Identification and quantification of mercury binding functional groups in natural organic matter and methylating bacteria

Baohua Gu (gub1@ornl.gov) - Oak Ridge National Laboratory (PI), Benjamin Mann; Hui Lin; Balaji Rao; Liyuan Liang (Co-PIs).

Our recent studies have emphasized the important role of thiols in controlling the fate of mercury (Hg) species, including highly toxic methylmercury, in both biotic and abiotic systems. Reactions of inorganic Hg species with naturally dissolved organic matter (DOM) results in both reduction of Hg(II) and oxidation of Hg(0), suggesting the involvement of two competing mechanisms: reduction by reduced semiquinones and oxidation by thiol-induced complexation. Similar effects of cellular thiols on Hg reduction, oxidation, and cell-surface binding have been observed on mercury-methylating bacteria, such as Geobacter sulfurreducens PCA and Desulfovibrio desulfurricans ND132. However, a robust and sensitive measurement approach for identifying and quantifying thiols present in complex DOM and bacteria remains an analytical challenge due to low abundance of thiols, their susceptibility to chemical oxidation, and the inherent absence of distinguishing spectroscopic characteristics. In this study, we describe the development of a thiol-specific fluorescent labeling technique to quantify thiols on bacteria and DOM in environmental samples. We report successful detection and quantification of nanomolar concentrations of thiols in washed cells of Gram-negative bacteria directly in phosphate buffered saline and DOM in aqueous solution. We further explore the use of high-throughput analytical approaches such as high-resolution mass spectrometry to profile molecular compositions of DOM and to describe the interrelated transformations of compounds in DOM following its exposure to Hg. We discuss the identification of the key molecular species that participate in Hg complexation and redox reactions with important implications to the bioavailability and microbial methylation of Hg in the environment. The diversity (or lack thereof) of reactive thiols requires additional study as this information could be useful in predicting the impact of Hg-cell binding or Hg-DOM complexation, Hg uptake by methylating bacteria, and Hg transformation in the environment.