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Bonding Of Hg²⁺ in Natural Organic Matter (NOM) Determined by X-Ray Absorption Fine Structure (XAFS)

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Beamline(s): X10C

Introduction: The strong binding of mercury in natural organic matter (NOM) is well known. The functional groups in NOM involved with Hg²⁺ binding are thought to be reduced sulfur (thiol, sulfide, and disulfide), oxygen (carboxylic and phenolic), or nitrogen. Recent research suggests that the strong affinity for Hg²⁺ is mainly due to reduced S. However, some researchers argue that O functional groups cannot be neglected because of the abundance of carboxylic groups and phenolic groups in NOM. In the current study we first determined the reduced S content in an HA sample with S K-edge x-ray adsorption near edge spectroscopy (XANES) then we added Hg²⁺ to the HA at concentrations equivalent to molar Hg/S_{red} ratios from 0.23 to 8.04 and determined the binding environment using XAFS.

Methods and Materials: A soil sample was taken from the upper 10-cm of an organic soil at the edge of a fen in the Marcell Experimental Forest, near the city of Grand Rapids in northern Minnesota. Humic acid was extracted using methods similar to those used by the International Humic Substance Society [1]. Total Hg content was determined using cold vapor atomic fluorescence spectroscopy (CVAFS). The S content was determined by total combustion. Mercury was added as Hg(NO₃)₂ to give five different Hg/S_{red} ratios ranging from 0.23 to 8.04. The S K-edge XANES analysis was carried out at beamline X-19A at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory. The results showed an S content of 0.2%. The Hg L_{III}-edge XAFS analysis was carried out at the beamline X-10C at NSLS and at the beamline ID26 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. The XANES data and the k³-weighted scattering curve and the radial structure function from XAFS data were computed using MacXAFS.

Results: Our data show the major peak in the experimental radial structure function (RSF) plot for the Hg/S_{red} = 0.23 sample appears at 2 Å and there are no other significant peaks. According to Xia et al. [2], this peak represents Hg-S binding. In the experimental RSF plot for Hg/S_{red} = 8.04, the major peaks are at 1.6 and 2.0 Å. The RSF spectra of the model compounds Hg-O and Hg(SET)₂ suggest the peak positions at 1.6 and 2.0 Å represent Hg-O and Hg-S bonding, respectively. Tabata et al. [3] reported that the peak position at 1.6 Å could be for Hg-N since the scattering patterns of Hg-O and Hg-N are very similar. In addition to the Hg-O (and Hg-N), and Hg-S peaks, there is a minor peak at 2.5 Å. Xia et al. [2] suggests that this is due to second shell scattering by C.

Conclusions: In NOM with high Hg/S_{red} ratios, the predominant inner sphere atom is O or N. With low Hg/S_{red} ratios, however, predominant bonding is with reduced S.

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