



Evaluation of the effects of Hg/DOC ratios on the reduction of Hg(II) in lake water

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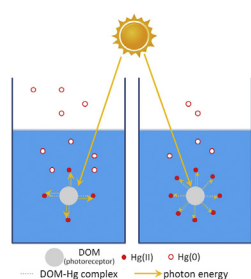
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HIGHLIGHTS

- Hg/DOC ratio has a dual role in the reduction of Hg(II) from natural waters.
- Maximum percentage reduction of Hg (~30%) occurred when Hg/DOC ratio was 1134 ng mg⁻¹.
- The reduction of Hg(II) may be inhibited by less amount of solar radiation on a single Hg atom.

GRAPHICAL ABSTRACT



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ABSTRACT

Reduction of mercury (Hg) in natural waters, which releases a substantial amount of gaseous Hg(0) to the atmosphere, has a close relationship to Hg/DOC ratios. However, the role of Hg/DOC ratio on the Hg(II) reduction in natural waters remains poorly understood. In this study, natural water collected from Hongfeng Lake, SW China, was used to study the effects of Hg/DOC ratio on the Hg(II) reduction. The lake water was spiked with variable amounts of Hg to make different Hg/DOC solutions. Through a 72 h Hg(II) reduction process, we demonstrated that the maximum percentage reduction of Hg ($29 \pm 3\%$) occurred when Hg/DOC ratio was 1134 ng mg⁻¹. Further increase or decrease of the Hg/DOC ratios would inhibit the reduction of Hg(II). This study clearly demonstrated that Hg/DOC ratio has a dual role in the reduction of Hg(II) from natural waters.

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1. Introduction

Mercury (Hg) is a persistent, bioaccumulative and semi-volatile pollutant that is ubiquitously distributed around the globe. Elemental Hg(0) is highly volatile and is the dominant form of Hg in

the atmosphere (Canario et al., 2017). Gaseous Hg(0) is oxidized in the atmosphere by atmospheric oxidants to form divalent Hg(II), which is highly soluble and is readily deposited to aquatic ecosystems (Garcia et al., 2005). In aquatic systems, Hg(II) is readily microbially methylated to form methylmercury (MeHg), a neurotoxin that can be bioaccumulated along the food chain (Harris et al., 2007). In natural waters, mercury occurs in many forms that depend on the oxidation-reduction conditions. Hg(II) in natural

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waters can be photochemically and microbially reduced to Hg(0) that is readily released to the atmosphere. The reduction of Hg(II) is of great importance in the global biogeochemical cycling of Hg (Bergquist and Blum, 2007; Schroeder and Munthe, 1998; O'Driscoll et al., 2005).

The reduction of aqueous Hg(II) is thought to be controlled by many factors such as temperature, pH, Eh, light radiation and dissolved organic matter (DOM) concentrations. DOM, primarily measured as dissolved organic carbon (DOC), occurs in natural waters and sediments usually at concentrations much higher than Hg (Morel et al., 1998; Barkay et al., 1997). DOM commonly forms complexes with many forms of Hg in natural waters (O'Driscoll et al., 2018). Therefore, the redox reactions of Hg in the presence of DOM play an important role in controlling the speciation of Hg in natural waters (Skylberg, 2008; Miller et al., 2007, 2009; O'Driscoll et al., 2004). It has been observed that the photoreduction of Hg(II) is positively correlated to DOM levels in natural waters (Grasby et al., 2013). In some experimental studies, the presence of DOM corresponds with a significant increase in Hg(II) photoreduction, as higher Hg(II) reduction rates were observed at higher DOM concentrations (Xiao et al., 1995; Costa and Liss, 1999). For instance, Wollenberg et al. (Wollenberg and Peters, 2009) suggested that Hg(0) emission rates in lake waters were positively correlated with DOC concentrations. Jeremiason et al. (2015) further demonstrated that DOC is the ultimate electron donor in Hg(II) photoreduction, and the DOC-bound Hg may be highly photosensitive. Orihel et al. (2007) reported that substantial amounts of Hg(II) deposited to lakes are quickly reduced to Hg(0) by solar radiation-driven reactions. In recent studies, it was suggested that DOM has a dual effect on the redox reactions of Hg in natural waters (Rocha et al., 2000; Maclair et al., 2008). A few studies demonstrated that the reduction of Hg(II) can be inhibited by DOC at high concentrations (Amyot et al., 1994; Tseng et al., 2004). In other words, the photoreduction of Hg(II) is largely related to Hg/DOC ratios.

The kinetics of aqueous Hg(II) photoreduction have been studied at low to high Hg/DOC ratios, ranging from 20 to 100,000 ng of

Hg per mg of DOC, by a number of studies at different times in different conditions (Zheng and Hintelmann, 2009; Gu et al., 2011; Haverstock et al., 2012; Driscoll et al., 1995). Although these studies provided some insights on the role of Hg/DOC ratios on aqueous Hg(II) photoreduction, each study focused on a certain range of Hg/TOC ratios using different types of water. To better understand the effects of Hg/DOC ratios on aqueous Hg(II) photoreduction, a controlled experiment covering a large range of Hg/DOC ratios using the same natural water at the same time is required.

In this study, natural waters were sampled from the Hongfeng Lake, SW China, and were spiked with variable amounts of Hg(II) to make different Hg/DOC solutions. These solutions were exposed to natural sunlight under room temperature for three consecutive days, and the reduction of Hg in these solutions was studied to understand the effects of Hg/TOC ratio on the Hg(II) reduction.

2. Materials and method

2.1. Materials and reagents

Hg standard solution (NIST SRM 3133) was purchased from the National Institute of Science and Technology (NIST, U.S. Department of Commerce). Other reagents (BrCl, HCl, NH₂OH·HCl, SnCl₂) used in this study were of analytical grade and were purchased from the Dongxing Chemical Group Co. Ltd., China. The 18.2 MΩ cm⁻¹ water (Millipore) was used to prepare the reagents. The glass vessels including 2 L Griffin beakers and 20 mL high borosilicate glass bottles were precleaned with 2% BrCl for 48 h, 20% HNO₃ for 24 h, washed by 18.2 MΩ cm⁻¹ water thoroughly, and were heated in a muffle furnace at 500 °C for 12 h to remove trace Hg before their use.

Surface water (depth: 10 cm) was collected in the middle of Hongfeng Lake in August 2019 (Fig. 1). The Hongfeng Lake (N 26°26'–26°36', E 106°19'–106°28'), located about 32 km west of Guiyang, SW China (Zhu et al., 2012; Wang et al., 2016), is a multi-functional water body that is used not only for drinking water, but

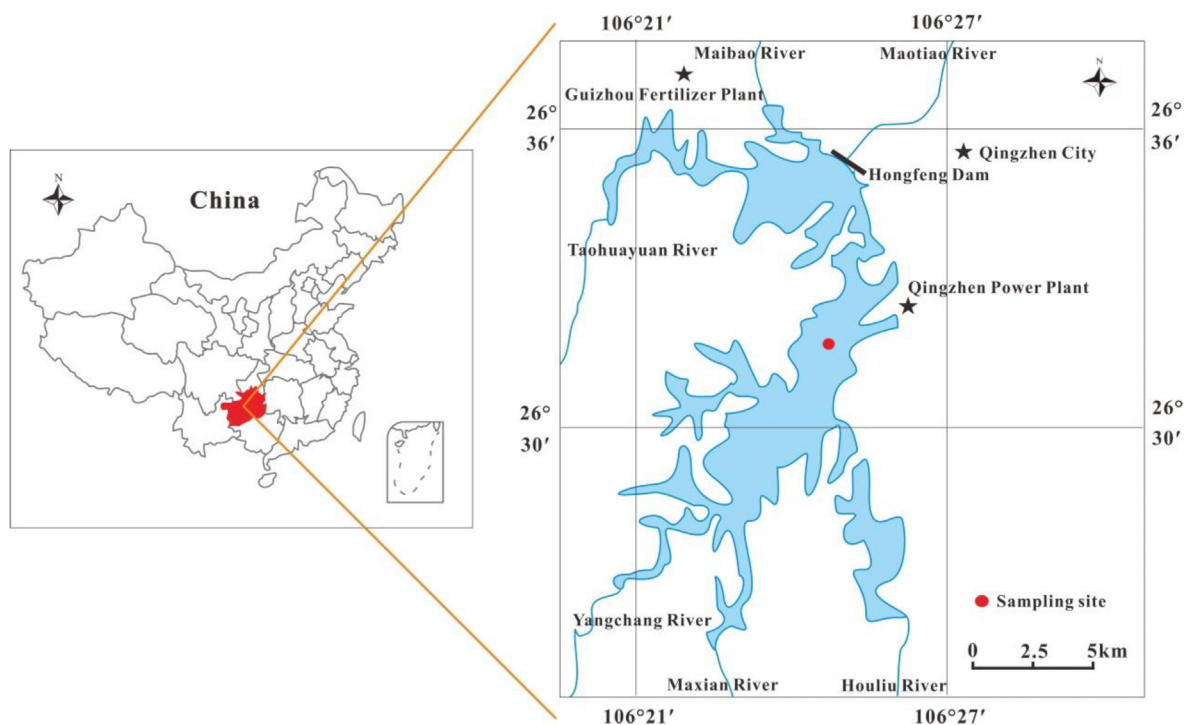


Fig. 1. Study area and sampling sites.

Table 1
Physical and chemical properties of water samples.

pH	Conductivity ($\mu\text{S}/\text{cm}$)	DO (mg/L)	DOC (mg/L)	Hg (ng/L)	Total Phosphorus (mg/kg)
8.83	264	8.69	4.41	30	1815

Table 2
Initial Hg and DOC concentration, and Hg/TOC ratios in the Hg(II) reduction experiment.

Breaker Number	Hg (ng/mL^{-1})	DOC (mg L^{-1})	Hg/DOC (ng mg^{-1})
P1, D1	2	4.41	454
P2, D2	5	4.41	1134
P3, D3	10	4.41	2268
P4, D4	20	4.41	4535
P5, D5	40	4.41	9070
P6, D6	80	4.41	18141
P7, D7	120	4.41	27211

also for hydropower, flood control, shipping, commercial aquaculture and recreation (He et al., 2012). The water was filtered through cellulose-acetate membrane filters (0.22 μm , Whatman) into the 2L polyethylene bottles, stored in dark conditions at 4 $^{\circ}\text{C}$, and transported to the laboratory prior to use. The physical and chemical properties of the collected water were immediately measured in the field (Table 1).

2.2. Photoreduction experiment and sample analysis

The experiment was performed from 6 a.m. on August 25, 2019 to 7 p.m. on August 27, 2019, in an open field. Sixteen precleaned 2L Griffin beakers, labeled P1-P7 and D1-D7, were used. Each beaker contained 1 L of the filtered water from the Hongfeng Lake. Different amounts of the Hg standard (NIST SRM 3133) were added into beakers, resulting in variable water Hg concentrations and Hg/DOC ratios in the beakers (Table 2). The beakers were stirred by a glass rod to ensure well mixing. The glass rod was carefully rinsed by 18.2 M Ω cm water between beakers.

Beakers P1-P7 were exposed to sunlight and the remainders (D1-D7) were placed in dark conditions for comparison. After 72 h, three subsamples of solution (20 mL each) from each beaker was pipetted into the precleaned borosilicate glass bottle and soon digested with 0.5% BrCl. The collected samples were then kept in a box to block out of sunlight and stored in the refrigerator before Hg concentration analysis the cold atomic absorption method used the F732-V mercury analyzer (Shanghai Huaguang Instrument Company). The relative standard deviations for duplicate samples were within 10%. The recoveries of THg for spiked samples were 90–110% ($n = 6$).

No rainfall events occurred during the experimental period. The evaporation caused the loss of water, therefore, the weights of water in the beakers were weighed before sampling. The meteorological parameters (temperature, total solar radiation) during the three days were obtained from the Guizhou Meteorological Bureau, China, based on data collected from the Guanshanhu Station, which is about 5 km away from our experiment site.

3. Results and discussion

3.1. Kinetics of Hg(II) reduction and its relationship with Hg/DOC ratios

The masses of Hg in different solutions ($\text{Hg}_{\text{solution}}$) were calculated by multiplying Hg concentrations by the volumes of the solution. The volumes of the solutions were calculated according to

the masses of the solution, assuming the density of the solution was 1 g mL $^{-1}$. Compared to the initial Hg masses ($\text{Hg}_{\text{initial}}$) added in the solutions, the $\text{Hg}_{\text{solution}}$ in different Hg/DOC solutions were gradually decreased during the experiment, at varying rates. The amounts of Hg reduction in different solutions are shown in Fig. 2A. The amounts of Hg reduction in solutions exposed to sunlight are variable, ranging from 371 to 2132 ng, however, it is interesting that the amount of Hg reduction peaked in breakers P2-P5, which has intermediate Hg concentration and the highest Hg/DOC ratio (Table 2). However, in other breakers with either higher or lower Hg concentration and Hg/DOC ratio, we observed a relatively small amount of Hg reduction. In comparison to those exposed to sunlight, the amounts of Hg in solutions placed in dark conditions are in general smaller, ranging from 11 to 520 ng. The larger amounts of Hg reduction in solutions exposed to sunlight are therefore hypothesized to be caused by photochemical reduction.

To compare the rate of Hg reduction in different Hg/DOC solutions, the percentages of Hg remained ($\text{Hg}_{\text{remained}}(\%)$) and the percentages of Hg reduction ($\text{Hg}_{\text{reduction}}(\%)$) in the solutions were calculated using the following equations:

$$\text{Hg}_{\text{remained}}(\%) = \text{Hg}_{\text{solution}}/\text{Hg}_{\text{initial}} \times 100\% \quad (1)$$

$$\text{Hg}_{\text{reduction}}(\%) = 100\% - \text{Hg}_{\text{remained}}(\%) \quad (2)$$

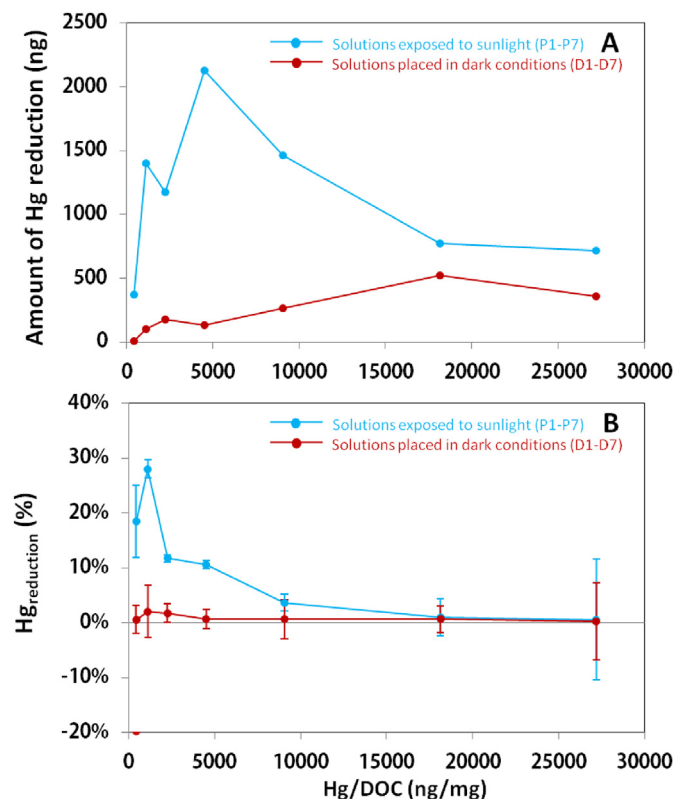
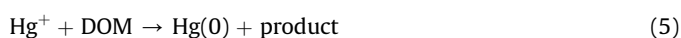


Fig. 2. (A) Relation between the amount of Hg reduction (ng) and Hg/DOC ratio (ng mg^{-1}) in the Hg reduction experiment; (B) Relation between the $\text{Hg}_{\text{reduction}}(\%)$ and Hg/DOC ratio (ng mg^{-1}) in the Hg reduction experiment.

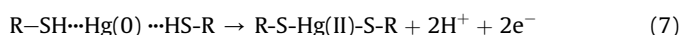
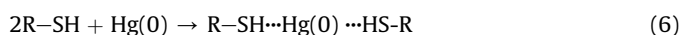
As shown in Fig. 2B, the $Hg_{reduction}(\%)$ in solutions (P1-P7) exposed to sunlight range of $1 \pm 12\%$ to $29 \pm 3\%$ (2SD, $n = 3$), suggesting Hg(II) reduction occurs at varying degrees. The $Hg_{reduction}(\%)$ was largely variable with different Hg/DOC ratios. The highest $Hg_{reduction}(\%)$ of $29 \pm 3\%$ was observed in solution with Hg/DOC of 1134 ng mg^{-1} . With further increase in Hg/DOC ratios beyond 1.134 ng/mL , however, the $Hg_{reduction}(\%)$ decreased gradually until $Hg_{reduction}(\%)$ was close to 0% at Hg/DOC of $>18141 \text{ ng mg}^{-1}$. On the other hand, relatively lower $Hg_{reduction}(\%)$ of $18 \pm 6\%$ was observed when Hg/DOC was $<1134 \text{ ng mg}^{-1}$. This indicates Hg(II) reduction was inhibited at either lower or higher Hg/DOC ratios than Hg/DOC of 1134 ng mg^{-1} . In comparison, no significant changes in Hg masses, with $Hg_{reduction}(\%)$ ranging from $0 \pm 7\%$ (2SD, $n = 3$) to $2 \pm 5\%$ (2SD, $n = 3$), were observed in solutions (D1-D7) placed in dark conditions. In this case, we concluded that the loss of Hg was mainly driven by photoreduction.

Fig. 2 clearly indicates that DOC/Hg ratios played a dual role in controlling the photoreduction of Hg(II). DOM molecule not only complexed with Hg(II) to form Hg-DOM complexes but also acts as a reducing agent. DOM acts as a photosensitizer and initiates the Hg(II) reduction by accelerating the electron transfer process. Active sites (e.g., carboxyl groups, phenolic hydroxyl groups, and amino groups) within the DOM molecule may play an important role in Hg(II) reduction (Zhang, 2006); DOM molecule absorbs light energy and decomposes into molecules or groups with relatively small molecular weight (Bertilsson and Tranvik, 2000; Kaiser and Sulzberger, 2004; Xiao et al., 1995). During these processes, some active sites in the DOM molecule undergo reduction and oxidation reactions to produce free radical intermediates ($R\cdot$, Hg_2^{2+} , and Hg^+). Hg_2^{2+} or Hg^+ species that are highly reactive, and can be quickly reduced to Hg(0) with the presence of excessive electron donors (e.g. organic compounds) (Horvath and Vogler, 1998; Kunkely et al., 1997). These reactions are simplified as follows:



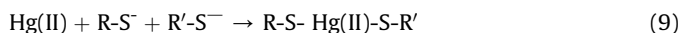
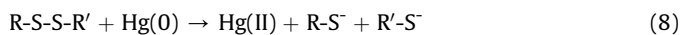
3.2. Low Hg/DOC ratios inhibit Hg(II) photoreduction

Our results suggest that at low Hg/TOC ranges ($0-1134 \text{ ng mg}^{-1}$), the increase of Hg/TOC can promote the Hg(II) photoreduction (Fig. 2). This is because DOM contains reduced sulfur groups (e.g., thiol and disulfide/disulfane functional groups) which have an affinity to Hg(II) (Drexel et al., 2002; Han and Gill, 2005). At low Hg/DOC ratios ($0-1134 \text{ ng mg}^{-1}$), the concentration of Hg is much lower than that of reduced sulfur in DOM. Hg primarily binds to these reduced sulfur groups with high stability constants, which results in lower Hg(II) reduction rates. Moreover, at high Hg/DOC ratios, the reduction of Hg(II) may be decreased due to the physicochemical sorption and ligand-induced oxidative complexation between DOM and Hg(0), as indicated in reactions (6) and (7), respectively (Arias et al., 2004; Lee et al., 2006; Makkuni et al., 2007).



In addition, due to Hg is a class B soft metal with a strong tendency to coordinate or complex with soft bases such as thiols

(Skylberg et al., 2006), Hg is formed by ligand-induced oxidative complexation at low Hg/DOC conditions. In this case, the reductant Hg(0) may be oxidized again and subsequently complexed with the intermediate thiolate products, according to the following reactions (R-S-S-R' represents DOM with oxidized sulfur or disulfides).



3.3. High Hg/DOC ratios inhibit Hg(II) photoreduction

Our results also indicate that at high Hg/TOC ratios ($>1134 \text{ ng mg}^{-1}$), the increase of Hg/TOC can inhibit the Hg(II) reduction (Fig. 2). Similar observations have been observed in previous studies (Amyot et al., 1997; Rolfhus and Fitzgerald, 2001). With the increase of Hg/DOC, the concentration of Hg far exceeds that of reduced sulfur. In this case, all reduced sulfur groups within DOM may be saturated by a small fraction of Hg, and the remaining part of Hg is expected to be combined with oxygen functional groups in DOM. Solar energy plays a critical role in the photoreduction of aqueous Hg(II), however, only when photoreceptors (e.g., DOM molecules) absorb enough photon energy, electrons are excited to initiate Hg(II) photoreduction (Balzani and Garassiti, 1970). The cleavage of bonds in the DOM-Hg complexes needs some time to absorb enough solar energy during photoreduction. During the experiment period, the surface solar energy was consistently weak ($0-2.9 \text{ mJ m}^{-2}$, Fig. A1). Therefore, at high Hg/TOC conditions ($>1134 \text{ ng mg}^{-1}$), a long time was needed for destroying a single Hg-DOM bond to initiate Hg(II) photoreduction. Meanwhile, the solar energy absorbed on the photoreceptors is thought to have released at night. More importantly, at high Hg/TOC ratios, the high Hg concentration led to the formation of more DOM-Hg complexities, which tended to dilute the solar energy on a single Hg-DOM bond. In this case, the solar energy in this study was expected to be not strong enough to initiate Hg(II) photoreduction at high Hg/TOC ratios ($>1134 \text{ ng mg}^{-1}$), thereby caused the decrease of $Hg_{reduction}(\%)$ at high Hg/TOC ranges ($>1134 \text{ ng mg}^{-1}$).

In earlier experimental studies, when the photoreduction of Hg(II) was under a single light source (e.g., visible light, UVA, UVB), the rate of Hg(II) reduction was shown to be negatively correlated with the wavelength of light (λ) (Lehnher and Louis, 2009). λ can be calculated using the following equation:

$$\epsilon = hc/\lambda \quad (10)$$

where ϵ is the energy of a photon; c is the speed of light; h is the Planck constant. In other words, the photoreduction of Hg(II) was positively correlated with ϵ , if λ remain consistent. In this study, the waters with different Hg/DOC ratios were placed under the same natural light, therefore no difference in λ was expected for different solutions. As the same size of beakers were used in this study, it is thought that the same amount of solar radiation was received by the solutions. Solar energy plays a critical role in the photoreduction of aqueous Hg(II), however, only when photoreceptors (e.g., DOM molecules) absorb enough photon energy, electrons are excited to initiate Hg(II) photoreduction (Balzani and Garassiti, 1970). In this case, the decrease of $Hg_{reduction}(\%)$ at high Hg/TOC ratios ($>1134 \text{ ng mg}^{-1}$) can be explained by the conceptual model as shown in Fig. 3. As DOM molecules are important receptors of photon energy that initiate Hg(II) photoreduction, the increase of DOM-Hg complexities tends to dilute (or decrease) the effective photon energy of photoreduction on DOM-Hg complexities,

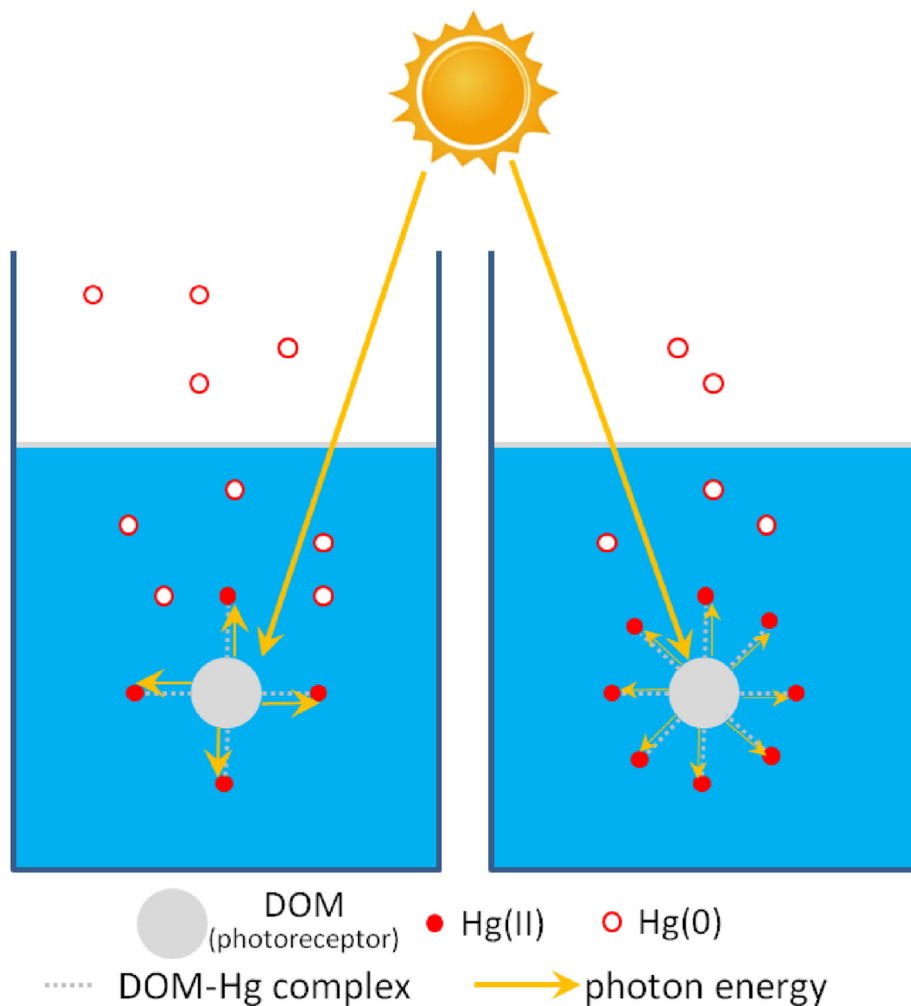


Fig. 3. A conceptual model showing the decrease of $Hg_{reduction}(\%)$ at high Hg/TOC ratios ($>1134 \text{ ng mg}^{-1}$).

thereby causing the lower efficiency of $Hg(II)$ photoreduction. We believed that the ratio between the masses of Hg (Hg_{mass}) in the solution and the amount of solar radiation ($Radiation_{solar}$), termed as $Hg_{masses}/Radiation_{solar}$, is reflective of the efficiency of $Hg(II)$ photoreduction. The $Hg_{masses}/Radiation_{solar}$ ratios in solutions exposed to sunlight (P1-P7) were calculated and shown in Fig. 4. Indeed, a significantly positive correlation between the $Hg_{reduction}(\%)$ and $Hg_{mass}/Radiation_{solar}$ ratio ($p < 0.02$) can be observed when Hg/DOC ratios were higher than 1134 ng mg^{-1} (Fig. 4), which suggests that low $Hg(II)$ photoreduction efficiency in high Hg/DOC solutions was driven by the decrease of photon energy on DOM- Hg complexes.

4. Conclusions and environmental implications

This study firmly proved that Hg/DOC ratios of natural waters can play a dual role in the photoreduction of $Hg(II)$ in natural waters. Regarding the Hongfeng lake water, the maximum $Hg(II)$ reduction rate occurs when $Hg(II)$ concentration was 2 ng/mL , with a Hg/DOC ratio of $\sim 1134 \text{ ng mg}^{-1}$. Further increase or decrease of $Hg(II)$ concentrations in the water, resulting in higher or lower Hg/DOC ratios, respectively, would inhibit the reduction of $Hg(II)$. In most natural waters, the $Hg(II)$ concentration is typically lower than 2 ng/mL and the Hg/DOC should be lower than $\sim 1134 \text{ ng mg}^{-1}$ as well. Within this low Hg concentration ($0\text{--}2 \text{ ng/mL}$) and Hg/DOC

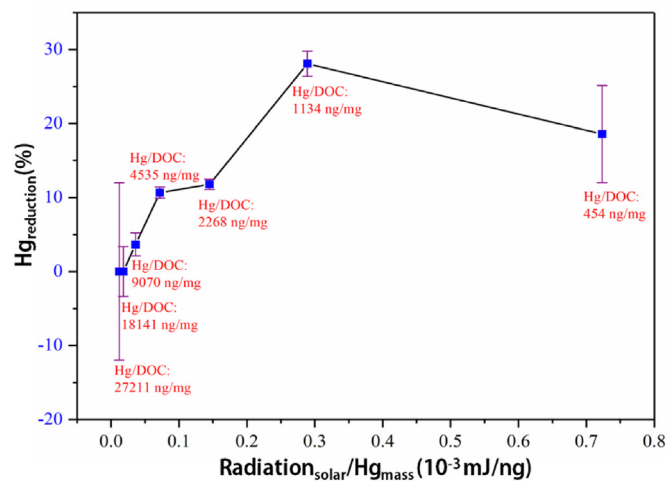


Fig. 4. Relation between $Hg_{reduction}(\%)$ and $Hg_{mass}/Radiation_{solar}$ ratio in solutions exposed to sunlight.

ranges ($0\text{--}1134 \text{ ng mg}^{-1}$), the reduction of $Hg(II)$ in natural waters should be commonly increased by the enhanced input of DOM to the water. This explains the positive correlation between $Hg(II)$ reduction rates and DOM levels observed in natural waters. This

study also suggests that the reduction of Hg(II) may be facilitated in Hg-polluted or organic-rich water bodies, in particular when the Hg concentration reaches 2 ng/mL and the Hg/DOC ratio reaches $\sim 1134 \text{ ng mg}^{-1}$. However, with the continued increase of Hg concentration ($>2 \text{ ng/mL}$) or Hg/DOC ratio ($>1134 \text{ ng mg}^{-1}$) in the water body, the reduction of Hg(II) may be inhibited by less solar energy on a single Hg-DOM bond. This study, thus, provides important insights into the biogeochemical cycling of Hg in the environment.

Declaration of competing interest

We declare that we have no financial and personal relationships with other people or organizations that can inappropriately influence our work, there is no professional or other personal interest of any nature or kind in any product, service and/or company that could be construed as influencing the position presented in, or the review of, the manuscript entitled.

CRediT authorship contribution statement

Zhuohong Wang: Conceptualization, Methodology, Writing - original draft. **Zhijun Fei:** Validation, Formal analysis, Writing - original draft. **Qixin Wu:** Writing - review & editing. **Runsheng Yin:** Conceptualization, Methodology, Writing - original draft.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemosphere.2020.126634>.

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