Molybdenum sorption in forest soils – mechanisms and modelling

JON PETTER GUSTAFSSON[1] AND CHARLOTTA TIBERG[1]

[1]Department of Soil and Environment, Swedish University of Agricultural Sciences, Box 7014, 750 07 Uppsala, Sweden. E-mail: jon-petter.gustafsson@slu.se, charlotta.tiberg@slu.se

Molybdenum is a contaminant from slags produced in steel processing, but is also an essential element important particularly for N_2 fixation. Usually molybdenum exists as hexavalent tetrahedral MoO_4^{2-} ions in solution. In soils it may be sorbed not only to Fe/Al (hydr)oxides, but also to organic matter. The binding is pH-dependent, with strong adsorption at pH < 5-6, and with low or insignificant adsorption at higher pH. By use of Mo K-edge X-ray absorption spectroscopy we studied the coordination environment of Mo(VI) on model sorbents, and on the O and B horizons of a Spodosol. The results were used to develop geochemical models able to predict the Mo partitioning in soils.

EXAFS spectroscopy showed MoO_4^{2-} ions to bind tetrahedrally to 2-line ferrihydrite as an edge-sharing bidentate complex, with Mo-O distances of around 1.76 Å and with a Mo···Fe distance at 2.80 Å. A minor contribution from a corner-sharing bidentate complex (Mo···Fe = 3.55 Å) was detected. An edge-sharing bidentate complex was dominant also on $Al(OH)_3$ (Mo···Al = 2.62 Å). XANES and EXAFS spectra collected for the Bs horizon sample were similar to those of $Al(OH)_3$, indicating an $Al(OH)_3$-type precipitate, probably allophane, to dominate Mo(VI) binding.

For Suwannee River Fulvic Acid at pH 4.0, and for the O horizon sample the EXAFS the results were different. Here Mo(VI) formed a complex in an octahedral configuration (2 Mo=O at 1.76 Å, 2 Mo-O at 1.99 Å and 1 Mo-O at 2.25 Å), with C atoms at larger distances (> 3.2 Å). Under the experimental conditions, no polycondensation was detected (i.e. no Mo···Mo distances were found).

The results were used to fine-tune the CD-MUSIC model for Mo(VI) adsorption to ferrihydrite, and to develop a new model for the prediction of Mo sorption to organic matter. Examples of model fits are shown in the presentation.