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Enhanced availability of mercury bound to dissolved organic matter for methylation in marine sediments

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Abstract

The forms of inorganic mercury (Hg^{II}) taken up and methylated by bacteria in sediments still remain largely unknown. From pure cultures studies, it has been suggested that dissolved organic matter (DOM) may facilitate the uptake either by acting as a shuttle molecule, transporting the Hg^{II} atom to divalent metal transporters, or by binding Hg^{II} and then being transported into the cell as a carbon source. Enhanced availability of Hg complexed to DOM has however not yet been demonstrated in natural systems. Here, we show that Hg^{II} complexed with DOM of marine origin was up to 2.7 times more available for methylation in sediments than Hg^{II} added as a dissolved inorganic complex ($Hg^{II}(aq)$). We argue that the DOM used to complex Hg^{II} directly facilitated the bacterial uptake of Hg^{II} whereas the inorganic dissolved Hg^{II} complex adsorbed to the sediment matrix before forming bioavailable dissolved Hg^{II} complexes. We further demonstrate that differences in net methylation in sediments with high and low organic carbon content may be explained by differences in the availability of carbon to stimulate the activity of Hg methylating bacteria rather than, as previously proposed, be due to differences in Hg^{II} binding capacities between sediments.

Keywords: Mercury; Methylation; DOM; Marine; Sediment

1. INTRODUCTION

Methylmercury (MeHg) is a neurotoxic form of Mercury (Hg) that is produced under anoxic conditions in sediments, soils and aquatic waters from inorganic divalent mercury (Hg^{II}) mainly by sulfur and iron reducing bacteria (Compeau and Bartha, 1985; Benoit et al., 2003). A fraction of the MeHg formed bioaccumulates in aquatic food webs to concentrations of concern for human and wildlife health (Mergler et al., 2007). Though anthropogenic emissions of Hg have decreased substantially in the US, predicting future concentrations of MeHg amidst changes in global Hg emissions remains a challenge (Mason et al., 2012; Driscoll et al., 2013). To address this challenge, a better understanding of the factors that control net methylation in aquatic systems is warranted (Benoit et al., 1999). While the ability to methylate Hg^{II} is restricted to specific strains of bacteria carrying the *hgcA* and *hgcB* genes, methylation is known to depend both on the activity and composition of the bacterial community as well as the pool of Hg^{II} available to Hg^{II} methylating bacteria (King et al., 2000; Jonsson et al., 2012; Parks et al., 2013).

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The Hg^{II} methylation potential has been widely studied across systems, using isotopically enriched Hg^{II} tracers in intact sediment cores or sediment slurries (Benoit et al., 1999; Hammerschmidt et al., 2008; Hollweg et al., 2010; Jonsson et al., 2012). The Hg^{II} methylated is assumed to be taken up from the dissolved pool which, in comparison to the amount of Hg^{II} methylated within a day at typically reported potential methylation rate constants (k_m) (0.01–0.12 d^{-1}) (Hammerschmidt et al., 2008; Hollweg et al., 2010; Jonsson et al., 2012; Schartup et al., 2013), is at least ten times smaller (a typical distribution coefficient between the solid and aqueous phase, K_D, of 10^3–10^5) (Hammerschmidt et al., 2008; Hollweg et al., 2010; Schartup et al., 2013). Therefore, desorption and dissolution of Hg^{II} from the much more abundant pool of Hg^{II} present in the sediment occurs to sustain the typically observed methylation rates (Jonsson et al., 2012). Hence, the speciation of Hg^{II} in both the dissolved and solid phase will influence the pool of Hg^{II} available to methylating bacteria. Previous work has shown that the availability for methylation of the adsorbed and solid forms of Hg^{II} found in sediments, differs up to two orders of magnitude, and that the rate of methylation was controlled by both the thermodynamic stability of the solid phase as well as the kinetics of Hg^{II} desorption/dissolution (Jonsson et al., 2012). Here, we present an examination of the methylation rates of isotopically enriched Hg^{II} tracers added as different solid, adsorbed and dissolved forms to four different sediments. Although the availability of both the adsorbed and solid forms will be discussed in this paper, the focus is primarily on the availability of dissolved Hg^{II} added to the sediment as Hg^{II} complexed with dissolved organic matter (DOM) extracted from coastal waters, or with inorganic ligands.

The dissolved forms of Hg^{II} complexes first proposed to be available for methylation included neutrally charged sulfide complexes, which have been assumed to passively diffuse into the cell of the bacteria (Benoit et al., 1999). This hypothesis was based on field data and pure culture experiments where the concentration of MeHg was related to the modelled concentration of neutrally charged Hg^{II}-S species (Benoit et al., 1999; Hammerschmidt and Fitzgerald, 2004; Hollweg et al., 2010). It should be noted that the stability constants used in the speciation models are highly uncertain (Skyllberg, 2011). More recent work done in pure bacterial cultures (Schaefer and Morel, 2009; Schaefer et al., 2014) has suggested that low-molecular weight thiol complexes facilitate the uptake of Hg^{II} by methylating bacteria, by serving as a transporting shuttle for Hg^{II} to the cell wall, where Hg^{II} is then taken up by a divalent metal ion transporter in place of Zn^{II} (an essential element) (Schaefer et al., 2014). The methylation rate was found to differ between different Hg^{II}-thiol complexes with the highest rate observed for Hg bound to cysteine (Schaefer et al., 2014). It has also been suggested that Hg^{II}-DOM complexes are more available because the DOM is taken up as a source of energy by the bacteria, resulting in the unintentional uptake of Hg^{II} (Chiasson-Gould et al., 2014; Schaefer et al., 2014) or alternatively that DOM may indirectly enhance the availability of Hg^{II} under sulfidic conditions by hindering the formation of β-HgS*(s)* particles large enough to reduce Hg^{II} availability (Graham et al., 2012, 2013). Although the different theories have been argued for in various pure culture studies, direct experimental support, except for DOM acting as a shuttle molecule for Hg^{II} to the divalent metal ion transporters, is missing (Schaefer et al., 2014).

One of the major challenges in studying bioavailable forms of Hg^{II} in natural samples comes from the multiple effects complexing agents (sulfide, thiols etc.) may have on Hg^{II} speciation and availability for methylation as well as their effects on bacterial activity. Here, we have compared the methylation rate constant (k_m, d^{-1}) determined from Hg^{II} added as chloride complexes, hereon referred to as Hg^{II}*(aq)* and Hg^{II} complexed to DOM (Hg^{II}-DOM) in four different estuarine sediments. To distinguish the effect that the added DOM may have on Hg^{II} availability and bacterial activity, we also examined the k_m of Hg^{II}*(aq)* in presence of an equal amount of simultaneously added DOM (as used to produce the Hg^{II}-DOM tracer). We also determined the k_m of Hg^{II} adsorbed onto particulate organic matter of marine origin (Hg^{II}-POM), and Hg^{II} precipitated with sulfide as micro or nanoparticles of metacinnabar (respectively, β-HgS*(s)*$_{micro}$ and β-HgS*(s)*$_{nano}$), as well as Hg^{II} equilibrated with two previously collected sediments.

2. MATERIAL AND METHODS

2.1. Preparation of Hg tracers

Methylation assay sets were used containing a ^{200}Hg and a ^{199}Hg enriched species specific Hg^{II} tracer, individually frozen in 15 ml falcon tubes. The isotopically enriched Hg^{II} tracers were prepared from $^{200}HgCl_2$ and $^{199}HgCl_2$ (Oak Ridge National Laboratory, TN, USA) dissolved in 0.1 M HCl (diluted and pH neutralized before use). Hg^{II} tracers complexed to dissolved or particulate organic matter (DOM and POM) were prepared by pre-equilibrating $^{200}Hg^{II}$ with DOM or POM for 24 h. The organic matter was extracted from water sampled at Eastern Long Island Sound (ELIS) using Bond Elute PPL cartridges for DOM (as described in the Electronic annex), and by filtering the water through a 1.0 μm plankton net, after which the collected particles were rinsed, freeze-dried and re-suspended in purified water for POM. Our experiments aimed at studying differences in the availability between different dissolved, adsorbed and solid Hg^{II} tracers for methylation. To complex Hg^{II}, it was thus desired to have a Hg^{II}:ligand ratio low enough to ensure that the binding sites to which Hg^{II} would complex under natural concentrations, are not saturated. At the same time, higher amounts of DOM and POM could alter the activity of Hg methylating bacteria and were thus avoided. For DOM, we used a Hg^{II}:ligand ratio of 1 μg Hg^{II} mg^{-1} DOC. A high and constant binding coefficient of Hg^{II} to DOM has been previously demonstrated at ratios equal to or less than the ratio we used (Haitzer et al., 2002). For POM, we used a concentration ratio of 2.4 μmol Hg^{II} g^{-1} POM. This is comparable to the Hg^{II}:POM ratio used in previous work