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Critical role of natural organic matter in photodegradation of methylmercury in water: Molecular weight and interactive effects with other environmental factors

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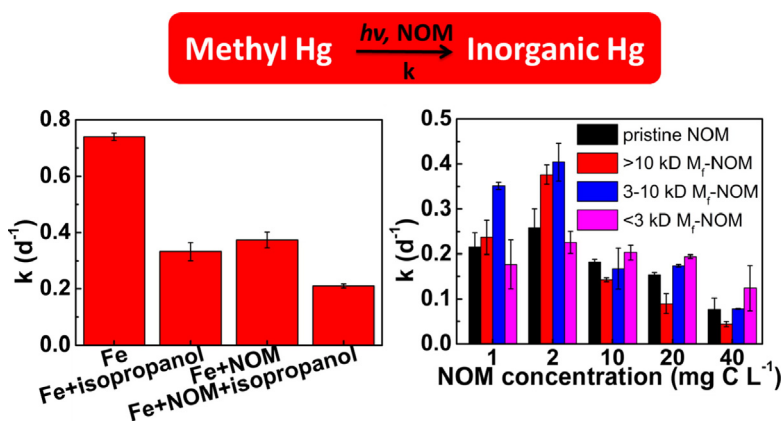
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HIGHLIGHTS

- NOM can significantly inhibit the Fe³⁺-induced degradation of MeHg.
- High molecular weight NOM shows higher light attenuation-induced degradation inhibition.
- Photodegradation-mediated by NOM is also affected by pH and co-existing Cl⁻ and NO₃⁻.

GRAPHICAL ABSTRACT



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ABSTRACT

Photodegradation is the main depletion pathway of methylmercury (MeHg) in surface water. However, the underlying mechanism of MeHg photodegradation is still not well understood. In this study, the critical role of natural organic matter (NOM) from Suwannee River natural organic matter of the International Humic Substance Society, especially its molecular weight, and the impacts of other related environmental factors in MeHg photodegradation were investigated. We observed that MeHg cannot photo-degrade in de-ionized water, excluding the direct photodegradation of MeHg. While either NOM or Fe³⁺ alone induced MeHg photodegradation, co-existing NOM significantly inhibited the Fe³⁺-induced degradation, highlighting the critical and complex role of NOM in MeHg photodegradation. Additionally, MeHg exhibited different photodegradation rates in the presence of molecular weight fractionated natural organic matter (M_f-NOM). More importantly, high concentration of NOM caused light attenuation significantly inhibited the photodegradation of MeHg, which was more significant for high molecular weight M_f-NOM. In the presence of M_f-NOM, MeHg photodegradation was also affected by light quality, pH and co-existing Cl⁻ and NO₃⁻. The study is helpful for a better understanding of the critical role of NOM and other environmental factors on MeHg photodegradation in surface water.

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1. Introduction

Methylmercury (MeHg), the most toxic mercury species, is ubiquitous in the aquatic environment (Mergler et al., 2007). It is a potent neurotoxin and easy to be accumulated and magnified in the food chains, posing a potential threat to wildlife as well as humans (Julvez et al., 2010; Morel et al., 1998). MeHg can be produced in sediment from inorganic mercury by a variety of anaerobic bacteria, especially sulfate-reducing bacteria and iron reducing bacteria (Fleming et al., 2006; Gilmour et al., 1992; Parks et al., 2013), and then released into the surface water. Toxic MeHg in the water can be degraded into less toxic inorganic mercury through biological and non-biological pathways (Whalin et al., 2007). Although the microbial degradation of MeHg occurs in sediment (Oremland et al., 1991) and water (Marvin-Dipasquale and Oremland, 1998; Schaefer et al., 2004), photodegradation is the main depletion way of MeHg from surface water (Hammerschmidt and Fitzgerald, 2006; Li et al., 2010; Sellers et al., 1996). It has been demonstrated that photodegradation can remove a large portion of MeHg in surface water (Hammerschmidt and Fitzgerald, 2006; Hines and Brezonik, 2007; Lehnher and St. Louis, 2009), resulting in the decrease in the concentration of MeHg in water. This photochemical process plays a critical role in the biogeochemical cycling of mercury in aquatic environments (Hammerschmidt and Fitzgerald, 2006; Sellers et al., 1996).

Revealing the underlying mechanism and controlling factors of MeHg photodegradation is of great importance to understand MeHg cycling and develop techniques to reduce the concentration of MeHg in aquatic environments. Although great efforts have been made in investigating MeHg photodegradation, there are still several open questions regarding this MeHg photodegradation. While some studies put forward that MeHg could be degraded in de-ionized water under sunlight (Black et al., 2012), other studies suggested MeHg cannot be photodegraded in deionized water (Hammerschmidt and Fitzgerald, 2010; Tai et al., 2014; Zhang and Hsu-Kim, 2010). An iron-mediated pathway of MeHg photochemical decomposition, involving the hydroxyl radical produced by photo-Fenton reaction, was also proposed (Hammerschmidt and Fitzgerald, 2010). However, although this iron-induced MeHg photodegradation was further demonstrated in de-ionized water (Kim and Zoh, 2013), it was observed that the addition of iron (at $10 \mu\text{mol L}^{-1}$) into natural surface waters showed negligible effect on MeHg photodegradation (Black et al., 2012). In contrast, recent studies suggested that the formation of MeHg-natural organic matter (NOM) complex may be a key step in MeHg photodegradation (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010). It should be noted that although the impact of inorganic ions (e.g. Cl^- , NO_3^- , and Fe^{3+}) (Kim and Zoh, 2013; Sun et al., 2013) on MeHg photodegradation has been investigated, most of these studies were performed in the absence of NOM. Since MeHg in surface water generally binds with NOM (Khawaja et al., 2010), the effect of co-existing ions on MeHg photodegradation should be studied in the presence of NOM. Moreover, as NOM is a polydispersed mixture with molecular weight from <100 Da to over 300 kDa (Mostofa et al., 2013), understanding the differential roles of different molecular fractions of NOM on MeHg photodegradation is also of great interesting, which unfortunately is still not well known. Our previous study showed that molecular weight fractionated natural organic matters (M_f -NOM) have differential structural and light attenuation characteristics (Yin et al., 2014). Thus, we proposed that these differences could also result in the different effects of various fractionated M_f -NOM in MeHg photodegradation.

The primary objective of this study was to assess the role of NOM and co-existing ions on MeHg photodegradation. To fulfill this aim, we investigated (i) the critical role of NOM and its effect on Fe^{3+} -induced MeHg photodegradation; (ii) the differential photodegradation of MeHg in M_f -NOM solution; and (iii) the effect of environmental factors and water constituents (i.e. light quality, pH, co-existing Cl^- and NO_3^-) on MeHg photodegradation in the presence of NOM.

2. Materials and methods

2.1. Materials

Suwannee River natural organic matter (SRNOM) obtained from the International Humic Substance Society (St. Paul, MN, USA) was used as a NOM model. Enriched $^{198}\text{HgCl}_2$ and $^{201}\text{HgCl}_2$ were purchased from Trace Sciences International (Ontario, Canada). Me^{198}Hg and Me^{201}Hg were synthesized by methylcobalamin according to our previous study (Ma et al., 2014). Amicon Ultra-15 centrifugal devices with molecular cut off 3 kDa and 10 kDa, respectively, were obtained from Millipore (Darmstadt, Germany).

Two types of films were used to evaluate the effects of light quality on the MeHg degradation. UV films from Energy-Film (Portland, OR), which can absorb UV-A and UV-B, were defined as UV-block film. Mylar films from United States Plastic Corp. (Lima, OH, USA), which can absorb UV-B, were used as UV-B-block film. The light transmissions of the films have been characterized in our previous study (Yin et al., 2014).

2.2. Preparation of SRNOM stock solution and M_f -NOM fractions

1 g L^{-1} stock solution of SRNOM was prepared in de-ionized water and shaken for 12 h at room temperature in the dark. Then the solution was filtered through $0.22 \mu\text{m}$ cellulose nitrate membrane. This filtered solution was defined as pristine SRNOM.

Ultrafiltration was used to prepare M_f -NOM with different molecular weights. The Amicon Ultra-15 centrifugal devices were initially rinsed with de-ionized water to remove glycerol. Then, add up to 15 mL of the pristine SRNOM into the 10 kDa Amicon Ultra-15 centrifugal device and centrifuged for 30 min at $6654g$ by a Sigma 3–18 K centrifuge (St. Louis, MO). The retentate was rinsed with de-ionized water and collected as $>10 \text{ kDa } M_f$ -NOM. Then the filtrate was transferred into 3 kDa Amicon Ultra-15 centrifugal device and centrifuged for 30 min at $8422g$. The retentate was collected as $3\text{--}10 \text{ kDa } M_f$ -NOM and the filtrate as $<3 \text{ kDa } M_f$ -NOM. All solutions were stored in the dark at 4°C in the refrigerator ahead of use.

2.3. Characterization of pristine and M_f -NOM

The concentrations of pristine and M_f -NOMs were analyzed by a Teledyne Tekmar total organic carbon (TOC) fusion analyzer (Mason, Ohio, USA). The molecular weight distribution of M_f -NOM fractions is shown in Fig. S1. The recovery of TOC was 88.7%. NOM loss during the fractionation was mainly ascribed to the membrane adsorption and the washing process.

The details regarding the UV-vis and fluorescence excitation-emission characterization of the pristine and M_f -NOM used in the experiment were available in the SI (Peuravuori and Pihlaja, 1997; Richard et al., 2004; Shen et al., 2015; Yin et al., 2014). These results (Fig. S2 and S3) suggested high molecular weight M_f -NOM contained more aromatic moieties, while low molecular weight M_f -NOM contained abundant carboxyl groups.

2.4. Measurement of MeHg photodegradation rate constants

The simulated sunlight was provided by a sunlight-simulator (TEMI880, Beifang Lihui, Beijing, China) equipped with three air-cooled Xe lamp (2500 W). The light intensity was set to 550 W m^{-2} and the temperature was controlled at $\sim 35^\circ\text{C}$. The experiments were performed in quartz bottles (100 mL) with quartz caps to avoid the adsorption of MeHg on the bottle surface. The total volume of the solution was 100 mL . Me^{198}Hg was spiked into quartz bottles to a final concentration of 15.0 ng L^{-1} . In previous study, it has been demonstrated that the pathway of MeHg photodegradation is controlled by MeHg/NOM ratio, but not the concentration of MeHg or NOM (Zhang and Hsu-Kim,

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