Hg isotope fractionation among atmospheric mercury species above a coastal suburban environment (Pensacola, Florida, USA)

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Mercury is a pervasive global pollutant that bioaccumulates in aquatic food webs after being methylated in the anoxic zones of aquatic systems. Atmospheric deposition of Hg from local, regional and global is the main contributor to Hg in ecosystems. The fate of Hg in the atmosphere is controlled by multiple processes. We measured the Hg isotopic composition of gaseous elemental Hg (GEM, gold coated quartz sand traps), reactive gaseous Hg (RGM, KCl soaked quartz fiber filters, QFF) and particulate aerosol Hg ($Hg_{(p),}$ QFF) in the atmosphere above the coast near Pensacola, Florida, during summer 2012. 4 rain samples were also collected. Both mass-dependent (MDF) and mass-independent (MIF) signatures of GEM were significantly different than those of Hg(II) species. GEM, more than 99% of the total Hg at this site, displayed positive δ^{202}Hg (0.7 to 1.2‰,) whereas both RGM and Hg(p) had negative δ^{202}Hg (-2.4 to -0.1‰). On the other hand, GEM (n=14) had slightly negative Δ^{199}Hg and Δ^{200}Hg average values -0.26±0.09‰ and -0.07±0.03‰, respectively, whereas Hg(p) (n=17) has slightly positive values (0.33±0.13‰ and 0.10±0.04‰, respectively). RGM displays no significant MIF (Δ^{199}Hg=0.02±0.14‰ and Δ^{200}Hg=-0.02±0.10‰). We suggest, in agreement with previous studies, that both oxidation and reduction processes are responsible for the patterns in the isotopic composition of RGM and Hg(p). Preferential scavenging of RGM and Hg(p) (rather than GEM) in wet and dry deposition result in significant variability of the isotopic composition deposited in coastal environments due to seasonal and sporadic changes in air mass trajectories and atmospheric physico-chemistry.

Molecular properties of anion-mineral surface complexes probed with infrared desorption and temperature-excursion experiments

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Surface complexation theory provides a framework to conceptually describe molecular-level interactions at water-mineral interfaces [1]. Central to this theory is the formation of local molecular entities (surface complexes) with well-defined structures and compositions. Typically, under a given experimental condition several surface complexes co-exist and a challenge in this research is to determine the molecular properties of the individual species. We need this information to make connections between the properties of these species and their influence on, for instance, surface catalytic, dissolution, and redox processes. Previously, mixtures of surface complexes have been disentangled via pH and ionic strength dependence experiments, thereby exploiting differences in the stability of different protonation states and surface bonding interactions. Here we will introduce infrared desorption and temperature-excursion experiments and their potential to differentiate between and characterize anionic surface complexes. For a series of carboxylic acids we will show that differences in desorption rates separate protonated and deprotonated surface complexes. We will also show that the number of bonds between the carboxyls and the surface is the decisive factor determining desorption rates, and not so much the character of the bond i.e. whether these are inner sphere or hydrogen bonded structures. Infrared temperature-excursion experiments distinguish surface complexes based on their fundamental thermodynamic properties. We will show how this approach helps to shed light on the controversy surrounding surface complexes of sulfate.

[1]. Stumm W. (1992) *Chemistry of the Solid-Water Interface*. Wiley, Inc., New York.

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