Chapter 6

Mn and Fe dynamics in the shallow groundwater adjacent to Lake Tegel, Berlin, Germany

Abstract

Water table oscillations due to on-off pump cycles in well fields have the potential to introduce dissolved oxygen into the shallow groundwater. As presented in Chapter 5, this amount of dissolved oxygen is sufficient to oxidize manganese (Mn), and presumably iron (Fe), in laboratory-scale experiments. In this study, we looked for evidence of Mn and Fe accumulation in shallow aquifer sediments adjacent to a bank filtration production well. However, XRF analysis of sediments showed no significant accumulation of Mn or Fe as a function of depth. The Mn sorption capacity of the deep aquifer sediments was relatively low as determined in sorption experiments with Mn-spiked artificial groundwater. Sorbed Mn concentrations under ambient conditions were estimated, on the basis of sorption experiments, to be between 7 and 16% of the total Mn concentration determined by XRF. Although XAS analysis of sediments revealed a slight increase in the relative proportions of Mn(II) and Fe(II) with depth, both elements' solid-phase speciation was dominated by clay- and primary-mineral-associated fractions, suggestive of the sediment background. The lack of evidence for *in situ* oxidation at this borehole suggests a chemical or hydrological inhibition of the oxidation process.

Introduction

In bank filtration, groundwater is extracted from a well near a river or lake. This induces infiltration from the surface water body, thereby improving the quality of water recovered and making it more consistent. Manganese (Mn) and iron (Fe) can be released into bank filtrate along its flow path to the production well to an extent that necessitates drinking water treatment after extraction (de Vet et al. 2010). In Berlin's bank filtration well fields, this involves aerated sand filtration (Massmann et al. 2007). Berlin's bank filtration well fields are also subject to well clogging, which is remediated by occasional injection of H_2O_2 pulses to remove Fe- and/or Mn-oxidizing biofilms from the well screen. Anecdotal evidence from observation boreholes suggests that Mn oxidation can also occur in the aquifer sediments adjacent to production wells. The conditions under which this occurs are unknown (C. Menz, personal communication).

Bank filtration sites with $\geq$ 1 m water table fluctuations at least every 2 days entrap sufficient air to oxidize Mn in the presence of a mature Mn-oxidizing community (Chapter 5). Bank filtrate in Switzerland was estimated to contain an excess of ~ 10% air due to entrapment of bubbles during flow with an oscillating water table (Beyerle et al. 1999). Excess air estimates in Berlin suggest that similar amounts of air entrapment occur at Lakes Tegel and Wann bank filtration sites, although significantly more air entrapment occurs at an artificial recharge basin adjacent to Lake Tegel (Massmann and Sültenfuß 2008). Modeling shows that air entrapment from water table fluctuations likely dominates dissolved oxygen delivery in bank filtrate (Kohfahl et al. 2009). Air entrapment in Berlin bank filtration sites thus affects dissolved oxygen delivery to the shallow subsurface, and could be responsible for the development of Mn oxide layers adjacent to production wells.

To search for evidence of *in situ* Mn oxidation, aquifer sediment samples were collected from an observation well borehole adjacent to a bank filtration production well at Lake Tegel, Berlin, Germany. The production well is between the lake shore and an artificial recharge pond, and its high water level fluctuates between 5 and 12 m below the ground surface. Depth-averaged sediment samples were taken in 1 m increments from 5 to 25 m below the ground surface to look for gradients in Mn and Fe concentrations and speciation that would reflect a gradient in the dissolved oxygen delivered to the shallow groundwater.

Experimental Section

Sample collection

Samples were collected from a well borehole 3 m inland of production well 18 of the Hohenzollernkanal well gallery, south of Lake Tegel, Berlin, Germany (Figure 6.1). Production well 18 is 40 m deep, screened between 20 and 37 m. The aquifer sediments at those depths are Pleistocene, porous, glaciofluvial and fluvial mainly fine- to medium-sized sands of the Saale and Weichsel glaciation. Below 40 m, a continuous organic-rich clay aquitard of the Holstein interglacial period limits the infiltration of the ambient deep groundwater (Massmann et al. 2007). As of March 2010, production well 18 had been in operation only 2 years, replacing an older well that was removed from service.

The sample borehole was drilled with a gauge driller, using ambient groundwater as drilling fluid and yielding 1 m depth-averaged samples. The samples were necessarily disturbed, and further, the drilling equipment had a rusty exterior. Upon removal from the borehole, sediments (5–25 m) were collected in sealed acid-washed plastic bags and stored on ice until they were frozen in the lab.

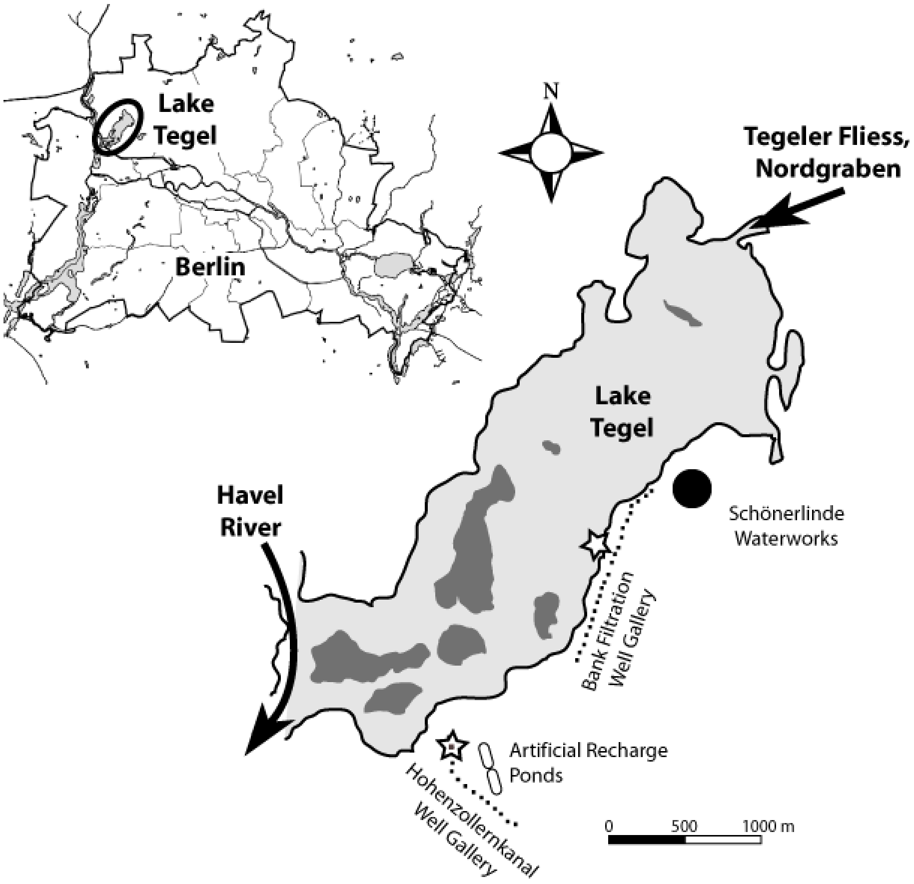

Figure 6.1. Map of sampling locations and bank filtration well galleries at Lake Tegel. Production well 18 is highlighted with a star in the Hohenzollernkanal Well Gallery. For reference, the shoreline sampling location in Chapter 4 is starred as well.

Sample analysis and characterization

Samples were freeze-dried before analysis. For XRF and XAS, samples were sieved (#25, < 707 μm) and milled for 30 s at 30 Hz with a ZrO_2 milling set (< 50 μm, Retsch MM400). XRF samples were diluted with wax and pressed into 32 mm pellets for analysis (Spectro XEPOS). Four samples (5–6 m, 8–9 m, 11–12 m, and 23–25 m) were loaded in plastic cells between Kapton tape for XAS analysis. Mn K-edge X-ray absorption near edge structure (XANES) and Fe K-edge XANES and extended X-ray absorption fine structure (EXAFS) spectra were measured at room temperature at the XAS beamline at the Angströmquelle Karlsruhe (ANKA, Karlsruhe, Germany). The Si(111) monochromator was calibrated by setting the first inflection point of the absorption edge of Mn and Fe metal foils to 6539 eV and 7112 eV, respectively. The Mn spectra were collected in fluorescence mode using a 5-element Ge solid state detector; the Fe spectra were measured in transmission mode. Spectral data processing and linear combination fitting (LCF) were performed using the software code Athena (Ravel and Newville 2005). Reference spectra for Mn included triclinic Na-birnessite, Mn(II)-reacted ferrihydrite, aqueous Mn^{2+} (100 mM $Mn(NO_3)_2$), chlorite (CCa-2, Source Clay Repository), and rhodochrosite. Reference spectra for Fe included 2-line ferrihydrite, lepidocrocite, Source Clay Repository clays illite (IMt-1) and chlorite (CCa-2), and aqueous Fe^{2+}.

Mn sorption experiments were conducted with the 23–25 m depth-averaged sample in artificial groundwater (AGW) at pH 8. Artificial groundwater was designed based on the adjacent artificial recharge water composition at Lake Tegel (Massmann et al. 2006) (Table 6.1). $MnCl_2$ concentrations (0–100 μM) were spiked in 20 ml AGW with 0.5 g sediment, with three replicates. After 24 h on an end-over-end shaker, supernatant samples were diluted with 1% HNO_3 for ICP-MS analysis (Agilent 7500cx). pH values at the end of the experiment were not significantly different from 8.0 (range 8.01–8.03).

Table 6.1. Composition of artificial groundwater for sorption experiments. Based on artificial recharge water composition at Lake Tegel (Massmann et al. 2006)

component	concentration (mM)
$CaCO_3$	2.1
NaCl	1.5
$MgCl_2$	0.4
$KHSO_4$	0.24
$NaNO_3$	0.15
HEPES	10
pH	8.0

Results and Discussion

Sediment composition and sorption capacity

Sediments were mainly sandy in appearance, with some bits of rock, shells, and black particulate organic matter interspersed. Sediments were visibly coarser with depth. A vertical gradient in sediment color was evident during drilling: light-colored sand down to 5 m below the ground surface, brown at 5–6 m depth, and fading of the brown to grey within 22 m. This corresponds with the local groundwater levels, which fluctuate between 5 and 12 m below the ground surface (Massmann and Sültenfuß 2008); the water table was approximately 6 m below the ground surface at the time of drilling. XRF data show declining values of Mn and Fe with depth, although the concentrations of both elements are relatively low (< 3.3% Fe, < 80 ppm Mn) and show heterogeneity between subsequent depths (Figure 6.2a). Plotted against each other, Mn and Fe appear to be linearly correlated (Figure 6.2b), although samples from the shallowest 4 depths (5–9 m below the ground surface) show some evidence of Fe accumulation relative to Mn. Other XRF-measured elements showed no significant trends with depth, sometimes with high heterogeneity for subsequent depths (not shown).

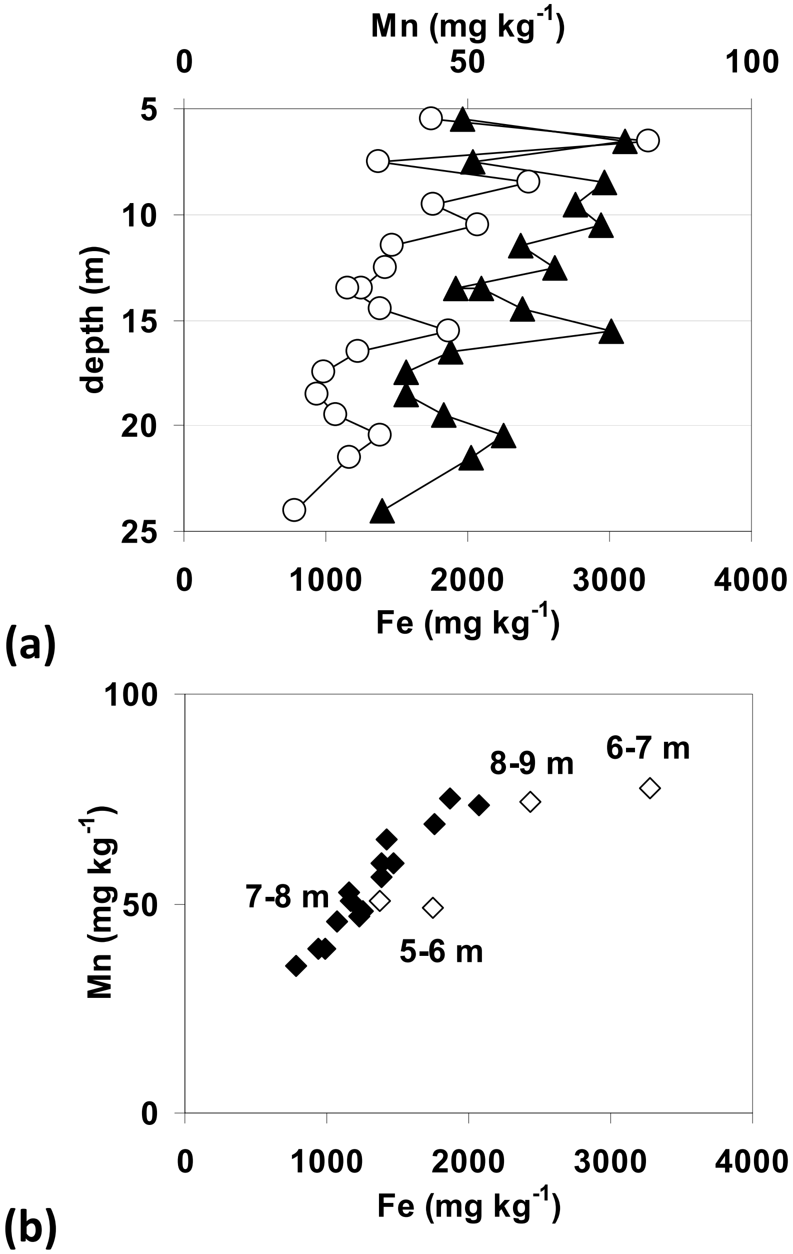

Figure 6.2. XRF concentrations of Mn (▲) and Fe (○) as a function of depth in the aquifer (a). Replicate samples at 13.5 m show the approximate variability of XRF data relative to inter-depth heterogeneity. For XRF Mn concentrations plotted against Fe concentrations (b), the top 4 m of sediments are labeled and plotted unfilled.

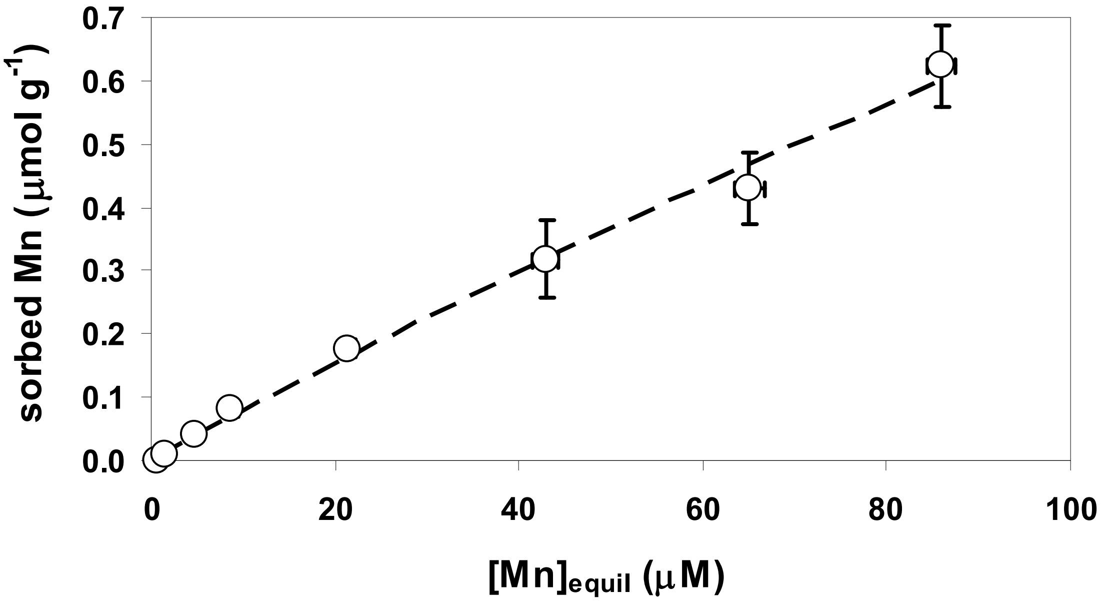

Figure 6.3. Mn sorption isotherm on aquifer sediments 23–25 m depth at pH 8. Dashed line shows the Freundlich isotherm (q_{max} = 4.6 μmol g^{-1}, K = 0.0017).

The sorption isotherm for Mn on the 23–25 m sediment showed nearly linear sorption up to 100 μM Mn in solution, with a maximum loading of 0.62 μmol Mn g^{-1} (Figure 6.3). At the average dissolved Mn concentrations in the groundwater (9 mM, Table 6.2), 0.1 μmol Mn are predicted to be adsorbed per g of aquifer sediments, or approximately 5.5 mg kg^{-1}. In comparison to XRF Mn concentrations of 35–78 mg kg^{-1}, the sorption capacity of the sediments is quite low (< 20% total Mn).

Table 6.2. Average groundwater composition in production well 18

parameter	**average value**
pH	7.3
redox potential	130 mV
electrical conductivity	750 µS cm^{-1}
DOC	5.1 mg l^{-1}
Fe^{2+}	7.2 µM
Mn^{2+}	9.1 µM
NO_3^-	18 µM
NO_2^-	3.5 µM
NH_4^+	13 µM
SO_4^{-2}	1.3 mM
total PO_4	1.6 µM
Cl^-	1.5 mM

Fe and Mn speciation

Speciation of Fe and Mn at four depths was determined with XAS. The depths included the highest groundwater level (5–6 m), the lowest groundwater level (11–12 m), an intermediate level (8–9 m), and a deep, presumably anoxic, level (23–25 m). If the water table fluctuations from pump operations indeed entrapped a gradient of dissolved oxygen in the shallow groundwater, the solid phase Fe and Mn speciation could reflect the change in sediment redox status as a function of depth.

Some significant limitations hindered this analysis. Mn concentrations were at the very low end for XAS measurements, which resulted in spectra inappropriate for EXAFS analysis. Mn XANES spectra were not very smooth, which interferes with LCF. The samples' redox status was unavoidably disturbed during the drilling process. Ambient groundwater was pumped into the borehole without concern for redox status, although the air temperatures were just above freezing (1–3°C) and samples were rapidly stored on ice in plastic bags. Although this would likely preserve reduced Mn, which is slow to oxidize (Morgan 2000), in samples, more rapid oxidation of Fe is possible. Furthermore, rust particles from the well borer likely entered the samples to some degree.

Nonetheless, Mn XANES show that almost all Mn was present in the reduced form (oxidation states II and III; Figure 6.4). There is a slight increase in the proportion of Mn(II) with depth, but none of the available reference spectra, including rhodochrosite ($MnCO_3$), provide a very good fit of this spectrum. This suggests the presence of some alternate Mn(II)-bearing phase (i.e., not Mn(II)-bearing ferrihydrite, aqueous Mn(II), chlorite, or rhodochrosite) in the aquifer.

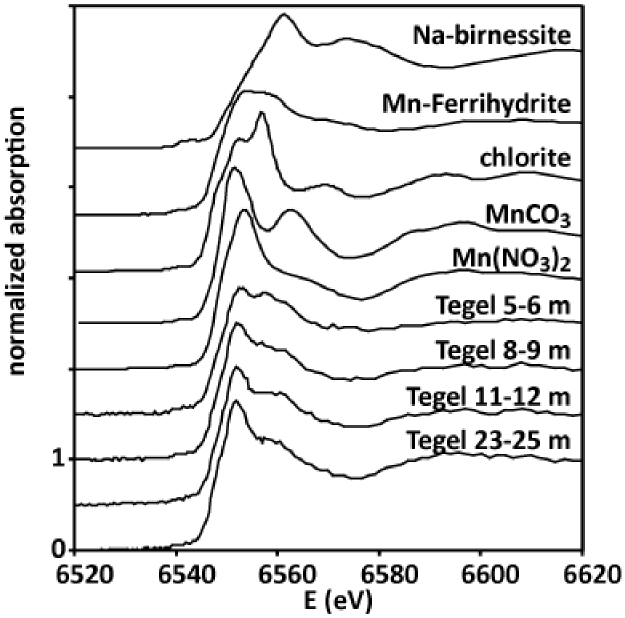

Figure 6.4. Mn K-edge XANES spectra of Lake Tegel aquifer samples from different depths compared to reference spectra of triclinic Na-birnessite, Mn^{2+}-reacted ferrihydrite (sorbed Mn likely partly oxidized to Mn(III)), aqueous Mn^{2+} (100 mM $Mn(NO_3)_2$), chlorite CCa-2 (Source Clay Repository), and rhodochrosite

Fe spectra show a slightly increasing proportion of Fe(II) with depth (Figure 6.5). Comparison to reference spectra suggests dominance of Fe(III) (hydr)oxides, like ferrihydrite and lepidocrocite (possibly from the well borer or air exposure), and Fe(II) and Fe(III) in phyllosilicates, like illite and chlorite. The presence of Fe(II) and Fe(III) in primary Fe-bearing minerals cannot be excluded.

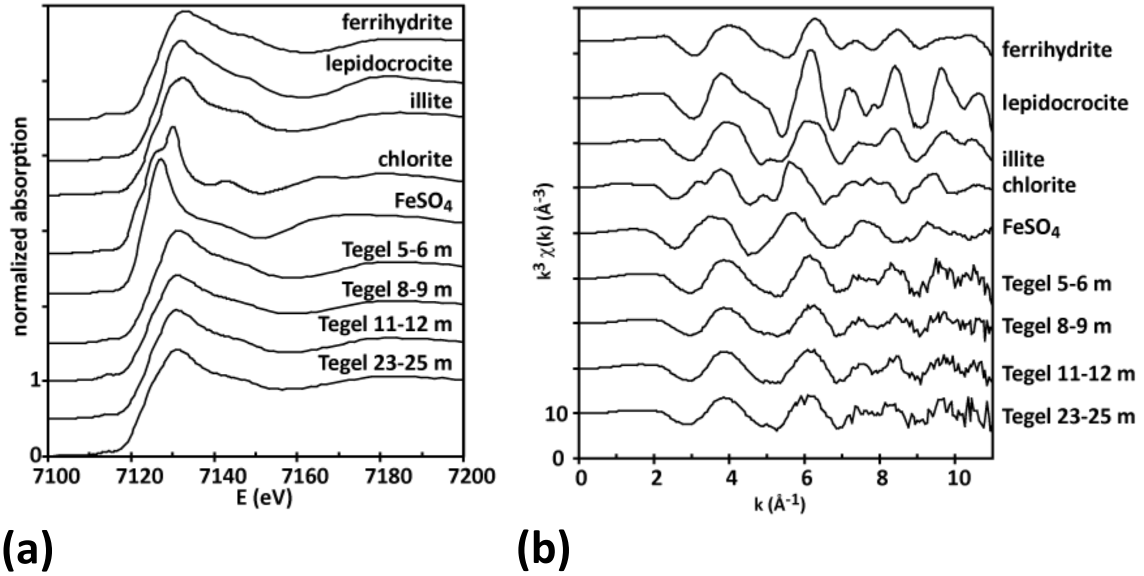

Figure 6.5. Fe K-edge XANES (a) and EXAFS (b) spectra of Lake Tegel aquifer samples from different depths compared to reference spectra of 2-line ferrihydrite, lepidocrocite, Source Clay Repository clays illite IMt-1 and chlorite CCa-2, and aqueous Fe^{2+}

The XAS data suggest much of the Fe and Mn is associated with clays, with low concentrations not indicative of significant accumulation. This suggests that these aquifer samples adjacent to Lake Tegel reflect the sediment background, rather than a significant change in solid-bound Fe and/or Mn. Both Fe and Mn bound in clays have complex redox chemistry that would have required a larger suite of standards at different redox conditions as well as better preservation of the sediment's ambient redox status, in order to analyze the speciation more precisely.

Lack of accumulation of Mn and Fe

Overall, the XRF and XAS data suggest no significant Mn or Fe accumulation in these aquifer sediments, despite favorable conditions for oxide formation upon the introduction of dissolved oxygen. Synchrotron data suggests that Fe and Mn are bound to clays, although whether that reflects sorption to a depth-dependent clay fraction or transport of Mn and Fe bound to clay colloids is unknown. Lack of significant accumulation of Fe, which rapidly oxidizes in the presence of oxygen (Wehrli and Stumm 1989), suggests that Fe and oxygen do not normally co-occur in the shallow groundwater. A nearby lake bank filtration site with similar hydrogeology has vertical redox zonation in the shallow groundwater, such that Mn^{2+}- and Fe^{2+}-containing groundwater are 12–15 m below the groundwater surface (Massmann et al. 2008b). If the groundwater is similarly zonated at the Lake Tegel site, the lack of accumulation could indicate that oxygen does not reach the depths of Mn^{2+}- and Fe^{2+}-containing groundwater.

Mn oxidation in particular depends on microbes at circumneutral pH (Morgan 2000), and is sensitive to the presence of ions in the groundwater that either inhibit or reverse oxidation. Fe(II), for example, reduces Mn oxides with a Fe(II, III) oxide by-product (Postma and Appelo 2000, Villinski et al. 2001). If all of the Mn in the local groundwater (9 μM, Table 6.2) were oxidized in the sediments, the local Fe concentration (7 μM, presumably Fe(II)) could reduce up to 3.5 μM, or 39% of the Mn. Ammonium (13 μM) inhibits Mn oxidation and must be fully removed before Mn oxidation can commence in sand filters (Frischherz et al. 1985, de Vet et al. 2010), although 4 mM

NH_4^+ in the MSTG minimal medium did not inhibit Mn oxidation in Chapter 5. Local groundwater concentrations from the production well reflect both temporal integration of contact with aquifer solids and spatial averaging over the groundwater volume accessed by well pumping, so it is difficult to hypothesize about the actual Mn, Fe(II), or ammonium concentrations at relevant depths in the aquifer. Although not assessed in this study, the prevalence of Mn oxidizing capacity is assumed to be ubiquitous (Francis and Tebo 2001) in this aquifer. The amount of time needed for the development of an active Mn-oxidizing microbial consortium is unknown. In sand filters this is normally 8–20 weeks (Frischherz et al. 1985, Mouchet 1992); production well 18 had been in operation for 2 years as of the sampling date.

The presence of Mn accumulations in shallow sediments in some locations around Berlin (C. Menz, personal communication) suggests that the conditions for Mn and Fe oxidation exist in some areas of the aquifer. The groundwater extracted from production well 18 comes from three sources: bank filtrate from Lake Tegel (~ 210 m away), recharged water from an artificial recharge pond (~ 170 m away), and the ambient groundwater. The hydrological balance between these sources strongly influences the entrapped air content in the groundwater (Massmann and Sültenfuß 2008) and the depth and concentration of dissolved Mn and Fe (Massmann et al. 2008b). Artificial recharge basins, for example, entrap large amounts of air, but the dissolved oxygen is consumed in the shallow sediments of the basins. Adjacent to wells, less air is entrapped from on-off cycles than from recharge basins, but more dissolved oxygen is transported deeper in the aquifer (Greskowiak et al. 2005, Massmann and Sültenfuß 2008). Future study of *in situ* Mn oxidation in this area should focus on more ideal hydrologic setting and groundwater composition: frequent water table fluctuation of high amplitude, low concentrations of Fe^{2+} and ammonium, and a shallow depth to the Mn-containing groundwater.

Acknowledgements

Christian Menz organized the well drilling in Berlin and provided the average groundwater composition at the production well. Andreas Voegelin performed all XAS measurements and data analysis. The Angströmquelle Karlsruhe (ANKA, Karlsruhe, Germany) provided beamtime at the XAS beamline, and Stefan Mangold assisted during XAS data collection.