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Trace Metal Speciation in Complex Aquatic Environments

*The Cu^{2+} , Cd^{2+} , Ferrihydrite, Phthalic Acid and Bacteria
System*

Yantao Song

*A thesis submitted in fulfillment of the requirements for the degree of Doctor of Philosophy,
The University of Auckland, 2009.*

Abstract

Trace metal speciation in aquatic environments is inherently complex due to the large number of possible interactions with dissolved and particulate components. Adsorption onto iron oxyhydroxide and bacterial surfaces, as well as the formation of metal-ligand complexes can play important roles in controlling the fate and transport of trace metals in natural environments. The objective of this study is to describe and understand metal speciation and distribution in a complex biogeochemical system by incrementally increasing the complexity from simple binary systems to a dynamic quaternary system containing a trace metal, iron oxide and bacteria that are active and metabolizing an organic ligand.

Copper, cadmium, and phthalic acid (H_2L_p) adsorption onto ferrihydrite in binary systems was well reproduced using the diffuse layer model (DLM). The adsorption of H_2L_p adsorption was analogous to that of inorganic diprotic acids in terms of the relationship between the adsorption constants and acidity constants. In ternary systems H_2L_p caused Cu^{2+} or Cd^{2+} adsorption to be either enhanced (due to surface ternary complex formation) or inhibited (due to solution complex formation) depending on the conditions. The DLM could only describe the effect of H_2L_p on metal ion sorption by including ternary complexes of the form $\equiv FeOHML_p^{(0)}$, where $\equiv FeOH$ is a surface site and M is Cu or Cd. The relationship between binary metal adsorption constants and the ternary complex adsorption constants from this and previous studies suggest several properties of ternary complexes. First, ternary complex structures on both ferrihydrite and goethite are either the same or similar. Second, those cations having large adsorption constants also have large equilibrium constants for ternary complex formation. Third, ligands forming stronger solution complexes with cations will also form stronger surface ternary complexes but because of the strong solution complexes these ligands will not necessarily enhance cation adsorption.

The bacterial strain *Comamonas spp.* was isolated from the activated sludge of a wastewater treatment plant. *Comamonas spp.* could effectively degrade H_2L_p in the presence of Cd^{2+} and ferrihydrite and was therefore chosen to study the effect of H_2L_p degradation on Cd^{2+} speciation. Proton, cadmium and H_2L_p adsorption onto *Comamonas spp.* were measured. The *Comamonas spp.* titration curve is flatter than that of ferrihydrite, indicating a higher degree of site heterogeneity at the bacterial surface. Adsorption edges of Cd^{2+} adsorption onto *Comamonas spp.* occurred over about 4~5 pH units compared to those of ferrihydrite which

occurred over ≈ 2 pH units on a dry weight basis. *Comamonas spp.* can accumulate a larger amount of Cd^{2+} than ferrihydrite especially under lower pH conditions. Proton and Cd^{2+} adsorption onto *Comamonas spp.* cells over a wide sorbent/sorbate and pH range was reasonably well described by a four site non-electrostatic model. The acid-base and Cd^{2+} adsorption behaviour of *Comamonas spp.* in this work were within the range of studies of bacteria adsorption. Phthalic acid adsorption onto inactive *Comamonas spp.* was negligible over a pH range of 3 to 8 and became significant only at $\text{pH} < 3$ where H_2L_p was fully protonated. This is consistent with the proposed mechanism for ligand adsorption onto bacterial surfaces which involved a balance between hydrophobic interaction and electrostatic repulsion. The presence of H_2L_p decreased Cd^{2+} adsorption onto *Comamonas spp.* due to competition for Cd^{2+} between the bacterial cell surface and the formation of solution complexes of Cd^{2+} . This was accurately modelled with the Cd-L_p solution species indicating that no significant surface ternary interaction occurred between Cd^{2+} , phthalic acid and *Comamonas spp.*.

Cadmium adsorption onto ferrihydrite-*Comamonas spp.* mixtures was slightly less than the simple additive predicted adsorption of ferrihydrite plus *Comamonas spp.*. This suggests there is a weak interaction between ferrihydrite and *Comamonas spp.* and this interaction could be modelled by including a generic reaction between the ferrihydrite and *Comamonas spp.* surface sites. Cadmium distribution in a system of inactive *Comamonas spp.*-ferrihydrite in the absence and presence of H_2L_p could be predicted by combining the ferrihydrite and bacteria models with the inclusion of the ferrihydrite-bacteria interaction. The effects of H_2L_p degradation on Cd^{2+} distribution were investigated in dynamic systems with live bacteria. Results showed that Cd^{2+} adsorption in these dynamic systems was reasonably estimated with the model parameters developed in the proceeding experiments though uncertainty exists in the dynamic process with regards to H_2L_p biodegradation products and changes in the bacteria population.

This thesis was therefore able to provide a better understanding of metal speciation in complex and heterogeneous realistic environments by experimentally examining and modelling metal speciation and distribution in various systems with increasing complexity. This helps to bridge the gap of quantitative description of metal speciation from simple laboratory experiment systems to real world systems, both natural and engineered.

Acknowledgements

Before saying heaps of thanks to a number of people, I would like first to express my appreciation for the New Zealand International Doctoral Research Scholarship, and the University of Auckland Scholarship for International Students. These scholarships made it possible to start and complete this work.

There are so many people that deserve special thanks for contributing to this thesis. First of all, my supervisors, Dr Naresh Singhal, Dr Peter James Swedlund and Dr Simon Swift whose research area is different from each other but have been always very supportive. Without their advice in engineering, geochemistry and bacteriology, it would have been impossible to achieve this work. I have been very impressed by their bravery at taking on a Chinese engineering student to undertake this project. Dr P. J. Swedlund has my unceasing gratitude for his boundless patience, loud laughs and endless answers to my unending chemistry questions. To me, he is a great mentor, just like Theodore Stephanides to little Gerald Durrel (Gerald Durrel, My Family and Other Animals). His insatiable interest, pure curiosity and enthusiasm for geochemistry, his ability and great patience to illuminate any question asked, coupled with an impish sense of humour made him an excellent supervisor. Without his guidance, I would have learnt nothing about geochemistry in New Zealand.

I am likewise grateful for the friendly and invaluable technical support of Mr Glenn Boyes, Mrs Maria Rowe, Mr Abel Francis, Ms Catherine Hobbis, Dr Alec Asadov, Dr Ron Etzion and Dr Sandra Uy, which meant a lot to me. I would also like to thank Dr Gordon Miskelly, Professor Jim Metson and Dr Sylvia Sander for not only being very generous letting me use laboratory instruments, but also providing inspiration ideas to solve some problems. Thank you.

The university library is one of the best libraries I have ever come across. The general library staff are always trying their best to get useful research material via various resources; while the engineering library staff have never let me down when I had problems using the library resource.

There are so many friends that I must say thank you. Latu Harper who has been very considerate and supportive, is one of the kindest, smartest and happiest friends that I have ever met. Denise Pilbrow, a patient and intelligent woman and an amazing expert in tricky

report templates and MS word. I learned a lot from her. Anthea, for her conversation and wit during tea breaks. Anthea along with the two Andrews (Andrew Rumsby and Andrew Baddeley), offered the first iron oxide field trip in New Zealand, which has, obviously built up my great enthusiasm in this project. Yuying Han, with whom working late and during weekend was a joy, not only was the work effectively done, but also the wonderful food we had cooked was shared together during lots of laughs. Maria Rowe, a great cook and elegant friend who taught me the meaning of bonhomie, has not only given me a lot of help since I started working in the molecular and pathology lab, but also provided her homemade tasty food and cheerful conversations during tea breaks. Chunxia Yang, one of my best friends, has taken the trouble to get and send documents overseas whenever required by my visa application. The long conversation on the phone with her has been always very enjoyable. Liangxin Wu's, a very friendly family, helped me move from place to place several times. Wanhua Feng, Eun Hea Jho, Anuradha Premathilaka, Claudia Kayser, Sasha Jattansingh, Avery Gottfried, Roy Elliot, Victoria Melville, Katherine Heays, Farhan Shams, Naeem Ejaz, Janine Louie, Benedic Uy, Emily Voyde, Jie Han and Buddhika Gunawardana are all great friends to work and talk with. Without them, I would not have learned different interesting research topics during the weekly group meeting, nor would I have enjoyed working in the postgraduate student office in the last few years. I have been very lucky to meet and get along with them.

My family, the most important support team in my life, have been given me endless support and care. While dad is always good at reminding me of study whenever he found that I have been talking too much about cooking or gardening, mum and all my sisters will never forget to remind me of getting sufficient rest during research. Andrew and his nice family, who have made studying overseas a little less hard, have given me very warm supportive care. Andrew, in the last few years during my study, has been busy driving between places during weekends, looking for my favourite food, showing me interesting natural iron oxide fields, beautiful beaches, amazing waterfalls, curious forests, marvellous plants, insects, birds and animals.

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