

Bilag 38

Abstract

Objectives. Mercury is a potent neurotoxin for humans, particularly if the metal is in the form of methylmercury. Mercury is widely distributed in aquatic ecosystems as a result of anthropogenic activities and natural earth processes. A first step towards bioaccumulation of methylmercury in aquatic food webs is the methylation of inorganic forms of the metal, a process that is primarily mediated by anaerobic microorganisms that are abundant in sediments. The production of methylmercury in the environment is controlled in part by the bioavailability of inorganic mercury Hg(II) to methylating microbes. In sediment porewater, mercury associates with sulfide and organic matter to form chemical species that include organic-coated **mercury sulfide nanoparticles** as reaction intermediates of heterogeneous mineral precipitation.

In this project, we investigated the geochemical processes that control the bioavailability of mercury to methylating bacteria in contaminated sediments. The research tested the hypothesis that kinetically-limited mercury sulfide mineralization reactions, rather than equilibrium porewater chemistry, controls the concentration of bioavailable mercury to sediment bacteria that convert it to methylmercury, the form that bioaccumulates in food webs (Figure E.1). We studied the relationship between mercury speciation and biouptake/methylation in sediments, a relationship that remains poorly understood. **The work focused specifically on the microbial methylation potential of nanoparticulate HgS in relation to bulk scale HgS and dissolved Hg-sulfide species.** The aim was to establish a premise that links the „age“ and chemical form of Hg in sediment porewater to the rate of MeHg formation. The kinetic data was incorporated in a conceptual model describing the fate of mercury. The overall goals of SERDP project #ER-1744 were to assess the importance of nanoscale mercuric sulfides for methylation potential in sediments and to develop a conceptual model that links mercury geochemical speciation to methylation potential in sediments.

1.4.4 Nanogeochemistry of mercury

In the last decade, geochemists and aquatic chemists have realized that nanoscale particles are ubiquitous in the environment¹³⁵⁻¹³⁷. Much of this work to document the presence of naturally-occurring nanoparticles has involved metal elements that are much more abundant than mercury (e.g. iron, aluminum, manganese, titanium, zinc).

Because of the high affinity between Hg(II) and inorganic sulfide, a portion of mercury in anaerobic settings could be expected to associate with metal sulfide clusters or nanoparticles, possibly through sorption of Hg²⁺ ions or coprecipitation of HgS on sulfide nanoparticle surfaces¹⁴³. Discrete nanoparticles of HgS have been detected directly in soil, sediment, and biofilms on plant roots^{122,144,145}.

Nanoscale particles are expected to behave differently than the compositionally identical, larger materials due to the high specific surface areas and unique reactivity of materials at the nanoscale^{135,137}. Indeed, the defining characteristics of nanoparticles are not only the small size (i.e., at least one dimension smaller than 100 nm) but also size-specific reactivity exhibited by the nanomaterials¹⁴⁶. Nano-specific reactivity is generally observed in monomer particles smaller than 30 nm and stems from the relatively large specific surface area and crystal lattice imperfections in a material with a large proportion of atoms on the surface.

Nano-specific reactivity may include increased sorption capacity (normalized to surface area), enhanced transport, and faster rates of dissolution and re-nucleation^{135,146}.

The reactivity of nanoparticles can lend them to unique pathways for uptake into organisms, and at the very least, will influence the microbial bioavailability of the metal constituents of the nanoparticle. Clues toward understanding the importance of nano-HgS for microbial uptake and methylation could be gained from more established research on biouptake of iron originating from nanostructured iron oxides. For example, in microbial iron reduction, nanosized iron oxide colloids exhibited up to 100 times greater iron transformation rates than their respective bulk minerals¹⁴⁷. This observation was attributed to the enhanced solubility¹⁴⁸ and larger mineral particle-bacteria contact for nanoparticulate Fe(III)^{149,150}. Moreover, microscopic analysis revealed that iron oxide nanoparticles could penetrate the outer membrane of iron reducing bacteria, *Shewanella putrefaciens*, without collapsing the cells¹⁴⁹, and this bacterium tended to dissolve Fe(III) at the bacteria-mineral interface¹⁵¹. Recent work has suggested that mercury derived from HgS nanoparticles is more available to methylating bacteria than bulk minerals (e.g., metacinnabar), even when normalized to surface area¹⁹. Greater dissolution rates of small, more amorphous particles may account for the observed relationship between MeHg production and the „age“ of the Hg-sulfide species

1.5 Research Needs

Key questions remain to be answered concerning the mechanisms by which microorganisms methylate mercury. An understanding of these mechanisms is critical to the development of models that predict methylation potential in contaminated settings, and particularly in settings altered by remediation or change in mercury deposition. The greatest gaps in knowledge are related to the molecular processes that control the speciation of mercury, the route of Hg(II) uptake into methylating bacteria, and the enzymatic pathways toward methylation. In this respect, recent developments in molecular biology and nanogeochimistry can lend clues to address these questions. The breakthrough discovery of the *hgcAB* systems⁵³ will undoubtedly pave the way for the development of a much greater understanding of mercury methylation mechanisms, the distribution of methylators in the environment and the factors that govern the rate of mercury methylation

In terms of the geochemical speciation of mercury at biological interfaces, recent developments in the nanogeosciences provide much promise for enabling the understanding of mercury reactivity in complex mixtures such as sediments and sulfidic bottom waters

While much progress has been made in understanding the multifaceted aspects of mercury methylation in the past decades, many fundamental questions remain. Hopefully, recent advances in the geochemical and biological sciences will help provide insights to those elusive questions. Ultimately, an improved comprehension of the factors that control MeHg production in the environment should enable the development of effective mercury remediation strategies, support the implementation of sound mercury emissions policies, and decrease human exposure to methylmercury

2.3.4 Environmental Implications

Our overall results challenge the longstanding view that mercury bioavailability (and methylation potential) can be represented by equilibrium speciation of dissolved mercury in water⁶². Our previous work¹⁵ has indicated that HgS(aq)0 (a form of dissolved mercury presumed to be bioavailable⁶²) represents HgS nanoparticles rather than a mononuclear aqueous mercury-sulfide complex.

Although the occurrence of nanoparticulate or colloidal HgS has been suggested in a number of studies 15,16,122,145,186,193, our investigation is the first to explore the potential of HgS nanoparticles to serve as an important, but previously unrecognized source of bioavailable mercury for methylating bacteria. Overall, our results points to a new approach for modeling mercury bioavailability that is needed for predicting and mitigating MeHg hotspots in the aquatic environment. **Given that mineral nanoparticles are ubiquitous in the environment 135, the importance of nanoscale processes for trace metal bioavailability and toxicity has yet to be fully realized. Our findings provide a new approach that may be applied to other metal-sulfide nanoparticles (e.g., ZnS, CuS, FeS) and their potential roles in biogeochemical metal cycling.**