Hg coordination in actively Hg-methylating bacteria

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Introduction

Anaerobic bacteria possessing the *hgcAB* gene cluster can transform inorganic Hg(II) into the potent neurotoxin methylmercury (MeHg) [1] and are the primary source of MeHg in the environment [2]. For Hg methylation to occur, Hg(II) must be internalized by the cell and hence interact with the cell surface. Hg(II) has a high affinity for reduced sulfur which exists both as thiols and sulfides in bacteria [3,4]. Thus, Hg(II) is likely transported into the cell while bound to reduced sulfur. However, the internalized Hg(II) species have yet to be identified. To better understand the mechanisms of Hg(II) uptake and methylation, this study determined the Hg coordination environments in actively Hg-methylating bacteria.

Main Results

We exposed *Geobacter sulfurreducens* in exponential growth phase to 50, 100, and 200 nM Hg(II) in a defined exposure medium and collected the cell pellet for Hg L_{III}-edge high energy resolution (HR)-XANES measurements. The HR-XANES spectra revealed that cells contain primarily $Hg(SR)_2$ species regardless of the total added Hg(II) concentration. In addition, we quantified the reactive cell surface thiol concentration with a fluorophore method. The fluorophore – monobromo(trimethylammonio)bimane (qBBr) – binds thiols via an S_N2 reaction, and the newly formed C-S bond is not broken upon the addition of Hg(II). HR-XANES show that the addition of qBBr and consequent blockage of ~ 60% of the reactive cell surface thiols had no effect on Hg(II) coordination in the cell. However, *G. sulfurreducens* exposed to 50 nM Hg and 100 µM cysteine, conditions which have been shown to greatly enhance MeHg production [5], contain ~40% $Hg(SR)_2$ and ~60% of a 4-coordinate Hg-S species that resembles β-HgS. Our results show that Hg coordination in actively Hg-methylating bacteria can be complex and further studies to selectively block functional groups involved in Hg(II) uptake are needed to identify the transported Hg species.

[1] Parks et al. (2013), *Science* 339, **6125** 1332-1335. [2] Driscoll et al. (2013), *Environ Sci Technol* 47, **10** 4967-4983. [3] Thomas & Gaillard (2017) *Environ Sci Technol* 51, **8** 4642-4651. [4] Mishra et al. (2017), *Chem Geol* 464, 137-146. [5] Schaefer, Szczuka, & Morel (2014) *Environ Sci Technol* 48, **5** 3007-3013.