CHARACTERIZATION OF CHROMOPHORIC DISSOLVED ORGANIC MATTER WITH IRON CHELATES IN RAIN WATER

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A Thesis Submitted to the
University of North Carolina at Wilmington in Partial Fulfillment
Of the Requirements for the Degree of
Master of Science

Department of Chemistry

University of North Carolina Wilmington

2005

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Dean, Graduate School

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ABSTRACT

The existence of Fe(II) and Fe(III) complexed CDOM has important ramifications for the speciation of iron in atmospheric waters. The Fe(III)-CDOM complex is a precursor to Fe(II) photochemical production where a ligand to metal charge transfer (LMCT) leads to the production of the reduced iron. Fe(II) and Fe(III) were added to Wilmington, NC rainwater containing chromophoric dissolved organic matter (CDOM). In general Fe(II) enhanced the fluorescence of CDOM while Fe(III) quenched CDOM fluorescence. The observation of fluorescence changes indicates complexation.

In authentic rain where Fe(II) and CDOM fluorescence were measured before and after irradiation there was a significant correlation between the photoproduction of Fe(II) and increased fluorescence. While in synthetic rainwater containing CDOM extracted from rainwater and added Fe(III) irradiation for 2 hours photoproduced Fe(II). The amount of Fe(II) produced was accurately predicted using a model calculation generated for predicting changes of Fe(II) in authentic rainwater using starting Fe(II), Fe(III), and H^+ concentrations. The accuracy of this equation in both authentic and synthetic rainwater with added rainwater CDOM demonstrates the importance of CDOM for Fe(II) photoproduction. Once irradiation ceased Fe(II) oxidized slower in synthetic rainwater containing CDOM relative to synthetic rainwater without CDOM with a rate constant of 1.66 nM h^{-1} which is similar to authentic rainwater oxidation studies where the rate of oxidation range for was 0.9 – 7 nM h^{-1}. After 22 hours the remaining Fe(II) was protected against further oxidation by complexation with the extracted CDOM. The reproducibility between authentic rainwater and synthetic rain with added CDOM indicates that the ligand responsible for protecting Fe from oxidation is CDOM.

A solution of CDOM extracted from rain with added Fe(II) remained stable in a synthetic rainwater solution for 24 hours similar to observation in authentic rainwater; however very different from synthetic rainwater without CDOM. A solution of CDOM with Fe(II) had constant Fe(II) concentrations when mixed 1:1 with seawater for at least four hours, however Fe(II) in synthetic rain with no added CDOM became undetectable within three minutes of mixing with seawater. This stability of Fe(II) with added rain CDOM suggests that CDOM is the organic ligand responsible for protected Fe(II) from oxidation and its soluble form in natural waters.

ACKNOWLEDGEMENTS

I would like to thank Dr. Robert Kieber, Dr. Joan Willey, and Dr Robert Whitehead for their constant guidance, support, and encouragement in completing this thesis. I send a special thank you to Leslie Bradshaw and Grant Pace for their friendship and amazing support though the many hard times both in the lab and out of the lab. I offer a blessing and namaste to the many yogis and yoginis that gave me strength and wisdom along the way. And finally with all my heart and love to Janice, my sister, Elaine, my beautiful grandmother, and Mike and Debbie Resetar, my parents, for their encouragement and goal orientation "Goal #1 Graduate!" We made it!

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