Elemental Mercury in Natural Waters: Occurrence and Determination of Particulate Hg(0)

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Supporting Information

ABSTRACT: Elemental mercury, Hg(0), is ubiquitous in water and involved in key Hg biogeochemical processes. It is extensively studied as a purgeable dissolved species, termed dissolved gaseous mercury (DGM). Little information is available regarding nonpurgeable particulate Hg(0) in water, Hg(0) bound to suspended particulate matter (SPM), which is presumably present due to high affinity of Hg(0) adsorption on solids. By employing stable isotope tracer and isotope dilution (ID) techniques, we investigated the occurrence and quantification of particulate Hg(0) after Hg(0) being spiked into natural waters, aiming to provide firsthand information on particulate Hg(0) in water. A considerable fraction of ²⁰¹Hg(0) spiked in water (about 70% after 4 h equilibration) was bound to SPM and nonpurgeable, suggesting the occurrence of particulate Hg(0) in natural waters. A scheme, involving isotope dilution, purge and trap, and inductively coupled plasma mass spectrometry detection, was proposed to quantify particulate Hg(0) by the difference between DGM and total Hg(0), determined immediately and at equilibration after spiking ID Hg isotope, respectively. The application of this newly established method revealed the presence of particulate Hg(0) in Florida Everglades water, as the determined DGM levels (0.14 to 0.22 ng L⁻¹) were remarkably lower than total Hg(0) (0.41 to 0.75 ng L⁻¹).

INTRODUCTION

Mercury (Hg), as a global pollutant, has received great attention due to accumulation and biomagnification of its methylation product, methylmercury (MeHg), through aquatic food chains. Elemental mercury, Hg(0), is an important species in Hg cycling, as considerable levels of Hg(0) are present in all environmental media, including the atmosphere (up to 95% of Hg being Hg(0)),^{1,2} soil³ and sediment,⁴ and water.⁵ Previous studies have shown that dissolved gaseous Hg (DGM), being mainly composed of Hg(0), is a ubiquitous form of inorganic Hg in seawater,^{5,6} fresh water,^{7–9} and groundwater.^{10,11} Hg(0) in water is involved in key processes of Hg biogeochemical cycling including air–water exchange,¹² oxidation–reduction,⁸ and methylation–demethylation.¹³ Hg(0) can be oxidized to Hg(II) by both chemical and biological processes in aquatic environments,^{6,7,14–17} and reduction of Hg(II) can produce Hg(0) in water, through photochemical processes,^{6,18–20} enzymatic catalysis by mercury-resistant microorganisms,^{7,21–23} or geochemical reactions involving humic acids and mineral-associated

ferrous ion.^{24–27} It was recently observed that dissolved Hg(0) could be methylated by *Desulfovibrio desulfuricans* ND132 to form MeHg,^{13,14} which was a previously unrecognized pathway in Hg cycling. MeHg photodegradation in natural waters could also produce Hg(0) as an end product.^{28–30} It should be noted that Hg(0) can be present in two forms in water, liquid Hg(0) droplet and aqueous Hg(0) (denoted as Hg(0)^{aq} for distinction in some cases), with the former being rarely observed in uncontaminated natural waters and the latter being ubiquitous and of more environmental relevance.^{8,17} The Hg(0) in this study is referred to the aqueous form, and Hg(0), instead of Hg(0)^{aq}, was used throughout the paper.

Despite being ubiquitous and playing a key role in Hg biogeochemical cycling, Hg(0) in natural waters has not been

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well understood with respect to its occurring forms and measurement. Hg(0) can be present as a dissolved species in water that has been the Hg(0) form being focused in the overwhelming majority of previous studies. In natural waters, Hg(0) could be bound to suspended particulate matter (SPM) and dissolved organic matter (DOM), with these forms of particulate Hg(0) and DOM-complexed Hg(0) being rarely studied. Although direct evidence for the presence of SPM-bound particulate and DOM-complexed Hg(0) in water is scarce, these Hg(0) species are presumably present in natural waters, reasoning from previously reported sorption of Hg(0) on various soils, clay minerals, and other solid materials. It has been shown that charcoal, peat, humic acid (HA), and illite were among the most effective materials adsorbing Hg(0),^{3,31,32} and Hg(0) could be rapidly adsorbed on lake sediment (likely related to organic matter).⁴ Recently, strong interactions between reduced HA and Hg(0) through thiolated ligand-induced oxidative complexation was observed under anoxic dark conditions with an estimated binding capacity of $\sim 3.5 \mu\text{mol Hg/g HA}$ and a partitioning coefficient $>10^6 \text{ mL/g}$, a value similar to the binding of Hg(II)-DOM.³³

The occurrence of and differentiation among dissolved, particulate, and DOM-complexed Hg(0) in natural waters present a challenge to a full understanding of cycling and fate of Hg(0) in aquatic environments. This is particularly true when considering that Hg(0) in water has been exclusively determined by procedures involving purge and trap aiming to directly purge Hg(0) out of water.⁶ Conventionally, water sample is purged for a certain period of time with nitrogen or argon, and the Hg(0) volatilized by purging was trapped on a gold-coated sand trap, followed by pyrolysis desorption and detection on atomic fluorescence spectrometry (AFS) or inductively coupled plasma mass spectrometry (ICPMS).^{6,9,16,17} This method is straightforward and easy to follow,^{6,18} but it has critical limitations depending on how the measured data is used. This conventional method measures only the volatile or purgeable Hg(0) fraction of the aqueous Hg(0), and as such the Hg(0) so measured is often operationally termed DGM. If particulate Hg(0) is present in water, one can reasonably presume that it could not be purged efficiently from water. Indeed, lower DGM levels have been observed in surface waters with higher SPM concentrations, probably due to SPM-bound Hg(0) being nonpurgeable.³⁴ The inability of the current Hg(0) determination method in differentiating particulate and dissolved Hg(0) could result in underestimation of total Hg(0) concentrations and incomplete information on Hg(0) transformation and fate in water.

The presence of particulate, nonpurgeable Hg(0) in water should be taken into account when studying Hg species transformation. As a common practice in studying the oxidation and reduction processes of Hg in water, a decrease in Hg(0) after being introduced in water is often attributed to the oxidation of Hg(0) to Hg(II).^{6,18} This practice, however, could result in misleading conclusions due to the fact that both oxidation from Hg(0) to Hg(II) and reduction from Hg(II) to Hg(0) can occur simultaneously and a fraction of Hg(0) could rapidly become nonpurgeable upon being adsorbed onto SPM in water. In a preliminary study on Hg photoreduction in Everglades water performed in our laboratory, a mass balance calculation of the spiked Hg showed a recovery of approximately 60% using the traditional purge and trap technique, indicating that a large fraction of Hg(0) is nonpurgeable. Therefore, quantification of both dissolved and particulate Hg(0) is necessary in order to fully

understand the role of Hg(0) in Hg transformation and cycling in water.

The objective of this study was to improve our understanding toward the behavior of Hg(0) in natural waters by evaluating the influence of SPM and DOM on Hg(0) purgeability and quantifying Hg(0) fractions that are both purgeable (as DGM) and nonpurgeable (as particulate Hg(0) being the difference between total Hg(0) and DGM), aiming to provide the first published study on the occurrence and quantification of particulate Hg(0) in water. Stable isotopic tracer $^{201}\text{Hg}(0)$ was spiked into natural water (with $^{199}\text{Hg}(\text{II})$ being added for comparison purpose). The behavior of Hg(0) and Hg(II) was monitored through determination of Hg species involved in the process using isotope dilution (ID) analysis (with $^{200}\text{Hg}(0)$ being ID isotope). Owing to the high accuracy and precision, both stable isotope tracer and isotope dilution techniques have been increasingly applied to Hg research such as determination of methylation/demethylation^{15,30,35–41} and reduction/oxidation rates³⁵ and ultratrace analysis of Hg species in complex matrices.⁴² On the basis of these two techniques, a scheme based on purge and trap-ID-ICPMS was proposed for quantification of dissolved and particulate Hg(0) in natural waters.

MATERIALS AND METHODS

Instrumentation, Materials, and Chemicals. A PerkinElmer Elan ICPMS (Elan DRC-e) was used for detection of Hg isotopes. Enriched stable Hg isotopes of ^{201}Hg , ^{200}Hg , and ^{199}Hg were obtained as HgO from Oak Ridge National Laboratory (Oak Ridge, Tennessee, USA) and Trace Sciences International Pilot Point (Texas, USA). Humic acids, HA1 from Acros (Sodium Salt, 50–60% as HA) and HA2 from International Humic Substance Society (Waskish HA, peat, 1R107H), were used. Detailed information for ancillary equipment (bubblers, traps, and desorption devices), other reagents (analytical grade or higher), reagent preparation, and glassware cleaning can be found in the [Supporting Information](#).

Preparation of Isotopic Hg(0) Stock Solutions. The stock solutions of isotopic Hg(0) were prepared through reduction of Hg(II) with acidic SnCl_2 solution, and detailed procedures can be found in the [Supporting Information](#). The Hg(0) stock solution was kept at 4°C in the dark and used for a period of about 30 days. For each use the concentrations of Hg(0) in the solutions were determined using the reverse isotope dilution by spiking natural Hg standard of known concentration and purity.^{43,44} Two Hg(0) stock solutions, $^{201}\text{Hg}(0)$ and $^{200}\text{Hg}(0)$, were prepared, with the former being used as tracer Hg isotope and the latter as the ID Hg isotope during ID-ICPMS quantification.

Evaluating Purgeability of Hg(0) from Water. All experiments in this study were conducted in triplicate and in the dark (with aluminum foil wrapping to eliminate the effect of radiation-induced reactions), unless stated otherwise. An initial experiment was conducted to evaluate the purgeability of Hg(0) spiked into natural water. To a quartz bottle, 100 mL of water collected from a small lake located at Florida International University (FIU) or DI water (as control) was added. The lake water was determined to have a pH of 8.0 and contain a SPM concentration of 5.2 mg L^{-1} and DOC of 5.7 mg L^{-1} . The lake water is primarily from rainwater runoff and contains little plant debris or algae, and the SPM is expected to be mainly composed of inorganic minerals (though which could be naturally coated with organic matter). Internal headspace was minimized to prevent loss of Hg(0) by volatilization. These water samples were

spiked with $^{201}\text{Hg}(0)$ stock solution to achieve a concentration of approximately 4.0 ng L^{-1} of $\text{Hg}(0)$, and the Hg spike levels used in all the experiments were about a few ng L^{-1} for the study to be environmentally relevant. The samples were slowly transferred to a 150 mL bubbler after being left at room temperature for 0, 1, and 4 h. Once being transferred into the bubbler, the sample was purged immediately with Ar ($350 \pm 35 \text{ mL min}^{-1}$) to collect $\text{Hg}(0)$ onto a gold trap. Release of the collected $\text{Hg}(0)$ was performed by heating the trap at 500°C with an Ar flow of $200 \pm 20 \text{ mL min}^{-1}$, followed by detection of Hg isotopes using ICPMS. The nonpurgeable Hg in solution was determined following BrCl oxidation for 24 h.^{33,45} After oxidation, Hg in the solution was reduced by SnCl_2 and determined using ICPMS.

Examining Effects of SPM and DOM on Purgeability of $\text{Hg}(0)$ from Natural Waters. As the initial experiment showed that not all $\text{Hg}(0)$ after spiking was purgeable with time, further experiments were conducted to examine if the nonpurgeable $\text{Hg}(0)$ is associated with SPM or DOM. To assess the effect of DOM on purging efficiency of $\text{Hg}(0)$, DI water (100 mL) with varying HA concentrations (0, 0.1, 0.3, 1.3, 5.3 mg L^{-1} for HA1 and 0, 0.2, 0.5, 1.8, 7.3, 14.5 mg L^{-1} for HA2) was spiked at approximately 4.2 ng L^{-1} of $^{201}\text{Hg}(0)$. After 4 h of equilibrium, the solutions were transferred to bubblers and analyzed for $\text{Hg}(0)$ following the similar purging, desorption, and detection procedures aforementioned. The influence of SPM on purging efficiency of $\text{Hg}(0)$ was determined by comparing the results of water samples with or without filtration using a $0.45 \mu\text{m}$ polyvinylidene fluoride (PVDF) filter. The water samples were spiked with 4.2 ng L^{-1} of $^{201}\text{Hg}(0)$ and left in the dark for 4 h before purging and analysis of $\text{Hg}(0)$.

A separate experiment was carried out to further evaluate the time-dependent purging efficiency of $\text{Hg}(0)$ and the kinetics of the equilibration between the spiked $\text{Hg}(0)$ isotope and ambient Hg . Lake water (100 mL) in quartz bottles was spiked with $^{201}\text{Hg}(0)$ at a final concentration of approximately 6.6 ng L^{-1} , and a series of bottles with such a sample was prepared. Three bottles (as triplicate) were taken, purged, and determined for purgeable $\text{Hg}(0)$ at 0, 0.5, 1, 4, 8, 24, 48, and 72 h, respectively. At each time interval, the water samples after purging were subjected to oxidation with BrCl , followed by reduction with SnCl_2 and purging with Ar for analysis of nonpurgeable $\text{Hg}(0)$ (so termed for discussion purpose). Similar experiments using DI water instead of lake water were carried out as controls. For mass balance calculation, the sum of purgeable and nonpurgeable $\text{Hg}(0)$ was compared with the amount of $\text{Hg}(0)$ spiked.

Fractionation of Dissolved and Particulate Hg in Natural Water after $\text{Hg}(0)$ Being Spiked. Our experiments suggest that significant loss of purgeable $\text{Hg}(0)$ after being spiked in natural water was attributed to adsorption on SPM present in the sample. To further examine the presence of SPM-bound particulate $\text{Hg}(0)$, i.e. the Hg adsorbed on SPM after $\text{Hg}(0)$ being spiked is still in the oxidation state $\text{Hg}(0)$ rather than being present in the mercuric form $\text{Hg}(\text{II})$, a series of speciation analysis experiments were conducted. Two Hg isotopes, $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$, were simultaneously spiked into the lake water at final concentrations of approximately 7.83 and 13.56 ng L^{-1} of Hg , respectively. Simultaneous addition of $^{199}\text{Hg}(\text{II})$ can provide useful information on species conversation and distribution during the course of experiments. The sample was equilibrated at $22 \pm 1.0^\circ\text{C}$ in the dark for 4 h. Control experiments using DI water suggest that loss of Hg and speciation transformation during the procedures are negligible,

as 87–92 and 91–96% of $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$ can be recovered. The Hg species was operationally divided into three fractions, including directly purgeable $\text{Hg}(0)$, particulate Hg , and dissolved Hg (Figure S2). The purgeable $\text{Hg}(0)$ was determined directly by purge-and-trap ICPMS. After purging, the sample solution in the bubbler was filtered with a $0.45 \mu\text{m}$ membrane (PVDF) to differentiate dissolved and particulate Hg .

The particulate Hg , which is retained on the filter membrane (termed as SPM- Hg), was investigated for the Hg oxidation state by using a thermal desorption method based on the fact that $\text{Hg}(0)$ and $\text{Hg}(\text{II})$ are released at different temperatures from the solid matrix. The thermal desorption method has been used before for Hg speciation in soils, which suggests that $\text{Hg}(0)$ in the solid matrix could be released at $150\text{--}200^\circ\text{C}$, while $\text{Hg}(\text{II})$ requires higher temperature ($200\text{--}250^\circ\text{C}$).^{46–48} Since $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$ were spiked into the water, it is expected that ^{201}Hg would be released at a lower temperature, whereas ^{199}Hg at a higher one. The filter containing SPM- Hg was transferred into a glass tube ($1/4'' \text{ od} \times 12 \text{ cm}$), with one end of tube being connected to Ar gas cylinder using Teflon tubing while the other to a soda lime drying column ($1/4'' \text{ od} \times 10 \text{ cm}$) and then to a gold trap. The glass tube was heated at 150°C for 40 min inside an oven to release particle-bound $\text{Hg}(0)$ which was collected on the gold trap at an Ar flow of $350 \pm 35 \text{ mL min}^{-1}$. After that a separate gold trap was connected to the glass tube which was then continued to be heated for another 40 min at 200°C for release and collection of $\text{Hg}(\text{II})$. The gold traps were then connected to ICPMS and thermally desorbed at 500°C with Ar ($200 \pm 20 \text{ mL min}^{-1}$) for Hg analysis.

For further fractionation of dissolved Hg , the filtrate was reacted with acidic SnCl_2 (20%, 0.2 mL) solution ($\text{pH} = 2\text{--}3$) and then purged with Ar . The Hg collected and measured by this treatment, representing the fraction of $\text{Hg}(0)$ that is weakly bound to dissolved substances (dissociated upon exposure to acidic solution) and/or the reactive SnCl_2 -reducible Hg^{2+} in the sample, was termed weakly bound Hg .^{49,50} The filtrate after SnCl_2 treatment was subjected to oxidation for 24 h after adding 2.0 mL of BrCl solution, followed by addition of 0.2 mL of $\text{NH}_2\text{OH}\cdot\text{HCl}$ to consume excessive BrCl . The Hg in the solution was then determined after adding 1.0 mL of SnCl_2 , followed by purge-and-trap-ICPMS. This fraction of Hg , representing the Hg that was strongly bound with dissolved materials that was not directly reducible by SnCl_2 , was defined as strongly bound Hg .^{49,50}

Determination of Dissolved and Particulate $\text{Hg}(0)$ in Natural Waters. Since we observed in the experiments that formation of particulate $\text{Hg}(0)$ through adsorption of $\text{Hg}(0)$ on SPM was primarily accountable for the nonpurgeable $\text{Hg}(0)$ and the interaction of spiked $\text{Hg}(0)$ with ambient Hg could approximately reach equilibrium in 4 h, we proposed a scheme for determination of both dissolved and particulate $\text{Hg}(0)$ in natural waters using the purge-and-trap ID-ICPMS technique. Surface water samples were collected from the Florida Everglades, and each sample was split into two aliquots for $\text{Hg}(0)$ analysis. First, one aliquot of water samples (100 mL) was spiked with $^{201}\text{Hg}(0)$ as ID Hg isotope upon arrival in the laboratory and immediately purged for 15 min at an Ar flow of $350 \pm 35 \text{ mL min}^{-1}$ to collect $\text{Hg}(0)$ onto a gold trap, followed by desorption and detection of the Hg collected on the trap using ID-ICPMS. This portion of $\text{Hg}(0)$ represents the purgeable $\text{Hg}(0)$ or DGM as commonly termed. Second, the other aliquot was spiked with $^{201}\text{Hg}(0)$ and left for 4 h for equilibration of the spiked ID isotope Hg with ambient Hg and then purged and

determined for total Hg(0). The Hg(0) measured by this treatment is compensated for the interactions between Hg(0) and SPM in the natural water and can reasonably represent the total Hg(0) present in the water sample. Particulate Hg(0) was then calculated by the difference between total Hg(0) and DGM.

RESULTS AND DISCUSSION

Purgeability of Hg(0) in DI and Lake Waters. In initial experiments with DI water spiked with Hg(0), the recovery of Hg(0) was calculated by the purgeable Hg(0) divided by the sum of purgeable and nonpurgeable fractions of Hg(0). It was found that Hg(0) was fully recovered ($99.1 \pm 0.6\%$, $n = 3$) when purge was carried out immediately (0 h) after Hg(0) being spiked into DI water, suggesting that the purge process was efficient and Hg(0) was not lost during the course of purging. Therefore, the Hg(0) purge recoveries in our other experiments were all calculated against the Hg(0) recovered at 0 h in Hg(0) spiked DI water. Recovery of the purgeable Hg(0) was further investigated after Hg(0) was spiked in DI water for 4 h. A recovery of $91.8 \pm 11.2\%$ ($n = 3$) of Hg(0) indicates that Hg(0) can be still efficiently recovered through purging.

Different results were observed when similar experiments were performed with lake water (Figure 1). Recoveries of the

eliminated. Our recent study on Hg redox reactions in Everglades water showed that dark oxidation of Hg(0) induced by microbial and chemical processes was insignificant, as evidenced by similarly slow oxidation rates of Hg(0) in sterilized and untreated water under dark conditions (unpublished data, see Figure S3). This observation is supported by a previous study where dark oxidation of Hg(0) in artificial and natural waters was not found to be statistically significant.¹⁶ Since photochemical reactions were eliminated in the experiments and microbial and chemical processes were not likely to oxidize a considerable amount of Hg(0) in the dark, we reasoned that the decrease in purge recovery of Hg(0) was plausibly due to the interaction of Hg(0) with particulate and/or dissolved substances (e.g., SPM and DOM) present in lake water, forming nonpurgeable SPM- and/or DOM-bound Hg(0).

Effect of SPM and DOM in Natural Waters on Hg(0) Purgeability. The filtered lake water was spiked with $^{201}\text{Hg}(0)$ to assess the role of SPM on Hg(0) purgeability. The recoveries observed at 0 and 4 h after spiking were $88.0 \pm 9.6\%$ and $81.0 \pm 3.5\%$, respectively (Figure 1). Compared to these results, the purgeable Hg(0) in the unfiltered lake water ($19.6 \pm 1.5\%$ recovered as aforementioned) significantly reduced after 4 h of equilibrium ($p < 0.01$, $n = 3$). These results provided evidence that Hg(0) in natural water could bind with particulates, subsequently influencing Hg(0) purge recovery from water.

Since the Hg(0) spiked into the filtered lake water could be almost fully recovered through purging even after 4 h treatment, it is clear that potential interactions between Hg(0) and the dissolved substances, including DOM, played a minor role in affecting the purgeability of Hg(0). Separate experiments using commercially available DOM prepared at different concentrations indeed supported this notion, as seen in Figure 2 where the effects of the two types of HA on the recovery of purgeable Hg(0) were illustrated. Since the HA solutions were filtrated prior to use, the influence of particulates can be excluded. No significant decreases in purgeable Hg(0) were observed for the concentration ranges tested for both types of HA. However, it seemed that a larger portion of Hg(0) was retained by HA2 than

Figure 1. Purgeable Hg(0) a) recovery and b) mass after spiking 0.42 ng of Hg(0) into 100 mL of deionized (DI) water, unfiltered natural water, and filtered (with 0.45 μm PVDF membrane) natural water. Error bars are standard deviations ($n = 3$).

purgeable Hg(0) were $93.9 \pm 7.6\%$ and $19.6 \pm 1.5\%$ after Hg(0) was spiked into lake water for 0 and 4 h, respectively, suggesting that a significant portion of Hg(0) was not purgeable in the water. One might speculate that a possible reason for the reduction in purge efficiency is that some Hg(0) may have converted to Hg(II) in lake water with time and hence cannot be purged out. However, these experiments were carried out in the dark, and thus photochemically induced Hg species transformation, i.e. oxidation of Hg(0) to Hg(II) or vice versa, can be

Figure 2. Recoveries of purgeable Hg(0) measured at 4 h after 0.42 ng of Hg(0) being spiked in 100 mL of solutions with varying dissolved organic matter concentrations. Humic acids purchased from Acros (Sodium Salt, 50–60% as HA) and from International Humic Substance Society (Waskish HA, peat, 1R107H) were used to prepare HA1 and HA2 solutions, respectively.

by HA1, suggesting that characteristics of DOM could determine its role in affecting the purgeability of Hg(0). Although reduced DOM has been previously found to have a high affinity to Hg(0), this strong affinity was not observed for oxidized DOM,³³ suggesting again that the differences in the DOM compositions and properties could affect the interactions between Hg(0) and DOM. Nevertheless, our results here indicate that DOM in natural water does not contribute significantly to the purge efficiency of Hg(0), in comparison to particulates.

Our experiments suggest the occurrence of SPM-bound Hg(0), presumably through adsorption of Hg(0) onto particles, which is nonpurgeable and in fact is the primary reason that causes low recoveries for the spiked Hg(0) when purging. It should be pointed out that particulate and dissolved phases are operationally defined terms as different sizes of filters have been used for fractionation, and here the 0.45 μm cutoff was used to distinguish particulate-Hg from dissolved-Hg. It is possible that there are still colloidal particles below 0.45 μm . In this study we did not observe the effect of these colloidal particles on Hg(0) purging, probably because these smaller particles were not the major fraction of the SPM used here or some small sized particles could be purged out of solution. The situation might be different in some other cases where smaller particles constitute a considerable portion or SPM concentration is high (the SPM was 5.2 mg L^{-1} in this study). Very limited research has been done on the adsorption of Hg(0) on SPM in an aquatic environment, although adsorption of Hg(0) has been studied for such sorbents as activated carbon or noncarbon^{51–53} soil,^{3,46} and aquatic sediment.⁴ As particles are vital components of natural water and often the major carriers for metals, the adsorption of Hg on particles is a key factor determining the concentration of dissolved Hg.^{4,34} Our results shown in this study call for a better understanding of the behavior of Hg(0) in aquatic environment, especially the interactions between Hg(0) and SPM.

Fractionation of Dissolved and Particulate Hg in Natural Water with Hg(0) Spiked. Knowing the concentration of total Hg(0), rather than the purgeable Hg(0) (or DGM) alone, in an aquatic environment is critical for a full understanding of the Hg biogeochemical cycle. Figure 3

Figure 3. Changes of purgeable Hg(0), nonpurgeable Hg(0), and total Hg with time after Hg(0) being spiked into natural water. Natural water was spiked with Hg(0) at a final concentration of approximately 6.6 ng L^{-1} and determined for purgeable and nonpurgeable Hg at different times. Error bars are standard deviations ($n = 3$).

illustrates the variations in the distribution of purgeable and nonpurgeable Hg(0) in the experiments studying the kinetics of formation of SPM-bound Hg(0) after $^{201}\text{Hg}(0)$ was spiked into the lake water. Initially, the purgeable Hg(0) was $96.5 \pm 5.4\%$ calculated against the amount of purgeable Hg(0) from DI water at 0 h, indicating that instantaneous adsorption of Hg(0) to SPM was minimum. A rapid decrease in the purgeable Hg(0) with time was observed until 4 h when the trend of change reached a plateau with a purge recovery of $14.7 \pm 1.9\%$. On the other hand, nonpurgeable Hg(0) was steadily increased and eventually reached a plateau of approximately $82.1 \pm 11.4\%$ at 4 h. Mass balance calculation indicates that about 20% of Hg(0) could be lost during the course of experiments, which is not unusual for experiments involving Hg(0) in an extended period of time.

Several processes could cause the conversion of the spiked $^{201}\text{Hg}(0)$ to nonpurgeable Hg. Again, the oxidation of $^{201}\text{Hg}(0)$ to $^{201}\text{Hg}(\text{II})$ could not be accountable for the loss of purgeable Hg(0), as all experiments were performed in the dark. Therefore, it seems reasonable to presume that the decrease in the purgeable Hg(0) with time could be the results of adsorption of Hg(0) onto SPM forming nonpurgeable particulate Hg(0) in natural water. Indeed, the fractionation of dissolved and particulate Hg using lake water spiked with both $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$, where directly purgeable Hg(0), SPM-Hg, and dissolved Hg were determined, supports this presumption. After 4 h equilibrium, only $18.8 \pm 3.3\%$ of $^{201}\text{Hg}(0)$ was directly purged out, confirming that the majority of $^{201}\text{Hg}(0)$ was nonpurgeable and associated with SPM and/or dissolved substances with the former and the latter being about 70 and 20% of Hg(0) spiked, respectively, as revealed by further speciation analysis after filtration (Table 1). The dissolved Hg in the filtrate was further fractionated into weakly and strongly bound Hg fractions (see Experiments section for their operational definitions), with the former accounting for $6.1 \pm 0.76\%$ of spiked ^{201}Hg and the latter $14.7 \pm 3.0\%$.

For the particulate fraction of $^{201}\text{Hg}(0)$, which accounts for $68.2 \pm 8.1\%$ of the spiked $^{201}\text{Hg}(0)$, $33.2 \pm 3.3\%$ and $35.0 \pm 6.3\%$ (calculated against the amount of ^{201}Hg spiked) were desorbed upon thermal desorption at 150 and 200 $^{\circ}\text{C}$ (Table 1), suggesting that the ^{201}Hg adsorbed on SPM should be primarily in the form of Hg(0). On the contrary, for SPM-bound $^{199}\text{Hg}(\text{II})$, only less than 10% of the spiked ^{199}Hg was released at 150 $^{\circ}\text{C}$ and about 25% at 200 $^{\circ}\text{C}$. Considering that thermal desorption at 150 $^{\circ}\text{C}$ would exclusively release Hg(0), and at 200 $^{\circ}\text{C}$ Hg(0) would still be the primary form of Hg released plus a small portion of other Hg species based on previous thermal desorption studies,^{4,46,48} it is conceivable that the majority of the spiked $^{201}\text{Hg}(0)$ became nonpurgeable due to the formation of SPM-Hg(0) through Hg(0) adsorption on SPM. Quantitative recovery of $^{201}\text{Hg}(0)$ spiked ($107.3 \pm 4.6\%$) lends further support on the SPM-bound ^{201}Hg being Hg(0) and also validates the procedures used here to evaluate the speciation and distribution of Hg(0) in natural water. For $^{199}\text{Hg}(\text{II})$ -spiked trials, total recovery was found to be $83.6 \pm 2.3\%$, indicating approximately 15–20% of the spiked Hg(II) were not recovered by this speciation protocol. This is probably because a fraction of Hg(II) associated with SPM could not be released from SPM after the thermal treatment used here (up to 200 $^{\circ}\text{C}$), as the complete release of Hg(II) from solids requires higher temperatures (e.g., 220–250 $^{\circ}\text{C}$).^{46,48} It should be noted that thermal desorption is not a precise method for Hg speciation analysis, as release of each Hg species occurs within a temperature range and is dependent upon a solid matrix. For

Table 1. Percentage (%) Distribution of Different Hg Species after Spiking $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$ (0.783 and 1.356 ng, Respectively) into Natural Water for 4 h

	purgeable Hg	SPM-Hg			weekly bound Hg	strongly bound Hg	total Hg
		150°	200°	total			
$^{201}\text{Hg}(0)$	18.8 ± 3.3	33.2 ± 3.3	35.0 ± 6.3	68.2 ± 8.1	6.1 ± 0.8	14.7 ± 3.0	107.3 ± 4.6
$^{199}\text{Hg}(\text{II})$	3.3 ± 0.3	10.0 ± 3.2	25.2 ± 4.2	35.2 ± 7.0	32.4 ± 4.76	12.7 ± 2.15	83.6 ± 2.3

Figure 4. A diagram depicting the presence and different behavior of dissolved and particulate Hg(0) in aquatic environments.

example, it was observed that, when heating airborne particles, a minor amount of HgCl_2 could be released even at 150 °C.⁵⁴ That is why we used a study design of simultaneously spiking isotopic $^{201}\text{Hg}(0)$ and $^{199}\text{Hg}(\text{II})$, where different behavior of SPM-bound Hg(0) and Hg(II) upon thermal desorption could be compared.

Determination of Dissolved and Particulate Hg(0) in Natural Waters. It can be seen from this study that determination of total Hg(0) in natural waters cannot be performed by direct purge with Ar, as currently employed in the conventional Hg(0) determination method, due to the presence of nonpurgeable particulate Hg(0). Even the employment of ID, which can overcome the potential Hg(0) loss during the sample treatment by being corrected by an equivalent loss of the ID Hg isotope,⁴⁴ would significantly underestimate the concentration of total Hg(0) if purged immediately after spiking ID isotope. This is because the Hg(0) spiked into water will interact with SPM and substitute endogenous Hg(0), and the interaction of the spiked and ambient Hg will take time to reach equilibrium.

The proposed scheme for determination of particulate Hg(0) was applied to Everglades water, and samples were collected and analyzed for both DGM and total Hg(0). The Everglades water has a pH of 7.2–7.8, DOC of 5.7–24.1 mg L^{-1} , and SPM of 1.7–3.1 mg L^{-1} . Before the application, it was estimated that the method detection limit (MDL), determined as three times standard deviation of seven replicate measurements of a blank solution, was 0.1 ng L^{-1} for Hg(0). The precision of the method, calculated as relative standard deviation of triplicate measurements of one sample, was approximately 5–15%. The determined DGM in Everglades water ranged from 0.14 to 0.22 ng L^{-1} , whereas total Hg(0) ranged from 0.41 to 0.75 ng L^{-1} .

The discrepancies between DGM and total Hg(0) indicate that nonpurgeable particulate Hg(0) is indeed present in Everglades water, and the fraction of particulate Hg(0) against total Hg(0) could vary from approximately 45–80%. It should be pointed out that the equilibrium time required after ID Hg(0) isotope being spiked may vary with the type of natural waters (4 h for this study), and the appropriate equilibration time should be determined prior to analysis for other water samples.

It is clearly demonstrated in our study the occurrence of particulate $^{201}\text{Hg}(0)$ through Hg(0) adsorption on SPM, which could account for the majority of Hg(0) spiked, after $^{201}\text{Hg}(0)$ was added into water samples. As the dissolved and particulate Hg(0) should be in a dynamic equilibrium, one can comfortably reason that the ambient Hg(0) originally present in the water samples should include both dissolved and SPM-bound forms. Since Hg(0) has a high affinity to be adsorbed on SPM as shown here, it seems reasonable to presume that particulate Hg(0) would be widely present in natural waters due to the ubiquity of SPM. The test results of Everglades water confirmed the presence of particulate Hg(0) in natural waters and as a major fraction of Hg(0). Therefore, particulate Hg(0) must be considered, in addition to DGM, to fully understand aquatic Hg cycling, as these two species have distinct characteristics. Figure 4 depicted the presence and different behavior of dissolved and particulate Hg(0) in aquatic environments, which sheds some light on exploring environmental implications of particulate Hg(0). First, particulate Hg(0) is nonpurgeable and thus could be easily omitted if the conventional direct purge and trap method is used to measure Hg(0) in water. The omission of particulate Hg(0) in this type of measurement may

affect the interpretation of results in Hg redox reaction studies. In a previous study on ocean water dynamics of Hg(0), Qureshi et al. observed different rate constants using instantaneous photoreduction and purging method, and they suggest this is due to Hg(0) binding to particles,⁵⁵ which is probably the case given our results presented here. Second, due to its non-purgeability, particulate Hg(0) is not expected to evade into the atmosphere, as opposed to DGM. However, little is known about the stability of particulate Hg(0) through time and how it will affect Hg(0) release and volatilization. For field studies purging samples to determine Hg(0) will particulate Hg(0) change during sample transport and storage and thus affect the measurement, if purging is not done immediately on site. Last, although dissolved Hg(0) could be (photochemically and microbially) oxidized to Hg(II) in water, little is known about the chemical, photochemical, and microbial reactivity of particulate Hg(0). Diurnal dynamics of DGM have been observed in natural waters, but how much of the patterns observed are due to Hg(0) binding to particulates rather than reoxidation. Further studies are warranted to examine the role of particulate Hg(0) in Hg oxidation/reduction, air–water Hg transport, and the global biogeochemical cycling of Hg.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b01940.

Detailed information on instrumentation, materials, and experimental procedures; discussion on the effect of HAs on Hg(0) purgeability; a figure showing microbial and chemical oxidation of Hg(0) in the dark insignificant; and a figure showing Hg(0) adsorption on magnetite particles (PDF)

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Notes

The authors declare no competing financial interest.

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