Air-snowpack exchange of bromine, ozone and mercury in the springtime Arctic simulated by the 1-D model PHANTAS

K. Toyota (1,2), A. P. Dastoor (3), R. M. Staebler (2), and J. C. McConnell (1)
(1) York University, Department of Earth and Space Science and Engineering, Toronto, Canada, (2) Environment Canada, Air Quality Research Division, Toronto, Canada (kenjiro.toyota@ec.gc.ca), (3) Environment Canada, Air Quality Research Division, Dorval, Canada

A dynamic exchange of halogens between the ocean, sea ice, snowpack, and the atmosphere is a main driver for the occurrence of ozone depletion episodes (ODEs) and atmospheric mercury depletion episodes (AMDEs) in the polar boundary layer particularly during the spring. Oxidized mercury is deposited to the snow/ice surface efficiently concurrent with the AMDEs and can be transformed to methyl-mercury, which subsequently bio-magnifies and imposes various health threats to northern communities and wild life. However, some field measurements of mercury in the snowpack and overlying ambient air, including but not limited to those in the polar region, indicate the photochemical reduction of oxidized mercury back to gaseous elemental mercury (GEM) on timescales of days to weeks whereas other studies show no evidence of rapid reduction. Such differences could be attributed not only to meteorological factors like temperature but also to chemical/biological factors that control the abundance of halogens and organic compounds, with a link to the redox chemistry of mercury. In order to understand the role of each driving process in the overall behaviors of mercury in the polar region, we have developed a one-dimensional model, PHANTAS (a model of PHotochemistry ANd Transport in Air and Snowpack), which describes multiphase chemistry in the gas phase, aerosols and the brine layer assumed to exist on the grain surface of saline snowpack. Henry’s law for Hg(II) gases and aqueous-phase stability constants for Hg(II)-halide complexes are re-evaluated including their temperature dependence. Photochemical reduction of Hg(II) to Hg(0) in the aqueous phase is handled simply by a prescribed first-order rate constant with diurnal variations. The model also handles the transport of gases and aerosols across the snowpack and the turbulent atmospheric boundary layer. The atmospheric profile of turbulent diffusivity down to the interfacial sublayer is diagnosed from an arbitrary chosen set of measured surface sensible heat fluxes, reference-height wind speed and static stability in the free troposphere. The model yields a shallower boundary layer depth with decreasing wind speed, leading to more rapid ODEs and AMDEs. On the other hand, the amount of Hg(II) deposition is simulated to increase with increasing wind speed. Ozone and GEM are actively destroyed in the snowpack interstitial air via bromine radical chemistry. However, apparent dry deposition velocities for ozone (and GEM where efficient Hg(II) reduction is not included in the model) reached only up to the order of $10^{-3}$ cm/s. The gas-particle partitioning of oxidized mercury in the air is strongly connected to bromine chemistry in that particulate mercury starts to build up mainly as $\text{HgBr}_2^-$ in sulfate aerosols after ozone is significantly depleted. In the saline snowpack above the sea ice, mixed-halide complexes like $\text{HgCl}_2\text{Br}_2^-$ and $\text{HgCl}_3\text{Br}_2^-$, as well as $\text{HgCl}_2^-$, are simulated to comprise a major component of inorganic Hg(II). A predominant fraction of Hg(II) entering from the atmosphere is captured in the top millimeter of the snowpack, whereas molecular diffusion in the brine and re-emission of GEM followed by re-oxidation in the interstitial air contribute to the downward migration of some of the Hg(II).