ABIOTIC REDUCTION OF MERCURY BY HUMIC SUBSTANCES IN AQUATIC SYSTEM - AN IMPORTANT PROCESS FOR THE MERCURY CYCLE

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ABSTRACT. The potential ability of humic substances to reduce Hg(II) to Hg(0) in aqueous systems and, consequently, strongly influence Hg speciation and mobility in the environment is known but has not been studied in detail. A demonstration of the redox behavior of Hg in the presence of humic substances is made in the present work. Calculations show that the reduction is thermodynamically possible. The effects of some chemical parameters (pH, aerobic/anaerobic conditions, presence of chloride) on the process were studied experimentally. Hg(0) production was highest in O_2-free systems in the absence of chloride at pH ca 4.5, when ca 25% of initially 2×10^{-6} M Hg(II) was reduced to Hg(0) in 50 hr. The presence of a competing ion (10^{-4} M Eu) in the system as well as methylation of the carboxyl groups in the humic substance considerably reduced the Hg(0) production. The practical importance of the abiotic reduction of Hg in the environment is pointed out.

1. Introduction

Despite the fact that the releases of Hg from antropogenic sources have been drastically reduced since the early 60-ies, Hg is still spreading in the environment. The transformation of Hg in water and sediments to volatile species (elementary Hg and organic forms) and the subsequent oxidation to Hg(II) in the air are the necessary requirements for the cycling and redistribution of Hg that will continue even in the absence of new sources. The reduction of Hg(II) to Hg(0) in soils and sediments are generally considered to be the result of microbial processes. It has, however, been suggested and clearly demonstrated experimentally, that natural organic matter, particularly humic substances, under certain conditions could initiate an abiotic reduction of Hg(II) (Alberts *et al.*, 1974; Miller, 1975; Miller *et al.*, 1975). These organics would also have an effect on the oxidation state and chemical speciation of other elements like Fe, V, Mo, I (summarized by Skogerboe and Wilson, 1981) as well as the actinides (Nash *et al.*, 1981). The reducing effect of natural organics would be less important in soils and sediments, where microbial processes are likely to dominate. However, in aqueous systems (pore waters as well as surface waters and shallow ground waters), where the concentrations of e.g. dissolved humic substances generally are in the range 1 to 10 mg L^{-1}, the abiotic redox processes might be of more relative importance. Turner *et al.*, 1989, suggested, that abiotic reduction could account for as much as 10 to 70% of the volatile Hg released from a contaminated stream under study.

Mercury forms very strong complexes with humic substances and would thus be stabilized as Hg(II) in natural waters. If, however, the formation of stable Hg-humic complexes also would lead to a subsequent reduction to Hg(0), e.g. by an intra molecular electron transfer, the

dissolved humic substances would be particularly important for the speciation and mobility of Hg in the aqueous environment, acting both as strong complexing (and solubilizing) agents as well as reducing agents even when the biological transformation of Hg is slow.

The aim of this study is to further illustrate the potential reduction of Hg(II) to Hg(0) in the presence of water soluble humic substances at environmental concentration levels as well as the role of some chemical and physical factors on the combined complexation and redox process.

2.   Redox Processes and Chemical Speciation

2.1. MERCURY

Solubility and chemical speciation of Hg in natural waters are governed by the redox conditions, determining the oxidation states (0, +I, +II) and the formation of inorganic and organic complexes as well as alkylated species (e.g. CH_3Hg^+, $(CH_3)_2Hg$, CH_3HgCl, CH_3HgOH and others) (Stumm and Morgan, 1981). Complexes with OH^- and Cl^- dominate in most fresh water systems ($Hg(OH)_n^{2-n}$, n=1,2; $HgCl_n^{2-n}$, n=1,4; HgOHCl) while other inorganic ligands (F^-, SO_4^{2-}, NO_3^-, PO_4^{3-}) would normally not significantly affect the speciation in solution (Gilmour, 1971; Hahne and Kroontje, 1973), although HgS(s) would be formed as a solubility limiting solid species in the presence of SH^-. Eh/pH-diagrams have been constructed, Figure 1, based on thermodynamic data from National Bureau of Standards, as given in Stumm and Morgan (1981). Organic forms as well as complexation with humics are not considered in these diagrams.
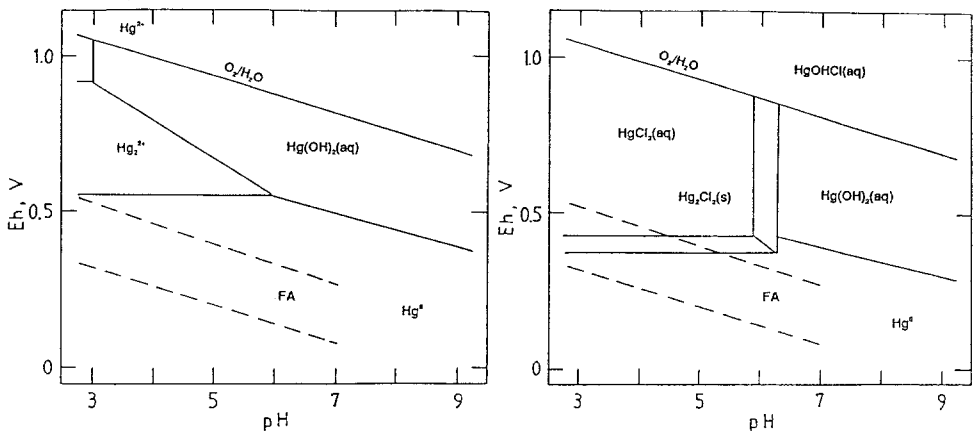

Fig. 1. Eh/pH-diagram for Hg
        ([Hg]=10^{-8} M; [Cl^-]=10^{-8} M (top) and 10^{-4} M (bottom);
        FA: FA(ox) + H^+ + e^- = FA(red) for E^0=0.5 and 0.7 V

The predominance of Hg^{2+} and $Hg(OH)_2$(aq) under oxic conditions and in the absence of chloride is obvious and well known. However, the existence of Hg(0) is possible even in the presence of air, considering that the effective redox potential generally is lower than the theoretical one set by the O_2 partial pressure. The presence of chloride leads already at

concentration levels of a few mg L^{-1} to the formation of the dominating species $HgCl_2(aq)$ at low pH ($HgCl_4^{2-}$ at high chloride concentrations) as well as $HgOHCl(aq)$. The over-all stability of the oxidation state +II is enhanced.

2.2. HUMIC SUBSTANCES

The reducing capacity of humic substances have been demonstrated in a number of systems (for V by Szalay and Szilágyi, 1967; Goodman and Chesire, 1975; Wilson and Weber, 1979; for Fe by Szilágyi, 1971; Langford *et al.*, 1977; Miles and Brezonik, 1981; for Mo by Szilágyi, 1967; for I by Skogerboe and Wilson, 1981; for actinides by Nash *et al.*, 1981; for Hg by Strohal and Huljev, 1971; Alberts *et al.*, 1974; Miller, 1975; Miller *et al.*, 1975; Skogerboe and Wilson, 1981). It is assumed that intermediates like semiquinones, which are present in the humics, are involved in these redox processes. A reaction according to

$$FA(ox) + e^- + nH^+ = FA(red), \quad E^0=0.5 \text{ V (FA) and } 0.7 \text{ V (HA)} \quad (1)$$
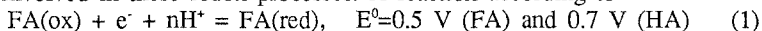
for fulvic acids (FA) and humic acids (HA), respectively, has been proposed (Wilson and Weber, 1979; Skogerboe and Wilson, 1981). A reducing capacity of 0.6 meq g^{-1} was suggested for a FA, based on the contents of quinone in the molecule (Senesi *et al.*, 1977). However, the exact mechanism for the electron transfer is not known. Evidently, humic substances are quite stable even under highly oxic conditions, where the presence of O_2 sets the over-all potential.

2.3. MERCURY COMPLEXES WITH HUMICS

Aquatic humic substances generally have a high metal complexing capacity due to the presence of carboxylic groups, typically in the range 4 to 8 meq g^{-1}. The stability of metal-humic complexes follows the Irving-Williams series (Mantoura *et al.*, 1978), i.e. Mg<Ca<Cd=Mn<Co<Zn<Ni<Cu<Hg. Possibly the presence of sulphidic groups in the humic substance (Huffman and Stuber, 1985) enhances the stability of particularly Hg complexes even further. The high stability of Hg-HA-complexes has been confirmed in several studies (Strohal and Hueljev, 1971; Cheam and Gamble, 1974; Miller, 1975; Mantoura *et al.*, 1978; Lu *et al.*, 1983; Pang *et al.*, 1983; Frimmel *et al.*, 1984; Lövgren and Sjöberg, 1989), although the reported formation constants cover an unreasonable range (from ca 10^5 to 10^{21}!). However, it is clear that already at concentrations of a few mg L^{-1} of humics, e.g. in fresh water systems, Hg speciation in solution is largely dominated by humic complexes.

The equilibrium between FA(red) and FA(ox) according to reaction (1) is given in Figure 1, using the E^0-values proposed by Skogerboe and Wilson (1981), and assuming n=1. It is clear, that Hg(II) would easily be reduced to Hg(0) by humic substances exept at very low pH and/or high chloride concentrations. On the other hand, the formation of the Hg-FA-complex would stabilize the divalent state. Still, the reduction would be favored, assuming an intra molecular process that is possible only when the complex has been formed.

3. Materials and Methods

Purified humic substances of aqueous origin were dissolved in water to a total concentration of 10 mg L^{-1}. A known volume (usually 30 mL) was put in a tube that was sealed. Nitrogen was bubbled through the solution to remove dissolved O_2. A spike of a Hg stock solution (labeled with ^{203}Hg) was added to give a total initial Hg concentration of 2.0×10^{-6} M. A pH of 4.5 to 5 was generally obtained (due to the buffering by the FA). Chloride was added to some of the systems (to give total Cl⁻ concentrations of 10^{-3} or 10^{-1} M; back-ground concentrations of Cl⁻ were estimated to be <10^{-6} M). In some systems pH was reduced (to ca

3) or increased (to ca 8 to 9). Bubbling of gas (N_2 or O_2) was continued, and the gas was led through a washing solution of cystein into an acidic $KMnO_4$-solution and then out of the system (cf. Figure 2). All volatile ionic and organic Hg species that might be formed would be trapped in the cystein solution (Clarkson and Greenwood, 1970), while elementary Hg would be quantitatively oxidized in the $KMnO_4$-solution. Aliquots were taken from the washing solution and the $KMnO_4$-solution as a function of time, and the activity was measured (scintillation counting).
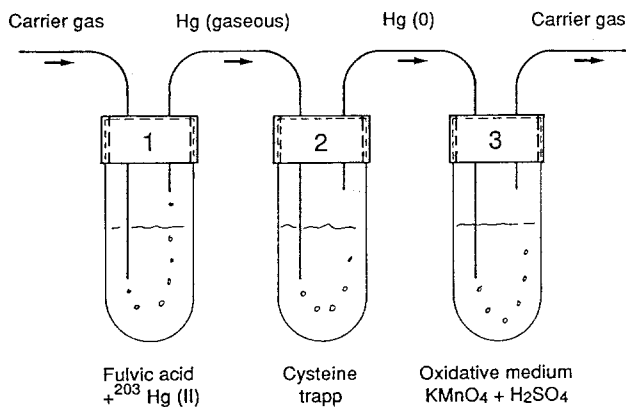

Fig. 2. System for the generation and recovery of Hg(0)

Experiments were also performed with a natural surface water (from the location where the FA and HA were sampled) and in a system with a competing cation present (10^{-4} M Eu) as well as with a derivative of the FA, where the complexing acidic carboxyl groups had been methylated (Arsenie *et al.*, 1990).

The humic material (FA and HA) used was isolated from a surface water in a bog area in Bersbo (about 200 km south of Stockholm, Sweden). The FA had a molecular weight of ca 1500 (M_n) and a total acid capacity (carboxylic) of 4.8 meq L^{-1}. The isolation and purification procedure as well as the chemical characterization of the materials have previously been described in detail (Ephraim *et al.*, 1989).

All experiments were performed at ambient temperature ($23\pm2°C$), mostly under light. A few experiments were also performed in the dark. Sterile equipment was used (autoclavation) and all solutions were filtered (0.22 μm ultra filter) to eliminate microbial activity in the system.

4. Results and Discussion

The generation of Hg(0) as a function of time is given in Figures 3 and 4 for the various systems. Background values, corresponding to the production in systems free from humics, are given in Figure 4. No significant Hg concentrations were detected in the cystein washing solution in any of the systems, which indicates that no organic Hg-species were formed and that the fraction recovered in the final $KMnO_4$-solution was entirely Hg(0).

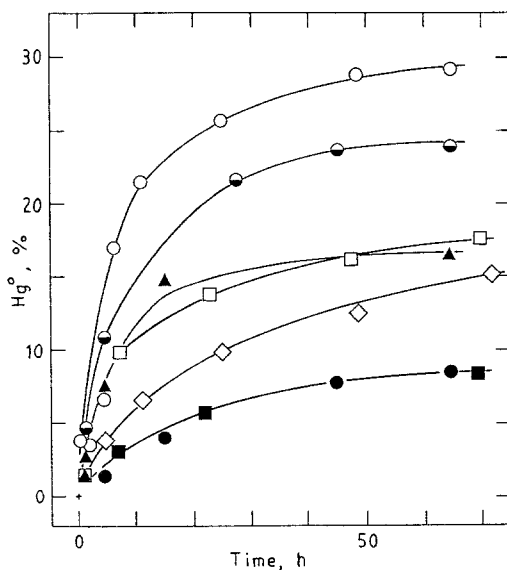The production of Hg(0) in the blank systems was not negligible, except for the system

Fig. 3. Generation of Hg(0) in the presence of FA
($[Hg]_{tot}=2.0 \times 10^{-6}$ M, $[Cl^-]<10^{-6}$ M, 10 mg L^{-1} FA;
● pH 2.9, N_2; ○ pH 4.5, N_2; ◗ pH 8.8, N_2; ■ pH 3.1, O_2; □ pH 5.3, O_2;
▲ pH 6.8, N_2, 10 mg L^{-1} HA; ◇ Nat. water, pH 6.3, $[Cl^-]=1.0 \times 10^{-4}$ M, 10 mg L^{-1} FA)
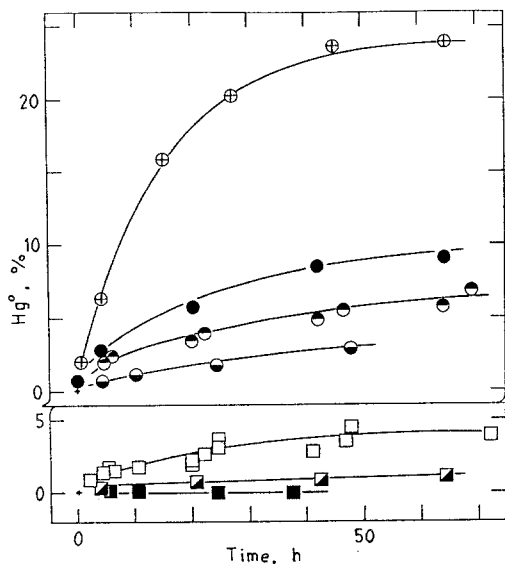

Fig. 4. Inhibited generation of Hg(0) in the presence of FA
($[Hg]_{tot}=2.0 \times 10^{-6}$ M, pH 4.1-4.8, 10 mg L^{-1} FA, N_2;
◖ 10^{-3} M Cl^-; ◗ 10^{-1} M Cl^-; ● Methylated FA, $<10^{-6}$ M Cl^-; ⊕ 10^{-4} M Eu, $<10^{-6}$ M Cl^-;
Background: No FA; □ $<10^{-6}$ M Cl^-; ◪ 10^{-3} M Cl^-; ■ $KMnO_4$ added)

with an oxidizing agent ($KMnO_4$) present. However, for all the systems containing humic substances the production of $Hg(0)$ was significantly above the blank values. For most of the systems, a fairly rapid generation was observed (during the first 10 to 30 hr) followed by a slower but continued generation.

The total production after 50 hr, with blank corrections, are given in Table I, expressed both in mol L^{-1} and in percent of the initial Hg-concentration (2.0×10^{-6} M).

TABLE I Production of $Hg(0)$ after 50 hr
    $[Hg]_{tot.} = 2.6 \times 10^{-6}$ M, $[FA]_{COOH} = 4.8 \times 10^{-5}$ eq L^{-1} (10 mg L^{-1})

		System		
[Cl⁻], M	pH	Carrier gas	Other	$[Hg(0)] \times 10^8$, M [a]
10^{-1}	4.4	N_2		4.2 (2.1)
10^{-3}	4.8	N_2, air		9.8 (2.1)
<[b]	4.5	N_2		50 (25.1)
<	8.2	N_2		38 (19.1)
<	2.9	N_2		8.6 (4.3)
<	5.3	Air		26 (12.9)
<	3.1	Air		8.6 (4.3)
<	4.1	N_2	10^{-4} M Eu	40 (19.9)
<	6.3	N_2	10 mg L^{-1} HA[c]	26 (12.9)
10^{-4}	6.3	N_2	Nat. water[d]	20 (9.9)
<	4.0	N_2	Methyl. FA[e]	11 (5.3)

[a] After blank correction; % of total within paranthesis
[b] $<10^{-6}$ M; estimated as maximum level from Cl⁻-impurities in chemicals
[c] Replacing FA with HA
[d] Diluted to give a FA-concentration of 10 mg L^{-1}
[e] Methylated FA-derivative

The highest production was observed in the O_2 free system at pH ca 4.5 and in the absence of chloride and in the light (a reduction of the original Hg concentration by ca 25% after 50 hr, corresponding to a reducing capacity of ca 0.1 meq g^{-1} FA). Lower values were obtained in the presence of air as well as for systems kept in the dark. The addition of chloride led to a drastic reduction of the production. Evidently, the formation of the competing strong chloride complexes had an inhibiting effect. Also the addition of Eu had a similar but less pronounced effect. Both these observations indicate that the Hg-FA-complex has to be formed before reduction can take place. The fact that the methylated FA, where the number of acidic

complexing sites had been reduced, also had a very strong inhibiting effect on the reaction confirms that the reduction appears to proceed through an intra molecular process.

The production of Hg(0) was reduced somewhat when pH was increased, except at very low pH (below pK_a of the dominating carboxylic groups of the FA). The general level of the suggested FA(ox)/FA(red)-curves in Figure 1 are reasonable, but the pH-dependence is not clear.

5. Conclusions

Some general conclusions can be drawn:
o Hg(II) was reduced by soluble humic substances (humic and fulvic acids) to Hg(0); a rapid initial phase could be observed (corresponding to a reducing capacity of 0.1 meq g^{-1} during the first 50 hr for the FA in the present study).
o The reduction was inhibited by competing ions (Cl⁻, that forms complexes with Hg(II) as well as Eu, that forms complexes with the FA).
o The reduction of the number of available complexing sites by methylation of the FA had a strong inhibiting effect on the Hg(0)-production, indicating an intra molecular process.
o The reduction was significant, although somewhat reduced, in the presence of air.
o The reduction is enhanced by light.

The exact mechanism behind the reduction process (including the quantitative effects of competing ions as well as the influence of pH) should be further elaborated. However, it is evident that the abiotic production of Hg(0) has to be considered as a part of the total mercury cycle in the environment.

Acknowledgments

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