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Biogeochemical Processes of Mercury in Natural and Contaminated Environments

S. C. Brooks, *Organizer*

ABSTRACTS

GEOC 38

Dissolved organic matter and mercury in aquatic systems

George R. Aiken, *graiken@usgs.gov*, U.S. Geological Survey, 3215 Marine Street, Boulder, CO 80303, and **David P Krabbenhoft**, US Geological Survey, 8505 ResearchWay, Madison, WI 53562

A number of biogeochemical processes that influence the fate, bioavailability and transport of mercury (Hg) in aquatic systems are often controlled by interactions with dissolved organic matter (DOM). Laboratory based research demonstrates that DOM binds with mercury very strongly and exerts controls on Hg solubility by the stabilization of nanocolloidal HgS. Field studies across a range of watershed types reveal strong correlations between DOM and total dissolved Hg concentrations in almost all systems, supporting the hypothesis that DOM controls the concentration and transport of dissolved Hg in aquatic systems. Last, mesocosm experiments designed to measure the influence of DOM on Hg biogeochemistry under field settings demonstrate that, in addition to increasing concentrations of dissolved Hg, DOM additions also substantially increased the bioavailability of Hg as evidenced by notable observed production of methylmercury.

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Kinetic controls on the formation of complexes between mercury and DOM in a contaminated environment

Carrie L Miller¹, *millercl@ornl.gov*, **Baohua Gu**², *gub1@ornl.gov*, **George Southworth**³, *southworthgr@ornl.gov*, **Scott C. Brooks**⁴, *brookssc@ornl.gov*, and **Liyuan Liang**⁴,

liangl@ornl.gov. (1) Environmental Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6038, (2) Environmental Science Division, Oak Ridge National Laboratory, P.O. Box 2008, Mail Stop 6036, Oak Ridge, TN 37831-6036, (3) Environmental Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6036, (4) Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6038

The interaction of Hg with dissolved organic matter (DOM) under equilibrium conditions has been the focus of many studies but the kinetic controls on this interaction has often been overlooked. This study examined the rate of Hg-DOM complexation through reactive Hg (HgR) measurements to differentiate inorganic and DOM complexed Hg in the Upper East Fork Poplar Creek (UEFPC) in Oak Ridge, TN. Results indicate that >90% of the dissolved Hg was present as HgR at the headwaters of the creek but a decrease in HgR was observed downstream (>25% of dissolved Hg at all sites examined). The presence of HgR throughout the creek suggests complexes other than Hg-DOM are present and equilibrium complexation has not established. The formation rate of Hg-DOM complexes was further examined in the laboratory using a DOM isolate and similarity between the rates measured in creek water and in DOM solutions suggests that the formation rate of the Hg-DOM complexes is important in controlling the complexation of Hg in UEFPC.

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Determination of Mercury(II) Complexation with Dissolved Organic Matter in a Contaminated Aquatic Environment

Wenming Dong, *dongw@ornl.gov, Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, MS 6038, Oak Ridge, TN 37831-6038, Fax: 865-576-8646, Liyuan Liang, liangl@ornl.gov, Environmental Sciences Division, Oak Ridge National Laboratory, Box 2008, MS 6038, Oak Ridge, Oak Ridge, TN 37831-6038, Carrie L Miller, millercl@ornl.gov, Environmental Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6038, George Southworth, southworthgr@ornl.gov, Environmental Sciences Division, Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6036, and Baohua Gu, gub1@ornl.gov, Environmental Science Division, Oak Ridge National Laboratory, P.O. Box 2008, Mail Stop 6036, Oak Ridge, TN 37831-6036*

The aqueous speciation of Hg(II) in the contaminated East Fork Poplar Creek (EFPC) at Oak Ridge, Tennessee, is not well understood despite the recognition of important roles played by dissolved organic matter (DOM) in controlling the transport, transformation and bioavailability of mercury in the system. In this study, subfractions of DOM (*i.e.*, hydrophobic and hydrophilic acids) were isolated from EFPC surface water, and their chemical structure and specific functional groups (*e.g.*, thiols, carboxyls and phenols) were characterized by chemical and spectroscopic techniques. The conditional stability constants of Hg(II) complexes with DOM-isolates were determined using a modified ion

exchange method and an equilibrium dialysis ligand exchange (EDLE) technique. Results indicate that Hg(II) forms the strong complexes with DOM through thiol-like functional groups (-SH). Model calculations suggest that Hg(II)-DOM complexes are the dominant species in EFPC surface waters and may control the reactivity and transformation of mercury under site-specific conditions.

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Mechanisms of the reduction and emission of HgCl₂ from surfaces

Anthony Carpi¹, *acarpi@jjay.cuny.edu*, **Nicholas D. K. Petraco**², *npetraco@jjay.cuny.edu*, **Daniel Cocris**³, *dcocris@yahoo.com*, **Anthony Ho**¹, *anthony.h718@gmail.com*, and **Jaimie Heslin**¹, *jaimie.heslin@jjay.cuny.edu*. (1) John Jay College, Department of Sciences, City University of New York, 445 West 59th Street, New York, NY 10019, (2) Science, John Jay College, 445 West 59th Street, New York, NY 10019, (3) Science, John Jay College, 445 West 59th Street, New York, NY 10019

Soils and other surfaces are significant sources of mercury to the atmosphere. Divalent mercury [Hg(II)], including HgCl₂, is deposited to surfaces via wet deposition and subsequently reduced to elemental mercury Hg(0) and volatilized from the surface. While numerous factors are known to facilitate the reduction and emission of Hg(II) from surfaces, the mechanisms involved in this process remain unclear. We have conducted a series of laboratory experiments in which HgCl₂, Hg(0), and other species of mercury were added to various artificial surfaces (sand, homogenized soil, and Teflon) and the flux of mercury from these surfaces was monitored using a standard Teflon dynamic flux chamber and Tekran 2537A. Results from these studies indicate that HgCl₂ can be reduced to Hg(0) in the absence of any third-party electron donor. Gaussian software was then used to model Density Functional Theory with a B3LYP functional to find electron density of ground state properties of HgCl₂. The molecule was found to be linear and approaches a transition state at a bond angle of 62 degrees. Further research is currently underway to model the products produced during this transition and the factors that can influence bond vibration to that angle. Results from this work will be presented.

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Effect of oxalate and cysteine on desorption of Hg(II) on kaolinite

Wasana U Senevirathna¹, *hrsenevira21@tntech.edu*, **Hong Zhang**¹, *hzhang@tntech.edu*, and **Baohua Gu**², *gub1@ornl.gov*. (1) Department of Chemistry, Tennessee Tech University, Foster Hall, 55 University Drive, Cookeville, TN 38505-0001, (2) Environmental Science Division, Oak Ridge National Laboratory, P.O. Box 2008, Mail Stop 6036, Oak Ridge, TN 37831-6036

Desorption of Hg(II) on kaolinite as affected by oxalate and cysteine was studied by varying pH (3-7), ligand concentration (0.25, 1.0 mM), and temperature (15-35 °C). The desorption strongly depended on pH, increasing with decreasing pH. Without organic ligands, >90% of Hg(II) desorbed at pH 3 within 2 h, but <10% at pH 7; the desorption was similar with oxalate. The pH effect was much less for cysteine, with similar desorption (~20-50% in 2 h) at all pH studied. These observations are consistent with the previous finding that Hg(II) is sorbed favorably as hydroxylated species at high pH, suggesting that oxalate is probably ineffective in enhancing the Hg(II) desorption because of its weak binding with carboxyl ligand. Cysteine greatly decreased the Hg(II) desorption, especially at low pH. This may result from the ternary complex formation between kaolinite and cysteine through carboxylic groups and between cysteine and Hg(II) through thiol groups.

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Allosteric control mechanism of the mercury-responsive transcriptional regulator MerR

Alexander Johs, *johsa@ornl.gov*, Environmental Sciences Division, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37831, **Hao-Bo Guo**, *guoh1@ornl.gov*, UT/ORNL Center for Molecular Biophysics, Oak Ridge National Laboratory, 1 Bethel Valley Road, Oak Ridge, TN 37996, **Anne O. Summers**, Department of Microbiology, University of Georgia, Athens, GA 30602, **Jeremy C. Smith**, *smithjc@ornl.gov*, UT/ORNL Center for Molecular Biophysics, Oak Ridge National Laboratory, P.O. Box 2008, Building 6011, MS-6309, Oak Ridge, TN 37831-6309, and **Liyuan Liang**, *liangl@ornl.gov*, Environmental Sciences Division, Oak Ridge National Laboratory, Box 2008, MS 6038, Oak Ridge, Oak Ridge, TN 37831-6038

Bacteria participate in mercury transformation in natural and industrial environments. The bacterial mer operon in transposons or plasmids mediates mercury resistance by encoding specific genes that facilitate uptake of mercuric species, cleavage of Hg-C bonds, and reduction of Hg(II) to Hg(0). MerR responds specifically to nanomolar levels of Hg(II) by activating the transcription of the mer operon genes. Small angle x-ray scattering experiments and molecular dynamics were applied to study the allosteric control mechanism of MerR in the presence and absence of Hg(II). Binding of Hg(II) induces a significant reorientation of the MerR homodimer that causes two DNA-binding domains to open and rotate. A population-shift mechanism is proposed causing DNA-underwinding by MerR. This mechanism could explain why the Hg(II)-bound MerR has a lower affinity to DNA than the Hg(II)-free form. Here, we present the complete dynamics of transcription activation by MerR upon Hg(II)-binding.

GEOC 44

Mechanism of Hg-C protonolysis in the organomercurial lyase MerB

Jerry M. Parks¹, parksjm@ornl.gov, **Hong Guo**², hguo1@utk.edu, **Cory Momany**³, cmomany@mail.rx.uga.edu, **Liyuan Liang**⁴, liangl@ornl.gov, **Susan M Miller**⁵, smiller@cgl.ucsf.edu, **Anne O. Summers**⁶, and **Jeremy C. Smith**¹, smithjc@ornl.gov. (1) UT/ORNL Center for Molecular Biophysics, Oak Ridge National Laboratory, P.O. Box 2008, Building 6011, MS-6309, Oak Ridge, TN 37831-6309, Fax: 865-576-7651, (2) Department of Biochemistry & Cellular & Molecular Biology, University of Tennessee, M407 Walters Life Sciences, University of Tennessee, Knoxville, TN 37996, (3) Department of Pharmaceutical and Biomedical Sciences, College of Pharmacy, The University of Georgia, Athens, GA 30602, (4) Environmental Sciences Division, Oak Ridge National Laboratory, P.O. Box 2008, Oak Ridge, TN 37831-6038, (5) Department of Pharmaceutical Chemistry, University of California at San Francisco, 600 16th Street, San Francisco, CA 94143, (6) Department of Microbiology, University of Georgia, Athens, GA 30602

The bacterial organomercurial lyase, MerB, catalyzes the demethylation of organomercurials via Hg-C protonolysis. Two Cys residues in the active site are required for catalysis, but the source of the catalytic proton and the detailed reaction mechanism have not been determined. Here, two proposed reaction mechanisms for MerB protonolysis are investigated using density functional theory calculations. A model of the active site was constructed from an X-ray structure of MerB. Calculations with the methylmercury substrate rule out direct protonation of the leaving group by Cys96. Instead, the calculations support a two-step mechanism in which Asp99 abstracts a proton from Cys96 and then protonates the nascent carbanion leaving group to cleave the Hg-C bond and release the hydrocarbon product. Computed activation barriers for three organomercurial substrates reproduce experimental reaction rates. Analysis of atomic charges using Natural Population Analysis reveals how MerB lowers the barrier in the Hg-C protonolysis reaction.

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Biogeochemical controls on mercury distribution and bioaccumulation in the Florida Everglades

Guangliang Liu, liug@fiu.edu, Department of Chemistry and Biochemistry, Florida International University, Miami, FL 33199, Fax: 305-348-3772, **Y. Cai**, cai@fiu.edu, Dept. of Chemistry and Southeast Environmental Res, Florida International University, University Park, Miami, FL 33199, **Yuxiang Mao**, yuxiang.mao@fiu.edu, Department of Chemistry and Biochemistry, Florida International University, 11200 SW 8th Street, Miami, FL 33199, **Daniel Scheidt**, Region 4, Water Management Division, United States Environmental Protection Agency, Athens, GA 30605, **Peter Kalla**, Region 4, Science and Ecosystem Support Division, United States Environmental Protection Agency,

Athens, GA 30605, and David Roelant, Applied Research Center, Florida International University, Miami, FL 33174

A variety of biogeochemical characteristics (including total mercury, THg, and methylmercury, MeHg) were analyzed for surface water, soil, flocculent detrital material (floc), periphyton, and mosquitofish samples collected from 228 randomly located stations in the Florida Everglades to investigate the biogeochemical controls on Hg distribution and bioaccumulation in this wetland ecosystem. Correlation and multiple regression analysis suggested that multiple biogeochemical characteristic, such as surface water dissolved organic matter (DOCSW), pH, chloride, and compositional properties of solid compartments, are important factors controlling Hg distribution and bioaccumulation. For example, significant correlations ($P < 0.001$) between Hg (THg and MeHg) and DOCSW were observed across the ecosystem. Moreover, the MeHg/THg ratio also correlated positively with DOCSW, suggesting Everglades DOC has stronger binding capability with MeHg than with THg. A strong inverse correlation between bioaccumulation factor (BAF) for MeHg in mosquitofish and DOCSW ($R = -0.639$, $N = 167$, $P < 0.001$) indicates that DOC may decrease bioavailability of MeHg in water.

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A mechanistic mercury cycling model of the NY/NJ Harbor used to relate mercury loadings to concentrations in water, sediment and biota.

Aaron Redman¹, aredman@hydroqual.com, Robert Santore², James R. Wands³, jwands@hydroqual.com, Robin L. Miller³, rmiller@hydroqual.com, and Kevin J. Farley⁴, kevin.farley@manhattan.edu. (1) HydroQual, PO Box 198, Logan, UT 84326, (2) HydroQual, 6700 Kirkville Rd, East Syracuse, NY 13057, (3) HydroQual, Inc, 1200 MacArthur Blvd., Mahwah, NJ 07430, (4) Department of Civil and Environmental Engineering, Manhattan College, Manhattan College Parkway, Riverdale, NY 10471

A goal in managing mercury (Hg) in the environment is to predict the response in Hg levels to decreases in loading. There are several key processes in the Hg biogeochemical cycle that do not necessarily respond linear with loading rates. Accordingly, a process-based Hg modeling framework is being applied to develop the Hg TMDL for the NY/NJ Harbor. The modeling framework is 3-D and time variable and includes linked hydrodynamic transport, sediment transport, and organic carbon production modules. Demethylation was modeled as an abiotic process in surface waters and as microbial processes in the sediment. Methylation was modeled as a function of anaerobic microbial activity and the chemical bioavailability. Mercury interactions with major ions, sulfide, dissolved and particulate organic carbon and other solid phases are modeled using chemical speciation calculations. Site-specific loading response relationships in the model suggest that mercury in the water, sediment and fish responds slowly (>30 years) and that projected drivers of future Hg are head-of-tide, runoff, and bed sediments.