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Mercury Sorption and Desorption on Organo-Mineral Particulates as a Source for Microbial Methylation

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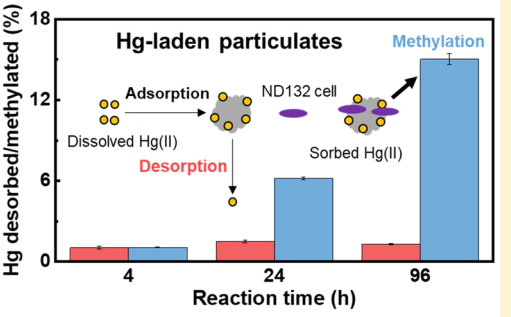
Supporting Information

ABSTRACT: In natural freshwater and sediments, mercuric mercury (Hg(II)) is largely associated with particulate minerals and organics, but it remains unclear under what conditions particulates may become a sink or a source for Hg(II) and whether the particulate-bound Hg(II) is bioavailable for microbial uptake and methylation. In this study, we investigated Hg(II) sorption−desorption characteristics on three organo-coated hematite particulates and a Hg-contaminated natural sediment and evaluated the potential of particulate-bound Hg(II) for microbial methylation. Mercury rapidly sorbed onto particulates, especially the cysteine-coated hematite and sediment, with little desorption observed (0.1−4%). However, the presence of Hg-binding ligands, such as low-molecular-weight thiols and humic acids, resulted in up to 60% of Hg(II) desorption from the Hg-laden hematite particulates but <6% from the sediment. Importantly, the particulate-bound Hg(II) was bioavailable for uptake and methylation by a sulfate-reducing bacterium *Desulfovibrio desulfuricans* ND132 under anaerobic incubations, and the methylation rate was 4−10 times higher than the desorption rate of Hg(II). These observations suggest direct contacts and interactions between bacterial cells and the particulate-bound Hg(II), resulting in rapid exchange or uptake of Hg(II) by the bacteria. The results highlight the importance of Hg(II) partitioning at particulate−water interfaces and the role of particulates as a significant source of Hg(II) for methylation in the environment.



INTRODUCTION

Mercury (Hg) is a global pollutant and can be methylated to form methylmercury (MeHg), a neurotoxin, which can bioaccumulate and biomagnify in food webs.[1,2] Certain microorganisms, such as sulfate-reducing bacteria,[3,4] iron-reducing bacteria,[5,6] and methanogens,[7−9] contain a two-gene cluster, *hgcAB*, responsible for converting inorganic mercuric Hg(II) to MeHg.[10] However, microbial methylation requires the initial step of Hg(II) cellular uptake from the extracellular environment,[11−13] and the physicochemical forms of Hg in the environment are known to affect its availability for uptake.[14−18] These different physicochemical forms of inorganic Hg present in natural waters and sediments include, but are not limited to, elemental Hg (Hg(0)), water-soluble Hg(II), mineral-bound Hg(II), dissolved and particulate organic matter (DOM and POM) bound Hg(II), and mercuric sulfide phases (cinnabar and metacinnabar).[14−17,19−21] In particular, minerals, DOM-coated minerals (or organo-minerals), and POM are ubiquitous, and up to 95% of the Hg(II) in fresh water and sediments are usually associated with these solids.[14,15,22−24]

Particulates may act as a sink for Hg(II) through sorption and occlusion or as a source by slowly and continuously releasing Hg(II) to solution for microbial uptake and methylation. However, under what geochemical conditions do these particulates become a sink or a source for Hg(II) remains unclear in complex environmental systems, where concurrent interactions may occur between Hg(II) and minerals, DOM or POM, microbes, and various dissolved ligands. Hg(II) is known to strongly sorb onto soil organic matter, minerals, and biomass,[11,14−17,23,25] although its mobility and bioavailability on particulates depend on the surrounding environment, such as the presence or absence of various Hg-binding ligands in solution. For example, low-molecular-weight (LMW) thiols are common in living organisms and often found in extracellular environments with concentrations ranging from nM to μM.[26−29] These thiol compounds have high affinities for Hg(II) binding and in particular, thiol functional groups on natural POM and DOM have been shown to form exceptionally strong complexes with Hg(II).[30−33] Therefore, Hg(II) binding with these environmentally relevant organic ligands may release and remobilize particulate-bound Hg(II), making it available for microbial methylation. Since minerals are often coated with DOM or POM, Hg(II) sorption and desorption behavior on these minerals could also be influenced by the coated organics or

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their exposed active functional groups. Previous studies suggested that aqueous Hg(II) species were more bioavailable than those bound to DOM or POM,[14,23] and particulate HgS was the least bioavailable form due to its extremely low solubility.[14,15,34−36] However, to date, systematic evaluations of particulate-bound Hg(II) for microbial uptake and methylation are lacking, especially concerning Hg(II) bound to organic matter or thiol-coated minerals and natural sediments. An improved understanding of the roles of complex organo-mineral particulates as a sink or source for Hg(II) sorption, desorption, and methylation under environmentally relevant conditions is needed to predict MeHg production in the environment.

The overall goal of this study was therefore to determine Hg(II) sorption and desorption behavior at the particulate−water interface and the bioavalability of particulate-bound Hg(II) for microbial methylation. Specifically, using the synthesized thiol- and DOM-coated hematite particulates and a Hg-contaminated natural sediment, we investigated the sorption/desorption kinetics and dynamics of Hg(II) and evaluated the potential availability of particulate-bound Hg(II) for microbial uptake and methylation by a known methylator, *Desulfovibrio desulfurians* ND132, in laboratory cultures.

EXPERIMENTAL SECTION

Chemicals. Cysteine, glutathione, and sodium 2,3-dimercapto-1-propanesulfonate monohydrate (DMPS) were used as LMW thiols. Elliott soil humic acids (HA) was obtained from the International Humic Substances Society (IHSS), containing 58.13% C (w/w) and 0.44% S (w/w). An EFPC-DOM was isolated from East Fork Poplar Creek (EFPC) water in Oak Ridge, Tennessee, as previously described,[37] and contained 54.77% C (w/w) and 1.93% S (w/w). A Hg-contaminated natural sediment, containing ∼2% iron oxides,[38,39] and a pure hematite mineral, as commonly observed in natural soil and aquatic environments, were selected for comparative studies. Hematite was purchased from Sterm Chemicals (Newburyport, MA) and used as received. The sediment sample was collected from EFPC, oven-dried at 45 °C until a constant weight, ground, screened with a 250-mesh sieve (63 μm openings), and then stored in a desiccator in the dark until use. The sediment contained about 16.1 μg/g total Hg, 10 mg/g C, and 0.2 mg/g S.

Mercury Adsorption Experiments. Four particulate samples were used to investigate Hg(II) adsorption and include pure hematite, cysteine-coated hematite, EFPC-DOM-coated hematite, and a Hg-contaminated EFPC-sediment. The organic matter-coated hematite was prepared by reacting hematite (5 g/L) with either cysteine (10 mM) or EFPC-DOM (0.24 g/L) in 1 mM NaCl solution in amber glass vials. The suspensions were shaken for 24 h and vacuum filtered through 0.45 μm membrane filters (Millipore). The organic-coated hematite was then washed three times with 1 mM NaCl (5 mL each), scraped off the filters, and oven-dried at 45 °C until a constant weight was obtained. Adsorption isotherms of Hg(II) were subsequently determined on these particulates with a solid concentration of 0.1 g/L in 1 mL NaCl at pH 6.5 in sealed glass vials under ambient conditions. An aliquot of the Hg(II) stock solution was added to a series of amber glass vials to obtain an initial Hg(II) concentration of 1 to 50 μg/L. Samples were then equilibrated on a rotary shaker for 24 h, which was found to be sufficient to reach an adsorption equilibrium based on initial kinetic studies. For detailed kinetic studies, the initial Hg(II) concentration was fixed at 10 μg/L, and samples were taken and analyzed at desired time intervals of 1, 2, 4, 12, 24, and 48 h. For Hg(II) analysis, duplicate sample vials were sacrificed, and samples were filtered through 0.2 μm syringe filters. The filtrate was preserved in 5% (v/v) BrCl solution (in 0.2 M HCl) overnight or longer at 4 °C, and an aliquot was used for determining Hg(II) concentration via reduction with $SnCl_2$ to purgeable Hg(0) and detection using a Lumex RA-915+ analyzer (Ohio Lumex Co., Cleveland, OH). The detection limit of the method was about 10 pg Hg.[11,37,40] The amount of Hg(II) adsorbed was calculated by the difference between the initial Hg(II) concentration and the amount measured in the filtrate solution. Data points in all figures represent an average of 4−6 replicate samples (at least duplicate batch experiments), and error bars represent the standard deviations.

Mercury Desorption Experiments. Hg(II) desorption from Hg-laden minerals and the EFPC-sediment was subsequently investigated in the presence of various organic ligands (HA and thiols). The Hg-contaminated EFPC-sediment was used without further treatment. The Hg-laden hematite, cysteine-coated hematite, and EFPC-DOM-coated hematite were prepared in laboratory by reacting Hg(II) (0.5 mg/L, 20 mL) with 0.2 g hematite, cysteine-coated, and DOM-coated-hematite, respectively, in 1 mM NaCl solution at pH 6.5 in sealed amber glass vials. Samples were then equilibrated for 24 h on a rotary shaker and vacuum filtered through 0.45 μm membrane filters. The particulates were again washed with 1 mM NaCl and oven-dried before use.

Desorption kinetics of Hg(II) was studied similarly with the DOM-coated hematite (1 g/L) and the EFPC-sediment (5 g/L). A higher sediment concentration was used because of its relatively low desorption. HA (8 mg C/L) or DMPS (100 μM) was added to the suspension, and the vials were shaken for desired time intervals (1, 2, 4, 8, 24, 72, and 120 h) for Hg(II) desorption. Similarly, Hg(II) desorption from Hg-laden particulates was also conducted in the presence of different concentrations of HA (0−40 mg C/L) and thiols (cysteine, glutathione, and DMPS at 0−200 μM) in 1 mM NaCl at pH 6.5. Samples were equilibrated for 24 h and then filtered and analyzed, as described in the sorption experiment.

Mercury Methylation Assays with Hg-Laden Particulates. The bioavailability of the particulate-bound Hg(II) was assayed by the production of MeHg by a known methylator, *Desulfovibrio desulfurians* ND132, under anaerobic conditions. The *D. desulfurians* ND132 strain was cultured, harvested, and washed using previously established protocols.[11,37,41] A series of 1 g/L Hg-laden cysteine-coated hematite and 2 g/L EFPC-sediment suspensions were prepared in deoxygenated phosphate-buffered saline (PBS), consisting of 0.14 M NaCl, 3 mM KCl, 10 mM Na_2HPO_4, and 2 mM KH_2PO_4 at pH 7.4. The washed ND132 cells were added to the suspension to a final cell density of 10^8 cells/mL and then supplemented with 1 mM pyruvate and 1 mM fumarate as the respective electron donor and acceptor. All vials were immediately sealed with PTFE-lined silicone screw caps and shaken in the anaerobic chamber in the dark. Control experiments were conducted similarly with particulates in PBS but without cells. At desired time intervals, replicate sample vials were collected and preserved in HCl (0.5% v/v) at 4 °C until analysis. An aliquot (0.05−0.2 mL) was used for total MeHg analysis with a modified EPA Method 1630, as previously described.[10,11,37,40,41] The detection limit for

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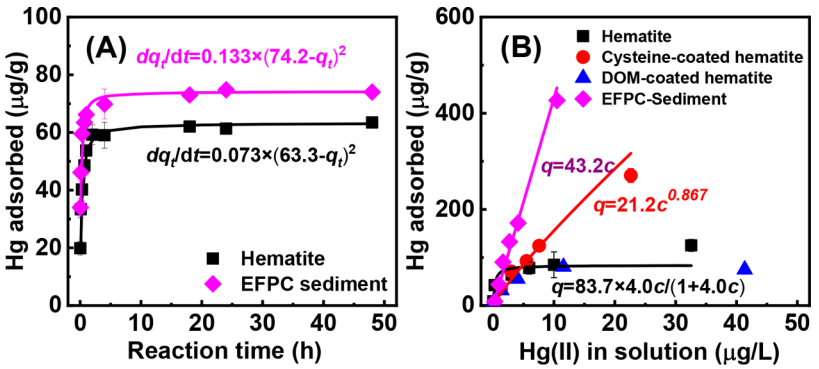

Figure 1. (A) Hg(II) sorption kinetics (at the initial Hg concentration of 10 μg/L) and (B) sorption isotherms on 0.1 g/L hematite and EFPC-sediment suspended in 1 mM NaCl solution at pH 6.5. Solid lines are fitted curves using linear (EFPC-sediment), Freundlich (cysteine-coated hematite), and Langmuir (hematite) model equations noted in the figure.

MeHg was ~6 pg/L Hg. The remaining aliquot was oxidized with BrCl (5% v/v) overnight and analyzed for total Hg using a Lumex RA-915+ analyzer. Control samples (without cells) were filtered through 0.2 μm syringe filters, and the filtrates were analyzed for total Hg(II) in the same manner.

RESULTS AND DISCUSSION

Mercury Adsorption on Organo-Hematite Particulates and EFPC Sediment. Sorption kinetics of Hg(II) were evaluated first on hematite and the EFPC-sediment (Figure 1A). In both cases, the sorption increased rapidly within the first 2 h, and the rate decreased and reached equilibrium in ~4 h. The kinetics appeared to follow a pseudo-second-order reaction with estimated rate constants of 0.073 and 0.133 g μg^{-1} h^{-1} on hematite and the EFPC-sediment, respectively (Supporting Information, Figure S1). The amount of Hg(II) adsorbed at equilibrium was 63.3 μg/g on hematite and 74.2 μg/g on the EFPC-sediment at the initial Hg(II) concentration of 10 μg/L and the particulate concentration of 0.1 g/L.

Hg(II) sorption isotherms were subsequently determined using hematite, cysteine-coated hematite, EFPC-DOM-coated hematite, and the EFPC-sediment (Figure 1B and Table S1), representing various organo-mineral particulates found in the natural environment. Hematite and the EFPC-DOM-coated hematite exhibited similar sorption behavior for Hg(II): the sorption first increased with increasing aqueous Hg(II) concentrations and reached a maximum sorption capacity of ~84 μg/g on both hematite and the EFPC-DOM-coated hematite. However, Hg(II) sorption on cysteine-coated hematite increased much more than that on the bare hematite or the DOM-coated hematite and did not show a maximum within the Hg(II) concentration ranges studied (up to 50 μg/L). The EFPC-sediment showed the highest affinity and capacity for Hg(II) sorption among all the particulates studied (Figure 1B).

The observed differences in Hg(II) sorption affinity and capacity on particulates (Figure 1) could be explained by different mineral surface characteristics and binding sites for Hg(II). Iron oxide adsorbs DOM through surface complexation-ligand exchange reactions with the carboxyl and hydroxyl functional groups on DOM.[42,43] The amount of DOM adsorbed on hematite was estimated to be ~1.5 mg C/g hematite (0.15 mg C/L) at pH 6.5 in 0.1 M NaCl, based on previous studies (Figure S2).[42,43] As a conservative estimate, if we assume that 50% of the sulfur (total 1.93%) on EFPC-DOM is reduced and the strong binding sites (−SH) represent 2% of the reduced sulfur,[31,44] the total binding sites on the EFPC-DOM adsorbed on hematite would be ~3.5 nmol/g hematite. This small amount of −SH on EFPC-DOM-coated hematite thus did not induce observable differences in Hg(II) sorption from the bare hematite. However, a much higher amount of cysteine was adsorbed on hematite at neutral pH (up to 26 mg/g, or ~0.2 mmol/g thiols on the surface) (S2),[45] although partial oxidation of cysteine is expected under ambient conditions.[45,46] A substantially higher amount of Hg(II) adsorbed by the cysteine-coated hematite than the bare hematite and the DOM-coated hematite (Figure 1B) suggests that the adsorbed cysteine remained effective in binding with Hg(II). For the EFPC-sediment, it exhibited the highest sorption capacity for Hg(II) (Figure 1B), although the sediment already retained a substantial amount of Hg(II) (Table S2). This high sorption capacity by the EFPC-sediment may be explained not only by surface adsorption but also immobilization by a heterogeneous mixture of various POM, biomass, and minerals in the sediment,[30,31,47] which contained about 10 mg/g C and 0.2 mg/g S. Soil organic matter and biomass, such as microbial cells and periphyton, are known to adsorb or rapidly take up Hg(II) from aqueous solution.[37,40,48−50] Taking into account the low sorption capacity of hematite and the DOM-coated hematite, it is reasonable to assume that the presence of organic matter and biomass in the EFPC-sediment are likely responsible for its higher Hg(II) sorption capacity.

Mercury Desorption from Hg-Laden Hematite Particulates and EFPC-Sediments. Hg(II) desorption kinetics from the Hg-laden DOM-coated hematite and the EFPC-sediment was investigated in the presence of either 100 μM DMPS or 8 mg C/L HA (Figure 2). The initial loading of Hg(II) on the DOM-coated hematite was 14.6 μg/g, which was ~20 times higher than the estimated thiols on the adsorbed DOM, suggesting that other functional groups on DOM (e.g., carboxyl and amine) or direct binding with hematite were also involved in Hg(II) adsorption. The EFPC-sediment was used without further treatment, with an initial Hg(II) loading of 16.1 μg/g (Table S2). Hg(II) desorption by DMPS proceeded rapidly within the first 24 h and reached a plateau between 24 and 120 h for both the DOM-coated hematite and the EFPC-sediment. However, a smaller fraction of Hg(II) was desorbed from the EFPC-sediment (0.72 μg/g, or <5% of the total Hg) than that from the DOM-coated hematite (~7.5 μg/g, or ~50%). Interestingly, Hg(II) desorption by HA was much lower than that by DMPS,

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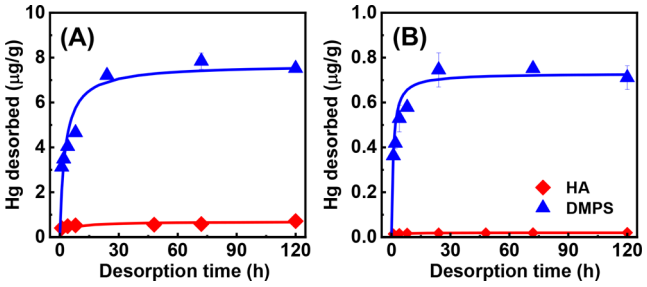

Figure 2. Hg(II) desorption kinetics from (A) Hg-laden EFPC-DOM-coated hematite (1 g/L) and (B) EFPC-sediment (5 g/L) with 8 mg C/L HA or 100 μM DMPS at pH 6.5 in 1 mM NaCl. Solid lines are fitted curves based on rate equations in Table S3.

although HA or DOM is also known to form strong complexes with Hg(II).[26,30,33] The amount of Hg(II) desorbed by HA was <4% and <0.15% from the Hg-laden DOM-coated hematite and the EFPC-sediment, respectively (Figure 2). The ineffectiveness of HA in desorbing Hg(II) was attributed to a lower amount of −SH functional groups on HA than on DMPS. It was estimated that the HA contained a reactive −SH concentration in the range of 21−310 nM at 8 mg C/L,[31,51] which is much lower than the added DMPS (100 μM, or 200 μM −SH). However, when normalized to the available concentrations of −SH functional groups, the ability of −SH in HA in desorbing Hg(II) was in fact comparable to that of DMPS, consistent with strong binding affinities of Hg(II) with both HA and DMPS.[30,52]

To further investigate Hg(II) desorption or mobilization, different concentrations of HA and LMW thiols (i.e., DMPS, cysteine, and glutathione) were used in Hg(II) desorption from three Hg-laden hematite particulates and the EFPC-sediment (Table S2). Without addition of HA or thiols, Hg(II) desorption upon wetting of the particles was generally low, ranging from 0.1 to 4% of the initially loaded Hg(II) (Figure 3). Desorption was higher from Hg-laden DOM-coated hematite (~4%) than from Hg-laden cysteine-coated hematite (~0.5%) and from Hg-laden hematite (~0.1%) (Figure 3), likely due to the desorption of some weakly bound Hg(II) or Hg-DOM or Hg-thiol complexes upon wetting. As expected, addition of HA or thiols resulted in substantially increased Hg(II) desorption due to strong competitive binding of HA and thiols for the adsorbed Hg(II), although the amount of desorption varied greatly with the type and concentrations of HA or thiols and the Hg-laden particulates themselves. Hg(II) desorption by HA from the three Hg-laden organo-hematite was relatively low but increased with increasing HA concentrations (Figure 3, left column). Hg(II) desorption by the LMW thiols (Figure 3, right column) was 4−40 fold higher than that by HA, resulting from the addition of a higher amount of available −SH functional groups. With the addition of 50 μM LMW thiols, Hg(II) desorption increased to ~20% from the Hg-laden hematite, and further increasing thiol concentrations (up to 200 μM) desorbed only a slightly higher amount of Hg(II). This trend of Hg(II) desorption by LMW thiols was similar on all three Hg-laden organo-hematite particulates. The ability of DMPS, cysteine, and glutathione in desorbing Hg(II) was comparable, with the exception of Hg(II) desorption by cysteine from the Hg-laden cysteine-coated hematite. In this case, a significantly lower amount of Hg(II) (~10%) was desorbed by cysteine than by glutathione or DMPS (~60%) since Hg(II) was already bound to cysteine

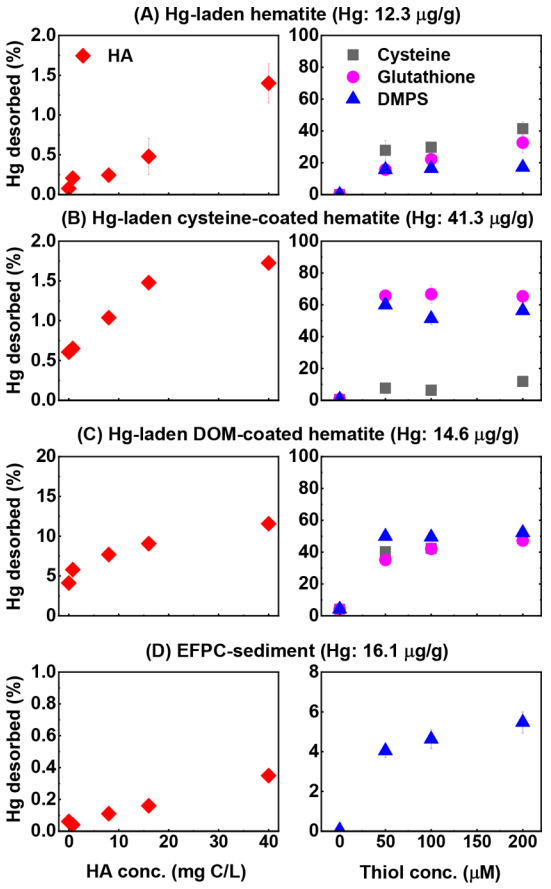

Figure 3. Hg(II) desorption from (A) Hg-laden hematite, (B) Hg-laden cysteine-coated hematite, (C) Hg-laden DOM-coated hematite, and (D) EFPC-sediment with varying concentrations of HA or LMW thiols (cysteine, glutathione, and DMPS) in 1 mM NaCl at pH 6.5 for 24 h. The added particulate concentration was 1 g/L for Hg-laden hematite and 5 g/L for the EFPC-sediment.

on the hematite surface. The result also implies that the adsorbed Hg(II)-cysteine on hematite was stable, but glutathione and DMPS were able to outcompete cysteine for Hg(II) desorption.

Interestingly, we observed a higher amount of Hg(II) desorption from the DOM-coated hematite (40−55%) or cysteine-coated hematite (50−70%) than the Hg-laden hematite (20−40%). This observation was surprising because Hg(II) bound to hematite surfaces was thought to be more readily desorbed by thiols than from the thiol-bound Hg(II) on the DOM- or cysteine-coated hematite, as Hg(II) would be strongly bound to the −SH functional groups.[23,30,33,51] The lower Hg(II) desorption from the Hg-laden hematite than from the Hg-laden cysteine-coated hematite suggests that Hg(II) was likely sorbed or immobilized more strongly on hematite, making it more resistant to desorption. Previous EXAFS studies proposed the formation of an inner-sphere complex between Hg(II) and goethite via two oxygen atoms bound to the Fe sites[53] and the potential formation of montroydite (HgO) during Hg(II) adsorption on montmorillonite and vermiculite.[54] Other studies speculated that Hg(II) can migrate and be incorporated into mineral solid matrix or diffuse into pores of minerals, making it unavailable for desorption.[36,55,56] These immobilization mechanisms of Hg(II) likely occur on hematite as well and may thus partially explain why lower amounts of Hg(II) were desorbed from the

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bare hematite than from the cysteine-coated hematite. Alternatively, the desorbed Hg(II) (or Hg-thiol complexes) could be readsorbed on hematite directly or by forming ternary complexes of hematite-thiol-Hg(II), as previously described.[23,57] Hg(II) readsorption would compete with its desorption, thereby resulting in an apparently low amount of Hg(II) desorption by increasing concentrations of thiols (Figure 3, right column). Similarly, for the Hg-laden DOM-coated hematite, a portion of the Hg(II) could be bound directly on hematite because of limited thiol-binding sites on DOM. Therefore, the amount of Hg(II) desorbed from the Hg-laden DOM-coated hematite was lower than that from the cysteine-coated hematite but higher than that from the bare hematite.

Of particular interest is the observation of a much lower amount of Hg(II) desorbed from the EFPC-sediment than that from the organo-hematite particulates by both HA and DMPS (Figure 3D). Less than 0.4% and 6% of the Hg(II) on EFPC-sediments was desorbed by HA and DMPS, respectively. We hypothesize three possible mechanisms as to why a low amount of Hg(II) desorption was observed from the EFPC-sediment. First, in complex natural sediments, Hg(II) not only binds with soil minerals (e.g., Fe/Mn oxides) and organic matter but also forms mineral precipitates such as metacinnabar (HgS) or nanoparticulate HgS.[14,17,39,58] The predominant forms of Hg in the EFPC-sediment were characterized to be metacinnabar and organic matter-bound Hg(II), with a small fraction of the Hg(II) present as the sorbed Hg(II) on Fe/Mn oxides.[17,39] We thus consider that HA and DMPS could desorb Hg(II) by competing with soil organic matter on the EFPC-sediment, as in the Hg-laden cysteine- or DOM-coated hematite. HA and DMPS could also enhance the dissolution of HgS or nanoparticulate HgS by forming Hg(II)-thiol complexes,[52,59] although previous studies have shown that HgS is quite resistant to desorption and dissolution by HA and thiols.[14,17] These results support our observation that lower amounts of Hg(II) could be desorbed from EFPC-sediment than from the Hg-laden organo-hematite particulates, where Hg(II) was bound to the surface-coated organics. The fact that Hg(II) desorption or dissolution increased with increasing HA or DMPS concentrations (Figure 3D) also suggests that Hg(II) on the EFPC-sediment was more resistant to desorption than that on the Hg-laden organo-hematite particulates. The second mechanism could be due to the incorporation or uptake of Hg(II) to biomass in the EFPC-sediment, as described earlier, making the Hg(II) less accessible for desorption or dissolution. Biomass such as microbial cells and phytoplankton is known to rapidly take up and internalize a large portion of Hg(II).[11,37,40,48−50] Once inside the cell, Hg(II) cannot be desorbed unless cells are lysed. Third, aging effects could be another factor contributing to the low desorption of Hg(II) from the EFPC-sediment due to potential phase transformations, changes in bonding environments, and migration of Hg(II) into stable soil and organic matrixes over time. Several studies have reported that fresh Hg(II) loadings to waters and sediments are more bioavailable and accessible than the previously deposited Hg(II),[14,36,60] consistent with our observations of lower Hg(II) desorption from EFPC-sediment (with a long deposition time) than from Hg-laden hematite particulates.

Particulate-Bound Hg(II) as a Source for Microbial Methylation. To evaluate whether the particulate-bound Hg(II) may serve as a sole source of Hg(II) for methylation, the Hg-laden cysteine-coated hematite and the EFPC-sediment were incubated directly with washed cells of *D. desulfurians* ND132 in PBS, and Hg(II) desorption and methylation were determined. Hg(II) desorption in the absence of ND132 cells (as a control) was found to be very low in PBS (Figure 4),

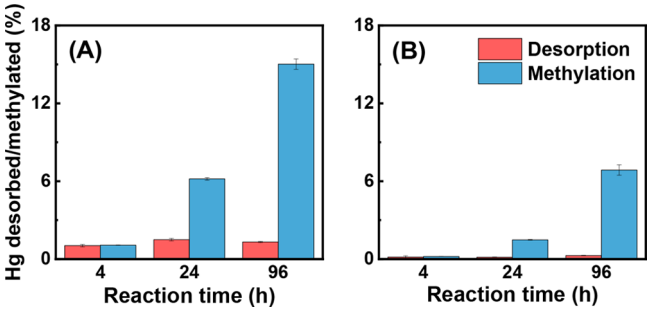

Figure 4. Hg(II) desorption (without cells) and methylation in the presence of washed cells of *D. desulfurians* ND132 (10^8 cells/mL) in PBS. (A) Hg-laden cysteine-coated hematite and (B) EFPC-sediments were used as the only Hg(II) source for Hg(II) desorption and methylation. The particulate concentration was 1 g/L for the Hg-laden cysteine-coated hematite and 2 g/L for the EFPC sediment.

similar to that observed in 1 mM NaCl solution at pH 6.5 (Figure 3). The amounts of Hg(II) desorbed were <1.5% and <0.3% after 96 h from the Hg-laden cysteine-coated hematite and the EFPC-sediment, respectively. Without ND132 cells, no MeHg production was observed in the EFPC-sediment control (data not shown), indicating negligible contributions of native microorganisms to Hg methylation in the sediment. However, a much higher amount of Hg(II) methylation was observed (Figure 4) in the presence of ND132 cells. With the Hg-laden cysteine-coated hematite, cells produced ∼2.2 to 31 nM MeHg after 4−96 h reactions, equivalent to about 1−15% of the total Hg(II) on the particulates (Figure 4A). Although lower, MeHg production in EFPC-sediment by ND132 cells ranged from 0.2% to 7%, but Hg(II) desorption was negligible (<0.3%) (Figure 4B). The lower methylation observed in EFPC-sediments than in the Hg-laden cysteine-coated hematite indicates that Hg(II) in the sediment was less bioavailable, since different forms of Hg(II) and its aging time could influence the rate of Hg(II) desorption, uptake, and methylation.

Importantly, the observed higher amounts of Hg(II) methylation than desorption (Figure 4) suggest that particulate-bound Hg(II) was available for microbial uptake and methylation. This observation questions the common notion that only soluble Hg(II) (and HgS nanoparticles) are available for microbial uptake or methylation.[14,15,61] Jonsson et al. proposed that aqueous or soluble Hg(II) was resupplied continuously by dissolution or desorption from the solids to sustain microbial methylation.[14,15] However, we estimate that the initial Hg(II) desorption rate from Hg-laden cysteine-coated hematite (Figure 4) was only ∼0.13 nM/h, much lower than the initial methylation rate of 0.53 nM/h. Similarly, the initial Hg(II) desorption rate from EFPC sediments was only ∼0.01 nM/h, but the methylation rate was ∼0.1 nM/h. The result cannot be attributed to the methylation of nanoparticulate HgS because of a low total Hg content observed in the filtrate solution. We hypothesize that direct contact and interactions between ND132 cells with the particulate-bound Hg(II) resulted in faster rates of Hg(II) uptake and

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methylation, possibly through ligand exchange with thiol functional groups on the cell surface rather than cell uptake of the Hg(II) in the bulk solution phase.[15] Abundant thiols or sulfhydryl functional groups (10^6–10^7 thiols/cell) are known to be present on ND132 cell envelops and cytosols[37,62] up to a thiol concentration of 0.17–1.7 μM at the cell concentration of 10^8 cells/mL, as used in this study. While it remains unclear exactly how cells take up Hg(II), cellular thiols are critically important in Hg(II) acquisition and uptake.[11,37,62,63] Another possible explanation is that bacterial exudates or extracellular substances may have made particulate-bound Hg(II) more available for methylation. These extracellular substances may include low-molecular-weight thiols or other organic ligands which form complexes with Hg(II) and thus enhance Hg(II) uptake and methylation.[13,27,29] However, regardless of the mechanisms, close contacts between particulate-bound Hg(II) and cells could lead to continuous Hg(II) complexation and exchange with the thiols on ND132 cells, resulting in subsequent Hg(II) uptake and methylation (faster than the rate of Hg(II) desorption without cells).

Environmental Implications. Mercury partitioning at particulate–water interfaces greatly affects its fate, transport, and transformation in natural water and sediments and ultimately its availability for biological uptake and methylation.[14,15,36] Natural sediments and organo-coated minerals, such as thiol- and DOM-coated hematite commonly found in soils, were all shown to have a large capacity to sorb Hg(II) under suboxic environmental conditions. They may represent one of the largest sinks when Hg(II) is discharged from a point source[23,47,64] or deposited from the atmosphere.[65,66] The result is consistent with the fact that most Hg(II) in soil and aquatic environments is associated with solids or particulates.[14,22–24,67]

However, Hg-laden particulates can also serve as a Hg(II) source for biological uptake and methylation. In particular, the presence of complexing organic ligands, such as small thiols, can result in significant desorption of Hg(II) and facilitate its release from particulates by 4–40 fold, depending on the types of particulate-bound Hg(II) and the thiol content. DOM at relatively low concentrations (e.g., < 5 ppm) shows a limited desorption capacity, in part because of its low thiol content and its competition with POM for Hg(II) binding. These observations agree with studies that have shown key roles of extracellular thiols in periphyton biofilms in influencing MeHg production during algal bloom.[29,68,69] Increased levels of low-molecular-weight thiols could enhance microbial methylation either through the formation of specific Hg(II)-thiol complexes[13] or through increased Hg(II) desorption from particulates or cellular materials and thus increased bioavailability.[11,37] Therefore, depending on the environmental conditions (e.g., minerals or organo-minerals, thiols, and DOM contents), particulates may exert significant controls on MeHg production in the aquatic environment.

Most significantly, we found that the particulate-bound Hg(II) is available for microbial methylation, evidenced by the higher methylation rates and extents than Hg(II) desorption using Hg-laden particulates as the only Hg(II) source (Figure 4). This is especially evident in experiments with the sediment-bound Hg(II), which resulted in >7% Hg(II) methylation but <0.3% Hg(II) desorption under same experimental conditions. The results signify important roles of particulates as an available Hg(II) source for methylation. We propose that direct contacts and interactions between particulate-bound Hg(II) and cell surface thiols likely facilitated the exchange of Hg(II) from particulates and consequently resulted in increased rate of cell Hg(II) uptake and methylation. These observations suggest an alternative pathway by which microbes take up Hg(II) that is more complicated than we previously thought: particulate-bound Hg(II) may not have to be desorbed or dissolved in the aqueous phase to make it available for microbial uptake and methylation. Microbial methylation of particulated-bound Hg(II) should thus be considered in predicting MeHg production in the natural aquatic environment.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b06020.

Hg sorption kinetics on particulates (S1), estimated DOM and cysteine adsorption on hematite (S2), Hg sorption isotherms on particulates (S3), Hg contents on Hg-laden particulates (S4), Hg desorption kinetics from Hg-laden particulates (S5) (PDF)

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The authors declare no competing financial interest.

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