

Final Report for Period: 03/2006 - 09/2006**Submitted on:** 02/14/2007**Principal Investigator:** Perdue, E. Michael .**Award ID:** 0129516**Organization:** GA Tech Res Corp - GIT**Title:**

U.S.-Germany Cooperative Research: An Integrated Analytical Approach for the Structural Characterization and Proton Binding of Size-Fractionated Natural Organic Matter

Project Participants**Senior Personnel****Name:** Perdue, E. Michael**Worked for more than 160 Hours:** Yes**Contribution to Project:****Post-doc****Graduate Student****Name:** Koprivnjak, Jean-Francois**Worked for more than 160 Hours:** Yes**Contribution to Project:**

This student took several samples of natural organic matter (NOM) that he isolated from southeastern rivers to Munich, where, in collaboration with our co-investigators at GSF, he conducted a wide variety of measurements to characterize the samples with respect to charge density, molecular weight, and chemical structure.

Name: Ritchie, Jason**Worked for more than 160 Hours:** Yes**Contribution to Project:**

This student took several molecular weight fractions of natural organic matter (NOM) that our research group isolated from the Suwannee River to Munich, where, in collaboration with our co-investigators at GSF, he conducted a wide variety of measurements to characterize the samples with respect to charge density, molecular weight, and chemical structure.

Undergraduate Student**Technician, Programmer****Other Participant****Research Experience for Undergraduates****Organizational Partners****GSF Forschungszentrum fuer Umwelt und Ges**

This project is a joint NSF-DAAD project. See the original proposal(s)!

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities:

The German (GSF) and American (GIT) co-investigators have met and worked together in Munich (May-June, 2002, August, 2003), Boston (July, 2002), Suwannee River, Georgia (May-June, 2003), and Atlanta (September, 2003, December, 2003, January, 2004). Two GIT graduate students have been trained in the use of capillary electrophoresis and related techniques and in the use of NMR spectrometry (^{13}C and ^1H). Samples of NOM that were collected and fractionated by those GIT students have been used for a wide variety of measurements in the labs at GSF. The co-investigators have finished writing a major paper that is based on this collaboration, and that manuscript was published in *Analytical Chemistry* in 2004.

The co-investigators from GIT and GSF also collaborated in preparation of a paper on ^{113}Cd NMR studies of metal complexation by humic substances at the 2005 Goldschmidt Conference, and a manuscript based on that paper is currently in press at *Applied Geochemistry*.

In the past two years (2/05 - 2/07), the GSF and Georgia Tech groups have met together in Atlanta and Munich to work on a new stochastic model called SPARIA (substitution patterns in aromatic rings by increment analysis). The work actually started in 2001 during Dr. Perdue's visit at GSF and has continued through the visits of GSF colleagues to GIT and finally through Dr. Perdue's recent visit to GSF in August, 2006. Based on the results of that collaboration, a manuscript describing SPARIA and its use to interpret two-dimensional heteronuclear NMR spectra of humic substances has been written and has recently been published in *Analytical Chemistry*.

Dr. Perdue and his GSF colleagues continue to collaborate informally on several topics and papers, and he will again visit GSF for six weeks in the summer of 2007 to further the collaboration (no longer supported by the NSF grant).

One of Dr. Perdue's Ph.D. students (Jason Ritchie) successfully defended his Ph.D. dissertation in August, 2005 on the topic of the pH-dependent distribution of charge in humic substances and their molecular size fractions. Central to this research are the capillary electropherograms that were determined in the laboratory of Dr. Philippe Schmitt-Kopplin at GSF. Dr. Ritchie has recently prepared two manuscripts that are being finalized for submission to peer-review journals.

Dr. Perdue's Ph.D. student (Jean-Francois Koprivnjak) is defending his dissertation in March, 2007. At least 50% of the content of the dissertation is based on his research collaboration with colleagues at GSF, and Mr. Koprivnjak has had several opportunities to take samples to GSF to obtain state-of-the-science analytical results that have been essential to the completion of his dissertation.

Findings:

We have found that Cd(II) ion is coordinated mainly by oxygen atoms in NOM. To a lesser extent, nitrogen donor atoms participate in complexation of Cd(II) , especially at higher pH. Weak evidence is also seen for binding of Cd(II) by sulfur donor atoms. Because NOM is a highly complex mixture of organic compounds that provides a rich variety of Cd(II) binding sites, there are no experimentally attainable conditions where chemical exchange of Cd(II) among binding sites is uniformly fast, intermediate, or slow. In fact, all three domains of chemical exchange rates are evident at all pH and Cd/C ratios that were investigated in this research.

The SPARIA model shows great promise for being able to predict the pattern of substituents on aromatic rings from the chemical shifts of a single C-H group in a heteronuclear 2-D HSQC NMR spectrum. Preliminary texts indicate that the same software will also be highly useful for interpreting homonuclear 2-D TOCSY and COSY NMR spectra of humic substances and natural organic matter.

The charge distribution model has shown promise of being able to reconcile data from three types of measurements (size exclusion chromatography, capillary electrophoresis, and alkalimetric titrations) through a common pH-dependent charge distribution that fits all data at all pH values that have been investigated (pH 4 -- 11).

Training and Development:

The two graduate students from GIT have received training at Georgia Tech in the isolation and fractionation of NOM. During their work at GSF in Munich, they have learned both the principles and practical application of capillary electrophoresis and NMR spectrometry for characterization of NOM and molecular weight fractions of NOM.

Outreach Activities:

Some of the findings of this research have already been integrated into the graduate course on Organic Geochemistry, which I taught in Fall, 2003. Additionally, some of the findings of this research were incorporated into a major review paper of dissolved organic matter in fresh

waters which the co-PI and one student (JDR) recently published in the Treatise on Geochemistry.

The research on the charge distribution of humic substances has been submitted for a presentation at the 2006 IHSS meeting in Karlsruhe, Germany, and the SPARIA model was presented at the 2005 National American Chemical Society meeting and at the 3rd European Symposium on NMR Spectroscopy in Soil, Geo and Environmental Sciences.

Journal Publications

N. Hertkorn, E. M. Perdue, and A. Kettrup, "A potentiometric and ^{113}Cd NMR study of cadmium complexation by natural organic matter at two different magnetic field strengths", Anal. Chem., p. 6327, vol. 76, (2004). Published

Books or Other One-time Publications

Web/Internet Site

Other Specific Products

Contributions

Contributions within Discipline:

Contributions to Other Disciplines:

Contributions to Human Resource Development:

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