Structural biogeochemistry of mercury in wildlife

A. Manceau[1], B.A. Poulin[2], P. Bustamante[3], Y. Cherel[4], J.P. Bourdineaud[5], A.C Gaillot[6], P. Glatzel[7], K.L. Nagy[8]

[1]ISTerre, Univ. Grenoble Alpes and CNRS, France (**manceau@univ-grenoble-alpes.fr**), [2]U.S. Geological Survey, Boulder, USA (bpoulin@usgs.gov), [3]LIENSs, CNRS-La Rochelle Univ., France (paco.bustamante@univ-lr.fr), [4]CEBC, CNRS-La Rochelle Univ., France (cherel@cebc.cnrs.fr), [5]IECB, Univ. Bordeaux and CNRS, France (jean-paul.bourdineaud@u-bordeaux.fr), [6]IMN, Univ. Nantes and CNRS, France (anne-claire.gaillot@cnrs-imn.fr), [7]ESRF, Grenoble, France (glatzel@esrf.fr), [8]Univ. of Illinois at Chicago, USA (klnagy@uic.edu)

Mercury, a global pollutant widely distributed in aquatic and terrestrial ecosystems, is highly toxic to life. It hinders the biological function of proteins by binding to cysteine and selenocysteine residues, bioaccumulating and biomagnifying in food webs as predators eat other organisms. The chemical forms of mercury are usually determined by chemical analysis, and the sources and cycling of mercury in environmental systems can be traced by stable isotope geochemistry. As powerful as these methods are, chemical analysis only differentiates "inorganic" (divalent mercury, Hg(II)) from "organic" (methylmercury, MeHg) mercury, and isotopy does not provide information on the underlying molecular mechanisms that control the fractionation of mercury isotopes (e.g., δ^{202}Hg). Precise knowledge of the molecular forms and transformation reactions of mercury in its biogeochemical cycle is key for understanding how it is bioaccumulated and detoxified, which is essential for protecting wildlife and designing treatment against mercury poisoning. The speciation of metals in environmental matter is obtained usually by X-ray absorption spectroscopy (EXAFS and XANES) and chemical reactions are modeled most often by the density functional theory (DFT). However, these two approaches have limited applications in the case of mercury for the following reasons: (1) the detection limit of standard EXAFS is at best 30-40 ng/mg (ppm), at least one order of magnitude too high to study the large majority of environmental samples, (2) L_3-edge XANES spectra are featureless because the width of the Hg($2p_{3/2}$) level is 5.8 eV and, (3) Hg is a 5d element with strong relativistic effects not well accounted for by DFT.

The two first limitations have been overcome by development of a high-luminosity multi-crystal analyzer on beamline ID26 through the EcoX Equipex project. The third limitation has been addressed by modeling reaction pathways at a high level of molecular orbital theory (post-Hartree-Fock).

We will demonstrate how this new instrumentation laid the foundation for identifying two new mercury species in three animal phyla (birds, fishes, and earthworms). One is a dicysteinyl Hg complex stabilized through interactions with secondary N/O electron donors, such as amine and amide nitrogen and carboxyl and carbonyl oxygen. This complex can transform into nanoparticulate metacinnabar (β-HgS). The second species is a tetraselenolate complex resulting from the demethylation of methylmercury. It is stable in waterbirds and transforms into tiemannite (HgSe) in seabirds. Calculations of the free and activation energies of the chemical reactions at the ccsd(t) level show that Hg is more selenophilic than thiophilic. Although HgSe is a detoxification product of methylmercury, its formation depletes the cell in Se, an essential element for selenoprotein synthesis and activity. The Hg-Se antagonism and Hg/Se toxicity threshold will be discussed.

Acknowledgement. The EcoX Equipex project is supported by the French National Research Agency (ANR) under Grant ANR-10-EQPX-27-01.