Molybdenum speciation and bioavailability in soils

T. WICHARD, B. MISHRA, A.M.L. KRAEPIEL AND
S. MYNENI

Department of Geosciences, Guyot Hall, Princeton University, NJ 08544 USA (twichard@princeton.edu)

Molybdenum is part of the active center of the nitrogenase and thus plays an essential role in N_2-fixation. However, typical concentration of Mo in soil is very low (2 ppm). As a result, the asymbiotic N_2-fixing soil bacteria (eg. *Azotobacter vinelandii)* has to acquire Mo for diazotrophic growth at such low concentrations in soils. Interestingly, the importance of molybdenum in the fertility and elemental cycles in terrestrial system is still unattended. The specific objective of this study is to achieve a detailed mechanistic understanding of the link between chemical speciation and the bioavailability of Mo for bacteria in soil.

Molybdenum speciation in soils is usually believed to be controlled by adsorption to particles such as iron oxides or clays at low pH. Contrary to this notion, X-ray absorption near-edge (XANES) spectroscopy result has shown that Mo binds preferentially to leaf leachate in a competition experiment to Fe under controlled environment. XANES spectra of a Mo rich natural soil collected from Pentagonia (Arizona) also confirmed binding to organic matter. X-ray micro fluorescence mapping (µXRF) of the natural soil did not show strong correlation between Mo and Fe/Mn either.

Molybdate exists as the tetrahedral $[MoO_4]^{2-}$ anion in aqueous solution but the degree of complexation of the aqueous molybdate ion with organic matter and its coordination geometry was found to be strongly dependent on the pH (4.0 – 9.0) conditions. Results of XANES- experiments ([Mo] = 1-10 mM) show that the coordination geometry of Mo changes from pure tetrahedral, to octahedral at pH 6.1. The linear combination fitting of XANES spectra of Mo treated with leaf leachte at pH 6.1 yields 85% and 15% contribution of azotochelin and cystein, respectively. Further investigation using, Extended X-ray Absorption Fine Structure (EXAFS) showed that Mo is bound by a 5-membered-ring in leaf leachates. We conclude that Mo may be bound to catecholate or α-hydroxy acid groups rather than iron oxides.

This result is particularly important in light of recent findings by our group showing that catechol-siderophores (e.g. protochelin) released by *A. vinelandii* affect the bioavailability of molybdenum [1], as these ligands form strong complexes with MoO_4^{2-} [2].

[1] Bellenger *et al.* (2007) *Nature Geosciences* **4**, 243-246. [2] Bellenger *et al*. (2007) *J. Biol. Inorg. Chem.* **12**, 367-376.

Hg isotopes in contaminated soils

J.G. WIEDERHOLD[1,2], B. BOURDON[2] AND
R. KRETZSCHMAR[1]

[1]Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Switzerland (wiederhold@env.ethz.ch)
[2]Institute of Isotope Geochemistry and Mineral Resources, ETH Zurich, Switzerland

Anthropogenic mercury pollution is a serious problem in natural ecosystems. Soils represent important sinks for anthropogenic Hg, but source allocation is often difficult and the fate of Hg in soils remains largely unknown. Mass-dependent (MDF) and mass-independent (MIF) fractionation of stable Hg isotopes provide a new tool to trace Hg sources and pathways in the environment. Here, we present Hg isotope ratios of total digests and sequential extracts of natural soil samples contaminated with Hg by different anthropogenic processes, and isotope ratios of Hg chemicals.

Cold-Vapor-MC-ICPMS (*Cetac HGX-200* coupled to *Nu Plasma*) was used to measure Hg isotopes in 5 to 20 ppb Hg solutions. Mass bias was corrected using Tl addition and standard-sample bracketing with NIST-3133. Masses between 194 and 208 encompassing all seven Hg isotopes, Tl, and potential Pt and Pb interferences were measured simultaneously. Our analytical protocol and data reporting follows the suggestions of [1]. δ^{202}Hg reproducibility was ±0.07‰ (2SD, n=11) based on replicate measurements of a Fluka Hg solution (-1.29‰) relative to NIST-3133. Analyses of the UM-Almadén standard (δ^{202}Hg = -0.52±0.06‰, 2SD, n=6) are identical within error to published values [1].

Total digests of contaminated soils exhibited significant MDF with $\delta^{202}Hg_{NIST3133}$ of -0.10‰ (NIST-2711, Montana, USA), -0.45‰ (Spittelwasser, Germany), and -0.64‰ (Gossau, Switzerland). Preliminary data indicated only small Hg isotope variations between different sequential extracts applied to separate Hg pools from soil samples [2]. Most soil samples and chemicals did only exhibit MDF with all Hg isotope ratios plotting on the theoretical lines in three-isotope plots (including ^{204}Hg). However, total digests and extracts of NIST-2711 (contaminated agricultural soil, collected from the till layer of a wheat field) exhibited small but significant depletions in the two odd Hg isotopes (Δ^{199}Hg and Δ^{201}Hg values of -0.2‰). This interesting finding of a negative MIF effect in a soil sample is complementary to published positive MIF data of odd Hg isotopes in biomass and photochemical reaction products. Hence, this soil might be the residue of a Hg transformation which preferentially removed the odd Hg isotopes by, for instance, a magnetic isotope effect.

[1] Blum & Bergquist (2007) *Anal. Bioanal. Chem.* **388**, 353-359. [2] Bloom *et al.* (2003) *Anal. Chim. Acta* **79**, 233-248.