

*Towards a mechanistic understanding of mercury –microbe/mineral interactions*Bhoopesh Mishra<sup>1</sup><sup>1</sup>University Of Leeds, Leeds, United Kingdom

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Complexation of Hg with high affinity thiol sites on bacterial cell surfaces under low metal loading conditions, followed by binding of Hg to lower affinity carboxyl sites upon saturation of cell surface thiol sites is a well-established paradigm (Mishra et al., 2011). Association of Hg with reduced S groups has also been shown to occur in phytoplankton (e.g., diatoms) under contaminated environments (Gu et al., 2014). Our recent studies have demonstrated that complexation of Hg with cell surface thiols is much more complicated than the formation of a single type of Hg-thiol complex at low Hg:biomass ratios. Hg can be complexed with cell surface thiols in a variety of stoichiometries depending on the biogeochemical attributes of the ecosystem in question. Stoichiometry of Hg-thiol complexes on bacterial cell surfaces depends on the Hg:biomass ratio, the abundance and distribution of thiol sites on the bacterial species in question, and whether the species is a Hg-methylator or not (Mishra et al., 2017). Hg-thiol complexes also play an important role in Hg-methylation. We have shown that Hg(0) oxidation is an intracellular process that occurs by reaction with thiol-containing molecules. Different stoichiometries of Hg-thiol complexes are produced by the oxidation of Hg(0) and the local coordination environment of the oxidized Hg evolves over time (Wang et al., 2016). Since the stability and reactivity of Hg-thiol complexes on cell surfaces is higher than those of Natural Organic Matter bound Hg-thiol complexes, the ultimate fate of these complexes after cell turnover raises new questions on our understanding of Hg biogeochemistry (Cheatham-Dunham et al., 2015).

Although Hg complexed with thiols on cell surfaces is not available for remobilization by mixed Fe(II/III) minerals (e.g., Magnetite), otherwise known to be a strong natural reductant (Mishra et al., 2011) – abiotic reduction of Hg by Fe mineral phases is known to be an important component of global Hg cycling. Over the last decade, reduction of Hg by Fe(II) (mixed Fe(II/III) mineral phases, Fe(II) sorbed to minerals, and aqueous Fe(II)) has been shown to be an important Hg(II) reduction pathway (Pasakarnis et al., 2013). Complementary to the previous studies, we have shown that Mn(II), which is not commonly considered a reductant, can also reduce Hg(II). Hg(II) reduction by Mn(II) is coupled with oxidation of soluble Mn(II) to highly insoluble Mn(IV) oxide. Formation of a Mn(IV) oxide mineral auto-catalyzes the reaction for first few hours, followed by significantly slower rates of reaction concomitant with changes in Mn(IV) mineral phase. Mn oxides thus formed, which are strong oxidants, would likely oxidize reduced Hg(0) in redox dynamic environments (Mishra et al., unpublished results). Since Mn can exist at fairly high concentrations in natural waters, Hg-Mn redox couple could have important implications on the overall mobility and bioavailability of Hg in subsurface and near surface environments.

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