuable discussion and advices, also to the two referees for suggestions on how to improve the manuscript. Work was supported partly by the Self- Management Council II for Scientific Research of S. R. Croatia and partly by the Environmental project of SAP Kosovo.

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### SAŽETAK

#### Model studije topljivosti anorganske žive u zagađenom priobalnom području

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Da bi se odredila moguća topljivost anorganske žive u zagađenom priobalnom području, izvršeni su paralelno eksperimentalne i modelne studije. Otapanje HgS u otopinama bikarbonata različitih koncentracija i različitih pH-vrijednosti, pokazalo je povećanje topljivosti žive s povećanjem pH i [CO<sub>3</sub><sup>2-</sup>]. U različitim razrjeđenjima morske vode s NaHCO<sub>3</sub> (10<sup>-3</sup> mol dm<sup>-3</sup>), otapanjem HgS dobivena je približno konstantna vrijednost od 40 μg dm<sup>-3</sup>.

Modelni proračuni pokazuju, da se u nazočnosti kisika, iz sedimenata može oslobađati elementarna živa, Hg<sup>0</sup>(aq), koja je u ravnoteži sa živinim parama, Hg<sup>0</sup>(g). Brzina oksidacije žive još je nepoznata. Nedavne pak studije pokazuju da je topljivost anorganskih i organskih soli žive(II) mnogo viša, nego topljivost elementarne žive. Iz eksperimentalnih rezultata i modelnih proračuna, moguće je predvidjeti kontinuirano oslobađanje topljive žive iz zagađenih sedimenata, dugo vremena pošto industrije-zagađivači prestanu s radom.

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Prispjelo 27. ožujka 1979.