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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HIGHLIGHTS

- NOM can significantly inhibit the Fe^{3+} -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 NO_3^- .

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 Fe^{3+} alone induced MeHg photodegradation, co-existing NOM significantly inhibited the Fe^{3+} -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 NO_3^- . 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 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 3–10 kDa M_f -NOM and the filtrate as <3 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,

2010). Therefore, MeHg concentration at 15.0 ng L^{-1} was used in our study to facilitate the sampling and analysis. 10 mmol L^{-1} phosphate was used to buffer the solution. Pristine- or M_F -NOM at different concentration was added to evaluate the role of NOM in the photodegradation of MeHg. Duplicate samples were prepared for each experiment. 5 mL solution was taken from each bottle after 0, 1, 2, 3, 4, 5 days of incubation. Isotope dilution technique based on aqueous ethylation and purge-and-trap pre-concentration followed by gas chromatography-inductively coupled plasma mass spectroscopy was applied in analysis of MeHg, and detailed instrumentation and procedure could be referred to our previous study (Ma et al., 2014). A model based on first-order chemical kinetics was used to describe the photodegradation of MeHg in the water (Eq. (1)) (Li et al., 2010; Tai et al., 2014). After integration of Eq. (1), $\ln(C_{\text{MeHg}})_t$ was simulated by $\ln(C_{\text{MeHg}})_0$, as described in Eq. (2). The rate constant of MeHg degradation, k , was then obtained by linear regression of $\ln(C_{\text{MeHg}})_t$ on t .

$$\frac{dC_{\text{MeHg}}}{dt} = -k \times C_{\text{MeHg}} \quad (1)$$

$$\ln(C_{\text{MeHg}})_t = \ln(C_{\text{MeHg}})_0 - k \times t \quad (2)$$

where C_{MeHg} is the concentration of MeHg (ng L^{-1}); k is the rate constant of MeHg photodegradation (d^{-1}), t is the incubation time (d).

2.5. Evaluation of light attenuation effect

The light attenuation effect from NOM was evaluated by using monochromatic irradiation (366 nm) provided with a mercury lamp (100 W) on the rotation reactor (XPA, Xujiang Electromechanics, Nanjing, China). The experiments were performed in 50 mL quartz glass tubes with quartz caps (50 mL, 2.2 cm diameter). The corrected MeHg photodegradation rate constant, $k_{\lambda, \text{corrected}}$ in the presence of pristine and M_F -NOM, was calculated following Eq. (3) (Yin et al., 2014),

$$k_{\lambda, \text{corrected}} = \frac{k_{\lambda}}{S_{\lambda}} = (2.303k_{\lambda}\alpha_{\lambda}l) / (1 - 10^{-\alpha_{\lambda}l}) \quad (3)$$

where k_{λ} is the degradation rate constant calculated from Eq. (2), S_{λ} is the light attenuation factor, α_{λ} is the decadic absorption coefficient of the solution at 366 nm, and l is the light path length of the reaction cell (2.2 cm). Detailed calculation of these parameters was given in our previous study (Yin et al., 2014).

2.6. Effects of light quality, pH, and other co-existing ions on MeHg degradation

Previous studies have demonstrated light quality has great impacts on MeHg photodegradation (Fernandez-Gomez et al., 2013; Lehnher and St. Louis, 2009; Li et al., 2010). To evaluate the effect of light quality in simulated sunlight on MeHg degradation, the quartz bottles were wrapped with UV-B-block film (UV-A + Vis), UV-block film (Vis) and without film (full radiation), respectively. Natural environment waters have different water chemistry such as different pH ranges (5 to 9; Zepp et al., 1992) and different concentration of Fe^{3+} (1.2 to $16.8 \mu\text{mol L}^{-1}$; Lofts et al., 2008), Cl^{-} (up to 0.5 mol L^{-1} ; Chen et al., 2003), NO_3^{-} (10^{-5} to $10^{-3} \text{ mol L}^{-1}$; Shankar et al., 2007), which could directly or indirectly influence MeHg photodegradation. To evaluate the influence of pH on MeHg photodegradation, the pH of the solution was adjusted to 5.0, 6.0, 7.0, 8.0, and 9.0, respectively, by using 10 mmol L^{-1} phosphate buffer. The effect of co-existing ions on MeHg photodegradation, including Cl^{-} (0 – 800 mmol L^{-1}), NO_3^{-} (0 – 2 mmol L^{-1}), and Fe^{3+} ($2 \mu\text{mol L}^{-1}$), was also investigated at pH 6.0 in the presence of 2.0 mg C L^{-1} pristine or M_F -NOM.

3. Results and discussion

3.1. Critical and complex role of NOM in MeHg photodegradation

Firstly, the possible direct photodegradation of MeHg in de-ionized water was investigated under simulated sunlight. Results (Fig. S4) showed that, under light radiation, the degradation of MeHg in de-ionized water was negligible, excluding the direct photodegradation pathway of MeHg. Most previous studies also proposed MeHg cannot be degraded in de-ionized water under the wavelength of the solar spectrum (Qian et al., 2014; Zhang and Hsu-Kim, 2010). However, a study suggested the photo-degradation of MeHg at relatively high rates in high purity water with no trace metals or NOM (Black et al., 2012). These different results could possibly be derived from the different adsorption of MeHg on the vessel materials (borosilicate/quartz vs. Teflon). The observed high “photodegradation” of MeHg in de-ionized water could possibly be ascribed to the adsorption of mercury on the coarse Teflon surface (Rong et al., 2001) in the absence of ligands (e.g. NOM, Cl^{-}), but not to real photodegradation.

Considering the “controversial” observation of Fe^{3+} and NOM on MeHg photodegradation, their effects on indirect photodegradation of MeHg were then investigated respectively. Fe^{3+} widely exists in the surface water, with a concentration ranging from 1.2 to $16.8 \mu\text{mol L}^{-1}$ (Lofts et al., 2008). In previous study, Hammerschmidt and Fitzgerald (2010) revealed that hydroxyl radical produced by Fe^{3+} -mediated photo-Fenton reaction was the main pathway of MeHg decomposition in an arctic Alaskan lake. This Fe^{3+} -accelerated MeHg decomposition (up to 7.5 times) was further demonstrated under UVA light (365 nm) by Kim and Zoh (2013). However, in another study, Black et al. observed that the addition of $10 \mu\text{mol L}^{-1} \text{Fe}^{3+}$ into surface waters from wetland field resulted in an 11% decrease of MeHg decomposition (Black et al., 2012). Therefore, the role of Fe^{3+} in MeHg photodegradation, especially in the presence of NOM, needs to be clarified further. As shown in Fig. 1, the addition of $2 \mu\text{mol L}^{-1} \text{Fe}^{3+}$ in the absence of NOM significantly induced MeHg photodegradation. The MeHg degradation was not observed in the presence of Fe^{3+} under dark conditions, suggesting a synergistic effect of Fe^{3+} and light. The fact of non-degradation of MeHg under dark conditions also indicated that the photodegradation in the presence of Fe^{3+} was not from an artifact of adsorption of MeHg on the iron colloids. Similarly, under dark conditions, degradation of MeHg was not evident in the presence of NOM (Fig. S4). However, in the presence of both NOM and simulated light, significant degradation of MeHg was observed. This was consistent with previous studies, which demonstrated that the formation of MeHg-NOM complex was a key step in the MeHg photodegradation (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010). Theoretically, the singlet-triplet excitation energies of MeHg-OH and MeHg-Cl are too high to undergo

Fig. 1. Effect of Fe^{3+} and NOM on MeHg photodegradation rate under simulated sunlight. Conditions: 10 mmol L^{-1} phosphate buffer (pH 6.0), $2 \mu\text{mol L}^{-1} \text{Fe}^{3+}$ or 2.0 mg C L^{-1} NOM. The concentration of isopropanol was 100 mmol L^{-1} .

degradation under the solar spectrum (Tai et al., 2014). However, as a soft Lewis base, thiol in NOM can form a strong bond with MeHg, which can weaken the C–Hg bond and subsequently facilitate the degradation of MeHg (Melnick and Parkin, 2007; Ni et al., 2006; Tossell, 1998).

Fig. 1 also showed that the addition of hydroxyl radical scavenger, isopropanol, significantly decreased the photodegradation of MeHg induced by Fe^{3+} , supporting the mechanism of hydroxyl radical-involved photo-Fenton reaction (Hammerschmidt and Fitzgerald, 2010). In addition, the MeHg photodegradation induced by Fe^{3+} significantly decreased in the presence of co-existing NOM, which could be ascribed to the depletion of hydroxyl radical by NOM (Vione et al., 2006; Westerhoff et al., 1999). This hypothesis was further validated by further adding isopropanol into the Fe^{3+} -NOM solution. The depletion of hydroxyl radical by isopropanol decreased the photodegradation of MeHg, and the resulting photodegradation rate ($0.210 \pm 0.007 \text{ d}^{-1}$) is comparable with that in the presence of NOM only ($0.205 \pm 0.006 \text{ d}^{-1}$). The inhibition of Fe^{3+} -induced photodegradation by NOM indicated that the underlying mechanism of NOM-induced MeHg photodegradation might be much different with that of Fe^{3+} . These results also suggested that although Fe^{3+} -produced hydroxyl radical can induce the degradation of MeHg, the catalytic role of Fe^{3+} in natural water could be inhibited by the ubiquitous NOM. As the concentrations of Fe^{3+} and NOM in natural waters varies in different ecosystems (Hudson et al., 2007; Loftis et al., 2008), the relative importance of Fe^{3+} and NOM in the photodegradation of MeHg may be different among various natural ecosystems.

3.2. Effects of pristine- and M_f -NOM on MeHg photodegradation

We further studied the effect of concentration of pristine- and M_f -NOM on the photodegradation of MeHg. As shown in Fig. 2a, the degradation rate of MeHg increased from 0.21 to 0.26 d^{-1} when NOM concentration increased from 1 to 2 mg C L^{-1} . However, further increase of NOM concentration significantly decreased the photodegradation of MeHg. This NOM-concentration dependent MeHg photodegradation should stem from a combined effect of NOM-concentration dependent formation of NOM-MeHg complex and light attenuation. It was reported that the formation MeHg-NOM complex is critical for MeHg photodegradation (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010). It is reasonable that with the increase of NOM concentration, the fraction of MeHg as NOM-MeHg complex increased accordingly, which could increase the photodegradation of MeHg. Similar enhanced MeHg photodegradation with the increase of NOM concentration was also observed in other studies by using NOM model other than SRNOM (Qian et al., 2014; Zhang and Hsu-Kim, 2010). However, the increase of NOM concentration also enhances the light attenuation, which potentially inhibits the degradation of MeHg (Li et al., 2010).

Different degradation rates were observed for MeHg in various M_f -NOM solutions, as shown in Fig. 2a, which should be attributed to the difference of M_f -NOM in structure and optical characteristics. Interestingly, differential M_f -NOM concentration dependent MeHg photodegradation was also observed. As shown in Fig. 2a, the light attenuation-induced inhibition of MeHg photodegradation was more significant for high molecular weight M_f -NOM in comparison with their low molecular weight counterpart, due to the higher absorbance in UV–vis region by high molecular weight M_f -NOM. For example, at 2 mg C L^{-1} concentration level of NOM, the degradation rate of MeHg in $>10 \text{ kDa}$ M_f -NOM solution was significantly higher ($p < 0.05$) than that in $<3 \text{ kDa}$ M_f -NOM solution, while at 40 mg C L^{-1} concentration level of NOM, the degradation rate of MeHg in $>10 \text{ kDa}$ M_f -NOM solution was quite similar to that in $<3 \text{ kDa}$ M_f -NOM solution. The effect of light attenuation on MeHg photodegradation was further evaluated by using a monochromatic radiation (366 nm) in pristine- and M_f -NOM. As shown in Fig. 2b, the corrected degradation rates of MeHg ($k_{\lambda, \text{corrected}}$) were comparable with that uncorrected in 2 mg C L^{-1} NOM solution, suggesting the impact of light attenuation on MeHg photodegradation is not significant at low NOM concentration. However, as shown in Fig. 2c, in NOM solution at 40 mg C L^{-1} , the corrected degradation rates of MeHg in the presence of M_f -NOM increased significantly and were quite similar with that in low concentration NOM solution. This result demonstrated that the lower apparent degradation rates (k_{λ}) in higher molecular weight M_f -NOM solutions at high NOM concentration were mainly ascribed to their stronger light attenuation effect than that of the lower molecular weight counterparts.

As light attenuation in water was primarily determined by NOM concentration (Donahue et al., 2003; Huovinen et al., 2003), the concentration of NOM should be one of the key factors controlling the photodegradation of MeHg in natural waters (Li et al., 2010). Our study further reveals that, in addition to NOM concentration, the NOM composition or molecular weight distribution also plays a critical role in the photodegradation of MeHg. As environmental waters from different origins could have different molecular weight distributions, the photodegradation of MeHg in these surface waters may be also site-specific, especially at high NOM concentration.

3.3. Effects of light quality on MeHg photodegradation

Effects of simulated light quality on MeHg photodegradation in pristine NOM and different M_f -NOM were quite similar, which were given in Fig. 3. Compared with that under full simulated sunlight, no significant MeHg degradation in NOM solutions ($K_d < 0.035 \text{ d}^{-1}$) was observed for that exposed under UV-block film, which indicated that the visible light in the simulated light played a minor role in the degradation of MeHg. This result also suggested that UV fraction in simulated sunlight played a major role (contribution $>83\%$) in the degradation. Meanwhile, significant degradation of MeHg still could be observed in

Fig. 2. Effect of pristine- and M_f -NOM concentration on MeHg photodegradation. (a), MeHg photodegradation rate with various concentrations of pristine- and M_f -NOM under simulated sunlight; (b and c) the apparent and corrected degradation rates of MeHg under monochromatic radiation (366 nm) in NOM solution at 2 mg C L^{-1} and 40 mg C L^{-1} concentration levels, respectively. Conditions: 10 mmol L^{-1} phosphate buffer (pH 7.4).

Fig. 3. Effects of light quality on MeHg photodegradation in the presence of pristine or Mf-NOM under simulated sunlight. Conditions: 10 mmol L⁻¹ phosphate buffer (pH 7.4), 2 mg C L⁻¹ pristine or Mf-NOM.

solutions exposed under UV-B-block film, suggesting that UV-A fraction played a critical role (average contribution ~73.3%) in MeHg photodegradation in our experimental settings. The contribution of UV-A fraction in MeHg photodegradation in our simulated sunlight was comparable with previous study under natural sunlight (~85%) (Li et al., 2010), although different light sources were used.

3.4. Influence of pH on MeHg photodegradation

The influence of pH (5.0–9.0) on MeHg photodegradation in de-ionized water was firstly investigated (Fig. S5). The results suggested that at all investigated pH the photodegradation of MeHg was negligible in de-ionized water. The effect of pH on MeHg photodegradation was further investigated in the presence of pristine- and Mf-NOM. As shown in Fig. S6, the pH had no significant effect on the degradation rate of MeHg at pH from 5.0–7.0. However, a decrease ($p < 0.05$ for pristine NOM and <3 kDa Mf-NOM, $p < 0.1$ for >10 kDa Mf-NOM) at pH 8.0 and then an increase ($p < 0.05$ for pristine NOM and all Mf-NOM) of degradation rate at pH 9.0 were observed. The influence of pH on the photodegradation of MeHg seemed complicated. On one hand, the influence of pH on MeHg photodegradation was mainly due to the coordination balance of NOM-MeHg complexes. Higher pH could promote the dissociation of thiol in NOM (Karlsson and Skjellberg, 2003) and NOM-MeHg complexes formation (Amirbahman et al., 2002), which could accelerate the subsequent MeHg photodegradation. On the other hand, lower pH could increase the photobleaching of NOM (Anesio and Granéli, 2003), which could then enhance the degradation of MeHg due to the increased light penetration (Tai et al., 2014) and concurrent photolytic degradation of NOM with MeHg (Fleck et al., 2014).

3.5. MeHg photodegradation in the presence of Cl⁻

Chloride ions widely exist in surface water at various concentrations (up to 0.5 mol L⁻¹). In our study, in the presence of 2 mg C L⁻¹ pristine- or Mf-NOM, the effect of Cl⁻ (0–800 mmol L⁻¹) on photodegradation of MeHg was investigated. As shown in Fig. 4, the degradation rates of MeHg increased with NaCl concentration up to 10 mmol L⁻¹. However, further increasing the concentration of NaCl from 100 to 800 mmol L⁻¹ significantly decreased the degradation rates of MeHg. The enhancement of MeHg photodegradation by Cl⁻ is probably a consequence of the photo-generated chlorine radicals-induced degradation of MeHg (Chen et al., 2003). In addition, the increasing ionic strength could also increase the absorbance of NOM (Gao et al., 2015), which could subsequently enhance the NOM-mediated MeHg photodegradation. However, with the further increase of Cl⁻ concentration, the fraction of MeHg complexed with NOM would decrease accompanying with the increasing fraction of MeHg as MeHgCl (Zhang and Hsu-Kim, 2010). As the direct photodegradation of MeHgCl (Tossell, 1998) was theoretically impossible under solar radiation or simulated light under our

Fig. 4. Effect of Cl⁻ on MeHg photodegradation in the presence of pristine or Mf-NOM under simulated sunlight. Conditions: 10 mmol L⁻¹ phosphate buffer (pH 7.4), 2 mg C L⁻¹ pristine or Mf-NOM.

experimental setting, high concentration of Cl⁻ is expected to inhibit the photodegradation of MeHg. Since the composition and structural characteristics of NOM varies in different ecosystems, the competitive binding behavior of Cl⁻ and NOM from different sources with MeHg might be different, possibly resulting in different degradation behaviors of MeHg in Cl⁻ and NOM-co-existing surface waters. For example, the minor influence of Cl⁻ on the photodegradation of MeHg in Florida Everglades water (Tai et al., 2014) could be ascribed to its higher abundance of reduced thiol in NOM, which can strengthen the binding of NOM with MeHg.

3.6. MeHg photodegradation in the presence of NO₃⁻

Previous studies have demonstrated that sunlight irradiation of NO₃⁻ can generate hydroxyl radicals (Shankar et al., 2007; Vaughan and Blough, 1998; Zepp et al., 1987), which can decompose MeHg (Chen et al., 2003; Gårdfeldt et al., 2001). The ubiquitous NO₃⁻ could also play a potential role in the photodegradation of MeHg through a hydroxyl radicals-involved decomposition of MeHgCl (Chen et al., 2003). However, the role of NO₃⁻ in MeHg photodegradation in the presence of NOM is still not known. As shown in Fig. 5, in 2 mg C L⁻¹ pristine- or Mf-NOM solutions (except for the 3–10 kDa Mf-NOM), the photodegradation rate of MeHg increased with the NO₃⁻ concentration up to 0.1 mmol L⁻¹, and then decreased with the further increase of NO₃⁻ concentration. This NO₃⁻-enhanced MeHg photodegradation could be ascribed to NO₃⁻-produced hydroxyl radicals (Mack and Bolton, 1999). However, the further increase of NO₃⁻ concentration also increases the accumulation of its photolysis product, NO₂⁻, which has strong light absorption at UV-A region (Vione et al., 2014). The accumulation of high concentration of NO₂⁻ could increase the light

Fig. 5. Effect of NO₃⁻ on MeHg photodegradation in the presence of pristine or Mf-NOM under simulated sunlight. Conditions: 10 mmol L⁻¹ phosphate buffer (pH 7.4), 2 mg C L⁻¹ pristine or Mf-NOM.

attenuation in the solution, which further inhibits the photodegradation of MeHg (Li et al., 2010). The almost constant photodegradation rate of MeHg at various concentration of NO_3^- in the presence of >10 kDa M_F -NOM could also ascribed to the strong light attenuation of high molecular weight NOM.

4. Conclusions

In this study, we investigated the effects of environmental factors on MeHg photodegradation. These factors included pristine- and M_F -NOM concentrations, light quality, pH, and co-existing Cl^- , NO_3^- , and Fe^{3+} under simulated sunlight. Our results demonstrated Fe^{3+} -mediated photo-Fenton reaction can induce MeHg photodegradation (Hammerschmidt and Fitzgerald, 2010), however, the co-existing NOM can partially inhibit the Fe^{3+} -induced MeHg degradation. The NOM-induced MeHg photodegradation was affected by its structure characteristics, complexation with MeHg (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010) and light attenuation (Fernandez-Gomez et al., 2013; Li et al., 2010). This light attenuation-induced degradation inhibition was more significant for high molecular weight M_F -NOM. Photodegradation-mediated by NOM is also directly or indirectly affected by pH and co-existing Cl^- and NO_3^- . The Cl^- and NO_3^- -enhanced MeHg photodegradation in the presence of NOM suggested multiple reaction pathways may be involved in MeHg photodegradation (Black et al., 2012), while photodegradation inhibition at high concentration of Cl^- demonstrated the importance of NOM-MeHg complexation in MeHg photodegradation (Qian et al., 2014; Tai et al., 2014; Zhang and Hsu-Kim, 2010). Considering the different water chemistry (concentration and composition of NOM, pH, co-existing Fe^{3+} , Cl^- , and NO_3^-) in surface waters from different sites, the photodegradation of MeHg in these surface waters should also be highly site-specific and multiple reaction pathways may be involved.

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Appendix A. Supplementary data

The supporting information includes a summary of the characterization of pristine and M_F -NOM, the molecular weight distribution of M_F -NOM fraction in SRNOM, UV-vis and fluorescence excitation-emission spectra of pristine- and M_F -NOM, MeHg degradation in deionized water under simulated sunlight or in NOM solution under dark, the effect of pH on MeHg photodegradation in deionized water or pristine/ M_F -NOM solution. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.scitotenv.2016.10.222>.

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