

INFLUENCE OF HUMIC SUBSTANCES ON PHOTOLYSIS OF DIVALENT MERCURY IN AQUEOUS SOLUTION

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Abstract. Mercury (II) solutions were irradiated by a simulated sunlight in the presence of humic acid (HA) or fulvic acid (FA). Results show that, under the experimental conditions and the FA and HA chosen, less than 20% of the Hg in solution was photolysed with a rate of $(1.63 \pm 0.29) \times 10^{-2} \text{ s}^{-1}$ (n=23) and the rest of $(2.38 \pm 0.40) \times 10^{-4} \text{ s}^{-1}$ (n=23) depending on the substitutes of humic substances to which Hg were bond. The sunlight photolysis lifetimes were estimated to be 4 and 250 sunlight hours respectively under summer conditions at Stockholm latitude.

1. Introduction

Atmospheric mobilisation and air-water exchange are important features of biogeochemical cycling of mercury (Hg) in the environment. Two main forms of Hg exist in the environment, the elemental mercury Hg^0 and the divalent Hg (II). The predominant species (> 90 %) in the air is Hg^0 with the remaining fraction consisting of Hg(II). Atmospheric Hg is mainly deposited with precipitation in the water-soluble form of Hg(II) to the environmental surfaces, while volatile Hg species formed in the water body, mainly Hg^0 , escapes into the atmosphere. This means that identifying the processes associated with cycling of elemental Hg between the atmosphere and natural water is of critical importance.

Mercury emissions from lakes (Schroeder and Fanaki, 1988; Xiao *et al.*, 1991, Fitzgerald *et al.*, 1991) and ocean water (Kim and Fitzgerald, 1986), probably in the form of Hg^0 and perhaps also $(\text{CH}_3)_2\text{Hg}$, have been measured. The volatile Hg species can be formed in sediments from Hg(II) both via biological or abiotic processes (Spangler *et al.*, 1973; Steffan *et al.*, 1988) or via a chemical reduction of mercuric ion in the presence of humic substances (Alberts *et al.*, 1974). The latter process was enhanced when the solution was exposed light (Allard and Arsenie, 1991).

Investigations conducted in this laboratory (Xiao *et al.*, 1994) show that a photoreduction in aqueous solution of Hg(II) to its elemental form is possible. In this experiment, pure $\text{Hg}(\text{OH})_2$ solution was prepared in Milli-Q[®] water and kinetic data obtained can only be applied to relatively "clean" water bodies with low concentration of humic substances, chloride or other compounds that could coordinate to the mercuric ions. However, in most natural water system, Hg(II) is probably bound to different ligands, e.g. humic substances.

Humic matter is known as heterogeneous copolymer of different chemical materials with different compositions and molecule weights depending on their sources and way of preparation. In aqueous systems such as surface water and shallow ground water, the concentration of dissolved humic matter generally is in the range of 1 to 10 mg l⁻¹. Humic substances are found to form complexes with many metal ions. Xu and Allard (1991) have shown that already in the presence of 1 mg l⁻¹ of FA that almost all Hg (II) is bonded to FA. The complexing constant for Hg(II) and humic matter was estimated to be $\log K = 18-21$ in a model natural freshwater with pH=7 and 21 °C (Munthe, 1991).

The aim of this investigation is to see the net effect of photolysis of Hg(II) in the presence of humic substances in aqueous solution. Mercury solutions together with humic substances were irradiated by a simulated sunlight under controlled conditions. Kinetic rate constants were obtained at different contents of humic substances and different concentrations of Hg both in Milli-Q and in natural waters. Finally the reactions half-lives under sunlight conditions were estimated.

2. Experimental

The experimental set-up is illustrated in Figure 1.

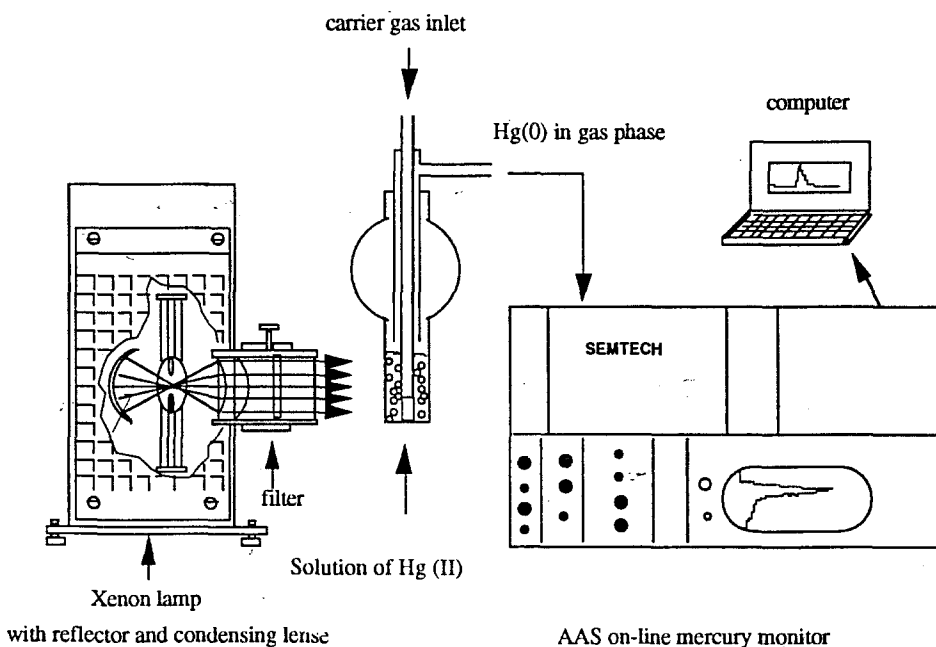


Figure 1. Experimental set-up.

A 400 W commercial xenon lamp, combined with a reflector and a condensation lens was used as a light source, which irradiates the reaction solution evenly at a horizontal direction. A colour filter was coupled to the system for cutting wavelength < 299 nm. A pyrex reaction bottle containing 20 ml solution was irradiated and the elemental mercury formed through photolysis was carried out by nitrogen. The flow rate

of the carrier gas was kept at 300 ml min^{-1} using a mass flow regulator. The changes of mercury concentration in gas phase were followed by Semtech[®] (Semtech Metallurgy AB, Lund Sweden), an instrument which can monitor Hg concentration directly and continuously. The working principle of this instrument is AAS with Zeem-effect. In order to eliminate the moisture influence, an extra washing bottle was placed between the reaction bottle and the Semtech. The concentration of Hg so measured was shown on the instrument screen directly and can also be collected by a personal computer for further data processing.

The light intensity of the xenon lamp was determined by a potassium ferrioxalate as a chemical actinometer (Xiao *et al.*, 1994). A Shimadzu[®] UV-2100 UV-Visible Recording Spectrometer was involved in determining the exposed actinometer solution. It was also used to record the absorbency spectra of FA and HA solutions selected for this study, see Figure 2.

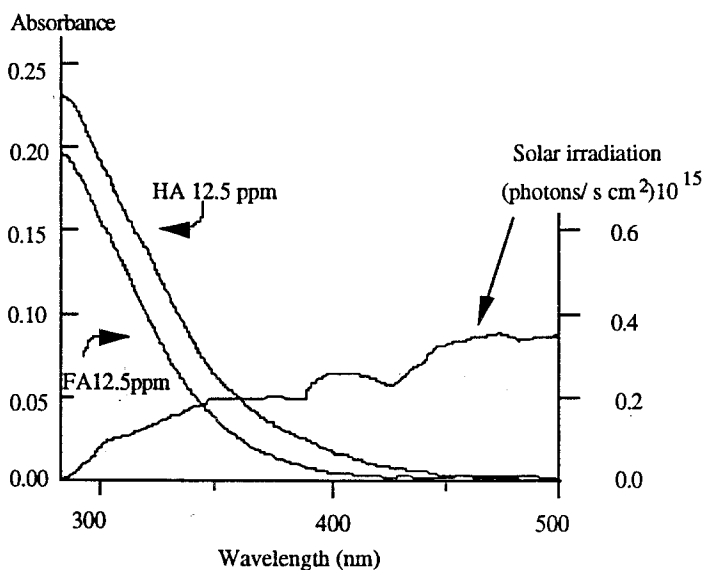


Figure 2. Absorption spectrum (pathlength of 1 cm) of FA and HA (12.5 ppm) solution and yearly maximum of daylight at 60°N (adapted from Svensson and Björndal, 1988).

Preparation of $\text{Hg}(\text{OH})_2$ solution ($\text{pH} = 7$) has been described previously (Xiao *et al.*, 1994). Diluted Hg working solutions were always prepared immediately prior to each experiment. HgCl_2 solutions were prepared from the neutral $\text{Hg}(\text{OH})_2$ solution by adding NaCl (pro analyse grade) to make the chloride concentration 0.1 or 0.2 M. At this range of chloride concentration and pH, Hg is in the form of HgCl_2 (Benes and Havlik, 1979).

Some samples of humic (HA) and fulvic (FA) acids were isolated from the Göte River water in Gothenburg. The preparing procedures and characteristics concerning their elemental composition and molecular weight distribution etc. can be found in Plechanov (1983) under items FA-1 and HA-1 for fulvic and humic acid, respectively.

Fulvic was dissolved in Milli-Q water directly while humic acid was dissolved in 0.1 M NaOH. The resulting solutions were stirred with a magnetic bar for several hours at 25 °C and then centrifuged for one hour at 15000 rpm in a Philip centrifugation apparatus. The supernatant was then diluted to desired concentrations with Milli-Q water.

Reaction solutions with Hg concentrations of 20 and 40 ppb, FA or HA concentrations of 10 and 18 ppm were prepared for this study. The final pH's of the artificial solutions were between 5.0-5.2.

3. Results and Discussion

Figure 3 presents the relative magnitudes of four different mercury solutions towards photolysis under the same experiment conditions. The elemental mercury formed in gas phase was recorded in the concentration unit of $\mu\text{g m}^{-3}$.

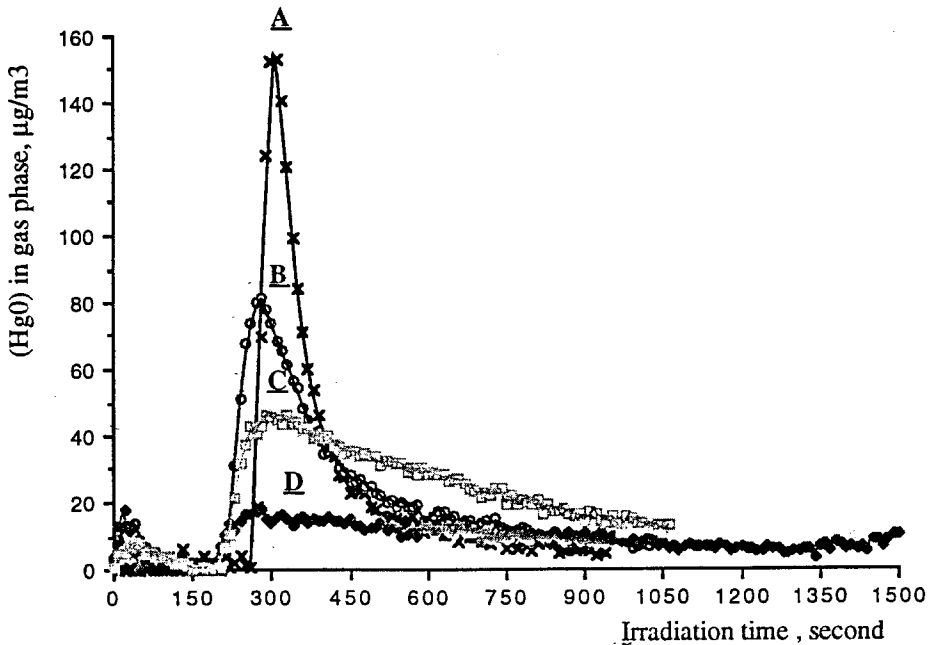


Figure 3. Relative magnitude of photolysis of divalent Hg in different solutions.. A. $\text{Hg}(\text{OH})_2$ 20 ppb in Milli-Q water in the presence of 10 ppm FA (pH 5.2), B. $\text{Hg}(\text{OH})_2$ 20 ppb in natural river water (pH 6.7), C. $\text{Hg}(\text{OH})_2$ 20 ppb in Milli-Q water (pH 7.0) only, and D. HgCl_2 20 ppb in Milli-Q water (pH 7.0) only.

It can be seen from Figure 3C that $\text{Hg}(\text{OH})_2$ can be photolysed directly, although its extinction coefficient of absorption at the wavelengths of interest is probably very small (Xiao *et al.*, 1994).

Principally speaking, no HgCl_2 could be photolysed in Milli-Q, due to the fact that it does not absorb light at wavelengths > 290 nm at all (Strömberg, 1990). The small amount of elemental Hg

formed, cf. 3D, when pure HgCl_2 solution was irradiated may probably be the contribution from small quantity of $\text{Hg}(\text{OH})_2$ which might exist in the HgCl_2 solution.

Water from the Göta River, which is used as the drain water sources for the city of Gothenburg, was sampled on January 1994. It was quite clean with concentration of Hg 3.1 ng L^{-1} and Total Organic Carbon (TOC) 5.0 mg L^{-1} . To this river water, 20 ppb $\text{Hg}(\text{OH})_2$ was added before exposure to the xenon lamp. Elemental Hg formed in the gas phase cf. 3B, was much more than the same concentration of $\text{Hg}(\text{OH})_2$ in Milli-Q water only.

Even more elemental Hg was formed when a 20 ppb mercury in Milli-Q water was irradiated in the presence of 10 ppm FA. This is illustrated by 3A, which shows the typical experimental result of the influence of humic substances on the photolysis of $\text{Hg}(\text{II})$ in aqueous solution.

Kinetic rate were evaluated by following the concentration decrease of the $\text{Hg}(\text{II})$ in solution. It was assumed that the elemental Hg formed through photolysis in solution was quantitatively transferred to the gas phase without losses in the system. Hence Equation (1) can be used:

$$[\text{Hg}^{2+}_{\text{tot}}]_t = [(n\text{Hg}^{2+})_0 - (n\text{Hg}^0)_t] / V \quad (1)$$

where $[\text{Hg}^{2+}_{\text{tot}}]_t$ is divalent Hg concentration in solution at time t , $(n\text{Hg}^{2+})_0$ is the mass of divalent mercury in the solution at time zero, $(n\text{Hg}^0)_t$ is the mass of elemental mercury in the gas phase at time t , and V is the volume of reaction solution. $(n\text{Hg}^0)_t$ can be calculated from the concentration of Hg measured in the gas phase, $(n\text{Hg}^{2+})_0$ and V are known.

At low concentration, photochemical reactions obey first order kinetics (Zepp, 1982), i.e. that the process can be described by Equation (2).

$$d[\text{Hg}^{2+}_{\text{tot}}]/dt = -k [\text{Hg}^{2+}_{\text{tot}}] \quad (2)$$

In Figure 4a, $\ln[\text{Hg}^{2+}]$ as a function of time is plotted, for a typical experimental result in order to see whether the reaction is a first order one. However, the plot is definitely not a straight line, and the conclusion must be that it is not an ordinary first order reaction. Identical curves pattern would be obtained for all the experimental results conducted in the presence of humic substances.

The best fit of the experimental data were achieved when an assumption of "two-reaction processes" was made :

$$[\text{Hg}^{2+}_{\text{tot}}]_t = [\text{HgA}^{2+}]_t + [\text{HgB}^{2+}]_t \quad (3)$$

Where, $[\text{Hg}^{2+}_{\text{tot}}]_t$ is the total concentration of Hg in the solution calculated according to equation (1); HgA^{2+} and HgB^{2+} are assumed to be of $\text{Hg}(\text{II})$ bound to different substitutes A and B of humic substances. The A or B can either be one single function group or several function groups of humic matter with the same photolysis characters when expose to the xenon lamp. First order rate expressions were then, applied separately to both the reactions:

$$[\text{HgA}^{2+}]_t = [\text{HgA}^{2+}]_0 E^{-k_A t} \quad (4)$$

$$[\text{HgB}^{2+}]_t = [\text{HgB}^{2+}]_0 E^{-k_B t} \quad (5)$$

The evaluation has been performed as follows: since one photolysis (the HgA) rate seems to be considerably higher than the other, almost no HgA will be left after a certain time interval, for example 200 seconds. Then, the contribution from $[\text{HgA}^{2+}]$ to $[\text{Hg}^{2+}_{\text{tot}}]$ may become negligible (see Figure. 3A for the typical experimental result) and $[\text{HgB}^{2+}] = [\text{Hg}^{2+}_{\text{tot}}]$. The concentrations of HgB^{2+} in the reaction solution from $t=200$ s to $t=800$ s can be calculated using Equation 1. By plotting $\ln[\text{HgB}^{2+}]_t$ against reaction time t , the rate constant, k_B , and $[\text{HgB}^{2+}]_0$ can be obtained, see Fig. 4c.

By rearrange of equation (3), $[\text{HgA}^{2+}]_t = [\text{Hg}^{2+}_{\text{tot}}]_t - [\text{HgB}^{2+}]_t$, the concentration of $[\text{HgA}^{2+}]_t$ in the reaction system can be calculated by using Equations (1) and (5). In the same way, k_A , and $[\text{HgA}^{2+}]_0$ can be obtained by plotting $\ln[\text{HgA}^{2+}]$ against reaction time t , see Fig. 4b. All the experimental results were treated in this way and the final results are summarised in Table 1.

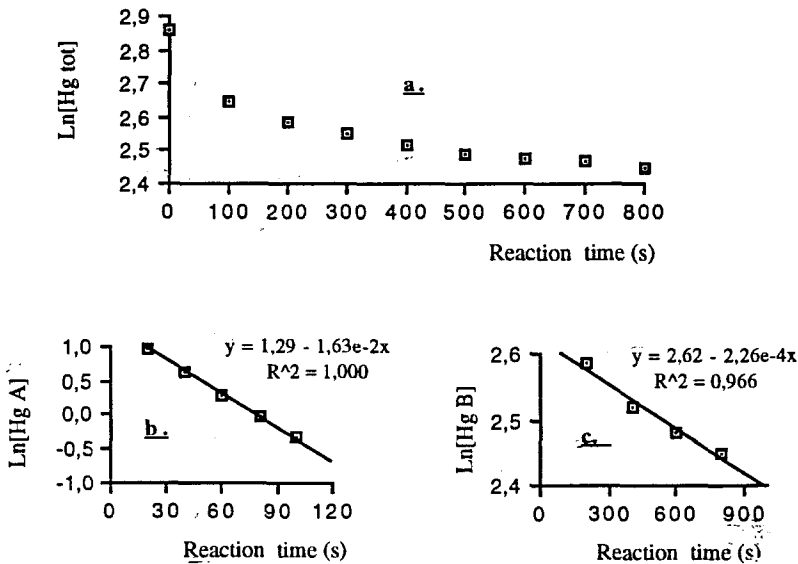


Figure 4. Typical calculating examples of first order plots. a. $\ln[\text{Hg}_{\text{tot}}]$ against reaction time, b. $\ln[\text{Hg A}]$ against reaction time, and c. $\ln[\text{Hg B}]$ against reaction time.

The linearity in Figure 4b is quite good, but in Figure 4c one can perhaps see a slight "banana shaped" curve, although a considerable improvement has been achieved compared to Figure 4a. Even better fitting

was obtained if "three-reaction processes" was applied to the experimental data. Figure 5 presents the plot for the slowest process (corresponding to Figure 4c), when three types of complexes Hg(II) are assumed.

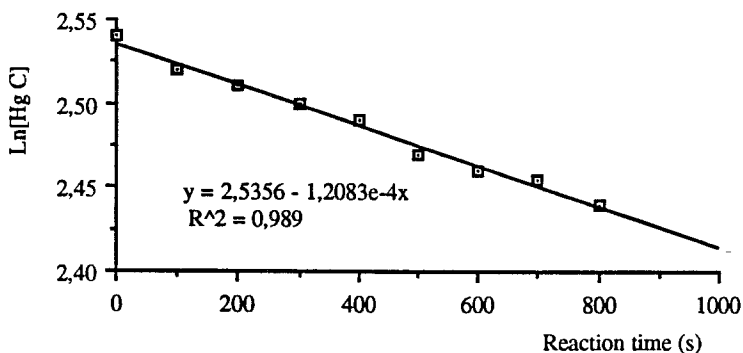


Figure 5. First order plot, Ln[HgC] against reaction time.

It is probable that Hg(II) is bonded to different types of sites of the very complex humic acid "molecule". Since, it has been shown that different Hg(II) complexes have different photolysis rates, see e.g. Xiao *et al.* (1994). It is not unlikely that a Hg(II) ion, bonded to one type of site of the humic acid has a photolysis rate that differs from a Hg(II) ion that is bonded to another type of site. This means that the photolysis of Hg(II) could very well be a sum of two or more photoreductions, which can be separately described by using ordinary first order reaction with their own reaction rates.

In Figure 5 the "banana shape" is disappeared. The third rate constants therefore, is obtained. An iterative method had to be used because at all times two fractions of Hg(II) were present. The new k_A was rather close to the k_A from Table I ($2.3 \times 10^{-2} \text{ s}^{-1}$ compare to $1.6 \times 10^{-2} \text{ s}^{-1}$). The "old" k_B is in between the new k_B and the new k_C , $2.3 \times 10^{-4} \text{ s}^{-1}$ respective to $4.1 \times 10^{-3} \text{ s}^{-1}$ and $1.2 \times 10^{-4} \text{ s}^{-1}$. The Hg_A fraction obtained with three different Hg(II) forms was $\approx 17\%$ (the old value $\approx 21\%$) and the corresponding Hg_B and Hg_C fractions were calculated to be 11% and 72%. The difference of results obtained using two or three forms of Hg(II) assumption is not significant considering the extrapolation of the photolysis rate constants to the natural waters. Hence, only results treated by "two-reactions processes" were summarized in Table I together with the percentage of $[HgA^{2+}]_0/[Hg^{2+}_{tot}]_0$.

It can be seen that the larger photolysis rate is approximately $k_A \approx 2 \times 10^{-2} \text{ s}^{-1}$. This is a much larger constant than the one for $Hg(OH)_2$ ($1.2 \times 10^{-4} \text{ s}^{-1}$) reported previously (Xiao *et al.*, 1994). The other rate constant, k_B , is approximately two magnitudes smaller, $\approx 2 \times 10^{-4} \text{ s}^{-1}$, which is in the same range as that of $Hg(OH)_2$. No significant difference between the experiments with HA and those with FA can be found. The Hg_A fraction varies between 10 to 23 % of the total Hg(II) with an average of $\approx 16\%$ in the artificial solution, the corresponding results are 9-17 and 14 % in the natural water.

When 20 ppb Hg was added to the Göte River waters, without the addition of FA or HA, the photolysis rate constants are $k_A = (1.3 \pm 0.3) \times 10^{-2} \text{ s}^{-1}$ ($n=4$) and $k_B = (1.8 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ ($n=4$), which are slightly lower than using the artificial FA and HA at a concentration level of 10-20 ppm.

Table I. Photolysis results of divalent mercury in aqueous solution with different content of humic substances

Experiment date	Reaction solution*	$k_B \times 10^4$ (s^{-1})	$k_A \times 10^2$ (s^{-1})	$(Hg_A)_0 / (Hg_{tot})_0$ (%)
9311303	FA18+Hg20	2.24	1.39	10.00
9311305	-----	2.93	1.30	14.77
9312015	FA18+Hg20	3.22	1.15	19.55
9312016	-----	2.65	1.32	14.99
9312022	FA18+Hg20	2.52	1.79	15.44
9312024	-----	3.22	1.56	15.00
940131	FA18+Hg20	2.75	2.69	17.00
940131-1	-----	2.84	2.02	17.14
940201-16	FA18+Hg20	2.75	1.68	10.09
940201-17	-----	2.65	1.45	10.37
940131-12	FA18+HgCl ₂ 20	2.13	1.96	22.90
940131-7	-----	1.92	2.53	23.30
9312025	FA10+Hg20	2.26	1.63	20.88
9312026	-----	2.60	1.54	20.95
940131-3	-----	1.53	1.65	11.05
940201-9	FA10+Hg40	1.92	1.68	17.19
940201-11	-----	2.68	1.61	11.35
9312027	HA18+Hg20	2.67	1.36	18.70
9312028	-----	2.26	1.44	21.50
940201-14	HA10+Hg20	2.08	1.67	14.66
940201-15	-----	2.13	1.69	13.21
940201-12	HA10+Hg40	2.10	1.56	12.89
940201-13	-----	2.04	1.54	12.63
940202-9	Hg20+GÄV	1.92	1.01	15.8
940202-10	-----	1.87	1.17	9.40
940202-7	HgCl ₂ 20+GÄV	1.61	1.52	15.43
940202-8	-----	1.80	1.62	16.88

* Number are concentrations for HA , FA (ppm) and Hg (ppb). If not specified, Hg was artificial solution in the form of Hg(OH)₂. GÄV= natural water from the Göte River.

The xenon lamp in this study gives an artificial sunlight. The sunlight at 60° N (Stockholm's latitude) has been calculated to be approximately 400 times weaker than the xenon lamp used in this study. This is based on actinometer measurements (Xiao *et al.*, 1994) and on a report by Svensson and Björndal (1988). This implies that the photolysis rate constant will be \approx 400 times smaller at outdoor conditions. This gives a half-life of \approx 4 sunlight hours for HgA²⁺ and 250 sunlight hours for HgB²⁺, respectively. In these roughly calculated examples, the ground averages for all k_A and k_B in Table I were used, except for those obtained with the Göte River water. Such a short half-life means that photolysis definitely could have an influence on the evaporation of Hg from a lake surface (see also the reasoning in Xiao *et al.*, 1994).

4. Concluding Remarks.

The photolysis of the Hg - HA/FA complex does not show an ordinary first order kinetics, but these data are possible to evaluate by assuming a sum of first order reactions, indicating that there is more than one type of Hg complex existing in the solution. This is not surprising, since humic and fulvic matter consist of complex "molecules" with many different functional groups to which the Hg^{2+} ions can bind.

The mechanism of the photolysis is still not clear, if the humic substances act as a photosensitizer to initialise the reaction through electron, energy transfer process (Cooper *et al.*, 1989) or as a complexing agent with the photolysis occurring on the bond of the humic-Hg complex directly. When HgCl_2 was applied in this study, instead of $\text{Hg}(\text{OH})_2$, both to Milli-Q water with humic substances and to the Göte River water, similar results were obtained as in the case of $\text{Hg}(\text{OH})_2$, which implies that Hg-humic complex is formed first. The results of many attempts to elucidate structures of humic substances and to correlate them to photoactivity have up to now been unsatisfying (Kotzias *et al.*, 1987). Hence, no efforts were done either in this investigation.

It should be pointed out that this is an experimentally determined rate constant, valid only under conditions similar to those of the experiments. In the real environment, situation may be quite different and much complicated, hence the magnitude of photolysis may vary significantly. However, there is no doubt that photolysis of divalent Hg in the natural water is an important process and the existence of humic substances in natural water does affect the distribution and mobility of Hg in the environment.

Further studies with improved methods to yield more accurate values for the rate constants are needed, for example, to find out if the rate constants discrepancies is influenced by the mass transfer of Hg^0 to the gas phase. In addition, different natural waters and wider ranges concentrations of $\text{Hg}(\text{II})$ and HA/FA should be tested.

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