Mercury Redox Chemistry in Waters of the Eastern Asian Seas: From Polluted Coast to Clean Open Ocean

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S Supporting Information

ABSTRACT: We performed incubation experiments using seawaters from representative marine environments of the eastern Asian seas to determine the mercury (Hg) available for photoreduction (Hgr(II)), to investigate the Hg redox reaction kinetics, and to explore the effect of environmental factors and water chemistry on the Hg redox chemistry. Results show that Hgr(II) accounted for a considerable fraction of total Hg (THg) (%Hgr(II)/THg: $24.90 \pm 10.55\%$, $n = 27$) and positively correlated with THg. Filtration decreased the Hgr(II) pool of waters with high suspended particulate matter (SPM). The positive linear relationships were found between pseudo-first order rate constants of gross Hg(II) photoreduction (k_r) and gross Hg(0) photo-oxidation (k_o) with photosynthetically active radiation (PAR). Under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$, the k_r were significantly ($p < 0.05$) lower than k_o (k_r/k_o : 0.86 ± 0.22). The Hg(0) dark oxidation were significantly higher than the Hg(II) dark reduction. The Hg(II) dark reduction was positively correlated to THg, and the anaerobic condition favored the Hg(II) dark reduction. Filtration significantly influenced the Hg photoredox chemistry of waters with high SPM. UVB radiation was important for both Hg(II) photoreduction and Hg(0) photo-oxidation, and the role of other wavebands in photoinduced transformations of Hg varied with the water chemistry.

1. INTRODUCTION

The marine ecosystem plays an important role in global Hg biogeochemical cycle.^{1,2} Globally, atmospheric deposition of divalent Hg (Hg(II)) was determined to be the primary pathway for Hg input to the ocean.³ Hg(II) in seawaters can be reduced to Hg(0), which tends to emit to overlying air due to its high volatility.³ This process lowers the Hg loading in marine ecosystems and promotes the redistribution of Hg in the global environment.^{1,2} In previous studies, researchers thought that Hg(0) was unreactive in aquatic environments. However, in the past decade, many studies have confirmed that Hg(0) can be oxidized to Hg(II) rapidly in salt waters.^{4–6} Hg(0) oxidation potentially reduces Hg(0) emissions from marine systems, thus enhances Hg residence times in waters and increases its potential to enter the food chain. Therefore, Hg(II) reduction and Hg(0) oxidation (known as Hg redox reactions) are important processes that influence the distribution, transport, and toxicological effects of Hg in marine ecosystems.^{1–3}

Over the past several decades, many efforts have been made to explore the mechanisms involved in the Hg redox chemistry.² Experimentally determined rate constants of Hg(II) reduction and Hg(0) oxidation in seawaters have been sporadically reported in the coast, estuary, offshore^{4–9} and open ocean.^{10,11} Studies show that Hg(II) reduction and Hg(0) oxidation in aquatic environments can be both photochemically and microbially mediated.^{12,13} Hg redox reactions in aquatic

environments are synergistically controlled by concentrations and speciation of Hg, intensity and wavebands of radiation, concentrations and structure of dissolved organic carbon (DOC), and other physical, chemical, and biological properties of waters (salinity, suspended particulate matter (SPM), dissolved ions, microbial activity, and so on).^{4–35} Therefore, a wide range of rate constants of Hg(II) reduction and Hg(0) oxidation have been reported.³⁶

As a key component of the regional and global Hg research framework, model study is an important tool for understanding the global Hg cycle.^{1,3} One of the most important knowledge gaps of current Hg model study is the lack of representative and comprehensive kinetic data of Hg redox reactions in seawaters.¹ The early models used empirically parametrized rate constants of Hg redox reactions to match observations.¹ Recently, modelers began to develop the parametrizations of Hg redox reactions based on the results of incubation experiments.^{37,38} However, previous incubation studies were performed either with a limited number of water samples or under certain well-defined, but not necessarily environment relevant conditions.^{4–6,8,10,39} This indicates that the data of these studies do

Received: November 4, 2015

Revised: January 20, 2016

Accepted: January 29, 2016

Published: February 10, 2016

not fully represent the characteristics of the global ocean and meet the need of Hg model.

In this study, we collected a number of seawaters from representative marine environments of the eastern Asian seas (from Hg-polluted coast to offshore and clean open ocean) to conduct a series of incubation experiments under conditions close to the real environment to explore the Hg redox chemistry. The goal of this study was (i) to determine the mass and fraction of Hg that was available for photoreduction; (ii) to investigate rate constants of Hg(II) reduction and Hg(0) oxidation; and (iii) to explore the effect of environmental factors (intensity and wavebands of solar radiation) and water chemistry (salinity, SPM, oxygen content, and DOC) on the Hg redox reactions.

2. MATERIALS AND METHODS

2.1. Samples and Instruments. In this study, 27 water samples were collected from the coasts, offshore and open ocean of the eastern Asian seas for incubation experiments. The sampling locations are illustrated in Figure 1. The coastal water

Figure 1. Sampling locations of 27 water samples in the eastern Asian seas. QHD (the coast of Qinghuangdao City), BS (the Bohai Sea), YS (the Yellow Sea), CD (the coast of Changdao Country), CJ (Changjiang Diluted Water), ECS (East China Sea), XM (the coast of Xiamen City), SCS (South China Sea), SY (the coast of Sanya City), WP (the West Pacific Ocean).

samples were manually collected into preclean 4 L brown borosilicate glass bottles. The surface water (~ 1 m) samples from offshore and open ocean were collected with the sampling system consisting of Teflon lined Go-Flo bottles on R/V *Kexue I*, *Dongfanghong II*, and *Beidou* and quickly decanted into 4 L acid-cleaned brown glass bottles for preservation and shipped to laboratory and kept in the dark until the time of experiments.

The preclean custom quartz bubblers (6 cm OD, 5.5 cm i.d., 10 cm height, a longitudinal section of 55 cm², approximately 160 mL in volume) were used as the vessel in incubation experiments. The structure of the quartz bubbler was almost identical to that of the Brooks Rand bubbler (08211, Brooks Rand), but all parts of the bubbler (including bottle, stopper, and bubbling frit) were made of quartz glass. The quartz glass is a suitable material for incubation experiments to explore the aquatic Hg photochemistry because of its high and identical ($\sim 85\%$) transmission of the radiation of 200–800 nm (see

Supporting Information (SI) Figure S1 for more details) and no Hg loss through the wall.⁴⁰ All materials in contact with seawaters and Hg(0) were preclean quartz glass, Teflon or borosilicate glass.

To investigate the effect of different wavebands of solar radiation on the Hg photochemistry, UVB and UV filters (3M) were used to wrap quartz bubblers to shield off the corresponding wavebands of solar radiation (see SI Figure S1 for more details).

The gold traps were used to collect Hg(0) released from waters. Hg(0) collected on the gold traps was quantified with a cold vapor atomic fluorescence spectrometry (CVAFS, model III, Brooks Rand).⁴¹

The incubation experiments using coastal waters generally were performed on site within 0.5–14 h after the water sampling to minimize the effect of storage of waters on transformations of Hg and the change of other factors. The incubation experiments using offshore and open waters were conducted within two months after water sampling.

2.2. Experimental Concept. A simple reversible reaction for Hg redox reactions (eq 1) was used to express the Hg(II) reduction and Hg(0) oxidation in aquatic environments.^{6,10,32}

where Hgr(II) refers the Hg pool that are available for photoreduction in waters. If the Hg(0) oxidation can be prevented, we can obtain the pseudo-first rate constant of gross Hg(II) reduction (k_r) according to eq 2.

$$\ln[\text{Hg(0)}_t/\text{Hg(0)}_0] = k_r t \quad (2)$$

where $[\text{Hg(0)}]_t$ and $[\text{Hg(0)}]_0$ represent Hg(0) concentrations at time t and at the beginning of the incubation experiment, respectively. k_r is the pseudo-first order rate constant of gross Hg(II) reduction. Similarly, if the Hg(II) reduction can be prevented, then the pseudo-first rate constant of gross Hg(0) oxidation (k_o) can be calculated.

According to eq 1, Hgr(II) is equal to the total Hg(0) released from the waters until cumulative released Hg(0) reaches a plateau in full solar radiation if the Hg(0) oxidation is prevented.

2.3. Experimental Design. **2.3.1. Hgr(II) and Hgr(II)/THg.** In a typical incubation experiment for determining the Hgr(II) pool, aliquots (150 mL) of water sample in triplicate were distributed to quartz bubblers for incubation from the morning of a cloudless day. Before the incubation experiment, the waters were purged with Hg-free air ($\text{Hg} < 0.01 \text{ pg L}^{-1}$) in the dark with the flow rate of 0.5 L min^{-1} to remove the natural Hg(0). After exposed to the solar radiation, the formed Hg(0) in waters was removed continuously by purging to prevent the Hg(0) reoxidation.^{30,42} The released Hg(0) was collected on gold traps with 0.5–1.5 h interval until the cumulative Hg(0) reached a plateau. Then the total Hg(0) released was equal to the amount of Hgr(II). Our data showed that the released Hg(0) in all incubated samples reached a plateau after approximately $12\text{--}27 \text{ mol m}^{-2}$ of cumulative photosynthetically active radiation (PAR). These cumulative PAR were lower than the daily cumulative PAR on experiment days ($\sim 35\text{--}42 \text{ mol m}^{-2}$), indicating that the Hg(II) photoreduction completed in one experiment day.

After the incubation experiment for determining Hgr(II), the subsamples were transferred to new 50 mL Falcon poly-

Table 1. Chemical Variables, Hg Available for Photoreduction, and the Rate Constants of Divalent Hg (Hg(II)) Reduction and Elemental Hg (Hg(0)) Oxidation for Water Samples Collected from Representative Marine Environments of the Eastern Asian Seas

sample no.	DOC (mg L ⁻¹)	salinity (PSU)	SPM (mg L ⁻¹)	Hgr(II) ^a (ng L ⁻¹)	remaining THg (ng L ⁻¹)	THg ^b (ng L ⁻¹)	%Hgr(II)/THg (%)	k_r^c (h ⁻¹)	k_o^d (h ⁻¹)	k_r/k_o	k_o in the dark (h ⁻¹)	k_r^e in the dark (pg L ⁻¹ h ⁻¹)
QHD-A	3.11	28.4	40.2	1.36 ± 0.18 ^f	22.31 ± 2.69	23.68 ± 2.88	5.77	0.32	0.33	0.97	0.08	22.3
QHD-B	2.49	28.4	43.2	1.30 ± 0.23	14.34 ± 3.62	15.64 ± 3.85	8.33					
BH-1	2.83	30.7	7.2	1.20 ± 0.19	7.43 ± 0.69	8.63 ± 0.88	13.94	0.34	0.35	0.97	0.06	11.4
CD-A	3.19	27.6	19.6	0.68 ± 0.09	3.02 ± 0.69	3.70 ± 0.78	18.39	0.41	0.33	1.24	0.06	4.3
CD-B	3.02	27.8	17.6	0.87 ± 0.12	4.12 ± 0.81	4.99 ± 0.93	17.38					
CD-C	3.49	26.6	19.5	1.13 ± 0.07	3.97 ± 0.53	5.10 ± 0.60	22.17					
CD-D	2.99	26.8	14.3	0.74 ± 0.10	4.36 ± 0.33	5.10 ± 0.43	14.47	0.34	0.36	0.94	0.05	5.2
YS-1	2.73	31.4	7.9	0.89 ± 0.12	6.36 ± 0.96	7.25 ± 1.08	12.25					
YS-2	2.35	31.9	5.3	0.42 ± 0.06	1.49 ± 0.13	1.90 ± 0.19	21.80	0.30	0.41	0.73	0.09	
YS-3	1.89	31.0	7.3	0.35 ± 0.10	1.27 ± 0.29	1.62 ± 0.38	21.78					
YS-4	1.07	32.0	5.2	0.51 ± 0.07	1.75 ± 0.26	2.26 ± 0.33	22.69	0.31	0.52	0.60	0.06	5.3
CJ-1	1.39	30.8	7.1	0.38 ± 0.10	1.58 ± 0.33	1.20 ± 0.42	19.18	0.28	0.36	0.78	0.05	4.4
CJ-2	1.44	30.3	7.6	0.41 ± 0.10	1.22 ± 0.41	1.63 ± 0.51	25.09	0.24	0.34	0.70	0.06	3.0
ECS-1	1.56	30.8	< 0.5	0.38 ± 0.07	1.09 ± 0.29	1.47 ± 0.36	26.06					
ECS-2	1.43	31.3	1.2	0.44 ± 0.08	1.15 ± 0.32	1.59 ± 0.40	27.57					
ECS-3	1.77	30.9	0.9	0.43 ± 0.06	0.59 ± 0.17	1.02 ± 0.24	42.24	0.25	0.41	0.61	0.08	3.3
ECS-4	1.58	32.0	1.2	0.38 ± 0.09	0.88 ± 0.20	1.26 ± 0.29	30.37					
XM-A	3.42	25.5	12.5	0.72 ± 0.06	2.22 ± 0.89	2.94 ± 0.95	24.58	0.32	0.30	1.07	0.05	3.2
XM-B	3.12	25.5	13.6	0.63 ± 0.13	2.59 ± 0.56	3.21 ± 0.69	19.52					
XM-C	3.33	25.6	17.9	0.94 ± 0.09	3.31 ± 0.12	4.26 ± 0.21	22.22					
XM-D	2.98	25.5	20.1	1.02 ± 0.12	2.35 ± 0.59	3.37 ± 0.71	30.33					
SY-A	2.23	30.8	2.3	0.47 ± 0.06	1.25 ± 0.26	1.72 ± 0.32	27.47	0.46	0.37	1.24	0.05	3.6
SY-B	2.09	30.7	3.6	0.50 ± 0.08	1.16 ± 0.11	1.66 ± 0.19	30.14					
SCS-1	1.42	31.0	< 0.5	0.37 ± 0.06	0.55 ± 0.31	0.92 ± 0.37	40.18	0.27	0.38	0.71	0.07	2.4
WP-1	1.65	32.4	< 0.5	0.44 ± 0.09	0.56 ± 0.16	1.00 ± 0.25	44.03					
WP-2	1.4	32.2	< 0.5	0.32 ± 0.08	0.34 ± 0.19	0.66 ± 0.27	48.52	0.29	0.44	0.66	0.13	2.1
WP-3	1.54	31.9	< 0.5	0.36 ± 0.08	0.65 ± 0.33	1.01 ± 0.40	35.82					

^aHg available for photoreduction. ^bTotal Hg (THg) = Hgr(II)+remaining THg. ^cThe pseudo-first order rate constant of gross Hg(II) reduction under the condition of PAR of 1 m mol m⁻² s⁻¹. ^dThe pseudo-first order rate constant of gross Hg(0) oxidation under the condition of PAR of 1 m mol m⁻² s⁻¹. ^eThe zero order rate constant of Hg(II) reduction in the dark. ^fAll numbers following a ± sign represent the standard deviation of three samples.

propylene tubes,³² preserved with 0.4% (v/v) 12 M trace-metal grade HCl, placed into double bags, kept in the dark for analysis of remaining Hg.^{41,43} The %Hgr(II)/THg was obtained by %Hgr(II)/(Hgr(II)+remaining THg).

2.3.2. Rate Constants of Gross Hg(II) Reduction and Hg(0) Oxidation. In this study, we designed four different exposure treatments to explore quantitative relationships between rate constants of gross Hg(II) reduction (k_r) and Hg(0) oxidation (k_o) and the intensity of the solar radiation. The 0%, 50% and 87.5% and 100% of effective exposure surfaces of bubblers were wrapped with aluminum foil to obtain 100% (i.e., the full solar radiation), 50%, 12.5%, and 0% (i.e., the dark condition) exposure treatments to the full solar radiation, respectively. The incubation experiments were conducted at midday (ca. 10:30 to 14:30, local time) on cloudless days. Both the theoretical calculation⁴⁴ and our measurements (data not shown) show that the solar radiation is relatively stable at midday on cloudless days because the small change of solar angle and little effect of cloud. We therefore assumed that the solar radiation was kept constant during incubation experiments. The bubblers were upright during incubation. The setup of sample radiation did not significantly influence the radiation reaching samples since all parts of bubblers were made of quartz glass with high solar radiation transmissions and the small change of radiation angle at midday. We used the PAR as the surrogate of full solar

radiation since PAR is easily measured and strongly correlated with full solar radiation and UV radiation (UVA and UVB),³² although we have known that PAR only represents a portion of full solar radiation to trigger the Hg photochemistry.^{4,45,46} The rate constants of Hg(II) photoreduction and Hg(0) photo-oxidation obtained directly from incubation experiments were scaled up to the PAR or different waveband of solar radiation according to the solar radiation transmission of quartz glass and UVB and UV filters.

Experiments for determining the k_r was similar to those of Hgr(II). In a typical incubation experiment, for each treatment, aliquots (150 mL) of water sample in triplicate were distributed to three quartz bubblers. Before the incubation experiment, the waters were purged in the dark to remove the natural Hg(0) (i.e., [Hg(0)]₀). After exposure to the solar radiation, the formed Hg(0) in waters was removed continuously by purging and collected on the gold trap with ~0.1–0.5 h interval (i.e., [Hg(0)]_t). Then the k_r was calculated according to eq 2.

To determine the k_o , we used a gastight syringe to inject Hg(0)-saturated air into seawaters in sealed brown glass bottle to spike the natural seawaters. The bottle was shaken slightly and then the seawaters were delivered to quartz bubblers by a peristaltic pump in short time (<5 min). Hg(0) concentrations of seawaters in the bubblers at the beginning of the incubation experiment were considered as the final Hg(0) concentrations

of seawaters spiked with Hg(0). The spike concentrations of Hg(0) (~ 1.5 – 3.0 ng L^{-1}) were about 20–100 times greater than the ambient levels of Hg(0) in the surface seawaters of the eastern Asian seas and other typical marine environments.^{47–53} For each treatment, aliquots (150 mL) of seawaters spiked with Hg(0) were distributed to five quartz bubblers quickly. A bubbler was removed and measured for the remaining Hg(0) with the interval of 0.1–3 h. The method for calculating the k_o was similar to that of the k_r . Theoretically, the rate constants of Hg(0) oxidation in this study should be reported as the rate constants of net Hg(0) oxidation since the Hg(II) reduction and Hg(0) oxidation occurred simultaneously.^{30,54} However, as mentioned above, the seawaters spiked with Hg(0) were used to conduct incubation experiments. In the early hours of the incubation experiments, the decrease of Hg(0) in seawaters dominated by the oxidation of spiked Hg(0), and the increase of Hg(0) from the Hg(II) reduction could be negligible.^{30,54} Therefore, this simplification of the gross Hg(0) oxidation has little effect on the k_o (because of the relatively high uncertainties of rate constants of Hg redox reactions in present study) and simplifies interpretations of comparisons of rate constants of Hg(II) reduction and Hg(0) oxidation.

To assess the influence of SPM on the Hg redox chemistry, filtered ($0.45 \mu\text{m}$) waters were used for incubation. To study the influence of O_2 content on the Hg redox chemistry, the waters were purged with Hg-free air and Hg-free Argon to generate aerobic and anaerobic condition, respectively. To explore the effect of the different wavebands of solar radiation on the Hg photoredox chemistry, the quartz bubblers were wrapped with UVB or UV filters to remove the corresponding wavebands from the full solar radiation.

2.4. Analysis and Measurement. **2.4.1. Hg.** The ultratrace Hg techniques were used to determine the Hg(0) collected on gold traps and THg in seawaters.⁴¹ Hg(0) collected on gold traps was quantified with CVAFS (model III, Brooks Rand) with the two-stage amalgamations. The determination of THg in seawaters used the EPA method 1631,⁴³ following BrCl oxidation, SnCl_2 reduction, two-stage gold amalgamation, thermal release and CVAFS quantification. The method detection limit (MDL) for Hg(0) on gold traps and THg in seawaters was 0.3 pg and 0.10 ng L^{-1} , respectively. More details of the ultratrace Hg techniques and QA/QC for Hg determination are given in SI and our previous literatures.^{41,47,48}

2.4.2. DOC. DOC in filtered ($0.45 \mu\text{m}$) waters were determined with an elemental analyzer (vario TOC select, Elementar, Germany) using the high-temperature catalytic oxidation (HTCO) method. The detection limit is 0.02 mg L^{-1} with a precision within 2%.

2.4.3. SPM. SPM in waters was determined by filtering a known aliquot (0.40 – 2.0 L) of sample through a preweighed $0.45 \mu\text{m}$ pore-size filter, rinsing out the salts with Milli-Q water, and drying before reweighing.^{41,55} The MDL was 0.5 mg L^{-1} for a typical volume of 1.0 L .

2.4.4. Salinity. The salinity of water (PSU) collected from the offshore and open oceans was recorded by the rosette-mounted conductivity–temperature–depth (CTD) probe. The salinity of coastal waters was determined with the portable conductivity/salinity sensor (DDBJ-350, INESA, China).

2.4.5. Ambient PAR. The ambient PAR radiation was monitored using the PAR sensor (GLZ-C, TOP, China) with 1–5 min interval in the unit of $\text{m mol m}^{-2} \text{ s}^{-1}$.

3. RESULTS

3.1. Hgr(II) and Hgr(II)/THg. We collected 27 water samples from representative marine environments of the eastern Asian seas, representing a great gradients of THg (0.66 – 23.68 ng L^{-1}), salinity (25 – 33), SPM (<0.5 – 102.1 mg L^{-1}), and DOC (1.07 – 3.49 mg L^{-1}) (Table 1), to investigate the Hgr(II) pool and its influencing factors. An example illustrating how to determine the Hgr(II) pool in seawaters is shown in SI Figure S2. In this study, the considerable amount of Hg (range: 0.32 – 1.36 ng L^{-1} , mean $\pm$ SD: $0.65 \pm 0.32 \text{ ng L}^{-1}$, $n = 27$) was available for photoreduction. Moreover, the Hgr(II) pool were positively related to the THg, and a logarithmic increase of Hg(II) pools with increasing THg was suitable to fit this relationship (SI Figure S2). The %Hgr(II)/THg varied from 5.8% to 48.5% with a mean of $24.9 \pm 10.6\%$, and was exponentially declined with THg, that is, the high % Hgr(II)/THg was observed in open ocean waters with low THg and the low %Hgr(II)/THg in coastal waters with high THg (Figure 2). There was a strong positive and significant linear relationship between Hgr(II) and DOC (SI Figure S4).

Figure 2. Relationship between %Hgr(II)/THg and THg in 27 water samples collected from the representative marine environments of the eastern Asian seas.

Three representative coastal water samples, QHD-B, CD-C, and SY-B, were filtered ($0.45 \mu\text{m}$) to explore the effect of SPM on the Hgr(II) pool. As shown in Figure 3, filtration significantly ($p < 0.001$) decreased THg for all three samples,

Figure 3. Effect of filtration ($0.45 \mu\text{m}$) on THg concentrations and Hgr(II) pools for three representative coastal water samples (QHD-B with high SPM and THg, CD-C with moderate SPM and THg, and SY-B with low SPM and THg, see Table 1 for details).

QHD-B (65.4%), CD-C (60.0%), and SY-B (42.8%). However, Hg(II) pools were insignificantly different between filtered and unfiltered waters for CD-C ($p = 0.23$) and SY-B ($p = 0.35$). Only the Hg(II) pool of QHD-B significantly ($p < 0.001$) decreased by 52.3% (from 1.30 ng L^{-1} to 0.62 ng L^{-1}).

3.2. Hg Redox Chemistry. **3.2.1. Hg(II) Reduction.** Thirteen samples were incubated to determine quantitative relationships between the k_r and the PAR intensity. A typical example is shown in SI Figure S5. For all incubated samples ($n = 13$), simple linear relationships were found to fit the k_r and PAR well with R^2 ranging between 0.96 and 0.99 ($p < 0.001$) (see SI Figure S5B, C for a typical example). Because of linear relationships, the slopes of regressions correspond to pseudo-first order rate constants of Hg(II) reduction under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$ (see SI Figure S5C for example and Table 1 for all data). This method allows comparisons among different treatments, different days and even different studies.

The k_r of 13 samples in full solar radiation at midday varied between 0.32 and 0.62 h^{-1} . The k_r under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$ ranged from 0.24 to 0.46 h^{-1} with a mean of $0.32 \pm 0.06 \text{ h}^{-1}$ (Table 1). There was no significant linear relationship between the k_r under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$ with DOC, salinity and SPM at significant level of 0.05 (SI Figure S6).

Theoretically, the intercepts of regressions correspond to the pseudo-first order rate constant of Hg(II) reduction in the dark, which varied between 0.002 to 0.015 h^{-1} . We plotted the cumulative Hg(0) produced during dark reduction incubation experiments versus the duration of incubation time and found strongly positive and significant linear relationships between them. A typical example is shown in SI Figure S7. The assumption of zero order rate constants of gross Hg(II) reduction in the dark generally leads to a good fit with experimental results. For all 12 incubated seawaters, strongly positive and significant correlations were observed between zero order rate constants of gross Hg(II) reduction in the dark and THg (Figure 4). The Hg(0) production rates ($2\text{--}20 \text{ pg}$

Figure 4. Zero order rate constants of Hg(II) reduction in the dark ($\text{pg L}^{-1} \text{ h}^{-1}$) versus THg concentrations in waters. Note that the linear regression was not constrained to pass through the origin.

$\text{L}^{-1} \text{ h}^{-1}$) in the dark were $\sim 10^2$ times lower than those in full solar radiation at midday ($130\text{--}2000 \text{ pg L}^{-1} \text{ h}^{-1}$). Because of the extremely low rate constants of Hg(II) reduction in the dark compared to those in the light, rate constants of Hg(II) dark reduction was ignored in the below relative calculations.

Figure 5 shows that the rate constants of Hg(II) dark reduction of seawaters purged with Hg-free Argon were

Figure 5. Effect of aerobic (Hg-free air as the purging gas) and anaerobic (Hg-free Argon as the purging gas) conditions on the rate of Hg(0) production in the dark.

significantly ($p < 0.05$) higher than those purged with Hg-free air. The highest increase of rate constants (140%) was observed in ECS-3, which has the lowest rate constants of Hg(II) reduction in the aerobic condition.

3.2.2. Hg(0) Oxidation. Thirteen samples used to determine rate constants of gross Hg(II) photoreduction were also incubated to determine rate constants of Hg(0) photo-oxidation. A typical example is shown in SI Figure S8. The k_o in full solar radiation at midday varied from 0.43 to 0.90 h^{-1} . Simple linear relationship was also found to fit the k_o and PAR well (R^2 ranging between 0.97 and 0.99, $p < 0.001$, see SI Figure S8B, C for a typical example). The slopes of regressions correspond to the k_o under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$ (see SI Figure S7C for a typical example). The slopes ranged from 0.30 to 0.52 h^{-1} with a mean of $0.38 \pm 0.06 \text{ h}^{-1}$ (Table 1). The k_o under the condition of PAR of $1 \text{ m mol m}^{-2} \text{ s}^{-1}$ were found to show a significant and positive correlation with salinity, a significant but negative correlation with DOC, and no significant correlation with SPM (SI Figure S9).

Similarly, the intercepts of linear regressions between the k_o and PAR correspond to the k_o in the dark. These intercepts for all regressions ranged from 0.05 to 0.13 h^{-1} with a mean of $0.07 \pm 0.02 \text{ h}^{-1}$ (Table 1), and was not significantly different from the values determined from incubation experiments of Hg(0) oxidation in the dark ($p = 0.453$). The rate constants of Hg(0) dark oxidation was positively and significantly correlated with salinity at significant level of 0.10 (SI Figure S10).

3.2.3. The Impact of SPM. The filtered samples of QHD-B, CD-C and SY-B were further incubated to explore the impact of SPM on the Hg photoredox chemistry. The data show that for all three samples, filtration significantly ($p < 0.001$) decreased the Hg(II) dark reduction, QHD-B (77.5%), CD-C (53.5%), SY-B (61.3%), but did not influence the Hg(0) dark oxidation (Figure 6A, B). Filtration significantly increased the k_r and decreased k_o of QHD-B in the light ($p < 0.05$), but did not significantly influence either the k_r or k_o of CD-C ($p = 0.23$) and SY-B ($p = 0.16$) in the light (Figure 6C).

3.2.4. The Impact of Different Wavebands of Solar Radiation. We incubated three representative samples, CD-B (the coast water), ECS-2 (the offshore water), and WP-1 (the open ocean water), to examine the effect of different wavebands of solar radiation on the Hg photoredox chemistry. For the

Figure 6. Using three representative coastal water samples (QHD-B with high SPM and THg, CD-C with moderate SPM and THg, and SY-B with low SPM and THg) to investigate the effect of SPM on the Hg redox reactions in the light and dark condition. (A) The effect of filtration on the Hg(II) dark reduction. (B) The effect of filtration on the pseudo-first order rate constants of gross Hg(0) dark oxidation. (C) The effect of filtration on the pseudo-first order rate constants of gross Hg(II) reduction and gross Hg(0) oxidation in full solar radiation at midday on cloudless days. The incubation experiments for filtered and unfiltered water of each sample were performed at the same time since the PAR intensity has important influence on the Hg photochemistry (see text).

Figure 7. Effect of different wavebands of solar radiation on the Hg(II) photoreduction and Hg(0) photo-oxidation for three typical water samples (CD-B with high THg and SPM, ECS-2 with moderate THg and SPM, and WP-1 with low THg and SPM). The incubation experiments included four radiation treatments: full solar radiation (UVB + UVA + visible light), no UVB (UVA + visible light), no UV (visible light only) and dark treatment. (A) The effect of different wavebands of solar radiation on the pseudo-first order rate constants of gross Hg(II) photoreduction. The rate constants of Hg(II) dark reduction was extremely low (see text) and the data are not shown. (B) The effect of different wavebands of solar radiation on pseudo-first order rate constants of gross Hg(0) photo-oxidation at midday.

Hg(II) photoreduction, UVB radiation accounted for ~30–55% of full solar radiation for these three samples (Figure 7A). The remaining photoreduction of Hg(II) mainly mediated by the visible light, except for the sample of CD-B, in which the UVA radiation contributed to the detectable fraction (~20%) of total Hg(II) photoreduction. For the Hg(0) photo-oxidation, UVB radiation accounted for ~25–50% of the full solar radiation (Figure 7B). Different from on the Hg(II) photoreduction, the contribution of UVA radiation on the Hg(0) photo-oxidation was comparable to or slightly higher than that of the UVB radiation (Figure 7). For WP-1 with low THg and SPM, UVA radiation was more important than UVB radiation on the Hg(0) photo-oxidation. The role of visible light in the Hg(0) oxidation was not so important, the Hg(0) oxidation triggered by the visible light were slightly but significantly higher than those in the dark ($p < 0.01$).

4. DISCUSSION

It is well-known that some fractions of Hg in both freshwaters and seawaters can be reduced to form Hg(0) under natural sunlight or artificial radiation.¹⁰ However, the focused

investigation of Hgr(II) pool and its controlling factors in seawaters are sparse. In this study, the measurements of waters from representative marine environments of the eastern Asian seas revealed that there was considerable amount of Hg available for photoreduction. The positive relationships between Hgr(II) pool and THg (Figure 2 and SI Figure S3) indicate that coastal waters with high THg had large potentials to produce more Hg(0) in the light, and high %Hgr(II)/THg in open ocean waters with low THg indicates the relatively rapid cycling of Hg in surface open ocean. The fact that the Hg in waters with high THg and SPM was less efficiently photoreduced is possibly subjected to the strong Hg complexation.⁵⁶ The positive correlations between Hgr(II) and DOC indicate that the presence of DOC possibly favored the Hg photoreduction.⁸

It is well documented that Hg mainly presents in particulate phase in aquatic environments, especially for the waters with high SPM.^{41,57,58} However, the effect of SPM on Hgr(II) pool is poorly investigated. In this study, as expected, filtration significantly decreased THg (Figure 3). However, the effect of SPM on Hgr(II) pool was more complicated. We found that in

seawaters with low SPM, Hg(II) primarily presented in dissolved phase, but in seawaters with high SPM, Hg(II) partly presented in particulate phase (Figure 3). It indicates that the involvement of SPM (including organisms and mineral particles) directly or indirectly increased the Hg(II) pool or stimulated Hg(II) photoreduction,^{9,22,23,31,59–62} although our study could not ascertain the threshold of the loadings and chemical or biological compositions of SPM that influence the Hg(II) pool.

At present, the nature of the photoreducible Hg(II) in aquatic environments is complex and unknown. Beside of concentrations of Hg, SPM, and DOC, the Hg(II) pool may also depend on many other factors, such as the structure of DOC, the concentrations of inorganic ligands, pH, the radiation, and so on.^{45,63} Although we reported a relationship between THg and Hg(II), the relationship may be different in other regions and even at different sampling times for the same regions due to the change of water chemistry. Therefore, additional field and laboratory works are required to understand the site-to-site differences in the photoreducible Hg.

In this study, the strongly positive linear relationships between rate constants of Hg photoredox reactions and solar radiation (PAR was measured as the surrogate of full solar radiation) indicate that the radiation was the dominant factor controlling photoinduced transformations of Hg, which is constant with many other studies.^{4,10,21,30,64} It suggests that the photochemical processes overwhelmingly dominate transformations of Hg in surface waters of oceans and seas. The rapid transformations of Hg among different species in the light also highlight that the waters sampled for Hg(0) determination must be kept in dark prior to analysis.

A direct comparison of rate constants of Hg photoredox reaction among different experiments is difficult since intensity and wavebands of radiation greatly influence the Hg photoredox chemistry and most previous studies did not report the detailed information of radiation. Furthermore, many different terms (reaction kinetics, gross reaction kinetics or net reaction kinetics) have been used to report rate constants of Hg redox reactions in different literatures with various incubation protocols and calculation methods.⁵⁴ Roughly, the rate constants of gross Hg(II) reduction ($0.24\text{--}0.46\text{ h}^{-1}$) at midday in full solar radiation in our study are comparable to previously reported values of salt waters ($0.1\text{--}1.5\text{ h}^{-1}$)^{6,10} and freshwaters ($0.1\text{--}1\text{ h}^{-1}$).^{32,64} The rate constants of gross Hg(0) oxidation ($0.30\text{--}0.52\text{ h}^{-1}$) at midday in full solar radiation were also comparable to other salt waters,^{6,65,66} but were clearly higher ($\sim 5\text{--}10$ times) than those of freshwaters, where Hg(0) oxidation was either not detectable or relatively slow.^{66,67}

Because of linear relationships between rate constants of Hg gross photoredox reactions and PAR intensity, the ratio of k_r/k_o for the same radiation should be more proper to compare the relative importance of Hg(II) reduction and Hg(0) oxidation. In our study, the ratios of k_r/k_o under the condition of PAR of $1\text{ m mol m}^{-2}\text{ s}^{-1}$ varied from 0.60 to 1.24 with a mean of 0.86 ± 0.22 ($n = 13$). These ratios were significantly lower than 1 ($p < 0.05$), indicating that the magnitude of Hg(0) photo-oxidation was greater than that of Hg(II) photoreduction in our seawaters. Similar results were also reported by Whalin et al.⁶ with a limited number of coastal waters from the Chesapeake Bay.⁶ Compared to freshwaters with relatively high rate constants of Hg(II) photoreduction,^{66,67} these ratios further suggest the importance of Hg(0) oxidation in salt waters. Previous studies suggest that the presence of chloride effectively

promotes the Hg(0) oxidation in salt waters.^{22,65,66} The above discussion highlights that the marine ecosystems are more vulnerable to Hg contamination compared to freshwater ecosystems since the enhanced oxidative process could greatly increase the Hg residence time in marine environments.

The effect of DOC on the Hg redox reactions in aquatic environments may be one of the most challenging issues on the Hg biogeochemistry.³⁶ Our results show that high DOC in seawaters favored the Hg(II) photoreduction (SI Figure S6) and decreased the Hg(0) photo-oxidation (SI Figure S9). This finding is consistent with the study of Costa and Liss,⁸ who observed that seawaters spiked with humic acid had enhanced Hg(II) reduction rates.

The effect of salinity on the Hg redox reactions seems to be relatively clear. It is well documented that high salinity promotes the Hg(0) oxidation in aquatic environments.^{22,65,66} We also found that high salinity induced high k_o in the light, and a positive correlation between salinity and the k_o in the dark was also found at significant level of 0.10 (SI Figure S10). This study and many other studies show that the k_r of fresh waters and salt waters in the light are comparable, indicating the salinity does not significantly influence the Hg(II) photoreduction.

The effect of SPM on the Hg redox chemistry seems to be more complicated. For all water samples incubated to study the Hg photoreaction kinetics, no significant correlation was found between the k_r and SPM (SI Figure S6B), and a negative correlation between the k_o and SPM at a significant level of 0.09 (SI Figure S9B). We further incubated filtered waters of three representative coastal waters and found the filtration only influenced the Hg photoredox chemistry of QHD-B with high SPM (Figure 6). The high k_r of filtered QHD-B in the light was likely caused by the increased light penetration and weak Hg complexation in dissolved phase.⁵⁶ The decreased k_o of filtered QHD-B in the light probably indicates that Hg(0) photo-oxidation occurred heterogeneously.³⁹ The decreased rate constants of Hg(II) dark reduction of filtered waters indicate that the involvement of SPM could promote the Hg(II) dark reduction. The most likely role of SPM in the Hg(II) dark reduction was the involvement of organisms since the Hg(II) dark reduction regulated by the biological process has been extensively identified in marine environments.^{9,68}

In our study, the Hg(0) photo-oxidation was mainly triggered by the UV radiation (UVB and UVA radiation), and the visible light was also significantly contributed to the Hg(II) photoreduction (Figure 7). Many studies suggest the complicated effect of different wavebands of radiation on the Hg photoredox chemistry in aquatic environments.^{4,45,46} In most instances of previous studies, the UV radiation was found to significantly promote the Hg(II) production and Hg(0) oxidation in both salt and fresh waters.^{4,46} However, Hg(II) photoreduction in some freshwaters with high DOC could not be triggered by the UVB radiation (e.g., ref 45). The above discussions suggest that the Hg photoredox chemistry for different water chemistry was sensitive to different wavebands of solar radiation.

The Hg(II) dark reduction was low but detectable and followed the zero order kinetics (SI Figure S7). The comparable rate constants of Hg(II) dark reduction were also reported in previous studies.^{9,69} The zero order rate constants of Hg(II) dark production was positively related to THg (Figure 4), which is constant with other studies.^{9,69} We speculated that the Hg(II) dark reduction was possibly

controlled by the chemical and biological mechanisms related to heterogeneous reactions that the SPM involved, such as microbe and mineral particles^{7,9,23–31,31,59–62,68} since filtration significantly decreased the rate constants of Hg(II) dark reduction (Figure 6A). The rate constants of Hg(II) dark reduction were enhanced under the anaerobic condition (Figure 5), which is constant with the finding of Beucher.⁶⁹ The above discussions indicate that Hg(0) can be produced continuously in the entire water column in the oceans throughout the entire day. The findings also highlight the important role of deep seawaters with enhanced THg (e.g., in coastal and marginal seas) in the marine Hg biogeochemical cycle since the high THg in these waters potentially induces the remarkable Hg(0) production in the dark and anaerobic condition. This finding might explain why the considerable Hg(0) has been extensively observed in deep waters in some coastal and marginal seas,^{48,70} where the photoreduction was unlikely to play a major role. The results also suggest that the long purging time with N₂ or Argon could potentially result in positive artifacts of purgeable Hg(0) measurements.

In some previous studies, the Hg(II) dark reduction was not observed in aquatic environments (e.g., ref 22). It is noted that in these experiments, incubated waters were generally not purged continuously to remove the produced Hg(0). Since the Hg(II) reduction and Hg(0) oxidation occur simultaneously in the dark, if the waters used for incubation are kept in the dark for long enough prior to incubation experiments, the Hg(0) in waters will have reached a plateau, then in the course of dark incubation, the change of Hg(0) is too little to detect because of the balance of Hg(II) reduction and Hg(0) oxidation in the dark.

In this study, rate constants of Hg(0) dark oxidation were $\sim 10^2$ times higher than those of Hg(II) dark reduction. The rate constants of Hg(0) dark oxidation were also clearly higher than those of freshwaters.^{18,66} The high rate constants of Hg(0) dark oxidation in seawaters suggest that the water samples used to determine the Hg(0) should be purged as soon as possible after sampling. A more recent study suggested that the Hg(0) might bond to SPM in lake waters,⁷¹ indicating the rate constants of Hg(0) dark oxidation obtained from incubation experiments probably have positive artifacts. However, in our study filtration did not significantly influence the Hg(0) dark oxidation kinetics (Figure 6B). Thus, the phase distribution of Hg(0) in fresh waters may differ from that in salt waters since freshwaters are generally low in ionic strength and high in alkalinity and DOC. It indicates that the interaction between Hg(0) and SPM in aquatic environments may be different system-to-system and even site-to-site.

■ ASSOCIATED CONTENT

■ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05372.

Figure S1–S10 and text (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was funded by the National Key Basic Research Program of China (No. 2013CB430002) and National Natural Science Foundation of China (Nos. 41203068, 41573117, 41176066, and 41371461) and Young Scientists Fund of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences (No. RCEES-QN-20130048F). We thank Hui Huang and Weihua Zhou (South China Sea Institute of Oceanology, Guangzhou) for their assistance in field experiments. We are grateful for the assistance of the captains and crews of the R/V *Kexue I* (Institute of Oceanology, Chinese Academy of Sciences), *Dongfanghong II* (Ocean University of China) and *Beidou* (Yellow Sea Fisheries Research Institute, Chinese Academy of Fishery Sciences, the Ministry of Agriculture) in the water sampling and data collections. We thank the reviewers for their valuable comments and suggestions.

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