Probing the DOM-mediated photodegradation of methylmercury by using organic ligands with different molecular structures as the DOM model

Xiaoyan Zhang [a], Yanbin Li [a, *], Gang Feng [b], Chao Tai [c], Yongguang Yin [d, e, **], Yong Cai [e, f], Jingfu Liu [d]

[a] Key Laboratory of Marine Chemistry Theory and Technology, Ministry of Education and College of Chemistry and Chemical Engineering, Ocean University of China, Qingdao 266100, China
[b] School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 401331, China
[c] Institute of Resources and Environment, Henan Polytechnic University, Jiaozuo 454000, China
[d] State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[e] Laboratory of Environmental Nanotechnology and Health Effect, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China
[f] Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, USA

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ABSTRACT

Photodegradation is the main depletion pathway for methylmercury (MeHg) in surface water. The formation of MeHg-dissolved organic matter (DOM) complexes has been found to be a key step in MeHg photodegradation. However, the major functional groups involved in the DOM-mediated process have yet to be clearly resolved. In this work, we systematically investigated the effects of DOM molecular structures on MeHg photodegradation by using a variety of organic ligands with different functional groups (e.g., thiosalicylate, thiophenol, and thioaniline). The results showed that thiol and phenyl groups may be the major functional groups governing DOM-mediated MeHg photodegradation, with photodegradation rates also dependent on the type (carboxyl, hydroxyl, and amino group) and position (ortho-, meta-, and para-) of other chemical substituents. The addition of "non-photochemically active" thiol ligands (e.g., mercaptoethanol and dithiothreitol) and high concentrations of Cl$^-$ can significantly inhibit the o-thiosalicylate-induced MeHg photodegradation, indicating that complexation of MeHg with these ligands is necessary for MeHg photodegradation. Sparging with O$_2$ had a negligible effect on MeHg photodegradation, while sparging with N$_2$ significantly enhanced MeHg photodegradation. This finding suggests that MeHg photodegradation may be a reductive process, which was further supported by identification of the degradation products of MeHg. A possible protonolysis mechanism of MeHg photodegradation in the presence of o-thiosalicylate was then proposed based on the findings of this study.

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1. Introduction

Methylmercury (MeHg) is the most toxic form of mercury in the environment, and it can be bioaccumulated and biomagnified through the aquatic food web, threatening aquatic biota and human health (Girard et al., 2016; Li et al., 2010; Sun et al., 2015). Great efforts have been made to investigate the cycling and fate of MeHg in aquatic environments (Coelho et al., 2010; Lehnherr et al., 2011; Matilainen and Verta, 1995; Morel et al., 1998; Tai et al., 2014) suggesting photodegradation is the main depletion pathway for MeHg in aquatic environments (Li et al., 2010; Hammerschmidt and Fitzgerald, 2006; Seller et al., 1996). For instance, it was reported that photodegradation of MeHg accounted for approximately 80% and 31.4% of the annual mobilization of MeHg from lake

(Hammerschmidt and Fitzgerald, 2010) and wetland (Li et al., 2010) sediments, respectively.

Considering the importance of MeHg photodegradation in Hg cycling, great efforts have been made to elucidate the possible mechanism of this process (Li et al., 2010; Sun et al., 2015; Tai et al., 2014; Zhang and Hsu-kim, 2010). Several pathways have been proposed, including both indirect (Hammerschmidt and Fitzgerald, 2010; Zhang and Hsu-kim, 2010; Chen et al., 2003) and direct (Black et al., 2012; Tai et al., 2014; Han et al., 2017) photochemical reactions. Indirect pathways mediated by reactive oxygen species (ROS) and free radicals (FR) (Hammerschmidt and Fitzgerald, 2006; Zhang and Hsu-kim, 2010; Kim and Zoh, 2013) were previously thought to play a crucial role in MeHg photodegradation. In recent years, direct photodegradation of MeHg-DOM has been reported to be the dominant pathway for MeHg photodegradation in an increasing number of aquatic systems (Tai et al., 2014; Qian et al., 2014; Han et al., 2017). Even for systems in which MeHg photodegradation is dominated by the FR/ROS-mediated pathway, complexation of MeHg with DOM was reported to be necessary for this process to occur (Fernandez-Gomez et al., 2013; Zhang et al., 2017; Zhang and Hsu-kim, 2010). These previous studies have highlighted the importance of DOM in MeHg photodegradation.

DOM composition has been deemed to be the key factor controlling the photodegradation of MeHg (Sun et al., 2015; Fernandez-Gomez et al., 2015; Jeremiason et al., 2015). Reduced DOM was found to be more effective than oxidized DOM in enhancing MeHg photodegradation (Qian et al., 2014). Thiol has been suggested to be the DOM functional group governing MeHg photodegradation (Zhang and Hsu-kim, 2010; Qian et al., 2014; Chandan et al., 2015), while phenyl groups may also be involved in the MeHg photodegradation but through an indirect pathway (Qian et al., 2014). In addition, the role of major functional groups (e.g., phenolic and amino group) in DOM-mediated MeHg photodegradation has yet to be clearly determined. Moreover, the type and position of other chemical substituents may also have a significant effect on DOM-mediated MeHg photodegradation by altering the bond energy of C-Hg. However, such effects remain poorly understood.

The major objective of this study was to probe the mechanism of DOM-mediated photodegradation of methylmercury by using organic ligands with different molecular structures as the DOM model. We examined (1) the importance of the thiol and phenyl groups, (2) the role of the type (carboxyl, hydroxyl, and amino group) and position (ortho-, meta-, and para-) of substituent functional groups, (3) the role of co-occurrence ligand ("non-photochemically active" thiol ligands) and Cl$^-$, and (4) the effect of O$_2$/N$_2$ sparging on MeHg photodegradation. Based on the results of these experiments, a possible mechanism for DOM-mediated photodegradation of MeHg was proposed. The results of this study will be useful for understanding the controlling factors and mechanism of DOM-mediated MeHg photodegradation.

2. Experimental section

2.1. Reagents

Enriched ^{198}HgCl$_2$ and ^{201}HgCl$_2$ were purchased from Trace Sciences International (Ontario, Canada). Me^{198}Hg and Me^{201}Hg were synthesized by using methylcobalamin (Li et al., 2010; Martin-Doimeadios et al., 2002). Thirteen organic ligands were adopted as DOM analogues, including o-, m-, and p-thiosalicylate; o-thioaniline; o-thiophenol; cysteine; dithiothreitol; 2-mercaptoethanol; 2-mercaptoacetic acid; 2-mercaptoethylamine; o-phthalic acid; catechol; and o-phenylenediamine. All reagents were prepared freshly with deoxygenated water in an anaerobic chamber to prevent the oxidation of thiol compounds (Hu et al., 2013).

2.2. Measurement of MeHg photodegradation rates under various treatments

Me^{198}Hg was spiked into 100 mL deionized water in quartz bottles to achieve a final concentration of 10 ng L^{-1}. Five milliliters of phosphate buffer (0.2 mol L^{-1}) was then added to achieve a solution pH of 7.0. The photodegradation experiment was carried out using a solar-simulator equipped with three air-cooled Xe lamps (2500 W), with the light intensity and temperature setting to 550 W m^{-2} and 35 °C, respectively. The spectrum of the simulated sunlight was the same as that reported in our previous study (Yin et al., 2014). Next, a 5 mL solution was sampled from each bottle following 0, 3, 6, 9, 15, 22, 30, and 40 h of incubation. Then, 5 ng L^{-1} Me^{201}Hg was added into the samples as an isotope dilution reagent for calculating the Me^{198}Hg concentration. The samples were then stored at 4 °C until analysis. Aqueous ethylation and purge-and-trap pre-concentration followed by gas chromatography-inductively coupled plasma mass spectrometry was used for detecting the MeHg content in samples. Detailed instrumentation and procedures for the analysis can be found in our previously published study (Ma et al., 2014).

For quality assurance and quality control (QA/QC) purpose, isotope dilution method was adopted to improve the accuracy and precision of the MeHg analysis. Triplicate analyses were employed for each treatment. The relative standard deviations (RSD) of triplicate samples ranged from 0.7% to 5.2%, which were within the acceptable ranges of the EPA 1630 method for MeHg analysis (<15%). The method blank was approximate 0.05 ng L^{-1}, within the acceptable value of EPA 1630 method (<0.1 ng L^{-1}). The absolute method detection limit for MeHg analysis was 0.75 pg.

2.3. MeHg photodegradation in the presence of non-thiol, aromatic thiol, and nonaromatic thiol ligands

To investigate the effect of thiol and phenyl groups on MeHg photodegradation, certain amounts of various DOM analogues, including three aromatic thiols (o-thiosalicylate, o-thioaniline, and o-thiophenol), five nonaromatic thiols (cysteine, dithiothreitol, 2-mercaptoethanol, 2-mercaptoacetic acid, and 2-mercaptoethylamine), and three non-thiol ligands (o-phthalic acid, catechol, and o-phenylenediamine), were added to 10 ng L^{-1} Me^{198}Hg solution to achieve a final concentration of 1000 nmol L^{-1}, respectively. MeHg photodegradation rates under these treatments were measured using the same method described above (section 2.2). Trials for MeHg degradation by these DOM analogues in the dark and MeHg photodegradation without addition of any DOM analogues were also included as controls.

2.4. MeHg photodegradation in the presence of aromatic thiol ligands with various substituents (carboxyl, hydroxyl, and amino) at different positions (ortho, meta, and para)

To determine the influence of substituent (carboxyl, hydroxyl, and amino) on MeHg photodegradation, certain amounts of o-, m-, and p-thiosalicylate; o-thiophenol; or o-thioaniline (aromatic carboxyl, hydroxyl, and amino ligands) were added to a 10 ng L^{-1} MeHg solution to achieve a final concentration of 0.1–10000 nmol L^{-1} and 10–10000 nmol L^{-1} for o-thiosalicylate and all the other ligands, respectively. MeHg photodegradation under these treatments was measured using the same method described above (section 2.2).