As(III) oxidation by delta-MnO_2: Kinetics, Mechanisms, and Inhibition

MATTHEW GINDER-VOGEL[1,2]*, BRANDON LAFFERTY[2,3], AND DONALD L. SPARKS[2]

[1]Present Address: Environmental Chemistry and Technology, Dept. of Civil and Environmental Engineering, University of Wisconsin – Madison, Madison, WI 53706, mgindervogel@wisc.edu
[2]Dept. of Plant and Soil Sciences, Delaware Institute for the Environment, University of Delaware, Newark, DE 19711
[3]United States Army Corps of Engineers, Engineer Research and Development Center, 3909 Halls Ferry Rd, Vicksburg, MS 39180

Abstract

In the environment, chemical reactions at the mineral/water interface occur over a range of temporal scales, ranging from microseconds to years. Many important mineral surface processes (e.g., adsorption, oxidation-reduction, precipitation) are characterized by a rapid initial reaction on time-scales of milliseconds to minutes, and are often limited by the formation of secondary mineral phases. Knowledge of these initial reaction rates combined with detailed characterization of secondary phases is critical to determining chemical rate constants, and reaction mechanisms.

Here we describe the reactions controlling the oxidation of As(III) by δ-MnO_2 (a poorly crystalline form of hexagonal birnessite) over time-scales rangin from sub-second to hours. Initial As(III) oxidation rates (< 30 s) were measured using batch reactions and quick-scanning X-ray absorption spectroscopy (Q-XAS). Longer-term reaction dynamics were examined using a combination of column and stir-flow reactors combined with molecular-scale characterization of the resultant solid-phases with both Q-XAS and traditional XAS. While the aqueous As(V) and As(III) concentrations were determined using LC-ICPMS analysis.

Q-XAS studies reveal that As(III) oxidation occurs most rapidly during the initial 30 seconds of reaction, followed by slow oxidation over the next several minutes, and that traditional analysis (i.e., ex-situ analysis of As$(III/V)_{aq}$) may underestimate As(III) oxidation rates due to As(V) removal from solution due to sorption on the HMO mineral surface.

In column and stirred-flow experiments, As(III) oxidation by δ-MnO_2 is also initially rapid but slows appreciably after several hours of reaction. Mn(II) is the only reduced product of δ-MnO_2 formed by As(III) oxidation during the initial, most rapid phase of the reaction. However, it appears that observed Mn(III) is a result of conproportionation of Mn(II) sorbed onto Mn(IV) reaction sites rather than from direct reduction of Mn(IV) by As(III). The only evidence of arsenic (As) sorption during As(III) oxidation by δ-MnO_2 is during the first 10 h of reaction, and As sorption is greater when As(V) and Mn(II) occur simultaneously in solution. Our findings indicate that As(III) oxidation by poorly crystalline δ-MnO_2 involves several simultaneous reactions and reinforces the importance of studying reaction mechanisms over multiple time-scales with multiple techniques.

Photodemethylation: a significant actor in the methylmercury budget of Arctic freshwater ecosystems

CATHERINE GIRARD[1*], MARC AMYOT[2]

[1]CEN, Université de Montréal, Département de sciences biologiques, Montréal, Canada, catherine.girard.7@umontreal.ca (* presenting author)
[2]GRIL, Université de Montréal, Département de sciences biologiques, Montréal, Canada, m.amyot@umontreal.ca

Results of field experiments in the Arctic

Photodemethylation of monomethylmercury (MMHg) into inorganic mercury (Hg) has recently been shown to play an important part in the mercury budget of aquatic ecosystems. The objective of our project was to assess photodemethylation potential as well as its chemical drivers in Arctic lakes and thermokarst ponds. In 2008-2011, *in situ* experiments were conducted on Bylot and Cornwallis Islands (Nunavut) to determine which natural compounds drove the process. After week-long incubations of natural water exposed to sunlight, we observed significantly lower levels of MMHg (losses of 34-63%), and the use of light filters showed that short wavelenghts of solar radiation (<410 nm) were most effective at mediating photodemethylation. The process appears to be abiotic, being unnaffected by filtration (0.45 μm). Furthermore, samples amended with sulfur-rich molecules (thiols), chlorides as well as reactive oxygen species producers and scavengers showed that the presence of glutathione, singlet oxygen and chlorides accelerated photodemethylation.

In 2011, another experiment was conducted during which solar radiation was obstructed (98,7% of radiation from 200-750 nm) from a thermokarst pond on Bylot Island to measure the impact of photodemethylation on the pond's total MMHg budget. Monitoring was conducted over a 14-day period, during which time Hg levels remained stable, indicating that the total Hg budget was unaffected. However, MMHg levels fluctuated significantly, with changes in water chemistry occuring concurrently. Hence, the absence of solar radiation induced significant changes in the MMHg budget of the thermokarst pond.

Conclusions

We conclude from both sets of experiments that photodemethylation is a major degradation pathway of MMHg in Arctic thermokarst ponds and lakes, and that it has the potential to significantly affect MMHg budgets in northern aquatic ecosystems. Our results show that the process is most effectively mediated by UV radiation, and that sulfur-rich compounds and singlet oxygen play a significant role in the *in situ* degradation of MMHg via solar radiation.