

Supporting Information

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

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There are total of 10 pages, 4 figures.

Instrumentation

Purging Hg(0) from water samples was performed using a 150 mL borosilicate glass bubbler (Ruyi LLC, Jiangsu, China). The traps used for retaining Hg(0) were glass tube (1/4" od \times 10 cm) packed with 3.4 cm of gold-coated quartz sand (45/60 mesh), purchased from Brooks Rand LLC (Seattle, WA, USA). The trap desorption module, including resistive heater, timer, power transformer and gas flow meter, was assembled in-house. Detection of Hg isotopes was conducted on ICPMS (Elan DRC-e, PerkinElmer). Makeup gas was introduced into ICPMS via a three-way Teflon connector after thermal desorption unit. Quartz bottles (100 mL, Ruyi LLC, Jiangsu, China) were employed as reaction vessels.

Materials and chemicals

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). Solution of SnCl_2 (20%, w/v) was prepared by adding 20 g of $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ and 20 mL of concentrated trace metal grade HCl to 100 mL deionized (DI) water, and the solution was cleaned by purging overnight with Hg-free N_2 at 400 mL min^{-1} .

Two different types of humic acid (HA), HA1 (Sodium Salt, 50-60% as HA) and HA2 (Waskish HA, peat, 1R107H) were purchased from Acros (New Jersey, USA) and International Humic Substance Society (IHSS, St. Paul, MN), respectively. The HA stock solutions were prepared by dissolving 16 mg HA in 10 mL NaOH solution (0.1%, w/v), followed by filtration with a $0.45 \mu\text{m}$ membrane. The final dissolved organic carbon (DOC) concentrations were 5.3×10^3 and $7.3 \times 10^3 \text{ mg L}^{-1}$ for HA1 and HA2, respectively.

Other reagents used were of analytical grade or higher. Nitrogen and argon gases used were passed through gold traps to remove Hg. Hydrophilic polyvinylidene fluoride (PVDF)

membrane filters (0.45 μ m) were purchased from Millipore (Millipore, USA). Quartz bottles and borosilicate glass bubblers were pre-cleaned by soaking in 30% (v/v) HCl for at least 48 hours and then baked for 3 hours in a muffle furnace at 500 °C before being used in all experiments. Interference from residual SnCl₂ (used as reductant during Hg(II) analysis) was found when the bubblers were reused. Trace levels of SnCl₂ constrained in the porous materials of the sparger could reduce Hg(II) present in the sample or reagents, leading to a false reading of Hg(0) concentration in the sample. It was found that a good cleaning can be achieved by soaking the spargers in 10% H₂O₂ for at least 3 hours and then rinsed with DI water. Baking in a muffle furnace at 500 °C for more than 12 hours is another method of choice to reduce the effect of residual SnCl₂.

Preparation of isotopic Hg(0) solutions

Stock solution of dissolved gaseous Hg, Hg(0), has been commonly prepared by bubbling N₂ gas saturated with Hg(0) vapor through DI water. The N₂ is saturated with Hg(0) in a U-shaped glass tube containing a small drop of liquid elemental Hg.¹⁻³ Although this method is easy to use, we decided to modify it by eliminating the use of liquid elemental Hg to avoid the risk of contaminating the laboratory. In our experiments, the production of Hg(0) was achieved through reduction of Hg(II) with acidic SnCl₂ solution in a 50 mL glass reaction vessel. A schematic diagram of the procedure is illustrated in Figure S1. The 50 mL reaction vessel, containing 10 mL SnCl₂ (20%, w/v), was equipped with a Teflon lined rubber cap with three pinholes for the purpose of introducing Ar bubbling gas, adding Hg(II) standard solution (100 μ g L⁻¹), and purging out produced Hg(0). Standard solution of Hg(II) was pumped into the reaction vessel at a flow rate of 0.35 ± 0.05 mL min⁻¹ using a peristaltic pump. The formed Hg(0) was purged out with Ar at a flow rate of approximately 5 mL min⁻¹ to a 500 mL volumetric flask filled with 510

mL DI water. A gold trap was connected to the outlet of the flask to capture gaseous Hg(0) that is not dissolved in water. After purging for 2 hrs, the concentration of Hg(0) in the volumetric flask was calculated using the reverse isotope dilution (the final Hg isotope solution was spiked with natural Hg standard of known concentration and purity).⁴⁻⁵ This solution, usually with final concentration of approximately $3 \mu\text{g L}^{-1}$ was used as Hg(0) stock solution. The Hg recovery calculated by the percentage of the formed Hg(0) against the total Hg(II) pumped into the reaction vessel reached over 30%. The Hg(0) stock solution was kept at 4°C in the dark and could be used for about 30 days. However, the Hg(0) concentrations were unstable and generally decreased to about $1 \mu\text{g L}^{-1}$ during the storage period. Thus, the Hg(0) concentration was calibrated and validated using the reverse isotope dilution method for every batch of the experiment. 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.

Effect of HAs on Hg(0) purgeability

Two type of HAs were used for the purpose of comparison, with HA1 being a commercial product extracted from lignite while HA2 an IHSS reference material extracted from Waskish peat from northern temperate regions. Both HAs have been widely used in DOM-related studies and much data regarding their typical properties exists. For example, for HA1, the H/C and O/C ratios were reported to be 0.97-1.15 and 0.51-0.57, respectively.⁶ For HA2, the H/C ratio is 0.88 and the O/C is 0.53, as calculated from the elemental composition data supplied by IHSS. Probably due to the differences in characteristics between these two types of HAs (as their source materials are different), we did observe different results when spiking Hg(0) into their solutions. More Hg(0) was retained by HA2 than by HA1, probably because HA2, a peat extract

which is more relevant to natural HAs, contains more abundant functional groups (e.g., thiol and carboxyl) that can complex Hg(0). Since it has been known that commercial HAs may not be able to be completely representative of natural HAs, our results suggest again that it is necessary to exercise cautions when extending laboratory results to the real environment and that, if possible, DOM isolated from field water sources should be used.

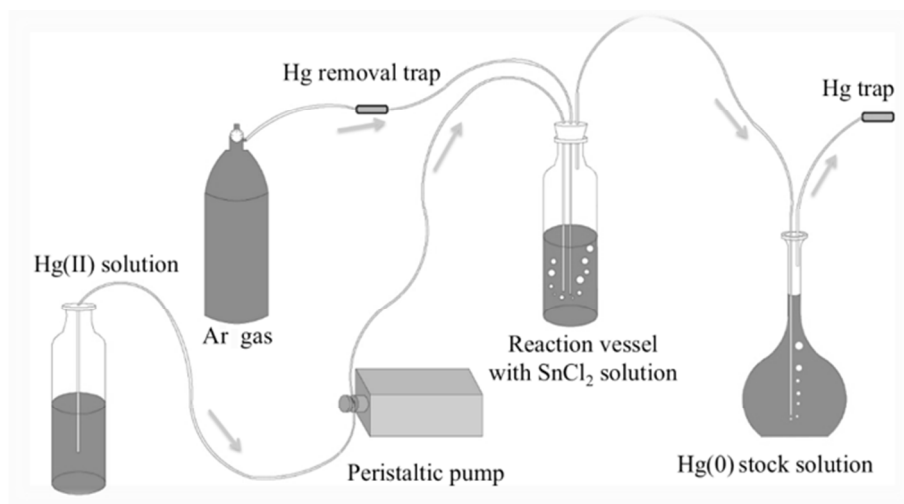


Figure S1. Schematic diagram showing the preparation of isotopic Hg(0) standard stock solutions using stannous chloride reduction method

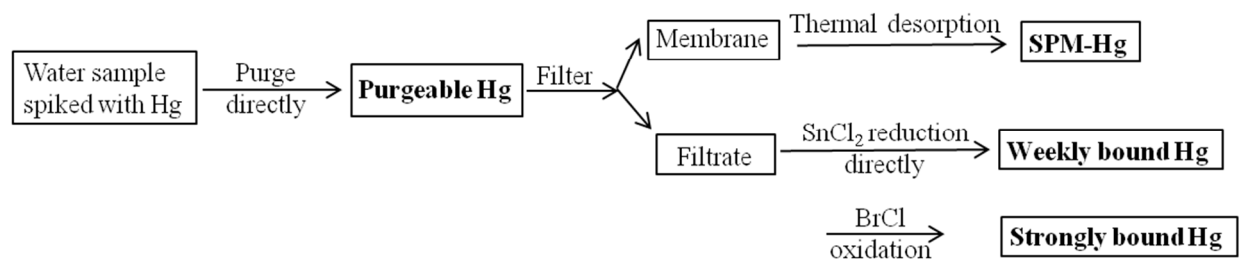


Figure S2. Mercury species operationally defined during fractionation and speciation analysis of Hg after Hg(0) being spiked into water. Dissolved Hg(0) was directly purged out of solution, and a 0.45 μm PVDF membrane filter was used to retain SPM-bound Hg.

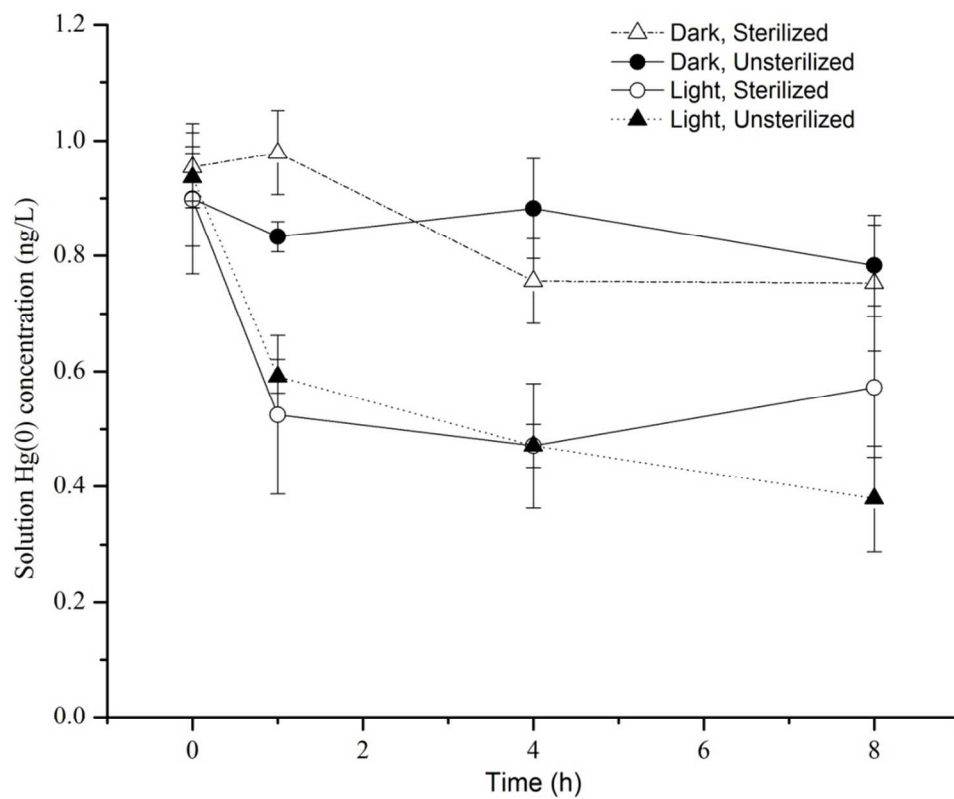


Figure S3. Photochemical reduction and oxidation reactions of Hg in natural waters under different conditions. It seems that dark oxidation of Hg(0) induced by microbial and chemical processes was insignificant, as evidenced by similarly slow oxidation rates of Hg(0) in sterilized and unsterilized water under dark condition.

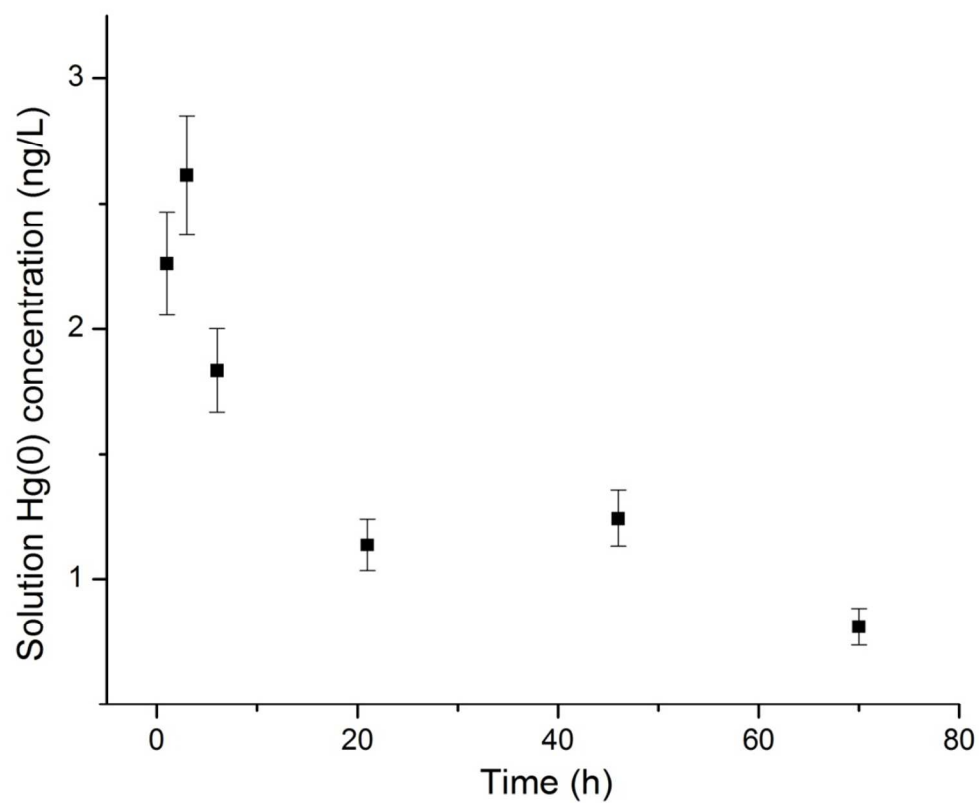


Figure S4. Adsorption of Hg(0) on magnetite (Fe_3O_4) particles as indicated by rapid decrease in solution Hg(0) concentrations after adding magnetite to Hg(0) standard solution. Thermal desorption experiments suggest Hg(0) being the primary form for the Hg adsorbed on magnetite.

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