

**PROCESSES CONTROLLING THE FATE AND  
TRANSPORT OF TRACE METALS IN THE SUBSURFACE  
DURING CHANGING REDOX POTENTIAL**

Thesis by

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In Partial Fulfillment of the Requirements

for the Degree of

Doctor of Philosophy

CALIFORNIA INSTITUTE OF TECHNOLOGY

Pasadena, California

2011

(Defended May 10, 2011)

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## Acknowledgements

First and foremost, I must thank Janet Hering, my advisor. I'm especially grateful for her editorial standards, financial and personal support, career guidance, and her invitation to move to Eawag. I attribute much of my personal growth over the course of my graduate work either directly or indirectly to Janet.

Jess Adkins, Michael Hoffmann, and Victoria Orphan have been supportive committee members from afar. Jim Morgan pointed me in the right direction towards some key papers and concepts early in my graduate work.

Rich Wildman became my unofficial graduate school mentor. From the shores of Lake Powell to the shores of Greifensee, Rich's enthusiasm and unwavering support gave me confidence and kept me going in the tough times. I thank both Rich and his wife, Zena Harris, for being my "training wheels" in Zürich. Vanessa Sternitzke listened to far more details of uncooperative Mn-oxidizing bacteria than any person should have to and made sure that I saw a bit of Switzerland as long as I was there. I would not have survived this Ph.D. without her patient friendship and our hiking adventures. Kate Campbell introduced me to gels and manganese in the lab. The consummate professional, it took me a couple of months to realize that she didn't already know the results of my doped-gel experiments.

I must acknowledge technical support from Nathan Dalleska at Caltech and Thomas Ruettimann, Caroline Stengel, Hermann Moench, Lisa Salhi, and Brian Sinnet at Eawag. Ich danke der Hydrogeologie-Gruppe des Freie Universität Berlins, namentlich Gudrun Massmann, Christian Menz, und Thomas Taute, für die gute Zusammenarbeit

beim Tegeler See. Sarah Griffis worked hard and asked good questions, besides getting in Lake Tegel on a cold day in July. I'm grateful to my microbiologist collaborators: Dianne Newman's group at Caltech, especially Alexa Price-Whelan and Yun Wang; Colleen Hansel's group at Harvard, especially Derek Learman and Cara Santelli; and Frederik Hammes, Hans-Ulrich Weilenmann, Karin Lautenschlager, and Johannes Wolf at Eawag. Andreas Voegelin performed all XAS sampling and analysis, and maintained good spirits throughout the long hours at the beamline.

Stephan Hug kindly let me be an unofficial member of his research group at Eawag. Edi Hoehn spent a full morning discussing bank filtration with me at the original Glattfelden site, and suggested collaboration with Gudrun Massmann. Peggy O'Day, Lars Maechler, and Matthias Brennwald had some key input in the initial design of my column experiments. Linda Roberts, Helen Rowland, Benoit Pernet-Codrier, Lenny Winkel, and Christine Wenk offered helpful discussions and friendship at Eawag. Megan Ferguson, Arthur Fitzmaurice, Azra Bilgin, Tom He, Diana Stefanescu, and Tao Cheng created a pleasant working group at Caltech. Maria Luisa Ruiz-Ripoll, Cristina Mojica, Yvonne Chen, and Katie Cychosz have provided six years' worth of graduate school sympathy and career advice. I'm grateful for Kathleen Wyss-Shore's professional guidance when I most needed it.

I credit Dan Giammar and Liyun Xie of the Aquatic Chemistry Lab at Washington University in St. Louis with teaching me good basic laboratory skills and making my enthusiasm for science productive. Jeanne Dalton taught me redox chemistry at St. Pius X Catholic High School, and her A.P. chemistry course, which presented us

with general hypotheses to be tested rather than explicit laboratory instructions, gave me my first taste in designing and executing chemistry experiments.

Finally, I would like to thank my parents, who have supported my intellectual pursuits, even as they take me further and further from home, and my siblings, who never cease to find ways to humble me, often in song. I must especially thank my grandparents, Sam and Carolyn Magruder, whose financial support during my Bachelor's studies started me on this path. I hope you agree it was a pretty good investment.

## Abstract

This study investigated the cycling of Mn and Fe as oxic surface water entered shallow sediments and was reduced, and as reduced groundwater became exposed to oxygen and was oxidized. A Mn-oxide doped gel probe sampler was developed to study *in situ* rates of reductive dissolution and was validated with laboratory studies with ascorbic acid and *Shewanella oneidensis* MR-1 as model reductants. The sampler was deployed in the bank sediments of Lake Tegel, Berlin, Germany. Modeling of the diffusion-controlled reaction converted the mass loss from the gels in the sampler to a profile of pseudo-first-order rate constants as a function of depth. The rate constants were highest at depths with high dissolved Fe and low operationally defined fractions of reducible oxides of Fe and Mn in the sediments.

A laboratory column experiment showed that 1.3-m water table fluctuations, as observed in bank filtration sites around Berlin, were able to provide sufficient dissolved oxygen delivery for *Pseudomonas putida* GB-1, an obligate aerobe, to oxidize Mn(II) *in situ*. Accumulation of Mn on the quartz sand in the column at the end of the experiment was limited to the top 60 cm, as measured with X-ray fluorescence (XRF), and X-ray absorption spectroscopy (XAS) analysis confirmed that the solid formed was a Mn(IV) oxide characteristic of biogenic origin. After a period of “filter ripening” in the column, rates of *in situ* oxidation were still lower than rates in engineered aerated sand filters.

Adjacent to a production well with a water table that fluctuates up to 7 m annually at Lake Tegel, however, sediments collected from a borehole did not show any significant accumulation of Mn or Fe with depth, as measured by XRF; analysis of the

speciation of Mn and Fe in the solid phase by XAS suggested a slight increase in the proportions of total Mn as Mn(II) and of total Fe as Fe(II) with depth. At this location, vertical zonation of groundwater may preclude the co-occurrence of reduced Mn and Fe with dissolved oxygen entrapped by water table fluctuations. Whether groundwater changes from oxidizing to reducing conditions or vice versa, the behavior of Mn and Fe reflects a complex interaction between sediments, solutes, microbial activity, and hydrology.

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