



The production of dissolved gaseous mercury from methylmercury photodegradation at different salinity

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ABSTRACT

Photodegradation of methylmercury (MeHg) is an important process in mercury cycling that maintains low concentrations of MeHg in freshwater lakes; however, less is known about importance of this process in marine waters. The photo-induced formation of dissolved gaseous mercury (DGM, Hg^0) from MeHg removal was investigated. This study examined the effect of various environmental factors (i.e. light wavelength and intensity, and MeHg concentration), and primary water constituents on the abiotic photodegradation of MeHg, especially under different salinity. MeHg photodegradation rates were positively correlated with the UV light intensity, implying that the attenuation of UV radiation had a significant effect on MeHg photodegradation. However, a high dissolved organic matters concentration and salinity inhibited MeHg photodegradation. DGM was always produced during the photodegradation of MeHg. Photodegradation rates of MeHg and DGM production decreased with increasing salinity, suggesting that the presence of chloride ions inhibited MeHg photodegradation. Therefore, this study implies that MeHg in freshwater could be more rapidly demethylated than that in seawater. In other words, MeHg flowing into the lake or river would be almost removed by photo demethylation. However, MeHg flowing to seawater would be hardly removed, which could have more chance for bioaccumulation in seawater.

Keywords: Methylmercury; Dissolved gaseous mercury; Photodegradation; Salinity

1. Introduction

The pollution of water with mercury and its compounds has received much attention due to the high toxicity of these species and their tendency to bioaccumulate, even at very low concentrations. Methylmercury (MeHg) is the form of mercury that generates most concern because it is readily biomagnified in aquatic food chains and can reach levels harmful to both humans and wildlife [1,2]. MeHg generally

accounts for >90% of the mercury found in most fish [3], and its biomagnification to harmful levels has resulted in fish consumption advisories throughout the US, Canada, and Europe [4]. The levels of MeHg in natural water bodies are influenced by both biological and photochemical processes. Although MeHg decomposition can be microbially mediated in water, many researchers have identified photodegradation as another important removal mechanism for MeHg degradation in freshwater lakes, thus, resulting

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in the reduced bioavailability of MeHg for accumulation through aquatic food webs [5–8].

Recent studies have reported that environmental factors, such as the intensity of solar radiation, water constituents (e.g. dissolved organic matters (DOM) and specific ions), are significant variables affecting abiotic MeHg degradation [9–12]. Sellers et al. [8] found that the MeHg concentration decreased in sunlight, but not in dark conditions. They also found that MeHg photodegradation followed first-order kinetics with respect to the MeHg concentration and light intensity. They further found that MeHg photodegradation rates decreased exponentially with depth below a lake surface due to the decrease in sunlight intensity. Benoit et al. [13] observed that the conditions that most favored photodegradation were oligotrophic freshwater with a low pH and DOM content. Naturally occurring constituents of surface waters such as nitrate (NO_3^-), ferric iron (Fe^{3+}), and bicarbonate (HCO_3^-) ions can also participate in the photodecomposition of MeHg [14–16]. Nitrate and ferric ions are known to produce OH radicals in water when excited by solar UV radiation. However, the bicarbonate ion does not absorb solar UV radiation, and is known to act as a scavenger of the OH radical [14,17,18]. DOM is ubiquitous in the aquatic environment and can also interact with mercury, affecting its speciation, solubility, mobility, and toxicity [15,19–23]. However, the effects of these parameters on the photodegradation of MeHg in the seawater environment are not fully understood, and relatively little research has been conducted on the fate and stability of MeHg in seawater. In fact, seawater could be potentially more important than other water sources as both a sink and source of MeHg because of its large global volume.

Dissolved gaseous mercury (DGM, Hg^0) is a major volatile species of mercury that is released from natural surface waters. DGM production in natural surface water is mediated by solar radiation and can be affected by other abiotic factors [24]. Although DGM can be released by the decomposition of MeHg, no studies have been published which have investigated the degradation of MeHg to DGM. Only studies investigating DGM production by the reduction of divalent inorganic mercury (Hg^{2+}) are available [24–27].

In this study, we investigated the effect of environment factors (i.e. light intensity and wavelength, salinity, and initial MeHg concentration), and primary water constituents (i.e. DOM, nitrate and bicarbonate ions) on the photo-degradation of MeHg under different salinity. We measured the production of DGM during MeHg photo-degradation, and investigated the photo-degradation kinetics of MeHg to determine the underlying mechanism.

2. Materials and methods

2.1. Sampling and materials

Seawater samples were collected from the Yellow Sea, located at latitude 37°N , and longitude 126°E . After filtering through a $0.45\text{-}\mu\text{m}$ nitrocellulose filter (Adventec, Tokyo, Japan), the samples were stored in the dark at 4°C until required for experiments. For the different salinity experiments, the seawater samples were diluted with deionized water by serial dilution. Nitrate (NO_3^-) stock solution was prepared with reagent grade KNO_3 . Standard Suwanee River humic acid was used to investigate the role of DOM in the photodecomposition of MeHg. Stock solutions of humic acid were prepared with deionized water and then filtered through a $0.45\text{-}\mu\text{m}$ nitrocellulose filter. A standard solution of MeHg ($1,000\text{ }\mu\text{g mL}^{-1}$) was diluted to make a MeHg stock solution (1 ng mL^{-1}). The initial concentration of MeHg was fixed at 20 ng L^{-1} by diluting the stock solution; this was kept constant throughout all experiments.

2.2. Photo reactor and experimental design

Fig. 1 is a schematic diagram of the photo reactor (Fig. 1). The PTEF bottles were placed inside a box-type photo reactor and irradiated for 180 min. The reactor was equipped with five UV lamps. UV

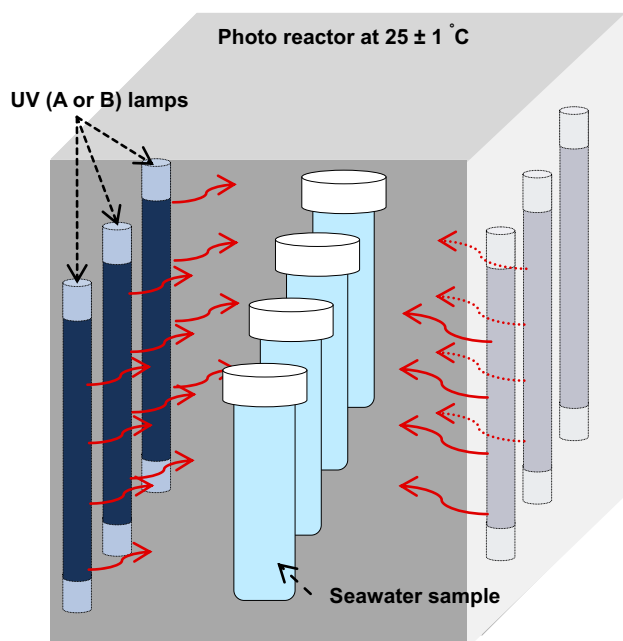


Fig. 1. A schematic diagram of the experimental design used to investigate the photochemical decomposition of MeHg.

intensity was controlled by the number of lamps used. The solutions were shaken after the addition of MeHg (20 ng L^{-1}) and natural water constituents, then immediately transferred into PTEF bottles (250 mL each) to leave no headspace inside. During the reaction, one bottle was removed every 30 min to determine MeHg and DGM concentrations. To provide dark conditions, PTEF bottles were covered with aluminum foil. The temperature of the reactor was maintained at $24\text{--}26^\circ\text{C}$ for the entire incubation.

2.3. Analytical methods

For the determination of MeHg, the samples were analyzed immediately before the digestion process commenced. A series of preliminary experiments indicated that no significant differences were observed in the MeHg concentration of samples analyzed both before and after distillation ($n=20$, paired t -test, $p < 0.05$). Therefore, the samples used for MeHg analysis were taken from the reactor at different reaction times, and were filtered through a nitrocellulose Millipore membrane (2.5 cm, $0.2 \mu\text{m}$). Filtered samples were transferred to a 125-mL purging vessel, adjusted to pH 4.9 with 2-M acetate buffer, then ethylated by the addition of sodium tetraethyl borate (NaBEt_4) in the closed vessel. After 15 min, ethylated Hg complexes were separated from solution by purging with nitrogen gas for 15 min and then trapped on Tenax. Trapped Hg complexes were carried through a gas chromatography column for separation, converted to Hg^0 via a pyrolytic column, and detected using cold vapor atomic fluorescence spectrometry (CVAFS).

DGM was measured using a mercury vapor analyzer (2537A: Tekran Instruments, Canada) connected to an automated purging system. This is a slightly modified version of the method described in Lindberg et al. [28]. The DGM was displaced by bubbling with zero-air gas and passed through the reaction bottle into the mercury vapor analyzer after humidity was removed from the solution by a soda-lime trap to protect the instrument. The DGM that entered the mercury vapor analyzer was adsorbed on a gold trap cartridge, and then thermally desorbed from the cartridge by a resistive heater. The response of the CVAFS detector was then integrated to provide a quantitative measure of the amount of DGM desorbed from the gold trap.

The intensity of the UVA ($\lambda = 365 \text{ nm}$) and UVB ($\lambda = 312 \text{ nm}$) regions in the photo reactor were measured regularly before the start of each experiment using a radiometer (VLX-3W: Cole-Parmer, Vernon Hills, IL).

The concentration of DOM was determined using a total organic carbon analyzer (TOC-VCPH: Shimadzu, Kyoto, Japan). The pH of water was measured using 415 CP pH/ISE/conductivity meter.

Results of replicated experiments were expressed as the mean values \pm standard deviation. We performed linear regression analysis using the SAS system for Microsoft Windows (version 9.1.3).

3. Results and discussion

3.1. Effect of UV light wavelength and intensity on MeHg degradation

Initially a blank test was conducted. In dark conditions, MeHg removal from a seawater sample was less than 5% within a 2 h period (data not shown). In contrast, exposure to UV radiation significantly enhanced MeHg photodegradation (Fig. 2). MeHg photodegradation in seawater was dependent on the source of the light (UVA or UVB), and intensity. Increasing the UV intensity resulted in an increase in the MeHg photodegradation rate (Fig. 2). MeHg photodegradation in seawater followed pseudo-first-order kinetics. A plot of $\ln(C_t/C_0)$ vs. reaction time (min) with changing UV radiation intensity produced a straight line with a correlation coefficient (R^2) greater than 0.98. This indicates that the direct photodecomposition of MeHg occurred following exposure to UV radiation, which is consistent with other recent reports [5–7,21]. There was a positive linear relationship between the MeHg photodegradation rate and UV radiation intensity at each UV wavelength (Fig. 3). UVB was more effective than UVA for MeHg photodecomposition. This may be because UVB radiation has a shorter wavelength and higher energy. The increase in the photodegradation rate constant with increasing UV radiation intensity implies that the photodegradation of MeHg in seawater is likely to decrease with water depth as a consequence of light attenuation.

Fig. 4 shows the variation in MeHg photodegradation at different initial MeHg concentrations (from 10 to 40 ng L^{-1}). Under UVA irradiation, the rate constant was 0.258, 0.162, and 0.096 h^{-1} at initial MeHg concentrations of 10, 20, and 40 ng L^{-1} , respectively. The rate constants also ranged from 0.276 to 0.114 h^{-1} under UVB irradiation across a range of initial MeHg concentrations. Increasing initial MeHg concentration led to a decrease in the rate constant. The lower photodegradation rates at higher MeHg concentrations were probably due to the competition for the photon flux between the increased number of MeHg molecules, and/or the MeHg photodegradation intermediates.

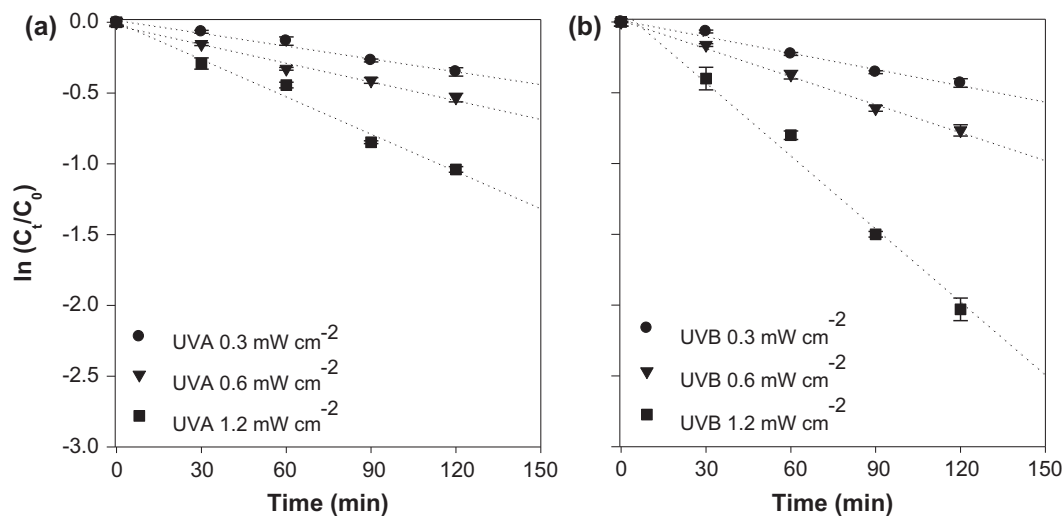


Fig. 2. Photodegradation kinetics of MeHg at pH 8.3, salinity = 30 ppt (parts per thousand), and $[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$, under (a) UVA and (b) UVB. Error bars represent the standard deviations of experiments performed in triplicate.

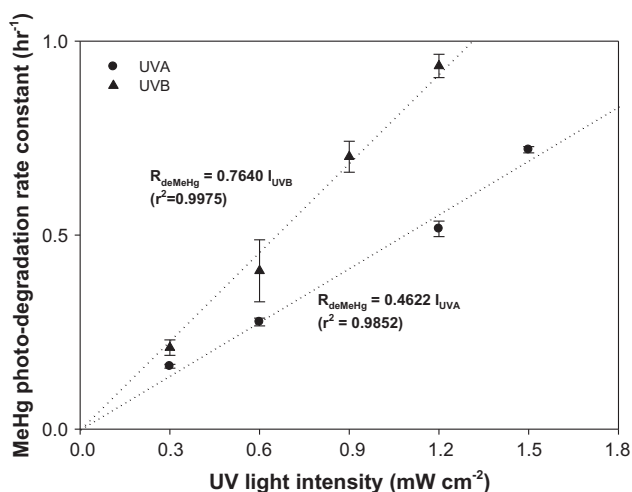


Fig. 3. Photodegradation rate constants as a function of different UV intensities. Error bars represent the standard deviations of experiments performed in triplicate.

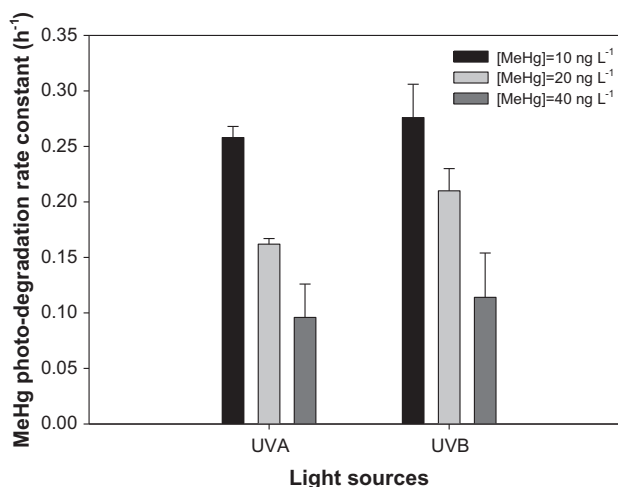


Fig. 4. The effect of the MeHg concentration on the rate of photodegradation under UVA and UVB at pH 8.3 and salinity = 30 ppt. Error bars represent the standard deviations of experiments performed in triplicate.

3.2. Effect of salinity on MeHg degradation

The first-order rate constants of MeHg photodegradation were calculated at different salinities (Table 1). The photodegradation rate decreased from 26.4 to 37.2% as salinity increased from 7.5 to 30 ppt, respectively. The decrease in photodegradation rates with increasing salinity agreed with recent reports [9,12,29,30], showing that photodegradation rates in water samples decreased with increasing chloride ion concentration.

Sun et al. [29] showed that the presence of high concentrations of chloride prevented MeHg chloride (CH_3HgCl) complexes from being readily converted into other mercury species. Their study revealed that, as the chloride ion concentration in water samples decreased, MeHg speciated gradually into CH_3HgOH . The strength of the Cl–Hg bond in CH_3HgCl is much greater than the strength of the Hg–OH bond in CH_3HgOH because of the strong complexation capacity of the chloride ion. Thus, the rate of MeHg

Table 1

The effect of salinity on the rate of MeHg photodegradation under UVA at $[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$

Salinity (ppt)	Rate constant (h^{-1}) \pm SD ^a	r^2
0.0	0.660 ± 0.005	0.987
7.5	0.486 ± 0.020	0.996
15.0	0.360 ± 0.080	0.984
22.5	0.258 ± 0.040	0.924
30.0	0.162 ± 0.030	0.947

Note: r^2 is the coefficient of determination.

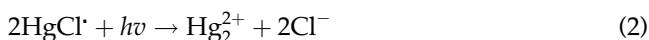
^aSD is the standard deviation of the average rate constant from experiments performed in triplicate.

photodegradation is considerably lower at high salinity than at low salinity. Zhang and Hsu-Kim [12] also reported that the chloride ion concentration has a significant effect on MeHg degradation. They suggested that CH_3HgCl complexes which are the main species of MeHg in coastal marine waters are less susceptible to photolytic decomposition at higher salinity. This also agrees with the results of a study by Black et al. [9]. These findings imply that salinity is an important parameter that affects various MeHg species and modulates the various photodegradation mechanisms and pathways.

3.3. DGM production during MeHg photodegradation

The photodegradation of MeHg in water is a key stage in the biogeochemical cycling of mercury in the environment. Many studies have investigated the photodegradation of MeHg in water systems, but few have considered the importance of the DGM flux resulting from MeHg photodegradation and the fate of inorganic mercury species from MeHg photodegradation. Therefore, we measured DGM which can be released from MeHg photodegradation in seawater under UV irradiation.

DGM can be produced from the photolysis of MeHg [29], as shown in Eqs. ((1)–(4));

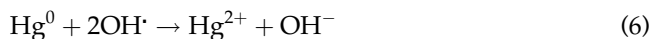
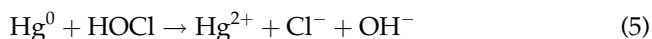


These equations imply that DGM can be generated from MeHg photodegradation, and therefore, it is an

important mercury species to study and understand the mechanism of MeHg photodegradation in seawater better.

Fig. 5 shows DGM production from MeHg photodegradation under UVA and UVB irradiation in seawater samples. As shown in Fig. 5, DGM was produced from the photolysis of MeHg. The total DGM production under UVB irradiation was higher than under UVA irradiation, which might be due to the shorter wavelength and higher energy of UVB radiation than UVA. Some recent studies have reported that reduced inorganic mercury and DGM emissions at the air/water interface were significantly and positively associated with solar radiation [31–33].

The trend of DGM production according to reaction time varied (Fig. 5). DGM production increased due to MeHg photodegradation from the initial reaction time to 60 or 90 min, while DGM production decreased after 90 min. This phenomenon is may be due to the re-oxidation of DGM by chlorine or the OH radical [34–36], as shown in Eqs. (5) and (6);



Therefore, we estimated the concentration of Hg^{2+} ion during reaction, and the result is shown in Fig. 6. In this study, total mercury analyzed included MeHg, DGM (Hg^0), and other species. We can easily consider Hg^{2+} ion as a main species for other species. As shown in Fig. 6, the portion of other species which is a mainly Hg^{2+} ion kept increasing during the reaction.

From these results, we suggest that DGM is produced by the photoreduction of MeHg and can also be rapidly oxidized in seawater. In seawater (pH 7.4–8.1), less than 50% of the chlorine is available as fast acting hypochlorous acid (HOCl). Previous studies have reported that the DGM oxidation rate increases in the presence of chloride ions [35,37].

3.4. Effect of salinity on DGM production in the presence of nitrate and bicarbonate ions

We then investigated the effect of salinity on DGM production through the photodegradation of MeHg. The results are shown in Table 2. DGM production decreased with increasing salinity, likely due to the salinity inhibiting the photoreaction of MeHg through a strong affinity between mercury and chloride. In addition, we assessed the effect of salinity in the presence of nitrate and bicarbonate ions on DGM production. Although seawater contains more dissolved ions

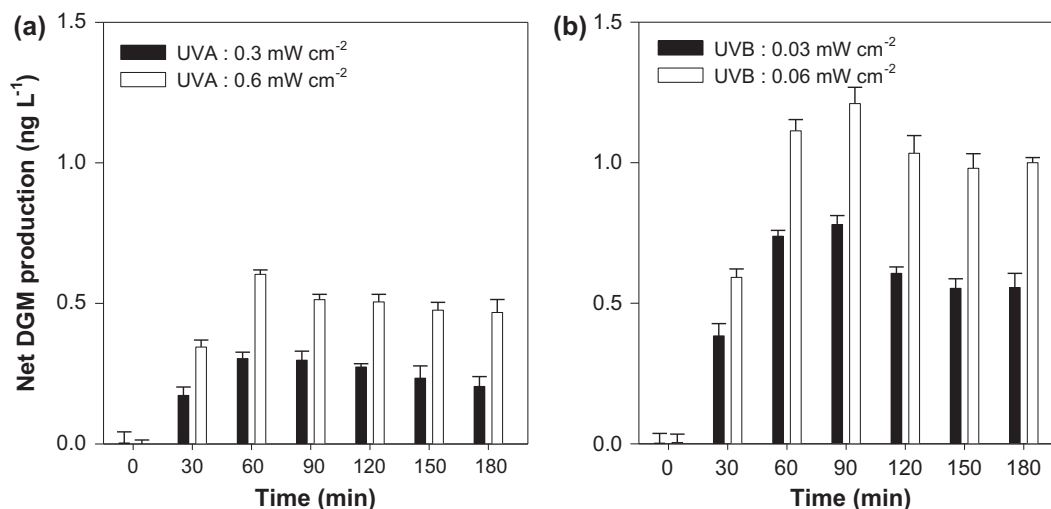


Fig. 5. DGM production from MeHg photodegradation under UVA and UVB at pH 8.3, salinity = 30 ppt, and $[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$. Error bars represent the standard deviations of experiments performed in triplicate.

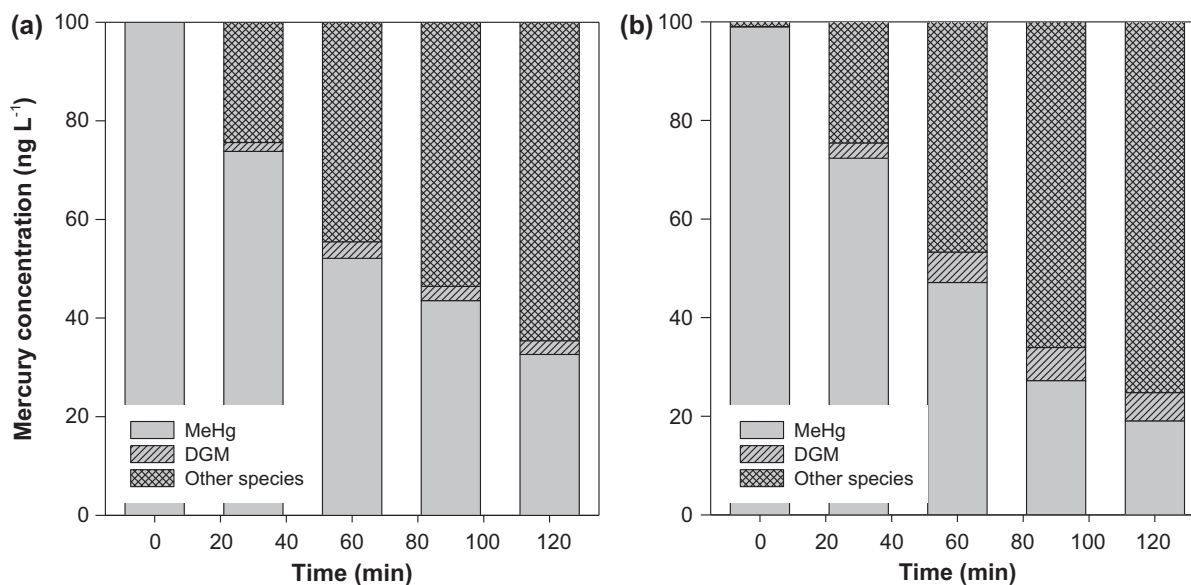


Fig. 6. Percentage concentration of mercury species in water during MeHg photodegradation under UVA and UVB at pH 8.3, salinity = 30 ppt, and $[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$.

than any freshwater system, the nitrate ion is present at lower levels in the ocean (from 0.01 to 0.08 mM) than other natural water sources, whereas the bicarbonate ion concentration in the ocean is only 2.8 fold higher than that in surface water. However, nitrate ion is known to produce the OH radical when excited by UV light [21,38–40], and plays an important role in MeHg transformation [21,39] (Eqs. (7)–(9)). In contrast, the bicarbonate ion is known to inhibit

the photodecomposition of MeHg through radical scavenging [18,21] (Eq. (10)).

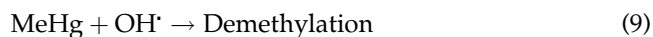
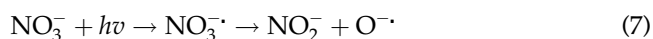


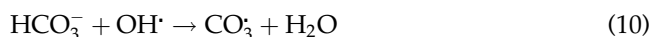
Table 2

The effect of salinity on DGM production from MeHg photodegradation under UVA at $[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$, reaction time is 180 min)

Salinity (ppt)	Gross DGM (ng L^{-1}) \pm SD ^a	r^2
0.0	2.4430 ± 0.02	0.986
7.5	2.2087 ± 0.04	0.948
15.0	2.0943 ± 0.02	0.973
22.5	1.9841 ± 0.05	0.961
30.0	1.4881 ± 0.03	0.986

Note: r^2 is the coefficient of determination.

^aSD is the standard deviation of the average rate constant from experiments performed in triplicate.



The effects of nitrate and bicarbonate ions on the MeHg photodegradation rate are shown in Tables 3 and 4, respectively. Under UVA irradiation, the MeHg photodegradation rate increased significantly in the presence of nitrate, whereas the MeHg photodegradation rate decreased dramatically in the presence of bicarbonate (Table 3). This suggests that nitrate can promote the photoreaction of MeHg by producing the OH radical when excited by UV light. Likewise, DGM production increased in the presence of nitrate, but decreased in the presence of bicarbonate (Table 4). However, the photodegradation of MeHg and DGM production decreased with increasing salinity in the absence and presence of both nitrate and bicarbonate. Therefore, we suggest that mercury may be more significantly affected by salinity (Tables 3 and 4).

3.5. Effect of DOM

DOM has various functions and plays important roles in chemical, biological, and even physical oceanography. In general, the major source of open ocean

DOM is planktonic primary producers, whereas the large amounts of DOM in coastal environments are mostly terrestrial humic and fulvic acids from rivers and run-off [41,42]. Previous studies have reported DOM concentrations in surface waters in the range 0.6–1.2 mg C L^{-1} in large areas of the ocean [42]. In coastal waters, more than 60% of the total dissolved mercury is associated with organic matter or suspended particles [43]. DOM appears to control the bioavailability of mercury due to its high Hg-binding capacity [12,13].

As the chromophoric portion of DOM, the role of humic acid in MeHg photodegradation presents a paradox. Humic acid can promote MeHg photodegradation by acting as a photosensitizer through the generation of the OH^\cdot and O_2^\cdot radicals [20,44,45]. Alternatively, humic acid can compete with MeHg for photons or reactive oxygen species, leading to the suppression of MeHg photodecomposition [14,15,21,22]. Thus, the overall role of humic acid in MeHg photodegradation depends on the balance between these two opposing effects.

In this study, we examined the effect of DOM concentrations on the rate of MeHg photodegradation and DGM production. The initial DOM concentration was 2 mg C L^{-1} in the seawater samples used, and humic acid was added to examine the effect of DOM. As shown in (Table 5), MeHg photodegradation was suppressed by increasing the DOM concentration under UV light exposure. This inhibition occurred due to the combined effect of photon attenuation and the competition for photons. MeHg photodegradation was suppressed by DOM added under UVA irradiation, which indicated that suppression due to photoabsorption or ROS quenching by DOM was more significant than photosensitization effects. Higher DOM concentrations inhibited MeHg photodegradation, which may be due to DOM competing with MeHg to absorb photons or interact with ROS.

Recently, Kim and Zoh [21] and Li et al. [7] investigated the role of DOM in MeHg photodegradation in

Table 3

The effect of salinity on the rate of MeHg photodegradation in the presence of nitrate or bicarbonate ions under UVA ($[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$, reaction time is 180 min, $[\text{NO}_3^-] = 0.08 \text{ mM}$, and $[\text{HCO}_3^-] = 20 \text{ mM}$)

Salinity (ppt)	Rate constant (h^{-1}) \pm SD ^a		
	Without $\text{NO}_3^-/\text{HCO}_3^-$	With NO_3^-	With HCO_3^-
0.0	0.660 ± 0.01	0.732 ± 0.01	0.354 ± 0.03
15.0	0.360 ± 0.08	0.480 ± 0.02	0.207 ± 0.04
30.0	0.162 ± 0.03	0.289 ± 0.01	0.140 ± 0.01

^aSD is the standard deviation of the average rate constant from experiments performed in triplicate.

Table 4

The effect of salinity on DGM production in the presence of nitrate or bicarbonate ion under UVA ($[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$, reaction time is 180 min, $[\text{NO}_3^-] = 0.08 \text{ mM}$, and $[\text{HCO}_3^-] = 20 \text{ mM}$)

Salinity (ppt)	Gross DGM (ng L^{-1}) \pm SD ^a		
	Without $\text{NO}_3^-/\text{HCO}_3^-$	With NO_3^-	With HCO_3^-
0.0	2.443 \pm 0.02	2.622 \pm 0.03	2.104 \pm 0.03
15.0	2.094 \pm 0.03	2.414 \pm 0.05	1.741 \pm 0.01
30.0	1.546 \pm 0.01	1.785 \pm 0.04	1.326 \pm 0.04

^aSD is the standard deviation of the average rate constant from experiments performed in triplicate.

Table 5

The effect of DOM concentration on the rate of MeHg photodegradation and DGM production under UVA ($[\text{MeHg}]_{\text{initial}} = 20.0 \text{ ng L}^{-1}$, pH 8.3, salinity = 30 ppt, and reaction time = 180 min)

DOM (mg C L^{-1})	Rate constant (h^{-1}) \pm SD ^a	Gross DGM (ng L^{-1}) \pm SD ^a
2	0.1620 \pm 0.03	1.8190 \pm 0.02
6	0.1200 \pm 0.03	1.3530 \pm 0.03
10	0.0767 \pm 0.01	1.1830 \pm 0.01
20	0.0300 \pm 0.01	1.1840 \pm 0.02

^aSD is the standard deviation of the average rate constant from experiments performed in triplicate.

freshwater under UVA irradiation. They found that the effect of increasing DOM concentration on the subsequent decrease in MeHg photodecomposition is related to the competition between MeHg and DOM to absorb UV radiation, which is the same result obtained in our study.

4. Conclusion

The photodemethylation experiments reported here demonstrated that while numerous chemical and physical factors can influence the rate of MeHg photodegradation, few exerted any substantial control of the transformation. The most important factors for predicting MeHg photodegradation rates in natural seawater were found to be UV wavelength, intensity, salinity, nitrate ion, and DOM concentration. MeHg photodegradation rate constants varied with the UV wavelength and intensity of radiation, demonstrating that MeHg photodegradation in seawater is dependent on the radiation source and its intensity. MeHg photodegradation rates and the DGM flux resulting from photodegradation decreased with an increase in the chloride ion concentration, suggesting that the presence of chloride could prevent MeHg photodegradation. The rate of MeHg photodegradation and DGM production recorded in this study under various conditions indicated that UV radiation is responsible for MeHg photodegradation together with chloride, and

that salinity has a significant influence on MeHg photodegradation and DGM photoproduction in seawater.

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