Chapter 7

Conclusions

Summary

In this study, we investigated the behavior of Mn and Fe under two types of changing redox conditions: as oxic surface water entered shallow sediments and was reduced, and as reduced groundwater became exposed to oxygen and was oxidized. The oxic-to-reduced transition was probed with a newly developed method to measure *in situ* reduction rates as a function of depth, with sub-cm resolution. The reduced-to-oxidized transition was investigated in a laboratory-scale column experiment, whose frequency and amplitude of water table oscillations were designed to simulate field conditions. For both types of redox transitions, laboratory study was complemented with a field investigation in the shoreline bank sediments and the aquifer sediments, respectively, at Lake Tegel, Berlin, Germany.

In situ rates of reductive dissolution

The Mn oxide-doped gels developed in Chapter 3 can assess *in situ* reduction rates in a variety of saturated settings. With the AQUASIM (Chapter 3) and MATLAB (Chapter 4) models, the mass loss of Mn from a gel over time can be easily converted to a pseudofirst-order rate coefficient for the reaction taking place at the Mn oxide surfaces inside the gel. Without accounting for diffusion in the model, the rate of Mn reduction would be underestimated by as much as 1–3 orders of magnitude.

Even with such accounting, the gels physically separate the electron acceptor (Mn oxide) from Mn-reducing microbes. Gel pore size is estimated to be between 2 nm and 1 μm (Chrambach and Rodbard 1971, Rüchel and Brager 1975, Patras et al. 2000); the dimensions of *Shewanella oneidensis* MR-1 are approximately 0.6 μm × 3 μm (Abboud et al. 2005). Modeling suggests that gels capture 35% of the reduction capacity of *S. oneidensis* MR-1, which may be attributable to extracellular electron shuttles and nanowires, but not to direct enzymatic contact with the Mn oxide (Nielsen et al. 2010).

More recent literature has identified flavins as the primary electron shuttle produced by *Shewanella* species (Marsili et al. 2008, von Canstein et al. 2008), and the kinetics of Fe oxide reduction by enzymes in the *S. oneidensis* MR-1 cell wall, mediated by riboflavin, have been modeled (Ross et al. 2009). A preliminary attempt to adopt the literature parameters in the AQUASIM model presented in Chapter 3, however, was unsuccessful. The modified model featured the enzyme omcA and reduced flavins (600 nM) initially in the bulk solution. The flavins could diffuse into the gel, become oxidized as they reduced Mn oxide, and diffuse out of the gel to be re-reduced by the enzyme omcA. Sensitivity analysis suggests that the diffusion gradient was too low for the rapid flavin recycling needed to reproduce the dissolved Mn concentrations observed in the bulk solution. This could be evidence for nanowires or some penetration of MR-1 in the gel, which would bypass the slow diffusive flux of low concentrations of an electron shuttle. Further research that takes advantage of the Mn-doped gels' physical constraints on microbial physiology could lead to interesting results. For example, in Chapter 5, this technique was used to quantify rates of Mn *reduction* by a Mn-*oxidizing* microbe.

The main practical limitations of Mn-doped gel probe deployment include the sediment's physical characteristics and chemistry. The ladder-like sample holder is deployable by hand in sandy sediments without gravel, which can rip the membrane covering the gels and block insertion; low porosity clayey sediments can also resist the force of insertion. Low porosity sediments can furthermore increase the time for diffusive equilibration of the porewater with the gels (Harper et al. 1997).

The data collected in Chapter 4 suggest that measured Mn oxide reduction rates from Lake Tegel reflect some interaction with dissolved Fe, presumably Fe(II), in the sediment porewater. If Fe(II) is the reductant directly responsible for Mn reduction in these sediments, then the time to reach diffusive equilibrium with the gels is important to consider. The MATLAB model in Chapter 4 does not consider the diffusion of the reductant into the gel, nor does it represent the reaction kinetics as second-order (first-order in both [reductant] and [Mn oxide]), as literature proposes for Fe(II) (Villinski et al. 2003) and sulfide (Burdige and Nealson 1986). With an infinite source of Fe(II) in the sediments, modeling suggests that diffusive equilibrium with the gels ($C_{gel} = 0.995$ $C_{porewater}$) should occur within 4 h. Further refinement of the MATLAB model could incorporate the second-order kinetics for Mn reduction by Fe(II) or sulfide and the diffusion of the reductant into the gel. This refinement could perhaps resolve the discrepancy between the *in situ* Mn oxide reduction rates and the rates expected from extrapolation of laboratory experiments to field conditions.

It is worth remembering, though, that the Mn-oxide-doped gels are single-point estimates of reduction rates. Modeling of the two end points (before and after deployment) and diffusion through the gel can generate a lot of data, but many assumptions underlie these rates. Nevertheless, comparisons with *in situ* Mn reduction rates from a variety of field settings suggest that the rates in Chapter 4 are reasonable. A recent compendium of bacterial Mn oxide reduction rates found that the average surface area normalized rate with zero-order kinetics was 1.47×10^{-7} mol m^{-2} h^{-1} (Bandstra et al. 2011), which is comparable to the shallow *in situ* reduction rates measured in Lake Tegel sediments (9.4×10^{-7} mol m^{-2} h^{-1}).

Finally, gel-derived *in situ* Mn reduction rates represent the potential for sediment to reduce Mn oxides rather than actual Mn reduction rates. Mn oxide reduction can be mediated by microbes with versatile electron transport chains (Ruebush et al. 2006), as well as by reduced porewater species such as Fe(II) and sulfide (Burdige and Nealson 1986, Villinski et al. 2003). These mobile constituents can occur in porewater independent of the location of Mn oxides, and thus solid-phase analysis of adjacent sediments should accompany Mn-oxide-doped gels in order to interpret the trends of rate constants with depth. At the shoreline of Lake Tegel, where deposition of Fe and Mn oxides is low, the highest Mn oxide reduction rates corresponded with depths most depleted in the operationally defined “reducible oxides” fraction. Increasing proportions of operationally defined “carbonate bound” and “organic and sulfide bound” Fe and Mn below this depth suggested that the highest measured rates did occur at the interface between more oxic sediments < 10 cm depth and more reduced, possibly sulfidic, sediments > 15 cm depth.

Oxidizing conditions induced by water table oscillations

In a quartz sand column with anoxic influent solution, downward percolation through unsaturated sand led to oxygen mass transfer to the dissolved phase, but no significant dissolved oxygen was acquired when the water table was high. Effluent dissolved oxygen levels, which reflect the "net" of oxygen transfer to the dissolved phase as well as consumption by microbial respiration, varied between a maximum concentration of 3.6 mg l^{-1} and minimum concentrations of < 1 mg l^{-1}. The actual dissolved oxygen delivered to the aqueous phase is unknown; the presence of oxygen-consuming processes (i.e., cellular respiration and Mn oxidation) enhances oxygen mass transfer across the air-water interface (Haberer et al. 2011).

Rates of Mn oxidation in the inoculated column increased with time and subsequent water table fluctuations, but were ultimately slower than those of pure cultures of *Pseudomonas putida* GB-1. The oxygen delivery likely played a role in this slower oxidation rate, because even under vigorous shaking, the dissolved oxygen (DO) concentration in early- to mid-logarithmic phase GB-1 cultures was nearly zero (Okazaki et al. 1997). That is, even with extremely high rates of delivery, cellular respiration was able to outpace oxygen mass transfer to the dissolved phase. Other *Pseudomonas putida* species are able to regulate gene expression based on DO concentrations (Martinez-Lavanchy et al. 2010), and their rates of aerobic biodegradation depend on DO levels (Bauer et al. 2009, Martinez-Lavanchy et al. 2010).

Oxidation is thus theoretically possible in shallow groundwater with water table fluctuations. The level of air entrapment, the groundwater flow rate, and the ambient microbial community all regulate the potential Mn oxidation rate in a sedimentary environment. Even so, maximum rates observed in the column were orders of magnitude lower than those observed in aerated groundwater treatment columns with beads coated in Mn oxides and a mixed *Gallionella* and *Leptothrix* biofilm community (Katsoyiannis and Zouboulis 2004). In an operational well field, post-extraction treatment specific to Mn and Fe removal may still be more efficient than any *in situ* oxidation process.

Field conditions necessary for *in situ* Mn and Fe oxidation

Despite the potential for water table fluctuations to induce oxidizing conditions in shallow groundwater (Chapter 5), no significant Mn or Fe accumulation was observed in aquifer sediments adjacent to a production well at Lake Tegel (Chapter 6). Solid-phase Mn and Fe, as determined by XRF, declined slightly with depth, but were generally low (< 3.3% Fe, < 80 ppm Mn). Less than 20% of the Mn accumulation was attributable to sorption, based on sorption experiments with Mn-spiked artificial groundwater. XAS-determined solid-phase speciation of Mn and Fe did show increasing amounts of phyllosilicate-bound Mn(II) and Fe(II) with depth, but evidence for a transition from metal oxides to reduced species with depth was modest at best.

Assuming that Mn oxidizing microbes were present in this sediment, which was subject to up to 7 m of annual water table change, why did no significant Mn or Fe oxidation occur in the solid phase? Ammonium, which inhibits microbial Mn oxidation in sand filters, and dissolved Fe, presumably Fe(II) which can reduce Mn oxides, were both present in the groundwater extracted from the production well 3 m from these sediments. Furthermore, other microbial respiration may dominate oxygen consumption in the capillary fringe and shallow groundwater. But the lack of significant Fe accumulation suggests that Fe(II) and dissolved oxygen do not co-occur in this groundwater, as abiotic Fe(II) oxidation by oxygen is rapid at circumneutral pH (Wehrli and Stumm 1989). Previous characterization of the redox conditions in Berlin's lake bank filtration sites found vertical redox zonation of the infiltrating groundwater (Massmann et al. 2008b). If reduced Fe and Mn travel at greater depths than dissolved oxygen is able to penetrate, no significant oxidation would be expected.

Physical flow thus affects both the introduction of dissolved oxygen and the location of the "plume" of reduced Fe and Mn. The presence of Fe and Mn oxide accumulations at other boreholes in Berlin suggests that spatial heterogeneity may make flow conditions near other production wells more ideal for *in situ* oxidation. Optimization of *in situ* oxidation, as a "natural" pre-treatment process for bank filtrate, should focus on maximum air entrapment (e.g., large, frequent water table changes), shallow depth to the reduced Fe and Mn, and relatively low concentrations of ammonium. There is a risk that Mn oxides formed in the capillary fringe at low water levels could be reduced by Fe(II) upon re-saturation with reduced groundwater, but even this step would remove Fe(II) *in situ* and thereby decrease the treatment burden of the extracted bank filtrate.

Future research in inorganic geochemistry relevant to bank filtration

As bank filtration use is expanded, many aspects of biogeochemistry remain open to further research. Organic micropollutant degradation, microbial pathogen removal, and viral inactivation remain active areas of research, especially as related to optimization of the bank filtration process (Tufenkji et al. 2002, Greskowiak et al. 2006, Massmann et al.

2006, Castro and Tufenkji 2008, Massmann et al. 2008a, Gupta et al. 2009, Toze et al. 2010). Fundamental to these aspects, as well as to inorganic geochemistry, is the transient redox status of the bank filtrate. Changing the water table elevation during pumping delivers oxygen to the subsurface (Kohfahl et al. 2009), with the potential to deliver amounts in excess of air saturation, via entrapped bubbles in the aquifer sediments. Quantification of the excess air delivered and its vertical extent in the aquifer remains site-specific (Cey et al. 2008, Klump et al. 2008, Massmann and Sültenfuß 2008); better predictions of excess air for given a water table fluctuation and frequency in terms of aquifer porosity and flow rates could enhance site managers' ability to optimize *in situ* redox conditions for target contaminant removal.

The location of reaeration along the flow path also impacts the sequestration of Mn and other trace elements released in the reducing zone. In the absence of newly generated sorbents or transition to precipitation, elements sequestered via sorption will eventually breakthrough at the production well (Appelo et al. 1999, Oren et al. 2007, Spiteri et al. 2007). The oxygen levels and the travel time along the flow path required to produce significant oxide minerals merit further study. Oxidation that occurs too close to the production well, or during mixing with deeper water in the production well, leads to well screen clogging and decreased well yield (Hässelbarth and Lüdemann 1972, van Beek 1984, van Beek et al. 2009). As rehabilitation of production wells susceptible to clogging is expensive in the long term (Dillon et al. 2006), cost-effective and sustainable management is important. This ranges from proper site selection (to avoid settings and screened intervals with potential mixing of oxic infiltrate and anoxic groundwater (van

Beek 1984, van Beek et al. 2009)), to novel solutions for well rehabilitation, such as addition of bacteriophages to degrade Fe- and Mn-oxidizing biofilms (Gino et al. 2010).

Global climate change will certainly affect the performance of bank filtration systems. As has already been observed with seasonal differences in temperature (von Gunten et al. 1991, Bourg and Bertin 2002, Massmann et al. 2008b), warmer conditions stimulate microbial activity both directly via higher temperatures and indirectly via higher organic carbon loads in surface waters. This enhanced microbial activity would extend the reducing zone further into the aquifer, and in existing bank filtration systems, this essentially decreases the travel time of the bank filtrate through areas of potential sequestration of trace elements. Higher intensity precipitation and more frequent flooding are also expected under climate change. Bank filtration systems with a sufficient travel time have performed effectively under flood conditions in the past (Eckert and Irmscher 2006), but floods could affect the redox status of soils (Borch et al. 2010). Additionally, the infiltration flow paths for microbes and viruses may be short-circuited under flood conditions (Gupta et al. 2009). Accordingly, new systems would need to allow more distance between the surface water and the production well. Further considerations of bank filtration design in light of climate change, both in drought and flood conditions, have been recently reviewed (Sprenger et al. 2010).

The simplicity of bank filtration makes it a desirable pre-treatment step for drinking water in many locations. It could furthermore offer significant benefits in the developing world, where water treatment infrastructure is minimal (Lorenzen et al. 2010). Long-term bank filtration on the Rhine River in Düsseldorf has been largely effective despite periods of low-quality surface water and a chemical “shock” load in 1986

(Schubert 2002). Due to contamination of surface waters by untreated wastewater and agricultural runoff, the organic carbon load on bank filtration systems can be much higher in the developing world than in the developed world; column studies in Addis Ababa, Ethiopia, and Mathura, India, suggest that bank filtration alone is not sufficient to produce high quality drinking water (Abiye et al. 2009, Singh et al. 2010). Nevertheless, a more efficient technical water cycle, where wastewater treatment plant effluent is combined with surface water for bank filtration or other managed aquifer recharge, as has been implemented in Berlin, Germany (Massmann et al. 2007), Orange County, California (Clark et al. 2004), and Shafdan, Israel (Oren et al. 2007), could begin to improve surface water quality in urban centers in developing countries (Jimenez and Chavez 2004). Extended organic carbon oxidation at the Israeli site has mobilized Mn from the aquifer sediments, a clear example of the complex management issues in these types of systems. Further studies on the long-term feasibility of joint water and wastewater management could have major impacts on the quality of drinking water in the developing world.

The use of bank filtration in concert with advanced wastewater management requires sufficiently advanced geochemical models. Some sites (more frequently, those used for ASR and ASTR) have more complex water-rock interactions than described here, such as fluorite (CaF_2) precipitation (Lorenzen et al. 2010) or dissolution (Gaus et al. 2002), or As release from Fe sulfides (Price and Pichler 2006, Wallis et al. 2010). Aquifers can also undergo physical changes during pumping, such as clay dispersion (Konikow et al. 2001), that affect the withdrawal rate; interrelated physical and chemical changes must be balanced effectively and efficiently to maintain high-yield bank filtration (Eusuff and Lansey 2004, Wiese and Nützmann 2009). Truly comprehensive models must incorporate these effects to optimize the desired treatment outcome and flow rate.

Wider implications

Bank filtration is far from the only setting in which water bodies undergo redox transitions. Natural infiltration in the hyporheic zone and in river- and lakebed sediments also induces a transition from oxic to reducing status. Permeable reactive barriers with Fe(0) intentionally create reducing conditions in oxic aquifers, usually for *in situ* remediation. In aquifer storage and recovery, oxic surface water is artificially introduced to reducing aquifers for storage. Oxidation of reduced groundwater is critical for aerobic biodegradation of organic contaminant plumes, and the impact of water table oscillations on the dissolved oxygen in those settings is an area of active research (Bauer et al. 2009). Surface waters, such as rivers, streams, and reservoirs, regularly undergo water level fluctuations. The interaction between those fluctuations and the adjacent groundwater could potentially create *in situ* reduction hotspots, due to infiltration of organic carbon from the surface water, as well as oxidation hotspots, due to the exposure of reduced solid-bound species to air-filled pores at low water levels. The behavior of Mn, Fe, and other trace metals in such dynamic redox conditions merits careful attention, especially when these water bodies are used for drinking water.