Springtime Deposition and Emission of Mercury from Arctic Snow

K.P. JOHNSON[1], J.D. BLUM[1], G.J. KEELER[1] AND
T.A. DOUGLAS[2]

[1]1100 N University Ave, University of Michigan, Ann Arbor, MI, 48109 (kelseyjo@umich.edu, jdblum@umich.edu, jkeeler@umich.edu)
[2]Cold Regions Research and Engineering Laboratory, P.O. Box 35170 Fort Wainwright, Alaska 99703-0170 (Thomas.A.Douglas@erdc.usace.army.mil)

Atmospheric mercury depletion events (MDEs) provide a pathway for gaseous elemental mercury (Hg^0) to be rapidly oxidized to Hg^{2+} and deposited to terrestrial surfaces. MDEs occur between polar sunrise and spring melt in many high-latitude locations. Projected changes in the Earth's climate this century will alter contaminant transport pathways (Macdonald, 2005) and may enhance Hg deposition and bioavailability in high latitude ecosystems (Lindberg, 2002).

We investigated net Hg deposition by MDEs to the Arctic cryosphere near Barrow, Alaska by (1) monitoring Hg concentrations in surface snow for 18 days, (2) quantifying emission of total gaseous mercury (TGM) from snow in flux chambers and (3) applying a newly developed analytical technique to measure Hg isotopic fractionation during (photo)chemical reactions. A nine-day MDE occurred during our intensive sampling campaign.

Daily monitoring of the upper 1 cm of the snowpack at two locations showed an increase in total Hg concentration throughout the MDE to maximum levels of 147 and 237 pg/g Hg. Twice-daily sampling at one site revealed a secondary trend of night-time Hg deposition. Mercury concentration in surface snow typically rose after exposure to darkness (~12 hours), while it remained unchanged or slightly decreased after exposure to daylight (~12 hours). Within two days of MDE cessation, Hg in surface snow returned to near-baseline levels and is probably the result of both Hg^0 emission and physical mixing of the snowpack (high-Hg surface layer diluted by low-Hg snow column).

Flux chambers were employed to elucidate the rate and mechanism of TGM emission from natural snow. The TGM emission pattern was typical of light and/or temperature dependent reactions: emission peaked shortly after solar noon and ceased overnight. Peak TGM emission from MDE and non-MDE snow reached > 15 $ng/m^2/hr$ and ~8 $ng/m^2/hr$, respectively. Blocking direct UV radiation decreased TGM emission by only 25%; UV_B was not wholly responsible for this flux. Hg isotopic ratios of snow samples before and after flux chamber incubation are being measured to help identify an isotope signature of Hg (photo)chemical reduction.

References

Lindberg, S. E., Brooks, S., *et al*. (2002) *Environmental Science & Technology* **36** 1245-1256.

Macdonald, R. W., Harner, T., *et al*. (2005) *Science Of The Total Environment* **342** 5-86.

Modeling glyphosate and metal-glyphosate speciation at solution-mineral interfaces

CAROLINE JONSSON, JOHN LORING, PER PERSSON AND
STAFFAN SJÖBERG

Department of Chemistry, Umeå University, S-90187 Umeå, Sweden (Caroline.Jonsson@chem.umu.se; John.Loring@chem.umu.se; Per.Persson@chem.umu.se; Staffan.Sjoberg@chem.umu.se)

Glyphosate (N-(phosphonomethyl)glycine, PMG, H_3L) is a widely used organophosphorous herbicide. It interacts with metal ions and mineral surfaces, which may affect its mobility, degradation and bioavailability in the environment. However, so far these interactions are far from fully understood.

This paper is a discussion on the complexation of PMG with metal ions in aqueous solution and the adsorption of PMG and Cd(II) on different mineral surfaces. EXAFS, ATR-FTIR, and XPS measurements showed that PMG adsorbs to the surfaces of goethite (α – FeOOH), aged γ-alumina (γ - Al_2O_3) and manganite (MnOOH) through one oxygen of its phosphonate group to singly-coordinated OH-surface sites.

The coadsorption of PMG and Cd(II) on the surfaces of goethite and manganite results in the formation of ternary mineral-PMG-Cd(II) surface complexes, as suggested from EXAFS results. In addition to the surface reactions in the binary Cd(II)-mineral and PMG-mineral systems, a single ternary complex with the stoichiometry $\equiv MeLCd(OH)^{1.5-}$ was sufficient to explain coadsorption data.

Surface complexation models consistent with the different spectroscopic results were fit to adsorption data using the 1pK reaction formalism involving charge distributions.