Mechanistic steps in the photoreduction of mercury in natural waters

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Abstract

Elemental mercury accounts for 10–50% of the dissolved mercury in lakes but plays a vital role in the cycling of this element in lacustrine environments. The view is advanced that a large fraction of the Hg(0) is generated by photochemical reactions in the surface waters. Possible mechanisms for the Hg(0) production are discussed including homogeneous photolysis of dissolved Hg species and photoreduction processes involving organic molecules and inorganic particulates in water.

Keywords: Photoreduction; Mercury pollution; Surface waters; Organic molecules

1. Introduction

The mercury cycle in lakes remains murky although the recent development of ultra-clean laboratory methodology for the sampling and analysis of mercury has provided some useful insights. One fact that has clearly emerged is that elemental mercury (Hg(0)) plays a pivotal role in the environmental mercury cycle. It constitutes about 98% of the mercury in the atmosphere which is dispersed globally and hence represents the dominant form of the element that is delivered into many lakes (Nriagu, 1993; Fitzgerald et al., 1991). About 10–50% of the dissolved mercury in lakes and the ocean is volatile Hg(0), enough to form oversaturated concentrations in many surface waters (Baeyens et al., 1991; Vandal et al., 1991, 1993). Since the Hg(0) can be lost to the atmosphere via gas exchange, many aquatic systems thus represent a source of atmospheric mercury. Short-term studies in temperate lakes show that during periods of high Hg(0) supersaturation, most of the mercury deposited from the atmosphere can be re-volatilized (Vandal et al., 1993). The venting of gaseous Hg(0) to the atmosphere (typical rate, $1-10 \times 10^{-7}/s$; Mason et al., 1993) reduces the Hg burden in the water (see Table 1) and may limit the methylmercury production and accumulation in fish. The self-cleansing pathway can thus serve to ameliorate the risks associated with mercury contamination especially in lakes.

The processes involved in the production of elemental mercury in natural waters remain equivocal. Many people invoke the activity of the bacterial mercuric reductase or indirect reduction by algal photosynthate (Barkay et al., 1991; Vandal et al., 1993). Mason et al. (1993) recently

Table 1

Concentrations of total dissolved mercury in lakes

Body of water	Location	Total Hg (ng/L)	Reference
Lake Ontario	USA/Canada	0.9	Gill and Bruland, 1990
Lake Erie	USA/Canada	3.9	Gill and Bruland, 1990
Lake Vernon	Ontario, Canada	2.3	Wright et al., 1993
Clay Lake[a]	Ontario	5–80	Driscoll et al., 1994
Onendaga[a]	New York	7–19	Bloom and Effler, 1991
Clear Lake[b]	California	3.6–104	Gill and Bruland, 1990
Lake Union	State of Washington	1.7	Bloom, 1989
3 drainage lakes	Manitoba, Canada	0.2–1.1	Bloom et al., 1990
14 drainage lakes	Adirondacks, USA	0.8–5.3	Driscoll et al., 1994
Drainage lake	State of Washington	0.2	Gill and Bruland, 1990
8 drainage lakes	Sweden	1.5–15	Lee and Iverfeldt, 1991
24 forest lakes	Sweden	3.7 (spring) 3.1 (summer) 6.2 (autumn)	Meili et al., 1991
4 seepage lakes	Wisconsin	0.9–1.9	Fitzgerald and Watras, 1989
2 seepage lakes	Adirondacks, USA	0.8	Driscoll et al., 1994
Alpine lake	California	0.6	Gill and Bruland, 1990

[a]Contaminated by effluents from chlor-alkali plants.

[b]Contaminated by mine effluents.

suggested that picoplankton (< 3 μm in size) may be the primary Hg reducers especially in seawater. Most studies, however, find abiotic processes (of unspecified nature) to be important in Hg(0) production especially in surface lake waters (Xaio et al., 1991; Mason et al., 1993; Vandal et al., 1993). Barkay et al. (1991), for instance, showed that abiotic reduction of Hg(II) accounted for 10–70% of the elemental mercury volatilized from surface waters. Photochemical processes have sometimes been imputed. Iverfeldt (1984) demonstrated photolytic formation of Hg(0) when a dilute solution of Hg(II) was illuminated with a xenon lamp. The reduction of Hg(II) by sunlight has been reported in distilled water as well as in precipitation samples (Brosset, 1987). Munthe and McElroy (1992) showed that Hg(II) in solution can be reduced to Hg(0) by simulated sunlight. The importance of photochemical reactions in the formation of Hg(0) in surface waters has not received the attention that it deserves. Possible mechanisms involved in the photoreduction of Hg(II), Hg(I), and to a limited extent, MeHg (methylated Hg species) are considered in this report.

2. Homogeneous photolysis of dissolved Hg species

In direct photolysis, the Hg species absorbs the incident solar energy and is reduced in its excited state. This can occur because many Hg species such as complexes with OH^-, HS^-, Cl^- and organic ligands (including CH_3Hg^0, $(CH_3)_2Hg$, CH_3Hg^+, CH_3HgCl, CH_3HgOH, CH_3HgSH, CH_3HgSR, and others) can absorb radiation in the highly energetic UV range (270–400 nm) of the solar spectrum (Fujita et al., 1973; Stromberg et al., 1991). Solid phases such as mercury oxides, hydroxides and sulfide can absorb the UV radiation and be photolytically reduced (Stromberg et al., 1991). Typically, the photons initiate a series of electron transfer reactions that result in the formation of reduced Hg ion and a free ligand radical. The photolytic reduction of dissolved $Hg(OH)_2$ can be schematized as follows:

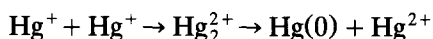$$Hg(OH)_2 \xrightarrow{h\upsilon} [Hg(OH)]^* \leftrightarrow Hg(OH)_{aq} + OH^{\cdot}$$
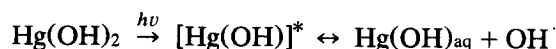
where $[Hg(OH)]^*$ refers to a complex at an excited state and $OH^{\cdot}$ is the hydroxyl radical. Since
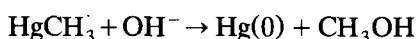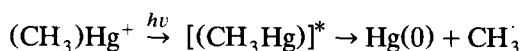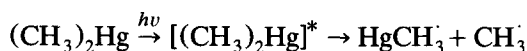
$Hg(OH)_{aq}$ is unstable in natural waters (Lindquist et al., 1991), it is quickly reduced to elemental mercury:

$$Hg(OH)_{aq} + H^+ + e^- \rightarrow Hg(0) + H_2O$$

$$Hg^+ + O_2^- \rightarrow Hg(0) + O_2$$
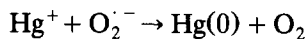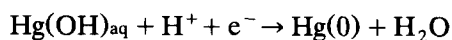
At low concentrations, $Hg(I)$ and Hg_2^{2+} can disproportionate to elemental mercury (Fujita et al., 1973):

$$Hg^+ + Hg^+ \rightarrow Hg_2^{2+} \rightarrow Hg(0) + Hg^{2+}$$

Little is currently known about the photolysis of dimethyl and monomethyl mercury, and possible pathways may include:

$$(CH_3)_2Hg \overset{h\upsilon}{\rightarrow} [(CH_3)_2Hg]^* \rightarrow HgCH_3 + CH_3$$

$$(CH_3)Hg^+ \overset{h\upsilon}{\rightarrow} [(CH_3Hg)]^* \rightarrow Hg(0) + CH_3$$

$$HgCH_3 + OH^- \rightarrow Hg(0) + CH_3OH$$

$$CH_3 + OH^- \rightarrow HCO_3^- + H_2O$$

$$CH_3 + CH_3 \rightarrow C_2H_6$$
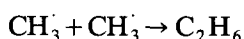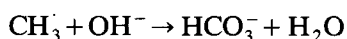
where CH_3 and $HgCH_3$ are free radicals. The quantum yield of a particular reaction sequence depends on the competition between the bond cleavage and the sinks for the metal ions as well as the free ligand radicals in the particular environment. It should be noted that the termination (or quenching) of the reactions by the formation of unreactive $Hg(0)$ should greatly enhance the quantum yield (moles of $Hg(0)$ produced per photon absorbed by the solution). The photolysis rate for Hg can be expected to be rather fast, in the order of seconds to hours, because (a) the formation of $Hg(0)$ greatly increases the quantum efficiencies of the photochemical reactions, and (b) the ligand-to-metal charge transfer absorption bands for many naturally occurring Hg species in natural waters fall in the 270–400 spectrum where the solar actinic flux is energetic enough (about 1.0 Einstein m^{-2} h^{-1}) to promote fast photolytic reactions. The few laboratory measurements that have been reported on Hg photolysis indeed show rates in the order of seconds to hours (Munthe et al., 1991; Brosset and Lord, 1991; Munthe and McElroy, 1992).

Although homogeneous photochemical reduction of methylated and other Hg(II) compounds has been demonstrated in the laboratory (Xiao et al., 1991; Brosset and Lord, 1991; Munthe and McElroy, 1992), its significance in natural waters is still not clear. Mason et al. (1993) observed that abiotic Hg(0) production in seawater is only about 40% of the rate in freshwater (1.0 $\times$ 10^{-6}/sec). The formation of strong Hg chloride complexes presumably modules the production of Hg(0) in seawater compared to freshwater. Such an ionic medium effect is evidence for some involvement of homogeneous photolysis.

## 3. Photoreduction involving inorganic particulates

Lakes and estuaries often have high concentrations of suspended particles (seston) which generally play an important role in the cycling of trace metals in such ecosystems (Jackson et al. 1980; Santschi, 1988; Balistrieri et al., 1992). Particles in water have a strong affinity for trace metals and scavenging by settling particles is widely regarded as the key process which controls the concentrations of many toxic metals in lakes. Although most of the previous studies have focused on the adsorption/desorption phenomenon, particles can also affect the speciation and hence the redistribution and toxicity of trace metals in other ways. For instance, particulates in water often contain mineral phases with semiconducting properties, including for instance TiO_2, Fe-oxides, Mn-oxides, Al_2O_3, ZnO, HgO, and Me-sulfides (Me, metal) (Litter et al., 1991). When such a semiconducting particulate is exposed to light of a wavelength more energetic than its band gap, an electron is excited from the valence gap into the conduction band leaving a hole in the valence band. The formation of the electron/hole pair can be schematized as:

$$Me_xO_y + h\upsilon \rightarrow Me_xO_y\{e^- ... h^+\} \rightarrow e_{cb}^- + h_{vb}^+$$
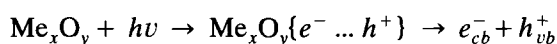
where Me_xO_y and $Me_xO_y\{e^- ... h^+\}$ are the semiconducting metal oxide in the natural and photoactive states, e_{cb}^- is conduction band electron and h_{vb}^+ is valence band hole. The charge carriers (e_{cb}^- and h_{vb}^+) are extremely reactive and can

affect the redox cycling of many trace metals in lakes.

The electrons being released are very energetic ($+0.5$ to -1.5 V vs. normal hydrogen electrode, or NHE) and can reduce many Hg compounds including phenyl mercuric chloride (Prairie et al., 1993; Foster et al., 1993), HgO and HgS (Lindquist et al., 1991). For instance:

$$Hg^{2+} + 2e_{cb}^- \rightarrow Hg(0)$$
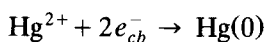
The valence band holes are powerful oxidants ($+1.0$ to 3.5 V vs. NHE) capable of oxidizing complex organic contaminants in water and this is the basis of the so-called photocatalytic detoxification that is currently the focus of much attention (Ollis et al., 1991). The reduction would most likely occur on the particulate surface between the charge carrier and the adsorbed Hg. Since e_{cb}^- is very unselective in its reaction, the probability for the electron to diffuse into the aqueous medium to react with the dissolved Hg ions in place of the much more abundant molecular oxygen is very low. However, any dissolved Hg can be reduced or oxidized by the transient species formed photolytically in solution (see below). In natural waters, the semiconducting particles are often coated with organic ligands which can serve as sacrificial reductants that scavenge the holes created in the light absorption process and would thus promote the Hg reduction.

Solid mercury compounds, especially HgO and HgS are likely to occur in such low concentrations in the suspended particulates that their effects on the cycling of mercury are likely to be minor. Whether other photoactive particles directly reduce Hg by the semiconductor mechanism in natural waters has yet to be demonstrated. It is more probable that the photoreduction of Hg in natural waters is indirect, mediated by iron and manganese photoredox reactions. Iron and manganese oxyhydroxides exercise a marked influence on the cycling of mercury in lacustrine environments (Jackson et al., 1980; Santschi, 1988; Bertino and Zepp, 1991), and photochemical (reductive) dissolution of iron and manganese has been documented in a number of freshwater systems (McKnight et al., 1988; Waite et al., 1988;

Moffett and Zafiriou, 1993; Waite and Szynczak, 1993a,b). The reduction may occur heterogeneously at the surface of the semiconducting particle (photochemical corrosion),

$$e_{cb}^- + Me_2O_3 \xrightarrow{h\upsilon} \{Me_2O_3\}^* \rightarrow Me^{2+} + products$$
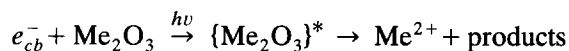
or homogeneously by the photolysis of dissolved metal species

$$MeOH^{2+} \xrightarrow{h\upsilon} \{Me^{2+}(OH)\}^* \rightarrow Me^{2+} + OH^-$$
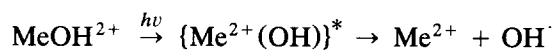
$\{Me_2O_3\}^*$ and $\{Me^{2+}(OH)\}^*$ in the above reactions refer to complexes in the excited state. For the reactions above to proceed, they must be linked to the oxidation of organic compounds (or appropriate charge acceptors) by the holes. The Fe^{2+} and Mn^{2+} so formed can easily reduce the adsorbed or Hg ions in solution:

$$Me^{2+} + Hg^+ \rightarrow Hg(0) + Me^{3+}$$
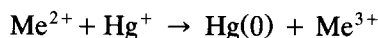
Since the Me^{3+} can then be reduced, the Fe and Mn essentially play a catalytic role in the Hg reduction process. Indirect photoreduction of Cr(VI) by Fe(II) has been shown to be common in natural waters (Kieber and Helz, 1992; Kaczynski and Kieber, 1993), and since Hg(II) and Hg(I) are more easily reduced, the involvement of a similar process in Hg(0) production would seem to be highly likely.

4. Photochemical reduction by organic molecules in water

The ability of dissolved organic matter (DOM) especially humic (HA) and fulvic (FA) acids to reduce mercury abiotically has been known for many years (Andersson, 1979; Allard and Arsenie, 1991). The reducing capacity of HA and FA is well documented, the redox reaction being represented as:

$$HA_{(oxidized)} + e^- + nH^+ \rightarrow HA_{(reduced)};$$
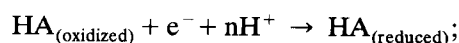
$$E^\circ = 0.7 \text{ V (HA) and } 0.5 \text{ V (FA)}$$

Although HA and FA can reduce some Hg species under some conditions, it is more usual

for Hg(II) to be stabilized by being strongly chelated by these organic molecules. HA and FA complexes are generally believed to be a key pathway in the transfer of Hg from the terrestrial watershed to the lakes (Mierle, 1990; Meili, 1991). Processes which favor the reduction of DOM-bound mercury should therefore be of particular concern in surface waters.

Solar radiation in the wavelength of 290–400 nm can be absorbed effectively by many organic compounds found in natural waters, including humic acids (HA), fulvic acids (FA), proteins, flavins and porphyrin derivatives (Larson and Marley, 1994). Environmental pollutants such as PAHs, synthetic dyes and drugs, some phenols and many oil components also absorb light in this wavelength region. These natural and synthetic organics form complexes with Hg in solution. Once irradiated, the molecule is excited to a new species which can release an electron to the aqueous medium or to an acceptor molecule with the resultant formation of radical cation, a hydrated electron e_{aq}^- or a radical anion (Frimmel et al., 1987; Serpone et al., 1993). The photoinduced reduction of mercury by DOM can be depicted as:

$$DOM \xrightarrow{h\upsilon} \{DOM\}^* \rightarrow \{DOM^+ + e^-\}^*$$

$$+ Hg_{(complexed)}^{2+} \rightarrow DOM^+ + Hg^0$$
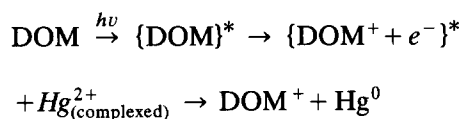
The reactions can occur either unimolecularly in which the molecule absorbs light and emits an electron or bimolecularly where the donor and acceptor form a charge-transfer complex and the electron transfer occurs within the complex. The later pathway should predominate in natural waters in which the complexed Hg is reduced directly by the hydrated electrons photoproduced by the DOM.

In a study of abiotic Hg reduction by humic acids, Allard and Arsenie (1991) observed the highest Hg(0) production rate (12%/day) in the illuminated system devoid of oxygen and chloride ions. The lowest rates were found in an aerated system kept in the dark. The reduction was inhib-
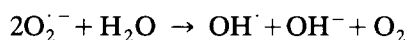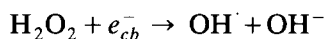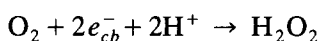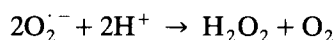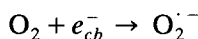
ited by the competing ions, Cl^- (which forms complexes with Hg(II)) and Eu (which forms complexes with the HA). These observations by Allard and Arsenie (1991) are difficult to interpret. The inhibition of Hg(0) production by reducing the available complexing sites on the HA by means of Eu would implicate an intra-molecular electron transfer process, however.

Another mechanism for light interaction with molecules in natural waters involves the conversion of molecules to the excited states capable of transferring some of their energy to ground-state acceptors. This phenomenon is commonly referred to as photosensitization. Most often, the energy is transferred from the sensitizing donor to molecular oxygen, resulting in the formation of singlet oxygen ($^1O_2$), but the transfer of the energy to another organic molecule is feasible. Naturally occurring substances with photosensitizing properties include HA, FA, porphyrin derivatives, chlorophyll degradation products, most pigmenting compounds, flavins and some quinones, and the pollutants that act as sensitizers include PAHs, synthetic dyes and phenols (Larson and Marley, 1994). Singlet oxygen, with its fully spin-paired electrons, can attack organic molecules effectively; it oxidizes protein amino acids (especially those with sulfurhydryl groups) and lipids (Straight and Spikes, 1985) and in the process can liberate Hg species which are then reduced by catenated photochemical reactions.

5. Role of transient reductants

The actual concentration of Hg(0) depends on its relative rates of formation and back oxidation in solution. The reoxidation can be driven by various species (including O_2^-, OH^-, H_2O_2, HO_2^-, and RO_2, and $^1O_2$) formed when UV light is absorbed by the semiconductors and DOM (Buxton et al., 1988; Faust, 1994). These reactive transients have been shown to be abundant in the photic zones of most natural waters (Cooper et al., 1988, 1989; Moffett and Zafiriou, 1990, 1993; Moore et al., 1993). Some of the common photolytic reactions that can generate the transient

species include (Bruccoleri et al., 1994; Prairie et al., 1993; Larson and Marley, 1994):

$$O_2 + e_{cb}^- \rightarrow O_2^{\cdot -}$$

$$2O_2^{\cdot -} + 2H^+ \rightarrow H_2O_2 + O_2$$

$$O_2 + 2e_{cb}^- + 2H^+ \rightarrow H_2O_2$$

$$H_2O_2 + e_{cb}^- \rightarrow OH^{\cdot} + OH^-$$

$$2O_2^{\cdot -} + H_2O \rightarrow OH^{\cdot} + OH^- + O_2$$

The nature of the oxidizing agent in the hole is still not clear, but the formation of the hydroxyl radical (in the hole) is generally depicted as follows:

$$OH^- + h_{vb}^+ \rightarrow OH^{\cdot}$$

$$H_2O + h_{vb}^+ \rightarrow OH^{\cdot} + H^+$$
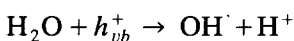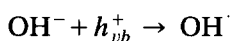
Irrespective of the origin of the oxidizing and reducing species, there is no doubt that these transients can play an important role in the reduction and oxidation of mercury and other metal species in natural waters.

Because of the very high first ionization potential for Hg (241 kcal/mol), which is similar to that of the inert gas Ra (248 kcal/mol) (Schroeder et al., 1991), elemental mercury is not attacked by mild oxidants in solution. The inertness is a key feature in the accumulation of Hg(0) in surface waters since once formed, it is not readily reoxidized by the transient species, a-la the Fe(II)/(FeIII) and Mn(II)/Mn(III) redox couples (Waite and Szymczak, 1993a,b; Faust, 1994). For example, Hg(0) is not oxidized but rather is reduced by H_2O_2 and O_2^- in natural waters (Schroeder et al., 1991; Brosset and Lord, 1991; Munthe and McElroy, 1992). It is unaffected by dissolved oxygen. Although the reactions with O_3, HClO and HSO_3^- are fast under atmospheric conditions (Munthe et al., 1991; Munthe and McElroy, 1992), these oxidant species are unlikely to be as abundant in natural waters. The transient species known to oxidize Hg(0), $(CH_3)_2Hg$ and CH_3Hg^+ rapidly is the $OH^{\cdot}$ radical (Lindquist et al., 1991; Munthe and McElroy, 1992). Since $OH^{\cdot}$ is unselectively reactive with a host of organic and inorganic molecules in solution, one would expect that its reaction with the volatile Hg(0) or

$(CH_3)_2Hg$ would be a rather slow process. Nothing is currently known about the reaction of Hg(II) and Hg(I) with singlet oxgen formed in natural waters.

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