

The mechanism behind the DOM effects on methylmercury photodegradation

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Methyl mercury (CH_3Hg^+), a neurotoxin, is the most toxic form of mercury that occurs in natural waters [1–4]. It is a cause of concern because of increasing worldwide pollution by mercury in both water and atmosphere [3, 5].

Photodegradation of CH_3Hg^+ is one of the main removal pathways from surface waters, and it has been shown to occur in the presence of dissolved organic matter (DOM) but not in ultra-pure water [2, 4]. Several mechanisms for the photodegradation of CH_3Hg^+ have been proposed, including: (1) direct photodegradation of CH_3Hg –DOM

complexes via intramolecular electron transfer [4] and (2) indirect photodegradation of CH_3Hg –DOM by free radicals/ reactive oxygen species such as singlet oxygen ($^1\text{O}_2$) and the hydroxyl radical ($\text{HO}\cdot$) [1, 2, 6]. Studies show that the photo-Fenton reaction or the reactive oxygen species, including hydroxyl radical ($\text{HO}\cdot$), $^1\text{O}_2$, triplet excited state of DOM ($^3\text{DOM}^*$), and hydrated electron (e_{aq}^-), play a minor role in CH_3Hg^+ photodegradation in aqueous media [3, 4, 6]. Interestingly, the photodegradation of CH_3Hg^+ depends on the wavelength-specific incident photon flux, on DOM contents and salinity, but does not depend on nitrate photolysis [3]. It has been shown that rates of CH_3Hg^+ photodegradation are decreased with increasing salinity and DOM contents [3]. Increasing DOM contents with the CH_3Hg^+ aqueous media can act as a barrier to reach the incident light intensity toward the CH_3Hg^+ component which could presumably decline the rates of CH_3Hg^+ photodegradation. Several gaps still exist concerning the proposed photodegradation pathways, including two unresolved key questions: (1) how does DOM form bonds with CH_3Hg^+ ?

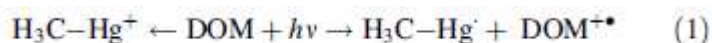
of considerations may help in shedding some light over this issue and could provide scope for further research in the field.

The first issue is the formation of p-electron bonding systems between CH_3Hg^+ [$\text{Hg}^{1+} = 1s2s22p63s23p64s23d104p65s24d105p66s14f145d10$] and DOM (CH_3Hg –DOM), through electron donation from the functional groups of high molecular weight DOM to an empty sorbital of CH_3Hg^+ (ligand-to-metal charge transfer) [7].

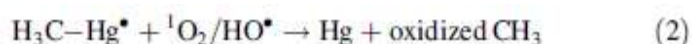
Note that the p-electron bonding system is not formed with low-molecular-weight DOM, because the formed complex would not be stable enough. The overall conditional complexation constants (K_0 DOM) between $\text{Hg}(\text{II})$ and DOM (extracted humic acids, fulvic acids and hydrophobic acids) show very strong interactions (K_0 DOM = 1023.2 ± 1.0 L/kg) at Hg/DOM ratios below approximately 1 lg Hg/mg DOM, which are indicative of mercury–thiol bonds [8].

Photodegradation of methylmercury can thus occur via a pathway that involves thiol complexation [2, 4]. In contrast, much weaker interactions ($K_0 \text{ DOM} = 1010.7 \pm 1.0 \text{ L/kg}$) are observed at Hg/DOM ratios above approximately 10 lg Hg/mg DOM, coherently with Hg binding to oxygen functional groups [8]. The second issue is that p-electrons are loosely bound and they are highly susceptible to radiative excitation [7].

The ligand-to-metal charge transfer could be triggered by the photolysis of the complex $\text{H}_3\text{C}-\text{Hg}^+ \leftarrow \text{DOM}$ (where the “ \leftarrow ” indicates electron donation), which could take place as follows (Eq. (1)):



Oxidized DOM ($\text{DOM}^{+\bullet}$) could undergo several processes. Interestingly, similar phenomena involving the charge-transfer photolysis of Fe(III)–DOM complexes ultimately cause DOM mineralization via decarboxylation [1]. The species $\text{H}_3\text{C}-\text{Hg}^\bullet$ might, for instance, react with HO^\bullet and/or $^1\text{O}_2$ [1, 2]. Oxidizing transients are expected to preferentially react with the methyl moiety of $\text{H}_3\text{C}-\text{Hg}^\bullet$, because the p-electron bonding system would provide an increased electron density on the methyl group and would lower the excitation energy of the carbon–mercury bond [9]. Such processes would lead to the demethylation of $\text{H}_3\text{C}-\text{Hg}^\bullet$, with the formation of elemental Hg and oxidation of the methyl group (Eq. (2)).



Note that the formation of Hg^{2+} from the reaction (Eq. (2)) would not occur, because irradiated Hg cannot release its outer electron from the s-orbital and also because of the high availability of hydrated electrons in waters under the light condition [7, 10].

The occurrence of inorganic compounds can also be important: for instance, increasing salinity can decrease the photodegradation of CH_3Hg^+ by several processes [3], including: (1) the scavenging of HO^\bullet by bromide (the main HO^\bullet scavenger in seawater) [7, 10] and (2) the different speciation of the CH_3Hg^+ cation in seawater compared to freshwater. In seawater, the formation of stable complexes/ion pairs with anions such as Cl⁻ and Br⁻ may hinder the formation of the photolabile species $\text{H}_3\text{C}-\text{Hg}^+ \leftarrow \text{DOM}$.

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