

Research Article

Kinetic Study of Biodangerous Methylmercury Degradation under Various Light Conditions

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Methylmercury (MeHg) has remarkable toxicological effects on humans, plants, and other lives in the environment, which may restrict the comprehensive utilization of biomass source in view of possibly forming biohazardous waste. In this study, a kinetic study of MeHg degradation under UVB, UVA, natural light, and dark was carried out. The result showed that light radiation enhanced MeHg degradation but had no significant influence on the final balance between MeHg and inorganic mercury (Hg^{2+}) in pure water. The balance is of great importance and can be used as a key fundamental to estimate MeHg cycling in other complicated aquatic environments. MeHg degradation was identified to be second-order reaction using the fitting optimization level of the regression equation, and the second-order rate constants were 1.61, 0.82, and 0.91 $\text{L}\cdot\text{ng}^{-1}\cdot\text{d}^{-1}$, half-lives were calculated to be 0.62, 1.3, and 1.08 d for UVB, UVA, and natural light, respectively. A possible MeHg degradation mechanism was proposed, and it could perfectly explain the results obtained in this paper and some previous studies.

1. Introduction

In the past decades, the extensive industrial and agricultural use of mercury and its compounds had resulted in serious contamination to fresh water and sea water [1–3]. Mercury-contaminated water may pose a risk to aquatic life [4] and subsequently to mankind through the food chains [5]. In addition, the possible formation of biohazardous waste from the toxin-rich biomass may restrict the comprehensive utilization of those renewable resources.

The ecological and toxicological effects of mercury are positively dependent on chemical species [6, 7]. As a potent neurotoxin to human and other lives in the environment, MeHg is many times more toxic than the corresponding inorganic metal ion [8], owing to its lipophilic and protein binding properties [9, 10]. Fortunately, aquatic MeHg content is kept at a low level because both of mercury

methylation and demethylation processes are going on in the environment. Research showed that photoinduced degradation of MeHg was thought to be an important process in the biogeochemical cycling of mercury [11, 12]. Both radiation intensity and light wavelength hold the capacity to influencing MeHg degradation [13]. Some kinetic studies were carried out to calculate the reaction rate of photoinduced MeHg degradation, but significant differences were observed in the obtained results, varying over orders of magnitude [11, 14–16]. These inconsistent results indicate that the mechanism of MeHg degradation may be different under various environmental conditions. Additionally, dissolved organic matter [17, 18], some ions (e.g., Cl^- and NO_3^-) [13, 19], and radicals (e.g., $\cdot\text{OH}$ and $^1\text{O}_2$) [20] in water also influence reaction rate significantly. However, no matter how many influencing factors act on and which mechanism undergoes in the process of MeHg degradation, the pure chemical balance between MeHg and inorganic mercury ion

(Hg^{2+}) is always the key fundamental to estimate the MeHg cycling in each aquatic ecosystem.

MeHg pool in an aquatic system was determined by the net result of processes, e.g., input, export, internal formation, and degradation of MeHg. Hence, experiments under simple conditions which start with only MeHg degradation and end with the chemical balance in an isolated system (without MeHg input or export) under constant temperature are most suitable to study the kinetic information of MeHg degradation. The kinetic data of these experiments can be used as a fundamental to establish the MeHg cycling model in a complicated aquatic system when other environmental factors were taken into account additionally. Therefore, this study was carried out in pure water and the objectives were to (1) establish chemical balances between MeHg and inorganic mercury under various light conditions and (2) estimate the kinetic data of MeHg degradation under UV irradiation, natural light, and darkness.

2. Materials and Methods

2.1. Preparation of Stock Solution. Clean techniques were used, and disposable gloves were worn throughout the experiments to minimize any exotic contamination. All the glassware was soaked in nitric acid for approximately 24 h and sterilized subsequently, and reaction solutions were prepared with ultrapure water ($18.2 \text{ M}\Omega\cdot\text{cm}^{-1}$). Stock solution of $1 \text{ ng}\cdot\text{Hg}\cdot\text{L}^{-1} \text{ CH}_3\text{HgCl}$ (GR, Seattle, WA, USA) solutions was prepared, and its pH was adjusted to be 5.5 with nitric acid or sodium hydroxide. The stock solution was stored in brown quartz bottles, which were wrapped in an aluminum foil and kept in a refrigerator at 4°C .

2.2. Experimental Design. 100 mL of $1 \text{ ng}\cdot\text{Hg}\cdot\text{L}^{-1} \text{ CH}_3\text{HgCl}$ solution was poured into bottles (borosilicate glass, 100 mL) and a very small space was left over the solution to minimize mercury lost from the reaction system. Then, the bottles were sealed with parafilm and incubated in a dark box whose inside wall was covered with aluminum foil to get ambient light. 8 UV bulbs (8 watt) were equipped in the box. The experiment lasted for 3 weeks, and 3 bottles were taken out each time at 1 d, 2 d, 4 d, 6 d, 9 d, 12 d, and 17 d for determination of MeHg concentration. Being the dominant component of UV in sunlight, UVA (365 nm) and UVB (310 nm) were employed to study the photoinduced decomposition of methylmercury in this study. The experiment was conducted under UVA, UVB, natural light, and dark, respectively, at 25°C in an air-conditioned room. Under natural light treatment, the dark box was open and the reaction solution was determined for MeHg concentration at midday to get similar light intensity (about 80–90 klx). Under dark treatment, the box was closed and all the bottles were wrapped with an aluminum foil. Under UV irradiation, 365 and 310 nm bulbs were employed to represent UVA and UVB radiations. A mini fan was equipped in a hole on the side wall of the box to keep air circulating and get constant

temperature when the UV bulbs were turned on. We verified the accuracy and the precision of the data in various aspects such as blank value assay, recovery rate experiment, and parallel determination experiment.

2.3. Data Analysis. MeHg concentration was determined using the method of 1630 [21], and all data were analyzed by SPSS 10.0 and Origin 8.0 software for Windows. The reaction kinetic order was determined using the fitting optimization level of the regression equation.

3. Results and Discussion

3.1. MeHg Demethylation Trend under Various Light Treatments. Many researchers have identified that solar UV could decrease MeHg content in surface water using field experiments [11, 16]. The photoinduced demethylation process was influenced by environmental factors (e.g., DOM, salinity, nitrate, photoreactive trace metals, and chloride) [13, 16, 20, 22]. The experiment in this study was conducted in lab, and all of the influencing factors were well controlled with light radiation as the only variable factor; data obtained in this study were much more purposeful and meaningful for further understanding of the photoinduced MeHg degradation process. MeHg concentration decreased at a faster rate in the first 6 days after the experiment started and at a lower rate in the following 15 days in all the treatments of dark, natural light, UVA, and UVB (Figure 1).

Although MeHg concentration decreased in all of the treatments with different radiations, a significant difference was observed in reaction rate between different light treatments, in an order of $\text{UVB} > \text{natural light} > \text{UVA} > \text{dark}$. As Figure 1 shows, 90% of MeHg degraded in the prior 6 days under UVB radiation; UVA which was similar to natural light resulted in about 80% of MeHg degradation. However, in the same 6 days, only 65% of MeHg degraded in the samples treated with dark. The result suggested that light wavelength has a great influence on MeHg demethylation. According to the previous reports, $\cdot\text{OH}$, produced in the Fenton reaction, should account for the fastest MeHg degradation induced by UVB treatment [20, 22]. Although UVB gave the fastest degradation rate in this study, it is noted that UVA dominates MeHg cycling in the aquatic environment [15], as it accounts for 98% UV light. Although samples treated under dark gave the slowest degradation rate, 90% MeHg degraded after 17 d as well, suggesting that photoinduced demethylation was not the only pathway accounting for the loss of MeHg which also occurred without light radiation.

In conclusion, light radiation indeed enhanced MeHg degradation rate, but it was not essential for MeHg demethylation in the aquatic system. Most probably, MeHg demethylation undergoes different mechanisms under corresponding light treatments.

3.2. Chemical Balance of MeHg Demethylation Reaction. It was unexpected to find such a similar final reaction state treated with UVB, UVA, natural light, and dark after

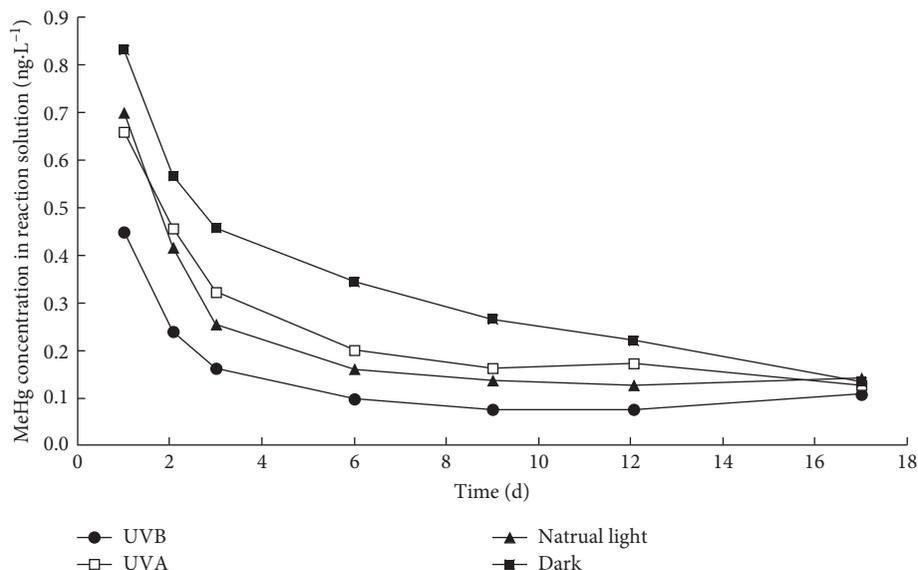


FIGURE 1: MeHg concentration variation with time. Initial MeHg concentration was $1 \text{ ng}\cdot\text{Hg}\cdot\text{L}^{-1}$.

incubation of 17 days, as Figure 2 shows. The ratios of MeHg to total mercury in the reaction solution were 10.51%, 11.45%, 11.60%, and 12.60% for UVB, UVA, natural light, and dark, respectively, and the differences between these ratios were rather less significant than imagined. This unexpected result verified that light radiation has a great influence on the MeHg degradation rate and most probably also to the reaction mechanism indeed, but it cannot significantly affect the final reaction balance of MeHg degradation in an isolated reaction system. However, in an open aquatic system, environmental factors such as dissolved organic matter, pH, sulfur, trace elements content, and so on will shift the balance to MeHg or Hg^{2+} side.

In this study, the experiments were conducted in a lab with constant pH and temperature, and the result was influenced entirely by light radiation. Hence, the similar balance between MeHg and inorganic mercury under various light irradiations is of great implication for the researchers to understand MeHg cycling (input, output, in situ formation, and decomposition) further in an aquatic system. For example, if the ratio of MeHg and total mercury was over than 12% in lake water, most probably, some environmental factors of this aquatic system were more suitable for MeHg formation or more external MeHg was inputted to this lake. These potential factors (in situ formation and external source) should be the focus when MeHg cycling in this lake was estimated.

3.3. Kinetic Study of MeHg Degradation under Various Light Radiations. Plots of $\ln[\text{MeHg}]_t/[\text{MeHg}]_i$ versus t and $1/[\text{MeHg}]_t$ versus t were used to validate whether MeHg degradation follows first-order or second-order reactions, respectively, where $[\text{MeHg}]_t$ means MeHg content ($\text{ng}\cdot\text{Hg}\cdot\text{L}^{-1}$) at time t and $[\text{MeHg}]_i$ means initial MeHg concentration, always $1 \text{ ng}\cdot\text{Hg}\cdot\text{L}^{-1}$ in this study. The fitting coefficients, reaction rate constants, and half-lives, which

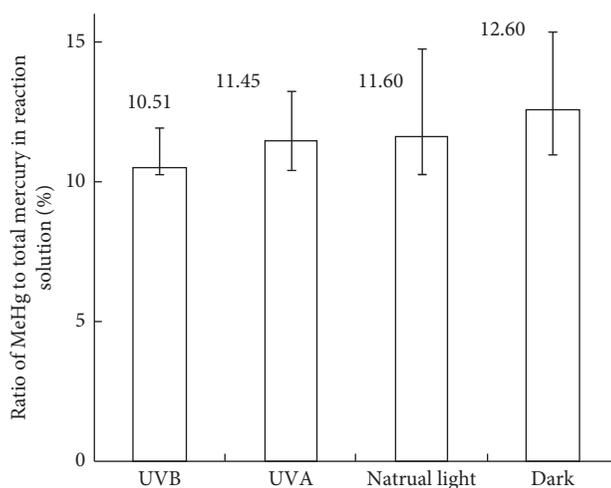


FIGURE 2: Ratio of MeHg to total mercury in reaction solution at the end of the experiment.

were calculated following both first- and second-order kinetic equations, are presented in Table 1.

It is noted that the data obtained after equilibrium conversion were not meaningful to calculate the rate constant. Hence, data obtained in the prior 9 days were used to study kinetic information for UVB, UVA, and natural light treatments and 17 days for dark treatment, respectively.

The results show that, under UVB, UVA, and natural light, the second-order equation is much better than the first-order equation to fit MeHg degradation. The fitting coefficients of the second-order equation were 0.94, 0.85, and 0.86, compared with that of first-order one 0.18, 0.38, and 0.48 for UVB, UVA, and natural light, respectively (Table 1). These data suggest that, under light radiation, MeHg degradation is a second-order reaction rather than

TABLE 1: Kinetic information of MeHg degradation under different light conditions.

Treatments	Rate constants				Fitting coefficients			
	UVB	UVA	Natural light	Dark	UVB	UVA	Natural light	Dark
First-order reaction (1 d^{-1})	0.35	0.19	0.21	0.13	0.18	0.38	0.45	0.83
Second-order reaction ($\text{L}\cdot\text{ng}^{-1}\cdot\text{d}^{-1}$)	1.61	0.82	0.91	0.43	0.94	0.85	0.86	0.90
Half-life (d)	0.62	1.30	1.08	—	—	—	—	—
ΔpH	0.2	0.1	0.1	-1.6	—	—	—	—

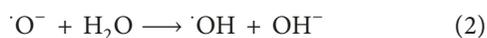
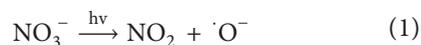
* ΔpH means the pH changes of the solution before and after the incubation period.

the first-order reaction. Under dark treatment, fitting coefficients of the first-order and second-order equations were very close, 0.83 and 0.89, and it is not enough to validate the reaction order. A hypothesis was proposed that MeHg degradation under light radiation follows an entirely different chemical mechanism from that under dark. Additionally, pH decreased by 1.6 (from 5.5 to 3.9) for solution treated under dark, while no significant pH change was observed in the solution treated under light radiation (Table 1). The difference in pH change under light and dark supports the hypothesis we proposed.

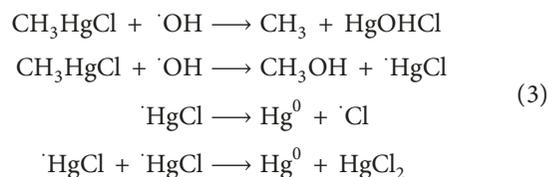
Under reaction conditions in this study, the second-order rate constants of MeHg degradation were 1.61, 0.82, and $0.91\text{ L}\cdot\text{ng}^{-1}\cdot\text{d}^{-1}$, and the half-lives were calculated to be 0.62, 1.3, and 1.08 d for UVB, UVA, and natural light, respectively. Kinetic data under dark treatment could not be calculated, because the reaction order under dark could not be decided based on the data obtained in this study (Table 1).

3.4. Proposed Mechanisms of Photoinduced Methylmercury Degradation. As shown in Figure 1 and kinetic data in Table 1, light irradiation can accelerate methylmercury degradation, as many previous studies have reported. Since methylmercury can be degraded directly by UV irradiation with wavelengths lower than 254 nm [23], direct degradation of methylmercury cannot occur with the light source of 310 and 365 nm in this study. Hence, we can conclude that indirect photolysis may be the dominant pathway for methylmercury degradation in this study. Previous studies have validated that hydroxyl radicals ($\cdot\text{OH}$) play an important role in the indirect photolysis process of methylmercury due to its powerful and nonselective reactivity. For example, Zepp et al. [24] and Chen et al. [20] determined the reaction kinetics of methylmercury and $\cdot\text{OH}$ using the steady-state kinetic technique. In this study, $\cdot\text{OH}$ can be produced through photolysis of nitrate ions which was introduced into the reaction system with nitric acid when adjusting pH of the solution.

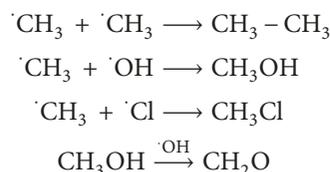
This hypothesis could be demonstrated with the following equations:



According to kinetic information obtained in this study, a possible mechanism was proposed as follows:



The possible side reactions are listed as follows:



The proposed mechanism gives perfect explanation to some previous studies. For example, Inoko and coworkers studied the photochemical decomposition of MeHg using mercury lamps and identified CH_3Cl and CH_3CH_3 as products in solution [23]. In addition, Chen et al. found CH_2O in MeHg decomposition products [20].

4. Conclusions

The MeHg degradation rate increases with decreasing radiation wavelength. Light radiation enhances the MeHg degradation but does not influence the final chemical balance between MeHg and inorganic mercury in an isolated aquatic reaction system. This ratio obtained in this study can be used as an important fundamental to estimate MeHg cycling in some complicated aquatic systems, where many environmental influencing factors are involved. Kinetic study shows that MeHg degradation is a second-order reaction and the half-life is 1.08 d under natural light in pure water.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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References

- [1] S. Heaven, M. A. Ilyushchenko, W. Tanton, S. M. Ullric, and E. P. Yanin, "Mercury in the River Nura and its floodplain, Central Kazakhstan: river sediments and water," *Science of the Total Environment*, vol. 260, no. 1–3, pp. 35–44, 2000.
- [2] W. Zhu, Y. Song, G. A. Adediran et al., "Mercury transformations in resuspended contaminated sediment controlled by redox conditions, chemical speciation and sources of organic matter," *Geochimica et Cosmochimica Acta*, vol. 220, pp. 158–179, 2017.
- [3] R. Cesário, L. Poissant, M. Pilote, N. J. O'Driscoll, A. M. Mota, and J. Canário, "Dissolved gaseous mercury formation and mercury volatilization in intertidal sediments," *Science of the Total Environment*, vol. 603–604, pp. 279–289, 2017.
- [4] Z. Y. Gao, M. M. Li, J. Wang, J. Yan, C. C. Zhou, and C. H. Yan, "Blood mercury concentration, fish consumption and anthropometry in Chinese children: a national study," *Environment International*, vol. 110, pp. 14–21, 2017.
- [5] G. J. Myers, P. W. Davidson, C. Cox, C. Shamlaye, E. Cernichiari, and T. W. Clarkson, "Twenty-seven years studying the human neurotoxicity of methylmercury exposure," *Environmental Research*, vol. 83, no. 3, pp. 275–285, 2000.
- [6] T. W. Clarkson, "Human toxicology of mercury," *Journal of Trace Elements in Experimental Medicine*, vol. 11, no. 23, pp. 303–317, 1972.
- [7] L. Mínguez-Alarcón, M. C. Afeiche, P. L. Williams et al., "Hair mercury (Hg) levels, fish consumption and semen parameters among men attending a fertility center," *International Journal of Hygiene & Environmental Health*, vol. 221, no. 2, pp. 174–182, 2018.
- [8] D. W. Boening, "Ecological effects, transport, and fate of mercury: a general review," *Chemosphere*, vol. 40, no. 12, pp. 1335–1351, 2000.
- [9] F. Zahir, S. J. Rizwi, S. K. Haq, and R. H. Khan, "Low dose mercury toxicity and human health," *Environmental Toxicology and Pharmacology*, vol. 20, no. 2, pp. 351–360, 2005.
- [10] D. Zhang, Y. Yin, Y. Li, Y. Cai, and J. Liu, "Critical role of natural organic matter in photodegradation of methylmercury in water: molecular weight and interactive effects with other environmental factors," *Science of the Total Environment*, vol. 578, pp. 535–541, 2016.
- [11] C. R. Hammerschmidt and W. F. Fitzgerald, "Photodecomposition of methylmercury in an Arctic Alaskan lake," *Environmental Science & Technology*, vol. 40, no. 4, pp. 1212–1216, 2006.
- [12] J. A. Fleck, M. Marvin-DiPasquale, C. A. Eagles-Smith et al., "Mercury and methylmercury in aquatic sediment across western North America," *Science of the Total Environment*, vol. 568, pp. 727–738, 2016.
- [13] R. Sun, D. Wang, Y. Zhang et al., "Photo-degradation of monomethylmercury in the presence of chloride ion," *Chemosphere*, vol. 91, no. 11, pp. 1471–1476, 2013.
- [14] P. Seller, C. A. Kelly, J. W. M. Rudd, and A. R. Machutcheon, "Photodegradation of methylmercury in lakes," *Nature*, vol. 380, no. 6576, pp. 694–697, 1996.
- [15] I. Lehnher and V. L. Louis, "Importance of ultraviolet radiation in the photodemethylation of methylmercury in freshwater ecosystems," *Environmental Science & Technology*, vol. 43, no. 15, pp. 5692–5698, 2009.
- [16] F. J. Black, B. A. Poulin, and A. R. Flegal, "Factors controlling the abiotic photo-degradation of monomethylmercury in surface waters," *Geochimica et Cosmochimica Acta*, vol. 84, pp. 492–507, 2012.
- [17] M. Ravichandran, "Interactions between mercury and dissolved organic matter—a review," *Chemosphere*, vol. 55, no. 3, pp. 319–331, 2004.
- [18] Y. Zhang, X. Chen, Y. Yang, D. Wang, and X. Liu, "Effect of dissolved organic matter on mercury release from water body," *Journal of Environmental Sciences*, vol. 23, no. 6, pp. 912–917, 2011.
- [19] W. Mao, R. G. Sun, D. Y. Wang, M. Ma, and C. Zhang, "Effects of nitrate ion on monomethylmercury photodegradation in water body," *Environmental Science*, vol. 34, no. 6, pp. 18–24, 2013.
- [20] J. Chen, S. O. Pehkonen, and C.-J. Lin, "Degradation of monomethylmercury chloride by hydroxyl radicals in simulated natural waters," *Water Research*, vol. 37, no. 10, pp. 2496–2504, 2003.
- [21] United States Environmental Protection Agency, *Method 1630: Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry*, United States Environmental Protection Agency, Washington, DC, USA, 2001.
- [22] C. R. Hammerschmidt and W. F. Fitzgerald, "Iron-mediated photochemical decomposition of methylmercury in an arctic Alaskan lake," *Environmental Science & Technology*, vol. 44, no. 16, pp. 6138–6143, 2010.
- [23] M. Inoko, "Studies on the photochemical decomposition of organomercurials—methylmercury (II) chloride," *Environmental Pollution Series B, Chemical and Physical*, vol. 2, no. 1, pp. 3–10, 1981.
- [24] R. G. Zepp, J. Hoigne, and H. Bader, "Nitrate-induced photooxidation of trace organic chemicals in water," *Environmental Science & Technology*, vol. 21, no. 5, pp. 443–450, 1987.



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