

Abiotic redox dynamics between Hg and Mn

SBR - ANL SFA (Laboratory Research Manager: Robin Graham)

Bhoopesh Mishra^{1,2}, Edward J. O'Loughin², Maxim I. Boyanov^{2,3}, Kenneth M. Kemner²

¹Physics, Department, Illinois Institute of Technology, Chicago, IL (USA); ²Biosciences Division, Argonne National Laboratory, Lemont, IL (USA); ³Institute of Chemical Engineering, Bulgarian Academy of Sciences, Sofia, (Bulgaria)

Our studies over the past few years demonstrated that Hg^{II} can be reduced to Hg⁰ by various forms of Fe^{II} due to the comparatively higher redox potential of many Hg^{II}/Hg⁰ couples. Hence we expanded our research and tested the potential for reduction of Hg^{II} by Mn^{II}, as Mn is Earth's second most abundant transition metal next to Fe and is similar to Fe in several aspects of its geochemistry.

Reduction of Hg^{II} by Mn^{II} was tested in batch experiments and solids were characterized by XAFS. Our results show that at pH 7.5, the majority of Hg^{II} is reduced to Hg⁰ within three hours. Hg^{II} reduction is coupled with oxidation of soluble Mn^{II} to highly insoluble Mn^{IV} oxide. Formation of a Mn^{IV} oxide mineral auto-catalyzes the reaction for the first few hours, followed by significantly slower rates of Hg^{II} reduction concomitant with changes in the Mn^{IV} mineral phase. The presence of redox inactive mineral surfaces (e.g. Al₂O₃ and TiO₂) inhibits the rate of Hg^{II} reduction. Hg^{II} reduction by Mn^{II} results in the formation of meta-stable Hg^I species when complexing ions such as sulphate are present, followed by slow transformation to Hg⁰ over an extended period of time.

Under an appropriate change in condition (e.g. pH fluctuation) due to rainfall or storm events, Mn^{IV}-oxides formed as a result of Hg^{II} reduction may become oxidants and re-oxidize Hg⁰, enabling Mn to play a dual role of reductant as well as oxidant of Hg in natural systems. Hence, we also tested the ability of Mn^{IV}-oxides to oxidize Hg⁰ in batch experiments characterizing solids using XAFS. Our results suggest that under acidic pH conditions Mn^{IV}-oxides (e.g. β-MnO₂) can oxidize Hg⁰. Even though oxidation of Hg⁰ by Mn^{IV} is not an unexpected result because Mn^{IV} has been shown to oxidize other contaminants (e.g. Cr^{III} and U^{IV}), the oxidative pathway of Hg⁰ by Mn^{IV} has immense implications on subsurface Hg biogeochemistry in light of recent findings showing biogenic Mn oxide mineral coatings on subsurface geomedia. Clearly, Hg-Mn interactions could have important implications in redox cycling environments due to coupled reduction and subsequent oxidation of Hg by Mn under circumneutral and acidic pH conditions, respectively. Incorporating these newly found Hg redox pathways in global Hg cycle models may improve the prediction of Hg transport, as well as the estimation of the size of the pool of bioavailable Hg for biochemical processes like methylation.