Methylmercury Detoxification in Wildlife: Novel Insights from HERFD-XANES and Stable Isotopes

A. Manceau[1,2], B.A. Poulin[3], Sarah E. Janssen,[4] P. Bustamante[5], Y. Cherel[6], A.C Gaillot[7], P. Glatzel[2]

[1]Ecole Normale Supérieure de Lyon (**alain.manceau@ens-lyon.fr**), [2]ESRF, Grenoble, France (**alain.manceau@esrf.fr**), [3]University of California Davis, CA 95616, USA (**bapoulin@ucdavis.edu**), [4]U.S. Geological Survey, Madison, WI 53562, USA (**sjanssen@usgs.gov**) [5]LIENSs, CNRS-La Rochelle Univ., France (**paco.bustamante@univ-lr.fr**), [6]CEBC, CNRS-La Rochelle Univ., France (**cherel@cebc.cnrs.fr**), [7]IMN, Nantes Univ. and CNRS, France (**anne-claire.gaillot@cnrs-imn.fr**), [2]ESRF, Grenoble, France (**glatzel@esrf.fr**)

Mercury, a global pollutant widely distributed in aquatic and terrestrial ecosystems, is highly toxic to wildlife and humans. It hinders the biological function of proteins by binding to cysteine and selenocysteine residues, bioaccumulating in individuals and biomagnifying in food webs as predators eat other organisms. The chemical forms of mercury are usually determined by wet chemistry 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 isotopes (*e.g.,* δ^{202}Hg) do not provide information on the underlying molecular mechanisms that control the fractionation. 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. We will show how Hg L_3-edge HERFD-XANES spectroscopy with high detection efficiency conducted on ID26 laid the foundation for identifying the detoxification pathway of MeHg to inert Hg selenide (HgSe) in top predators (giant petrels and toothed whales) following the stepwise demethylation reaction: methylmercury cysteine (MeHgCys) → tetraselenolate ($Hg(Sec)_4$) → HgSe). The isotopic fractionation of mercury at each step of the chain reaction was obtained by mathematical inversion of the bulk-averaged spectroscopic and isotopic data. Each of the three Hg species has a unique δ^{202}Hg value that is uniform across tissues and individuals. This finding illuminates the cycling of Hg in the body and provides insight on how MeHg is transformed internally, redistributed between tissues, and depurated.

Formation of the $Hg(Sec)_4$ and HgSe species in the detoxification of MeHg has unwelcome implications, however. It depletes the pool of bioavailable Se needed for selenoenzyme synthesis and activity as five Se atoms (four for $Hg(Sec)_4$ and one for HgSe) are required to fully demethylate just one MeHg molecule. The Hg-Se antagonism will be discussed. Lastly, we will report current efforts seeking to determine how methylmercury is detoxified in other marine mammals, including bottlenose dolphins, and mesopredators, such has penguins and reptiles.

References

[1] – A. Manceau et al., Environmental Science & Technology **55**, 1515 (2021)
[2] – A. Manceau et al., Environmental Science & Technology **55**, 1527 (2021)
[3] – A. Manceau et al. Environmental Science & Technology **55**, 13942 (2021)
[4] – A. Manceau et al. ACS Earth and Space Chemistry, **5**, 1591 (2021)
[5] – B.A. Poulin et al. ACS Earth and Space Chemistry, **5**, 990 (2021)

[6] From Antarctica to California: how birds detoxify mercury: https://www.youtube.com/watch?v=qyzic-YI5js
[7] On dolphins, mercury and climate change: https://www.youtube.com/shorts/5DQqywwKmqI