

**Poster #188**

**Elucidating Mechanisms of Natural Dissolved Organic Matter (DOM) in Influencing Mercury Chemical Speciation and Microbial Methylation**

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The chemical speciation and bioavailability of mercury (Hg) for methylation are markedly influenced by its redox transformation and complexation with DOM in aquatic environments. However, to date the effects of DOM on Hg complexation, species transformation, and microbial methylation remain obscure, partly due to heterogeneous nature and unknown molecular composition of DOM. In this study, we systematically investigated and compared the effects of DOM on Hg methylation by an iron-reducing bacterium *Geobacter Sulfurreducens* PCA and a sulfate-reducing bacterium *Desulfovibrio desulfuricans* ND132 under anaerobic conditions. We also utilized ultra-high resolution Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) to identify Hg-DOM complexes and to profile DOM compositional changes during photochemical transformation of Hg in water. We demonstrate that DOM effects on microbial methylation are bacterial strain-specific, time- and DOM-concentration dependent. Addition of small amounts of DOM greatly inhibits Hg methylation by *G. Sulfurreducens* PCA but enhances Hg methylation by *D. desulfuricans* ND132 cells in the dark. The result suggests that the effects of DOM on Hg methylation vary due to DOM competitive interactions with microbial cells for Hg uptake and are likely influenced by relative binding affinities of Hg with DOM and microbes. We also found that photochemical reactions of Hg-DOM complexes result in decrease in Hg reactivity and methylmercury production by *G. sulfurreducens* PCA cells. Decrease in Hg reactivity proceeded at a faster rate with a decrease in the Hg to DOM ratio and is attributed to the photolysis of Hg-thiolate complexes in DOM leading to the formation of mercury sulfide (HgS) and loss of S-containing DOM molecules. This observation reveals a potential new pathway of abiotic photochemical formation of HgS in surface water and provides a mechanism whereby freshly deposited Hg is readily methylated but, over time, progressively becomes less available for microbial uptake and methylation. For the first time, we also demonstrate the use of FTICR-MS to unambiguously identify specific DOM molecules in Hg binding. We found that heteroatomic molecules, especially those containing multiple S and N atoms, are among the most important in forming strong complexes with Hg. Major Hg-DOM complexes such as  $C_{10}H_{21}N_2S_4Hg^+$  were identified based on both the exact molecular mass and patterns of Hg stable isotope distributions detected by FTICR-MS. Together our results provide new insight into the roles and mechanisms of DOM on Hg chemical and photochemical transformation and its bioavailability leading to the formation of neurotoxic methylmercury in natural aquatic ecosystems.