Hg methylation and demethylation kinetics in aquatic environments: Role of biotic and abiotic pathways on Hg isotopic fractionation

VINCENT PERROT[1], MARIA JIMENEZ-MORENO[1,2], ROMAIN BRIDOU[1,3], REMY GUYONEAUD[3], MATHILDE MONPERRUS[1], AND DAVID AMOUROUX[1]*.

[1] Laboratoire de Chimie Analytique Bio-Inorganique et Environnement, IPREM, CNRS-UPPA-UMR-5254, Pau, France (*david.amouroux@univ-pau.fr)
[2] Department of Analytical Chemistry and Food Technology, Faculty of Environmental Sciences and Biochemistry, University of Castilla-La Mancha, Toledo, Spain
[3] Equipe Environnement et Microbiologie, IPREM, CNRS-UPPA-UMR-5254, IBEAS, Pau, France

Hg methylation and demethylation pathways in aquatic ecosystems are kinetically controlled mechanisms, which critically affect monomethylmercury (MMHg) occurrence and accumulation in food webs. Various biotic, chemical and physical parameters can thus influence the overall net methylation of inorganic Hg(II) in aquatic systems [1]. Because Hg isotopic composition in environmental samples may allow tracking Hg sources and cycling, laboratory experiments on Hg species kinetics and isotopes fractionation during the main Hg transformations are essential. The aim of this study was to investigate Hg reversible methylation/demethylation mechanisms via 1) metabolic pathways using sulphate-reducing bacteria (SRB) cultures and 2) chemical non-enzymatic pathways by naturally occurring methyl group donor methylcobalamin (MeCo). Kinetics of the transformations and related Hg compounds isotope fractionation were measured and compared between the different experimental conditions.

Abiotic methylation processes driven by MeCo showed production of both MMHg and DMHg (dimethylmercury). Successive and reversible kinetics of methylation and demethylation were identified. Hg(II) methylation rate constants were 10 to 100 times higher than dimethylation and demethylation ones. Under dark conditions DMHg isotopic composition varied significantly during the time course of the experiment (48 h), being progressively enriched in heavier isotopes (δ^{202}DMHg varied from -1.37 to +0.66‰). Demethylation of DMHg was then identified to promote Hg isotopes fractionation when compared to MMHg methylation. Presence of chloride (0.5M) avoided DMHg production but enhanced Hg species fractionation (δ^{202}Hg from -1.44 to 2.48‰ for inorganic Hg and MMHg, respectively). Pure cultures of SRB incubated with Hg(II) produced significant amounts of MMHg and were also capable of MMHg oxidative degradation. Rate constants were 100-times lower and to the same order of magnitude, for methylation and demethylation respectively, than in abiotic experiments. Physiologies and global metabolism of the bacteria (i.e. fermentative or sulphate-reducing activity) did not affect significantly Hg species production/degradation kinetics and isotope fractionation. At steady state, 20% of MMHg was produced by SRB activity, resulting in MMHg enriched in lighter isotopes (δ^{202}MMHg between -0.88 and -0.45‰) and inorganic Hg enriched in heavier isotopes (δ^{202}IHg between +0.32 to +0.62‰).

Overall, both abiotic / biotic pathways of methylation and demethylation induced Hg mass-dependent isotopic fractionation which was influenced by the respective kinetics of these reversible pathways. Our results exhibit that isotopic composition of Hg in aquatic natural samples (biota, sediments) should be interpreted with care since reversibility of main Hg transformations need to be taken into account.

[1] Ullrich et al. (2001). Critical Reviews in Environmental Science and Technology, **Volume 31**, pp241-293

Neptunium (V) adsorption to a halophilic bacterium at 2 and 4 M ionic strength: Surface complexation modeling in high ionic strength systems

DAVID A. AMS[1*], JULIET S. SWANSON[1], JENNIFER E. S. SZYMANOWSKI[2], JEREMY B. FEIN[2], MICHAEL M. RICHMANN[1]AND DONALD T. REED[1]

[1]Earth and Environmental Sciences Division, Los Alamos National Laboratory, Carlsbad, New Mexico, U.S.A., dams@lanl.gov (* presenting author)
[2]Department of Civil Engineering and Geological Science, University of Notre Dame, Notre Dame, Indiana, U.S.A.

Abstract

The mobility of neptunium (V) in high ionic strength aqueous environmental systems, such as in the vicinity of salt-based nuclear waste repositories and high ionic-strength groundwater at Department of Energy sites, may be strongly influenced by adsorption to the cell wall of halophilic bacteria. This is the first study to evaluate the adsorption of neptunium (V) to the surface of a halophilic bacterium as a function of pH at the relatively high ionic strengths of 2 and 4 M. The experimental adsorption data were incorporated into a surface complexation model that was adapted for high ionic strength conditions where traditional corrections for aqueous ion activity are invalid.

Adsorption was significant over the entire pH range evaluated for both ionic strength conditions and was shown to be dependent on the speciation of the sites on the bacterial surface and neptunium (V) in solution. Strong electrostatic attraction controlled the adsorption behavior of the positively charged neptunyl ion to the negatively charged bacterial surface at pH below circum-neutral. At pH above circum-neutral, the influence of negatively charged neptunium (V) carbonate complexes resulted in decreased, although still significant, adsorption. Adsorption in 4 M $NaClO_4$ was enhanced relative to adsorption in 2 M $NaClO_4$ over the majority of the pH range evaluated, apparently due to the effect of increasing aqueous ion activity at high ionic strength.

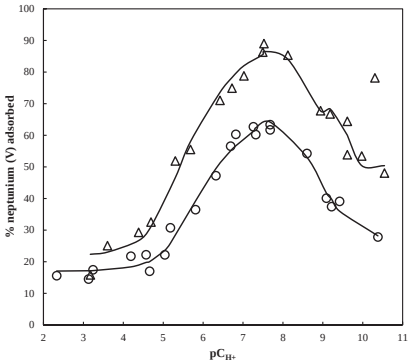

Figure 1: Experimental data for neptunium (V) adsorption onto *Chromohalobacter* sp. in 2 (open circles) and 4 (open triangles) M $NaClO_4$. Solid curves represent calculated surface complexation models. The adsorption data were modeled by testing likely reaction stoichiometries involving the adsorption of neptunium aqueous species (neptunyl: NpO_2^+, hydroxyl: NpO_2OH^0, $NpO_2(OH)_2^-$, and carbonate: $NpO_2CO_3^-$, $NpO_2(CO_3)_2^{3-}$, $NpO_2(CO_3)_2^{5-}$) to the four bacterial surface sites determined from bacteria titration modeling.