Chapter 2

Inorganic Geochemistry and Redox Dynamics in Bank Filtration Settings

Abstract

Bank filtration induces flow of surface water through a hydraulically connected aquifer by excess pumping from a production well in the aquifer. This chapter presents the four main geochemical processes relevant for inorganic geochemistry, with a focus on iron (Fe) and manganese (Mn), during bank filtration: reduction near the bank, oxidation near the production well, carbonate dissolution, and sorption to aquifer materials. Physical and transport processes affect these geochemical processes and influence the redox state of the infiltrate. The presence of Fe and Mn in bank infiltrate is directly related to its redox status and can necessitate drinking water treatment after extraction. Long-term, *in situ* sequestration of Fe and Mn requires precipitation of oxide or carbonate solids, since a sorption front can break through at the production well.

Introduction

Anthropogenic pressure on existing water resources management is growing due to population growth and the expansion of irrigated agriculture and may be exacerbated by climate change. The frequency and intensity of both drought and precipitation are anticipated to increase as a result of climate change; glaciers are already retreating. In the western U.S., observations over the past 50 years include more winter precipitation falling as rain instead of snow, earlier snow melt, and associated changes in river flow, as well as drier summer conditions due to regional warming (Barnett et al. 2008). Major Asian river basins that depend on glacial melt water are also susceptible to altered, and eventually decreased, flows as glaciers retreat and disappear (Immerzeel et al. 2010). Episodic groundwater recharge may also be significantly impacted by changes in precipitation events (Eckhardt and Ulbrich 2003, Ng et al. 2010). Population growth continues in areas of limited water resources (NRC 2008, Vorosmarty et al. 2010), and overdraft of groundwater, both seasonal and year-round, is a more and more common problem (Wada et al. 2010). In some coastal areas, existing use of groundwater resources has had to be curtailed or modified due to saltwater intrusion (Jha and Peiffer 2005, Brown and Misut 2010). Expansion of irrigated agriculture to feed burgeoning populations will further stress limited water resources; northern China, for example, contains 65% of the country's arable land, but only 18% of its water resources (Piao et al. 2010).

As a result of these pressures, water shortage is forecast for 36% of the global population by 2050 under a climate change and population growth scenario (Rockström et al. 2009). Moreover, 80% of the world's population would currently be exposed to high levels of threat to water security if not for massive investments in water infrastructure in developed countries (Vorosmarty et al. 2010). The lower Colorado River basin may already be in overdraft, as inflows have decreased to Lakes Powell and Mead while outflows from Glen Canyon and Hoover Dams continue at legally mandated rates (Barnett and Pierce 2008). Indeed, surface water storage may become impractical in arid and semi-arid areas due to lower streamflows and excessive evaporation (Bouwer 2002, Brikowski 2008). In addition, it is estimated that 1 billion people still lack access to safe drinking water, and in the developing world, the cost of building and maintaining conventional water and wastewater treatment can be prohibitive (Buros and Pyne 1994). Clearly, demand exists for more water management in the coming decades, but existing large-scale dam and irrigation projects may be unable to provide adequate water resources under the increasing anthropogenic pressure (Gleick 2002). Therefore, alternate water management schemes are necessary to take increasing advantage of water reuse and to reduce the capital- and energy-intensity of water treatment systems.

Many of these alternate management schemes fall under heading of “managed aquifer recharge” (MAR) or “managed underground storage”. Forms of MAR involve engineered delivery of water into the subsurface, which is later recovered after some storage and passage through aquifer material (Figure 2.1). Delivery modes can range from direct injection to passive spreading ponds, and the quality of the water delivered to the recharge systems can range from ambient surface water to wastewater treatment plant effluent (Bouwer 2002). Aquifer storage and recovery (ASR) and aquifer storage transfer and recovery (ASTR) inject water directly into an aquifer for storage. In ASR, essentially the same parcel is later recovered from the injection well itself. In ASTR, water is recovered from a down-gradient well and can, at early recovery times, include a substantial component of the native groundwater. Infiltration ponds are usually constructed off-stream where surface water is diverted and allowed to infiltrate (generally through an unsaturated zone) to an underlying unconfined aquifer. In soil-aquifer treatment (SAT), treated sewage effluent, or reclaimed water, is infiltrated intermittently through infiltration ponds to facilitate nutrient and pathogen removal in passage through the unsaturated zone for recovery by wells after residence in the aquifer. Bank filtration refers to extraction of groundwater from a well or caisson near or under a river or lake, which induces infiltration from the surface water body, thereby improving and making more consistent the quality of water recovered (NRC 2008).

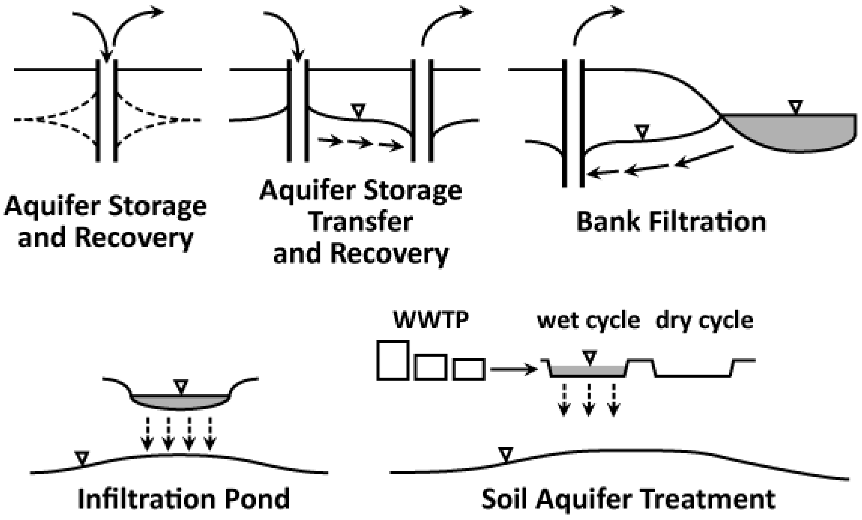

Figure 2.1. Schematics of various types of managed aquifer recharge. Adapted from Dillon (2005). WWTP denotes a wastewater treatment plant.

In contrast with some MAR schemes, bank filtration has a long history in Europe, with some sites in use for more than 130 years in Germany (Ziegler 2001, Eckert and Irmscher 2006). Bank filtration relies upon natural processes to remove nutrients, organic carbon, and microbes, especially pathogens, present in the source water (Schwarzenbach et al. 1983). Recent research in bank filtration settings has focused extensively on understanding the processes behind effective pathogen removal (Castro and Tufenkji 2008, Metge et al. 2010, Toze et al. 2010) and on quantifying the removal of persistent organic micropollutants (Massmann et al. 2008a, Hoppe-Jones et al. 2010), both of which are critical to determine the post-extraction treatment required for bank filtrate to meet water quality standards. The effects of inorganic geochemical processes along the infiltration flow path on the quality of extracted bank filtrate have received much less attention, despite the observed exceedance of WHO drinking water guidelines for iron (Fe) of 0.3 mg l^{-1} or 5 μM and manganese (Mn) of 0.1 mg l^{-1} or 2 μM at various well fields in Canada (Thomas et al. 1994), Germany (Hässelbarth and Lüdemann 1972), and the Netherlands (de Vet et al. 2010). Although the treatment to remove Fe and Mn is relatively simple in practice (often aeration and sand filtration (de Vet et al. 2010)), the presence of these elements can lead to well screen clogging (van Beek 1984, van Beek et al. 2009) and can also indicate conditions where trace metals associated with Fe and Mn oxide solids are released along the flow path (von Gunten and Kull 1986). Thus, *in situ* sequestration of Fe and Mn could potentially decrease both the risk of breakthrough of Fe, Mn, and any associated trace metals at the extraction well and the need for post-extraction treatment. If the sequestration occurs at some distance from the well screen, this could also decrease the likelihood of well clogging.

Both reductive dissolution of Fe and Mn oxides and subsequent sequestration of dissolved Fe and Mn in bank filtration are dependent upon the spatial and temporal variation of the redox state along the flow path. Furthermore, transient redox conditions can be significant for inorganic geochemistry and pathogen and organic micropollutant removal alike (von Gunten et al. 1991, Castro and Tufenkji 2008, Massmann et al. 2008b). This review presents the fundamental geochemical processes of bank filtration systems, with a focus on Fe and Mn, in light of relevant physical and transport processes.

Geochemistry of Bank Filtration

The evolution of groundwater along the infiltration flow path in bank filtration involves four key geochemical processes that can affect the efficiency of the system as well as the quality of the extracted water: reduction near the bank, oxidation near the production well, dissolution of carbonate minerals in the aquifer, and sorption-desorption to the aquifer material (Figure 2.2). These processes are also relevant in other MAR schemes, but specific aspects of other forms of MAR are not considered here.

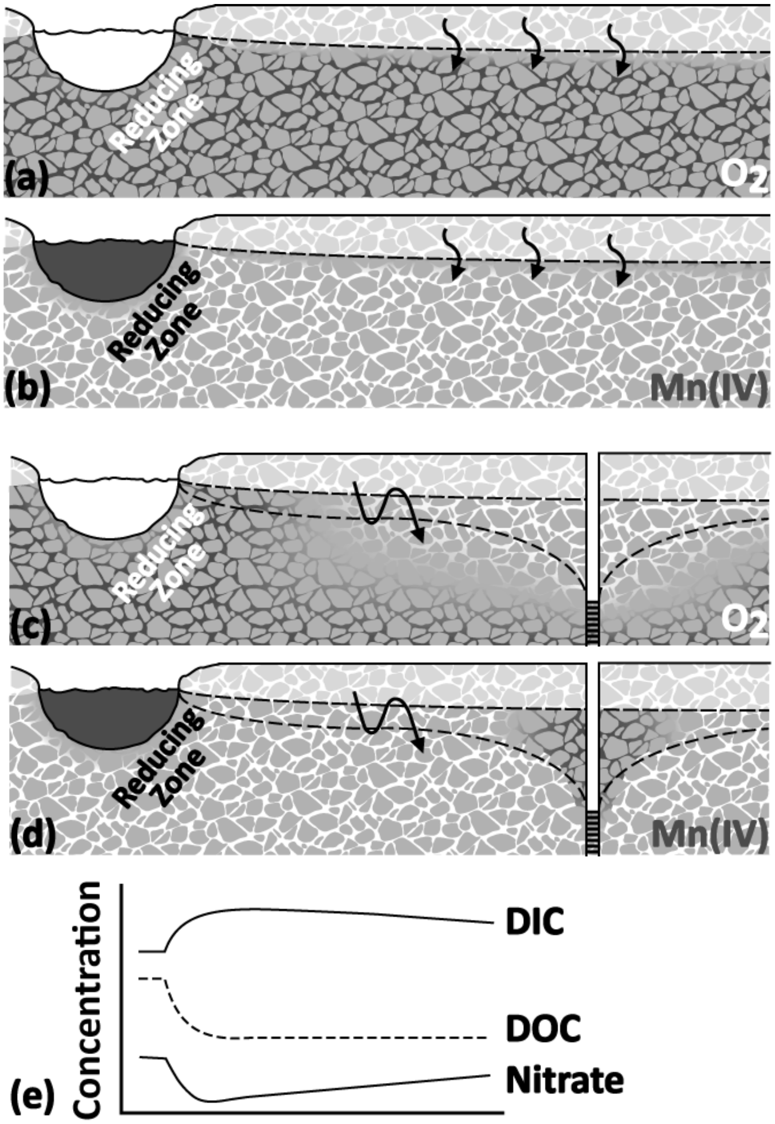

Figure 2.2. Profile of geochemical changes along a natural (a,b) and bank filtration (c,d) flow path. Dissolved oxygen levels are indicated by white (a,c), and oxidized Mn by dark grey (b,d). Arrows indicate the dominant mechanisms of reaeration: diffusion and rain infiltration under natural conditions and water table oscillations during bank filtration. The relative concentration profiles of dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and nitrate in bank filtration are shown in (e) after Bourg and Bertin (1993).

Bank filtration settings generally have different flow conditions than natural riverbank settings. A natural riverbank may be gaining or losing, relative to the adjacent aquifer, but bank filtration induces losing conditions. Furthermore, a bank filtration well's cone of depression draws down the water table, sometimes as far as to the bank itself (Massmann and Sültenfuß 2008), and on-off cycles of the production well cause oscillations of the water table (Figure 2.2), which affects oxygen delivery to the infiltrate (Kohfahl et al. 2009). Bank filtration wells may additionally induce native groundwater, which would not normally interact with surface water, to mix with infiltrate in or near the production well. This can help dilute and buffer concentrations in the infiltrate (Schubert 2002), or it can lead to undesirable geochemical processes such as Fe or Mn precipitation in production well screens (van Beek et al. 2009).

Fe and Mn are used to illustrate the geochemical processes below. Briefly, Mn has three common oxidation states in the environment (+II, +III, and +IV), and Fe has two (+II and +III) (Figure 2.3). Fe(II) and Mn(II) are soluble at low-to-neutral pH, and precipitate as $Fe(OH)_2$ (s) and $Mn(OH)_2$ (s), respectively, at very alkaline pH values (e.g., higher than pH 9 in Figure 2.3). Depending on the carbonate concentrations, which can be elevated in the subsurface, Fe(II) and Mn(II) can precipitate as siderite ($FeCO_3$) and rhodochrosite ($MnCO_3$). Mn(III) and Mn(IV) are largely insoluble, found most frequently in Mn oxides and oxyhydroxides such as birnessite ($K(Mn^{3+},Mn^{4+})_2O_4 \cdot 1.5H_2O$), pyrolusite ($MnO_2$), hausmannite ($Mn_3O_4$), and manganite (MnOOH) (Post 1999). Fe(III) is also largely found in insoluble oxides and oxyhydroxides, which are stable under more reducing conditions than those of Mn(III/IV) (Figure 2.3). Reductive dissolution of Fe and Mn oxides is largely microbially mediated (Lovley 1991, Lloyd 2003), and oxidative precipitation of Fe(II) and Mn(II) can be as well (Corstjens et al. 1992, Tebo et al. 2004). Although kinetics of abiotic Fe(II) oxidation by oxygen are relatively rapid at circumneutral pH, Mn oxidation is slow below pH 9 (Morgan 2005), with abiotic Mn oxidation orders of magnitude slower than microbially Mn oxidation (Hastings and Emerson 1986, Davies and Morgan 1989, Luther 2005). Recent studies of microbially-mediated Mn oxidation have suggested that the majority of naturally-occurring environmental Mn oxides are derived either from direct biogenic Mn(II) oxidation or from the subsequent alteration of biogenic oxides (Tebo et al. 2004).

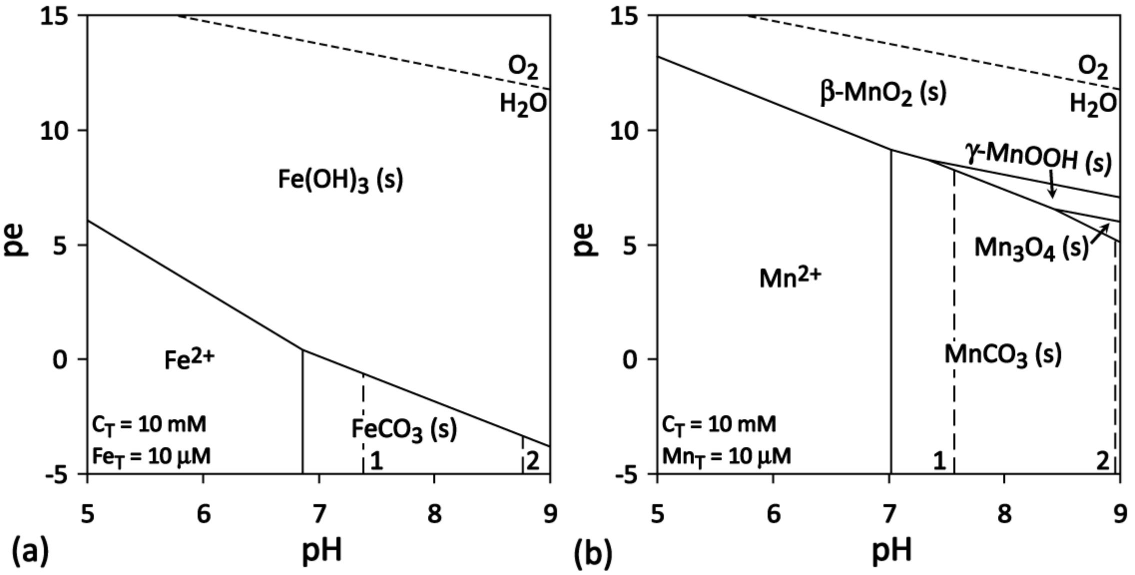

Figure 2.3. pe-pH predominance plot for (a) Fe (total = 10 μM) and (b) Mn (total = 10 μM) under typical pH and redox conditions for groundwater (C_T = 10 mM). Dashed vertical lines show the (a) Fe^{2+}/ $FeCO_3$ (s) and (b) Mn^{2+}/ $MnCO_3$ (s) equilibria for (1) C_T = 5 mM, $Mn_T = Fe_T$ = 5 μM, and (2) C_T = 1 mM, $Mn_T = Fe_T$ = 1 μM. Concentration changes slightly expand the γ-MnOOH (s) and Mn_3O_4 (s) predominance areas to lower pe and pH (not shown).

Reduction near the bank

Reducing conditions near the bank have been documented in many field sites (Jacobs et al. 1988, Bourg and Bertin 1993, Thomas et al. 1994, Massmann et al. 2008b). The influx of organic carbon from the overlying body of water into shallow sediments drives sufficient microbial activity to exhaust the supply of oxygen and often nitrate, leading to the reductive dissolution of Mn and Fe oxides (Berner 1980). Seasonal variation in the organic carbon load to the sediments correlates with the extent of reduction in the groundwater. Higher surface water temperatures in the summer lead to increased algal and phytoplankton growth, which yield higher summer loads of dissolved organic carbon. Secondary to these higher loads are increases in microbial respiration rate in the shallow sediments due to higher summer temperatures; this temperature signal is, however, damped as the infiltrate travels along the flow path (Greskowiak et al. 2006). These seasonal effects lead to a greater extent of reducing conditions as compared to the winter (von Gunten and Kull 1986, von Gunten et al. 1991, Bourg and Richard-Raymond 1994, Hoffmann and Gunkel 2011a). Solid organic carbon in the aquifer sediments can additionally promote reduction of oxygen, nitrate, and Mn oxides further along the flow path (Kedziorek et al. 2008).

On one hand, bank filtration is effective precisely because much of the organic carbon from the surface water is oxidized in the sediments and removed from the bank filtrate. At Lake Tegel in Berlin, bank filtration eliminates 20–45% of the dissolved organic carbon present in the surface water (Ziegler 2001, Hoffmann and Gunkel 2011a). Included in the dissolved organic carbon load are trace organic pollutants that persist through upstream wastewater treatment. Removal of any of these trace compounds in bank filtration is an added benefit. On the other hand, some trace organic compounds are only minimally removed under reducing conditions. Organic micropollutant removal at bank filtration sites has been studied extensively elsewhere (Schwarzenbach et al. 1983, Massmann et al. 2006, Massmann et al. 2008a, Hoppe-Jones et al. 2010).

The increase of the biomass of microbes that actively oxidize organic carbon can negatively impact the hydrologic properties of a bank filtration system. Microbial overgrowth leads to a clogged layer, especially in settings that are relatively stagnant compared to riverbanks. The development of a clogged layer at the bottom of an artificial recharge pond in Berlin caused a decrease in infiltration rate of one order of magnitude, at which point the layer was mechanically removed (Greskowiak et al. 2005). In a more natural lake bank filtration setting, the clogging layer cannot be removed. At Lake Tegel in Berlin, long-term pore water velocities were the same order of magnitude as the minimum at the above artificial recharge pond (Hoffmann and Gunkel 2011b). A significant portion of the pore volume of the shallow sediments was filled with algae, which occurred at concentrations nearly 1000× that in the overlying lake water (Gunkel and Hoffmann 2005). Nevertheless, transport through the clogged sands at the lake margins accounts for the majority of the bank filtrate in this site, so this issue is not likely to be prohibitive.

The other half of the redox reactions is also significant. Coupled to the oxidation of organic carbon, microbial reduction of nitrate in bank filtration systems is a distinct asset, whereas reduction of Mn and Fe oxides can be problematic. Nitrate reduction to N_2 (the most common end product) decreases the nutrient load in the infiltrate (Doussan et al. 1997, Doussan et al. 1998). Mn- and Fe-oxide reduction result instead from interactions between microbes and the native sediments at the site (Lovley 1991, Lloyd 2003). Significant overlap in enzymatic activities exists within microbial populations such that microbes able to reduce Mn oxides are often also capable of Fe oxide reduction (Beliaev and Saffarini 1998), and those rates of reduction are quite comparable (Blakeney et al. 2000, Ruebush et al. 2006). Mineralogy plays a key role in both the reactivity (Burdige et al. 1992, Ruebush et al. 2006) and the sorption capacity (Post 1999) of Fe and Mn oxides; more crystalline solids are less reactive and have lower sorption capacities.

When solid-phase oxides in the sediments are reductively dissolved, Fe and Mn are released to sediment porewater. High levels of dissolved Fe and Mn in bank filtrate can be problematic in and of themselves (Thomas et al. 1994, Petrunic et al. 2005), but both Mn and Fe oxides are major sinks for trace metals (Lovley 1991), and sorbed metals are released to solution during their reduction (Davranche and Bollinger 2000). This was observed for Cd, Cr, Cu, Pb, U, and Zn, as well as phosphate, at the Glatt River site (von Gunten and Kull 1986, Jacobs et al. 1988, von Gunten et al. 1991, Lienert et al. 1994). Subsequent reduction in the P concentration in sewage effluent, as required by regulations, resulted in lower levels of eutrophication in the surface water of the Glatt, effectively decreasing the organic carbon load in both the river and the bank filtrate. The decreased organic carbon load no longer supported extensive Fe- and Mn-oxide reduction, and dissolved metal concentrations were no longer elevated (Lienert et al. 1994), which illustrates the direct and indirect impacts of the reductive dissolution of Fe and Mn oxides on the quality of bank filtrate.

Oxidation near the production well

Along the flow path from the reducing zone near the bank to the production well, air reenters the water and can restore oxic conditions in the shallow infiltrate. Three main pathways for oxygen entry to the shallow groundwater are often considered: diffusive flux from the overlying unsaturated zone, vertical infiltration of oxic rain water, and gas entrapment due to water table oscillations (i.e., induced by intermittent production-well use). Modeling at Lake Wann (Berlin, Germany) clearly indicated that the dominant reaeration pathway was gas entrapment due to water table oscillations, once oscillations were greater than 0.5 m (Kohfahl et al. 2009). Laboratory studies predict dissolved gas saturation in excess of air equilibrium when gas bubbles are entrapped and collapse under sufficient water pressure; subsequent water table oscillations induce downward propagation of this “excess air” (Williams and Oostrom 2000). Excess air has been observed in the shallow groundwater of Berlin’s bank filtration sites (Massmann and Sültenfuß 2008), in support of the laboratory and model results. The generalized dissolved oxygen profile for bank filtration sites in Figure 2.2c reflects the reaeration of bank filtrate as the production well is turned on and off, especially in the vicinity of the cone of depression. In the winter, lateral infiltration of oxic surface water through the banks is an additional reaeration pathway as the extent of the near-bank reducing zone is limited by lower organic carbon loads and lower microbial respiration rates and dissolved oxygen solubility is higher (von Gunten et al. 1991, Massmann et al. 2008b). Thus, reaeration of the infiltrate is heavily influenced by the production well pump operation, seasonal nutrient loads, and temperature.

The oxic zone near to the production well has significant implications. Dissolved Mn and Fe from the reducing zone may precipitate as oxides in the presence of oxygen. In Figure 2.2, the spatial extent of Fe oxidation would be expected to align more closely with the oxygen profile (Figure 2.2c) rather than the Mn profile (Figure 2.2d) due to the rapid oxidation kinetics of Fe(II) (Luther 2005) and its potential (microbially-mediated) oxidation by nitrate (Senn and Hemond 2002). Mn oxidation only occurs in the presence of oxygen (Boogerd and de Vrind 1987, Morgan 2005), and can be assumed to be microbially mediated based upon the relative rates of abiotic and microbial oxidation (Morgan 2000). Despite its slow oxidation kinetics, dissolved Mn at the Lot River (France) displayed an inverse trend with dissolved oxygen in the wells along the flow path (Bourg and Bertin 1993, Bourg and Bertin 2002). However, breakthrough of elevated, dissolved Mn at an oxic production well could occur either because of slow oxidation kinetics or a nearby reduction hotspot (Bourg and Richard-Raymond 1994). Attempts to use E_h-based measurements or thermodynamic calculations to predict locations susceptible to elevated Mn have been very limited in their success (Kedziorek and Bourg 2009).

Similar processes can influence Fe, Mn, and other trace metals; for oxidative processes, Mn may be more significant than Fe either because Mn(III/IV) oxides can directly oxidize reduced species such as As(III) (Manning et al. 2002) or because metals such as Co(II) and Cr(III) can be indirectly oxidized by Mn(II)-oxidizing microbes (Murray et al. 2007). Field studies of streambed sediments downstream of acid mine drainage showed Co, Ni, and Zn sequestration concomitant with Mn and Fe oxidation at circumneutral pH, rather than with upstream Fe oxidation at more acidic pH (Gandy et al. 2007). The Glatt River bank filtration site (Switzerland) experienced seasonal changes in dissolved oxygen (due to surface water organic carbon loads discussed above), which affected the stability of Fe and Mn oxides. Reduction of Fe and Mn corresponded with seasonal release of trace metals, whereas winter Mn oxide formation in observation wells corresponded with seasonal sequestration of trace metals (von Gunten and Kull 1986).

The location and extent of reaeration can significantly affect the water quality at production wells and their flow rates as a result of clogging. In one site at the Seine River (France), a thick clayey sand layer inhibited the reaeration of the bank filtrate, and the prolonged reducing conditions generated elevated ammonium concentrations in the production well (Doussan et al. 1998). Dutch well fields often clog due to well-screen mixing of mildly oxic shallow groundwater and anoxic deep groundwater with elevated dissolved iron (van Beek et al. 2009). Iron oxidation is not generally observed far from the production wells in these well fields, which suggests that the infiltrate is not as readily reaerated along the flow path as other sites, given the fast kinetics (Luther 2005) of iron oxide precipitation. Many wells across Germany also clog with microbial Fe and Mn oxide encrustations, which require regular removal to maintain well yield (Hässelbarth and Lüdemann 1972). Bank filtration adjacent to polder settings in both Germany (Massmann et al. 2004) and the Netherlands (de Vet et al. 2010) is susceptible to elevated concentrations of sulfide, ammonium, and methane in the infiltrate, which tends to require post-extraction treatment for drinking water purposes. As polders are typically clay and peat soils reclaimed via extensive groundwater pumping and/or levees, their low hydraulic conductivity, long residence times, and sustained anoxic conditions are unsurprising (Massmann et al. 2004).

Dissolution of carbonate minerals in the aquifer

Disequilibrium between the bank filtrate and the native aquifer can lead to mineral dissolution and/or precipitation during the water's passage. Other than redox-sensitive minerals as described above, carbonate minerals (e.g., $CaCO_3$, $MgCO_3$) are most susceptible to dissolution during bank filtration. Silicate mineral dissolution tends to be less extensive than carbonate mineral dissolution (Bourg and Bertin 1993, Bourg and Richard-Raymond 1994, NRC 2008). Sulfide mineral dissolution is often considered in deep-well ASR and ASTR (Herczeg et al. 2004), but significant sulfide mineral abundances or dissolved sulfide concentrations are atypical in the shallow alluvial aquifers targeted for bank filtration. Polder settings are an exception, as they can result in anoxic groundwater with enough sulfide to precipitate sulfide minerals (Massmann et al. 2003).

Infiltrate with lower alkalinity and/or pH than the ambient groundwater has been observed to promote calcite ($CaCO_3$) dissolution in many field sites (von Gunten et al. 1991, Bourg and Bertin 1993, van Breukelen et al. 1998, Petkewich et al. 2004, Greskowiak et al. 2005) and some laboratory studies (Rinck-Pfeiffer et al. 2000, Patterson et al. 2010). Even if the infiltrate is chemically similar to the ambient groundwater, CO_2 and H^+ generated by oxidation of organic carbon in the bank can push the infiltrate to disequilibrium with the local aquifer (Bourg and Richard-Raymond 1994, van Breukelen et al. 1998, Rinck-Pfeiffer et al. 2000). Since only low levels of trace elements are typically affiliated with calcite (Morel and Hering 1993), its dissolution has different implications than the dissolution of Fe or Mn oxides. Increases in dissolved Ca and Mg from carbonate dissolution contribute to water hardness, but changes in hardness have been negligible in field and lab studies (Bourg and Bertin 1993, Johnson et al. 1999, Patterson et al. 2010). In one column study, calcite dissolution contributed to a locally higher hydraulic conductivity (Rinck-Pfeiffer et al. 2000). There is some concern that overly aggressive water could dissolve enough calcite grains so as to destabilize the soil, especially with reverse-osmosis-treated water in SAT sites (Johnson et al. 1999), but it is unlikely that natural surface water would threaten an aquifer's structural stability during bank filtration.

Past the reducing zone near the bank, reprecipitation of calcite can sometimes be anticipated based upon geochemical transport models (van Breukelen et al. 1998, Petkewich et al. 2004) and laboratory studies (Rinck-Pfeiffer et al. 2000). Many field studies do not explicitly consider reprecipitation, but if enough calcite has been dissolved, significant amounts of reprecipitated calcite could clog the pores of the aquifer, as has been observed in column studies (Rinck-Pfeiffer et al. 2000). Field-scale geochemical transport models nevertheless suggest that the reprecipitated quantities of calcite should not affect the aquifer's porosity (van Breukelen et al. 1998, Petkewich et al. 2004).

Although carbonates are not major sinks for trace elements, in locations with sufficiently high alkalinity, carbonate minerals can control dissolved Fe, Mn, and other trace cation concentrations (Tessier et al. 1979). The carbonate solids of Fe (siderite) and Mn (rhodochrosite) are more soluble than those with most other trace metals. The potential control on dissolved trace metal concentrations by carbonate precipitation is illustrated in Figure 2.4 (in which equilibrium with calcite is assumed). Besides metal-carbonates, some trace metals can form even less soluble mixed hydroxycarbonates or co-precipitate in calcite (Rimstidt et al. 1998), so the concentrations in Figure 2.4 can be considered an upper bound of the solid-phase-controlled equilibrium concentrations expected for the given conditions. One caveat to this approach is that the kinetics of precipitation could be slow, as suspensions of bentonite precipitation seeds, supersaturated in calcite and rhodochrosite or siderite, took more than 100 d to reach steady state (Jensen et al. 2002).

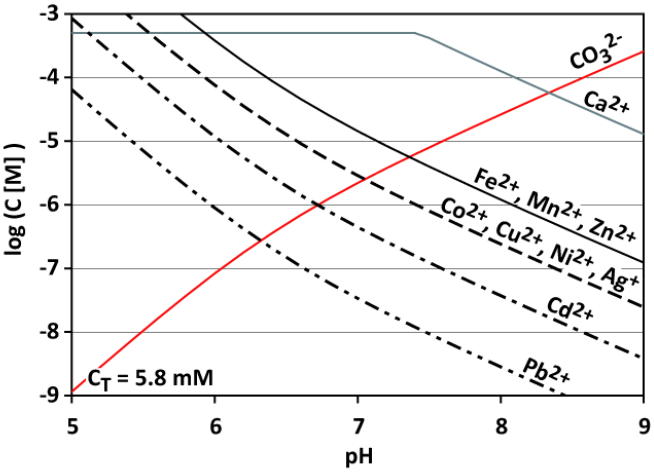

Figure 2.4. Soluble metal concentrations in equilibrium with calcite and metal carbonates (C_T = 5.8 mM; Ca_T = 0.5 mM, the average value for North American fresh water (Morel and Hering 1993)). Solubility products (in the form MCO_3 except Ag_2CO_3) taken from the MINTEQa2 database (2006). For simplicity, concentrations have been plotted with one line for each cluster of solubility products labeled on the figure (log K_{sp} within 0.5 units).

Multiple field sites have significant fractions of carbonate-bound Mn and Fe. In a polder setting in eastern Germany, dissolved Mn in groundwater was controlled by a combination of Mn and Ca carbonates (Massmann et al. 2004). Similarly, in an *in situ* groundwater treatment plant in Switzerland, short residence time in an aerated aquifer with high calcite abundance precluded the formation of Mn oxides. Dissolved Mn down-gradient of aeration wells was controlled by Mn- and Ca-carbonates with no evidence of Mn oxide accumulation (Mettler et al. 2001). At the same site, Fe oxides were associated with calcite, suggesting that Fe(II)-calcite interaction led to preferential oxidation sites during aeration (Mettler et al. 2001). Vernal calcite dissolution due to microbial respiration in the Glatt riverbank released significant Mn and Fe, suggesting both were carbonate-bound (von Gunten et al. 1994). Trace cations have also been released during calcite dissolution, e.g., Zn, Co, Cd, Ni, and Pb in batch incubations of aquifer sediments (Descourvières et al. 2009), and sequestered via carbonate preciptitation, e.g., Cd at the Glatt river site (von Gunten et al. 1991).

Sorption in the aquifer

Sorption and ion exchange also occur because of disequilibrium between the bank filtrate and the native aquifer. Surface-associated ions of the aquifer material desorb, while ions from the bank filtrate adsorb, during infiltration. Significant desorption from contaminated aquifer sediments would render the bank filtrate unusable without substantial post-treatment, and therefore such sites are avoided for bank filtration. In bank filtration settings, major ions dominate any ion exchange process, and as such, ion exchange rarely affects the quality of the bank filtrate. At one ASR site, exchange of carbonate for chloride in sediments did increase the chloride concentration beyond drinking water standards, and exchange of sodium in aquifer clays may have caused clay expansion and subsequent decreased permeability (Mirecki et al. 1998, Parkhurst and Petkewich 2002).

In contrast, sorption is the main retardation process for dissolved components during infiltration, especially for trace elements released to the bank filtrate in the reducing zone. Net sorption of dissolved components can enable the aquifer sediments to “buffer” the composition of the bank filtrate (Bourg and Darmendrail 1992). Trace cations such as Cd and Zn were released in the reducing zone, then sequestered via sorption at sites in Switzerland and France (von Gunten et al. 1991, Bourg and Darmendrail 1992, Bourg and Bertin 1993). Copper, often bound to organic matter, was not as readily adsorbed as Cd and Zn (von Gunten et al. 1991). Similarly, ammonium generated under prolonged reducing conditions at the Seine River (France) only penetrated the first 10–20 m of aquifer sediments after twenty years of passage, due to sorption (Doussan et al. 1998).

Sorption depends upon the surface area of the sorbent and the affinity of the dissolved species for the sorbent surface sites. Trace element sorption on Al, Fe(III), and Mn(III/IV) oxides has been described extensively in the literature (Gadde and Laitinen 1974, Murray 1975, Axe and Trivedi 2002, Lee et al. 2002). Field observations of Al-, Fe(III)-, and Mn(III/IV)-oxide sequestration of trace metals support a strong correlation between the sorption of Mn(II) and other trace metals (Fuller and Harvey 2000, Kay et al. 2001, Lee et al. 2002). (Iron(II) sorption on oxide surfaces is complicated by rapid surface-catalyzed oxidation in the presence of oxygen (Wehrli and Stumm 1989).) Exceptions to this trend occur in sites with high levels of organically-bound Cu and Zn (von Gunten et al. 1991, Bourg and Darmendrail 1992), which remain mobile under conditions otherwise favorable to sorption on aquifer sediments.

The limitation of sorption in long-term bank filtration (e.g., sites in Berlin have been active since the late 1800s (Ziegler 2001)) results from saturation of the surfaces of the aquifer sediments. This causes an advancing sorption front in the aquifer, which can eventually reach the production well, as has been observed for Mn in Israel (Oren et al. 2007) and modeled for P in Canada (Spiteri et al. 2007). Sorption also plays a key role in *in situ* iron removal. Injection of aerated groundwater oxidizes adsorbed Fe(II) to Fe(III) oxides, and low-Fe groundwater is subsequently extracted, while Fe(II) adsorbs to newly formed Fe(III) oxides, until Fe(II) breaks through at the well again (Appelo et al. 1999). Dilution with native groundwater and dispersion can significantly damp any sorption front moving through an aquifer for bank filtration. For example, in the 1980s along the Rhine River, elevated surface water concentrations of As, Co, Cu, Ni, and Pb did not penetrate further than 50 m along the infiltration path (Stuyfzand et al. 2006). Similar data comparing surface water and infiltrate for a German site (Duisberg) along the Rhine have been presented as a percentage "removed" from the infiltrate (e.g., 51–93% removal of As, Cu, Ni, and Pb) (Sontheimer 1980, Schmidt et al. 2003), but this terminology should be avoided. Trace elements sequestered via sorption to Fe and Mn oxides can readily desorb (Gadde and Laitinen 1974) if the composition of the bank filtrate changes, e.g., due to seasonal changes or shock loads in the source water body. Geochemical modeling of wastewater-derived P in two Canadian aquifers suggested that a P plume would move 20 m down-gradient in 17 years, upon removal of the wastewater source (Spiteri et al. 2007). Stable, long-term sequestration thus requires more than sorption alone for trace elements. Since actual breakthrough of trace metals in bank filtration wells is rare, alternate sequestration (i.e., precipitation of oxides and interactions with carbonates), coupled with dispersion and dilution, likely occurs in long-term bank filtration sites still in use.