Surface reactions can alter both perceived and actual composition of atmospheric Hg(II)

Mercury is a persistent and bioaccumulative environmental pollutant. It enters the atmosphere mostly in elemental form and leaves it in various oxidized forms, Hg(II). We still know little of the Hg(II) chemical makeup and most of this knowledge comes from quantum chemical calculations. Measurements in the atmosphere provide only an operationally defined speciation (elemental, oxidized, and particulate mercury), and this limited knowledge hinders our understanding of atmospheric mercury chemistry and global cycling. Achieving molecular speciation of atmospheric Hg(II) is a major challenge because of its extremely low abundance (10-50 pg/m^3), requiring pre-concentration of Hg(II) on adsorbents, where it can be altered in exchange reactions with itself and co-adsorbed atmospheric chemicals. Here I will talk about our work to develop an analytical technique for gaseous Hg(II) detection based on the chemical ionization mass spectrometry (CIMS). This technique can provide molecular composition of gaseous Hg(II) directly, skipping the pre-concentration step. Presently, the sensitivity is sufficient for laboratory studies of mercury chemistry, and I will talk about our recent projects focusing on Hg(II) gas-surface interactions and exchange reactions. These exchange reactions were studied in aqueous solutions and on surfaces, and the products were analyzed in the gas, solution, and in solid form. In all cases, we observed a rapid formation of exchange products, which can readily volatilize from the surface. We propose that a similar exchange may occur on the surfaces of aerosol particles in the atmosphere and on adsorbents during sample collection, scrambling both the actual and perceived makeup of atmospheric Hg(II). I will wrap up my talk by describing how the sensitivity of CIMS can be further improved for analyzing gaseous Hg(II) directly in the atmosphere.