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## Microbial formation of thiols control the chemical speciation and methylation of Hg(II)

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The formation of the neurotoxin methylmercury (MeHg) is a biotic process where anaerobic bacteria methylate inorganic divalent Hg (Hg(II)) intracellularly. The cellular uptake mechanisms are still not identified, but low molecular mass (LMM) thiols play an important role together with thiol groups on the outer membrane in controlling the chemical speciation of Hg(II). For example, increased concentration of specific LMM thiols, especially cysteine, is known to enhance the formation of MeHg. A recent study showed that metabolically active anaerobic microorganisms produced LMM thiols *in vivo* and exported them to concentrations up to 100 nM in the assay medium. The concentration range was sufficient to significantly affect the chemical speciation, uptake and methylation of Hg(II) without any external addition of LMM thiols.

In this study we investigate the kinetics of microbial formation and cellular export of LMM thiols by the iron-reducing bacterium *Geobacter sulfurreducens* and the sulfate-reducing bacterium *Desulfovibrio* sp. ND132 in high time resolution and the impact on the chemical speciation and methylation of Hg(II).

LMM thiols were separated by liquid chromatography and determined by electrospray ionization tandem mass spectrometry (LC-ESI-MS/MS). Hg(LMM-RS)<sub>2</sub> complexes were determined by thermodynamic modeling and by direct measurements using LC-Inductively coupled plasma MS (LC-ICPMS).

Results will be presented for the production of LMM thiol compounds, formation of Hg(LMM-RS)<sub>2</sub> complexes and how this change in Hg speciation impacts the Hg(II) methylation rate in short-term washed cell assays. Characterizing the time-dependent molecular composition of LMM thiols associated with methylating microbes are important to further understand their multiple roles on Hg(II) uptake and MeHg formation in bacteria assays and in the environment.