

Mercury Complexation with Dissolved Organic Matter as a Function of Redox Potential in Natural Aquatic Systems

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Several different chemical species of the heavy metal mercury are found in natural waters. The organic form, methyl mercury (MeHg) is an especially dangerous neurotoxin that concentrates in the fatty tissues of higher level predators and humans. Bacteria in the anaerobic regions and bottom sediments of lakes produce MeHg. In order to produce this dangerous product, the bacteria must have access to specific mercury containing reactants. Mercury binding with dissolved organic matter (DOM), called complexation, is one form of mercury that controls the access bacteria have to the starting products they need to make MeHg. These bonds are directly related to the amount of MeHg available for poisoning an aquatic environment. These complexed forms, in turn, may depend a great deal on the potential energy of the water system available for reduction and oxidation reactions (redox potential). Many of the Hg binding sites on DOM are sulfur and oxygen functional groups. These groups readily change from when there is a shift in the availability of electrons for reaction. For this reason it is suspected that redox potential has a direct impact on the complexation of mercury with DOM. The goal of this research is to quantitatively describe the impact redox potential has on complexation in aquatic systems by deriving an equilibrium coefficient to describe Hg-DOM binding.

The affirmation of a redox potential dependant relationship between DOM and mercury is accomplished through a mass balance approach. Initially, unbound mercury will be added to an environment containing a known amount of DOM. Free mercury ions in solution will be able to pass through a dialysis membrane that will separate two compartments of the experimental setup. However, the majority of the DOM molecules are too large, and will not be able to move through the membrane. A small fraction of the DOM is small enough to pass through the membrane, and this movement must be accounted for in the final calculations. The system will be in equilibrium when the free mercury ions are of equal concentration on both sides of the membrane, and mercury-DOM complexes (which are too large to pass through the membrane) are at a constant level. By measuring the amount of free mercury and the amount of DOM that is capable of passing through the membrane, the mass balance of free versus bound mercury can be completed.

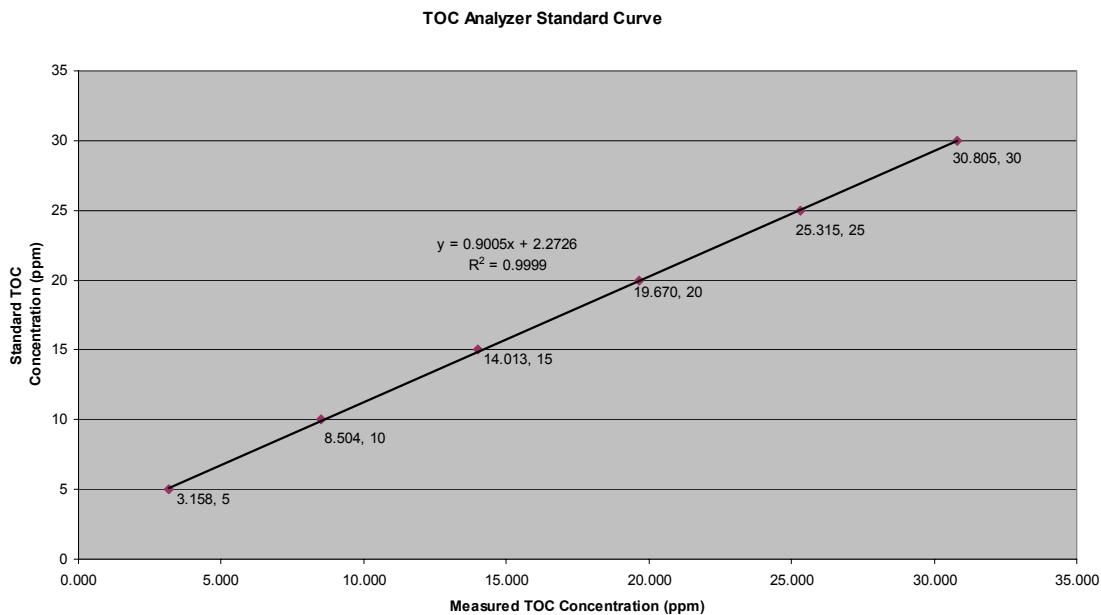
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Manipulation of the redox potential in which this dialysis experiment is carried out will yield a relationship between mercury-DOM complexing and redox potential. The redox potential will be varied from normal, surface water conditions in which dissolved oxygen controls to completely anoxic sulfur reducing conditions.

The detailed method for carrying out these experiments has been completed. Specifically, the details of the DOM interactions with the dialysis membrane have been established. Also, it was necessary to use the chemical equilibrium modeling software MINEQL+ to determine the concentrations of the various components required to create environments of specific redox potentials. The method for measuring mercury is very complex, and must be done in an extremely clean environment. It has taken a significant amount of time for us to be able to start making mercury measurements. Now that all of the pieces have come together, we will begin adding mercury to our samples and begin collecting significant data.

To date data collected has included measurements required to calibrate the Total Organic Carbon (TOC) analyzer. The TOC analyzer does not measure well at low concentrations similar to what might be found in natural waters. Therefore, a manual correction of the data must be made to ensure valid measurements. A measurement of standards of known concentrations yields the following graph.



In order to read low concentrations (5-100 ppm) the readings given by the TOC analyzer must be corrected with the linear regression shown above. After the regression, the TOC readings are very accurate.

Different organic carbon samples have shown different transitive properties across the dialysis membrane. There is a significant difference between natural samples, and samples prepared from dissolving freeze dried humic and fulvic acids (the main constituents of natural DOM) in water. The percent of dissolved carbon passable through the membrane in one experiment is shown below.

Sample	Passable %
Pahokee Peat Humic Acid	95.94
Fluka Humic Acid	94.37
Fluka Humic Acid	93.28
Fluka Humic Acid	92.23
Natural Sample	66.24
Natural Sample	65.40
Natural Sample	68.18

The Pahokee Peat and Fluka Humic Acid samples are both prepared from a freeze dried solid, whereas the natural sample is simply an analysis of natural water known to contain DOM.

Different redox potentials are required for the determination of Hg-DOM complexing as a function of redox potential. Using MINEQL+, three different redox conditions have been developed. The systems and predicted redox potentials are shown in the table below.

Redox System	Concentrations	Redox Potential
O ₂ /H ₂ O	P _{O₂} =0.21	14.6
NO ₃ ⁻ /NH ₄ ⁺ /H ₂ O	[NO ₃ ⁻]=[NH ₄ ⁺]=10 ⁻³ M	7.4
SO ₄ ⁻² /HS ⁻ /H ₂ O	[SO ₄ ⁻²]=10 ⁻⁵ M [HS ⁻]=10 ⁻³ M	-2.8

*Solution pH=6.0 for all systems

All of this information is critical for the analysis of mercury. The next phase of the experiment with mercury addition to systems with DOM is next. We hope to have preliminary mercury data available for the SURE conference.