Linking Trace Metal Biogeochemistry and Carbon-Nutrient Cycling: The Role of Metallophores

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BER Program: ESS

Project: Critical Interfaces Science Focus Area (Oak Ridge National Laboratory)

Project Website: https://www.esd.ornl.gov/programs/rsfa/

Project Abstract: Metal ions are essential components of metalloenzymes, which drive many biogeochemical carbon and nutrient cycles at the molecular scale. Microorganisms have developed strategies to overcome potential trace metal limitations by utilizing metallophores to facilitate the efficient uptake of trace metals. Thus, metallophores assume a significant role in controlling the bioavailability of trace metals. Metalloenzymes catalyze many key reactions driving critical metabolic processes, and they work at the interface between the cycling of trace metals and macronutrients, such as carbon and nitrogen. Methanobactin, a small peptide produced by some methanotrophs, is an example of a metallophore involved in copper (Cu) acquisition by methanotrophic bacteria linking the trace metal copper to the cycling of carbon (methane) in the environment. Additionally, methanobactins are known to form strong complexes with other transition metals, such as Hg, Zn, and Cd, affecting their biogeochemical transformations and bioavailability.

In this work, we present several case studies, such as discoveries of two novel methanotroph strains, *Methylomomas* sp. strain EFPC1 and *Methylococcus* sp. strain EFPC2, isolated from East Fork Poplar Creek, a Hg-contaminated stream in Oak Ridge, Tennessee, and interspecies interactions among methanotrophs. We show that some methanotrophs lacking genes for methanobactin biosynthesis are not limited for Cu by utilizing methanobactins produced by others. Certain methanobactins are also found to enhance the rate and efficiency of Hg methylation by the mercury-methylating bacteria, *D. desulfuricans* ND132 and *G. sulfurreducens* PCA, due to the formation of Hg-methanobactin complexes. We also investigate the interplay between solution-phase configurations, metal interactions and the spectroscopic signatures of methanobactin-metal complexes. Our results represent the first combined computational and experimental spectroscopy study of methanobactins and shed new light on molecular interactions and dynamics that

characterize complexes of methanobactins with Group 12 transition metals. Collectively our results underscore the complex roles of exogenous metallophores produced by microbes in controlling bioavailability and biogeochemical transformation of metals, which in turn exert a modulating influence on carbon and nutrient cycling in the environment.