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Inorganic Geochemistry and Redox Dynamics in Bank Filtration Settings

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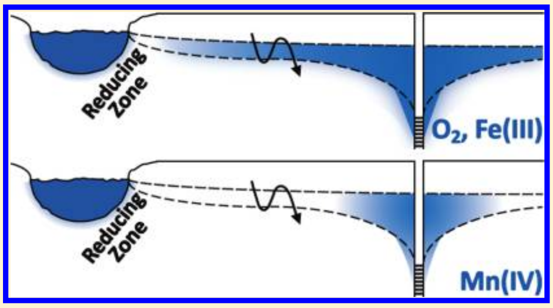
ABSTRACT: Bank filtration induces flow of surface water through a hydraulically connected aquifer by excess pumping from a production well in the aquifer. This review presents the four main geochemical processes relevant for inorganic geochemistry, with a focus on iron (Fe) and manganese (Mn), during 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 breakthrough 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. 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.[1] 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.[2] 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.[3] Indeed, surface water storage may become impractical in arid and semiarid areas due to lower streamflows and excessive evaporation.[4,5] 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.[6] 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.[7] 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 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.[5] 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.[8]

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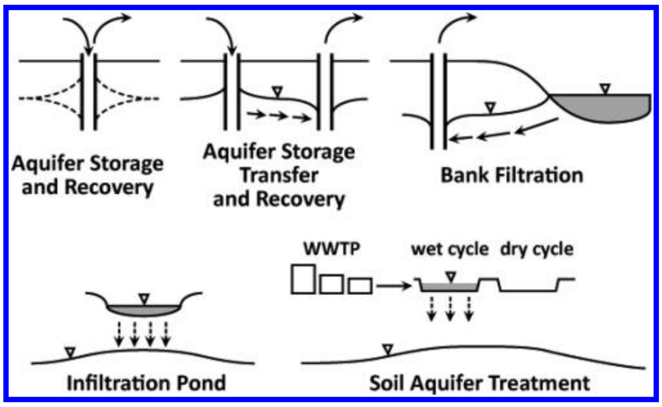

Figure 1. Schematics of various types of Managed Aquifer Recharge. Adapted from Dillon (2005).[9] WWTP denotes a wastewater treatment plant.

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.[10,11] Bank filtration relies upon natural processes to remove nutrients, organic carbon, and microbes, especially pathogens, present in the source water.[12] Recent research in bank filtration settings has focused extensively on understanding the processes behind effective pathogen removal[13−15] and on quantifying the removal of persistent organic micropollutants,[16,17] both of which are critical to determine the postextraction 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,[18] Germany,[19] and the Netherlands.[20] Recent research suggests Mn at levels above the (aesthetic) guidelines in drinking water may impair children's intelligence.[21,22] Although the treatment to remove Fe and Mn is relatively simple in practice (often aeration and sand filtration[20]), the presence of these elements can lead to well screen clogging[23,24] and can also indicate conditions where trace metals associated with Fe and Mn oxide solids are released along the flow path.[25] 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 postextraction 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.[14,26,27] 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). These processes are also relevant in other MAR schemes, but specific aspects of other forms of MAR are not considered here.

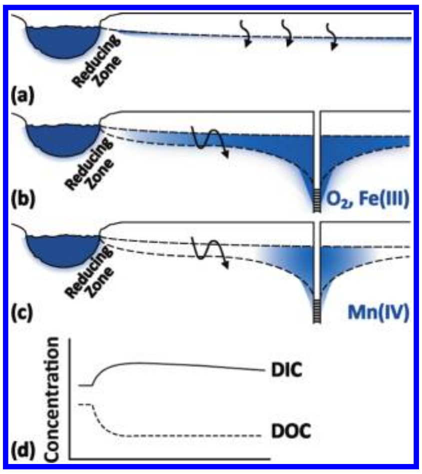

Figure 2. Profile of geochemical changes along a natural (a) and bank filtration (b,c) flow path. Oxidizing conditions and the corresponding occurrence of dissolved oxygen and oxidized Fe and Mn are indicated by blue coloration. Arrows indicate the dominant mechanisms of reaeration: diffusion and rain infiltration under natural conditions and water table oscillations during bank filtration. The relative concentration profiles of dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) in bank filtration are shown in (d) after Bourg and Bertin (1993).[28]

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,[29] and on−off cycles of the production well cause oscillations of the water table (Figure 2b, c), which affects oxygen delivery to the infiltrate.[30] This method of oxygen delivery is not included in the standard conceptual model for bank filtration geochemistry (presented by Bourg and Bertin[28]). In a natural setting, diffusion from the unsaturated zone and infiltration of rainwater provide limited oxygen delivery to the shallow groundwater (Figure 2a). 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. The standard conceptual model[28] suggests that this "mixing zone" extends for tens of meters from the production well toward the river- or lakebank, and is responsible for diluting and buffering concentrations, especially Mn and Zn, in the infiltrate. However, the dilution and buffering capacity depend on the solid-phase composition and groundwater concentration at a given site; mixing of aerated infiltrate with reduced groundwater can also lead to undesirable geochemical processes such as Fe or Mn precipitation in production well screens.[24]

The four geochemical processes are illustrated with Fe and Mn, whose relevant species are shown in Figure 3. Briefly, Mn has three common oxidation states in the environment (+II, +III, and +IV), and Fe has two (+II and +III). 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.,

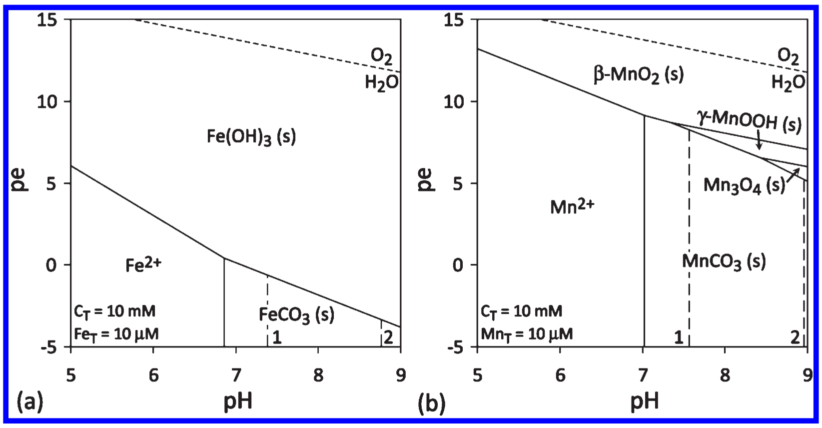

Figure 3. pe−pH predominance plot for (a) Fe (total = 10 μM) and (b) Mn (total = 10 μM) under typical pH and redox conditions for groundwater (C_T = 10 mM). Dashed vertical lines show the (a) Fe^{2+}/ $FeCO_3$ (s) and (b) Mn^{2+}/ $MnCO_3$ (s) equilibria for (1) C_T = 5 mM, Mn_T = Fe_T = 5 μM, and (2) 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).

higher than pH 9 in Figure 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 ($K(Mn^{3+}, Mn^{4+})_2O_4 \cdot 1.5\ H_2O$), pyrolusite ($MnO_2$), hausmannite ($Mn_3O_4$), and manganite (MnOOH).[31] Fe(III) is also largely found in insoluble oxides and oxyhydroxides, which are prone to dissolution under reducing conditions, but less so than those of Mn(III/IV) (Figure 3). Reductive dissolution of Fe and Mn oxides is largely microbially mediated,[32,33] and oxidative precipitation of Fe(II) and Mn(II) can be as well.[34,35] Although kinetics of abiotic Fe(II) oxidation by oxygen are relatively rapid at circumneutral pH, Mn oxidation is slow below pH 9,[36] with abiotic Mn oxidation orders of magnitude slower than microbial Mn oxidation.[37−39] 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.[34]

Reduction near the Bank. Reducing conditions near the bank have been documented in many field sites.[18,26,28,40] 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.[41] 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.[42] These seasonal effects lead to a greater extent of reducing conditions as compared to the winter.[25,27,43,44] Solid organic carbon in the aquifer sediments can additionally promote reduction of oxygen, nitrate, and Mn oxides further along the flow path.[45]

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.[11,44] 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.[12,16,17,46]

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 1 order of magnitude, at which point the layer was mechanically removed.[47] 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-mentioned artificial recharge pond.[48] 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.[49] 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.

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.[50,51] Mn- and Fe-oxide reduction result instead from interactions between microbes and the native sediments at the site.[32,33] 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,[52] and those rates of reduction are quite comparable.[53,54] Mineralogy plays a key role in both the reactivity[54,55] and the sorption capacity[31] of Fe and Mn oxides; reactivity and sorption capacity decrease with increasing crystallinity.

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,[18,56] but both Mn and Fe oxides are major sinks for trace metals,[33] and sorbed metals are released to solution during their reduction.[57] This was observed for Cd, Cr, Cu, Pb, U, and Zn, as well as phosphate, at the Glatt River site.[25,27,40,58] 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,[58] 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 rainwater, 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.[30] 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".[59] Excess air has been observed in the shallow groundwater of Berlin's bank filtration sites,[29] in support of the laboratory and model results. The generalized dissolved oxygen profile for bank filtration sites in Figure 2b 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.[26,27] Thus, reaeration of the infiltrate is heavily influenced by the production well pump operation, seasonal nutrient loads, and temperature.

The oxic zone near 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, the spatial extent of Fe oxidation is expected to align more closely with the oxygen profile (Figure 2b) rather than the Mn profile (Figure 2c) due to the rapid oxidation kinetics of Fe(II)[37] and its potential (microbially mediated) oxidation by nitrate.[60] Mn oxidation only occurs in the presence of oxygen,[36,61] and can be assumed to be microbially mediated based upon the relative rates of abiotic and microbial oxidation.[62] 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.[28,63] However, breakthrough of elevated, dissolved Mn at an oxic production well could occur either because of slow oxidation kinetics or a nearby reduction hotspot.[43] Attempts to use E_h-based measurements or thermodynamic calculations to predict locations susceptible to elevated Mn have been very limited in their success.[64]

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)[65] or because metals such as Co(II) and Cr(III) can be indirectly oxidized by Mn(II)-oxidizing microbes.[66] 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.[67] 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.[25]

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.[50] Dutch well fields often clog due to well-screen mixing of mildly oxic shallow groundwater and anoxic deep groundwater with elevated dissolved iron.[24] 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[37] 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.[19] Bank filtration adjacent to polder settings in both Germany[68] and the Netherlands[20] is susceptible to elevated concentrations of sulfide, ammonium, and methane in the infiltrate, which tends to require postextraction 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.[68]

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.[8,28,43] Sulfide mineral dissolution is often considered in deep-well ASR and ASTR,[69] 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.[70]

Infiltrate with lower alkalinity and/or pH than the ambient groundwater has been observed to promote calcite ($CaCO_3$) dissolution in many field sites[27,28,47,71,72] and some laboratory studies.[73,74] 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.[43,72,73] Since only low levels of trace elements are typically affiliated with calcite,[75] 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.[28,74,76] In one column study, calcite dissolution contributed to a locally higher hydraulic conductivity.[73] There is some concern that overly aggressive water could dissolve enough calcite grains so as to destabilize the

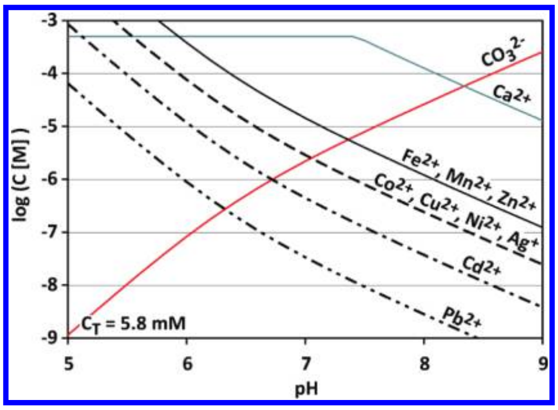

Figure 4. Dissolved metal concentrations in equilibrium with calcite and metal carbonates (C_T = 5.8 mM; Ca_T = 0.5 mM, the average value for North American fresh water[75]). Solubility products (in the form MCO_3 except Ag_2CO_3) taken from the MINTEQa2 database.[80] For simplicity, concentrations have been plotted with one line for each cluster of solubility products labeled on the figure (log K_{sp} within 0.5 units).

soil, especially with reverse-osmosis-treated water in SAT sites,[76] 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[71,72] and laboratory studies.[73] 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.[73] Field-scale geochemical transport models nevertheless suggest that the reprecipitated quantities of calcite should not affect the aquifer's porosity.[71,72]

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.[77] 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 4 (in which equilibrium with calcite is assumed). Besides metal—carbonates, some trace metals can form even less soluble mixed hydroxycarbonates or coprecipitate in calcite,[78] so the concentrations in Figure 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 days to reach steady state.[79]

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.[68] 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.[81] At the same site, Fe oxides were associated with calcite, suggesting that Fe(II)-calcite interaction led to preferential oxidation sites during aeration.[81] Vernal calcite dissolution due to microbial respiration in the Glatt riverbank released significant Mn and Fe, suggesting both were carbonate-bound.[82] Trace cations have also been released during calcite dissolution, for example, , Zn, Co, Cd, Ni, and Pb in batch incubations of aquifer sediments,[83] and sequestered via carbonate preciptitation, for example, Cd at the Glatt river site.[27]

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.[84,85]

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.[86] Trace cations such as Cd and Zn were released in the reducing zone, then sequestered via sorption at sites in Switzerland and France.[27,28,86] Copper, often bound to organic matter, was not as readily adsorbed as Cd and Zn.[27] 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.[50]

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.[87−90] 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.[90−92] (Iron(II) sorption on oxide surfaces is complicated by rapid surface-catalyzed oxidation in the presence of oxygen.[93]) Exceptions to this trend occur in sites with high levels of organically bound Cu and Zn,[27,86] 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[11]) 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[94] and modeled for P in Canada.[95] 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.[96] 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.[97] 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),[98,99] but this terminology should be avoided. Trace elements sequestered via sorption to Fe and Mn oxides can readily desorb[88] if the composition of the bank filtrate changes, for example, 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 downgradient in 17 years, upon removal of the wastewater source.[95] 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.

RESEARCH NEEDS

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.[14,15,17,42,46,100,101] 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,[30] 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;[29,102,103] 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.[94−96] Ayotte and others recently proposed a flowchart for water managers to determine if pumping at a public supply groundwater well is likely to mobilize trace elements.[104] 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, decreased well yield, and in some cases requires abandonment of production wells.[19,23,24] As rehabilitation or replacement of production wells susceptible to clogging is expensive in the long term,[105] 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[23,24]), to novel solutions for well rehabilitation, such as addition of bacteriophages to degrade Fe- and Mn-oxidizing biofilms.[106]

Global climate change will certainly affect the performance of bank filtration systems. As has already been observed with seasonal differences in temperature,[26,27,63] 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 interaction of the bank filtrate with oxic sediments that potentially sequester 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,[10] but floods could affect the redox status of soils.[107] Additionally, the infiltration flow paths for microbes and viruses may be short-circuited under flood conditions.[100] 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.[108]

The simplicity of bank filtration makes it a desirable pretreatment step for drinking water in many locations. It could furthermore offer significant benefits in the developing world, where water treatment infrastructure is minimal.[109] 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.[110] 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.[111,112] 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,[113] Orange County, California,[114] and Shafdan, Israel,[94] could begin to improve surface water quality in urban centers in developing countries.[115] 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[109] or dissolution,[116] or As release from Fe sulfides.[117,118] Standard geochemical reactive-transport models (e.g., PHREEQC[72,116]) can incorporate unusual geochemical processes, and have been used within sophisticated 3-D groundwater flow models (e.g., PHT3D[116,119]) to predict the behavior of bank filtration systems.[72,120] Aquifers can also undergo physical changes during pumping, such as clay dispersion,[121] that affect the withdrawal rate; interrelated physical and chemical changes must be balanced effectively and efficiently to maintain high-yield bank filtration.[122,123] Truly comprehensive models must incorporate these effects to optimize the desired treatment outcome and flow rate.

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REFERENCES

(1) Rockström, J.; Falkenmark, M.; Karlberg, L.; Hoff, H.; Rost, S.; Gerten, D. Future water availability for global food production: The potential of green water for increasing resilience to global change. *Water Resour. Res.* **2009**, *45* (7), W00A12.

(2) Vorosmarty, C. J.; McIntyre, P. B.; Gessner, M. O.; Dudgeon, D.; Prusevich, A.; Green, P.; Glidden, S.; Bunn, S. E.; Sullivan, C. A.; Liermann, C. R.; Davies, P. M. Global threats to human water security and river biodiversity. *Nature* **2010**, *467* (7315), 555–561.

(3) Barnett, T. P.; Pierce, D. W. When will Lake Mead go dry?. *Water Resour. Res.* **2008**, *44* (3), W03201.

(4) Brikowski, T. H. Doomed reservoirs in Kansas, USA? Climate change and groundwater mining on the Great Plains lead to unsustainable surface water storage. *J. Hydrol.* **2008**, *354* (1−4), 90–101.

(5) Bouwer, H. Artificial recharge of groundwater: hydrogeology and engineering. *Hydrogeol. J.* **2002**, *10* (1), 121–142.

(6) Buros, O. K.; Pyne, R. D. G. Extending water-supplies in water short areas. *Desalination* **1994**, *98* (1−3), 437–442.

(7) Gleick, P. H. Water management: Soft water paths. *Nature* **2002**, *418* (6896), 373–373.

(8) NRC. *Prospects for Managed Underground Storage of Recoverable Water*; National Academies Press: Washington D.C., 2008; p 350.

(9) Dillon, P. Future management of aquifer recharge. *Hydrogeol. J.* **2005**, *13* (1), 313–316.

(10) Eckert, P.; Irmscher, R. Over 130 years of experience with Riverbank filtration in Düsseldorf, Germany. *J. Water Supply Res. T.* **2006**, *55* (4), 283–291.

(11) Ziegler, D. H. Untersuchungen zur nachhaltigen Wirkung der Uferfiltration im Wasserkreislauf Berlins. Dr.-Ing. Thesis, Technical University of Berlin, Berlin, Germany, 2001.

(12) Schwarzenbach, R. P.; Giger, W.; Hoehn, E.; Schneider, J. K. Behavior of organic compounds during infiltration of river water to groundwater. Field studies. *Environ. Sci. Technol.* **1983**, *17* (8), 472–479.

(13) Metge, D. W.; Harvey, R. W.; Aiken, G. R.; Anders, R.; Lincoln, G.; Jasperse, J. Influence of organic carbon loading, sediment associated metal oxide content and sediment grain size distributions upon *Cryptosporidium parvum* removal during riverbank filtration operations, Sonoma County, CA. *Water Res.* **2010**, *44* (4), 1126–1137.

(14) Castro, F. D.; Tufenkji, N. Role of oxygen tension on the transport and retention of two pathogenic bacteria in saturated porous media. *Environ. Sci. Technol.* **2008**, *42* (24), 9178–9183.

(15) Toze, S.; Bekele, E.; Page, D.; Sidhu, J.; Shackleton, M. Use of static quantitative microbial risk assessment to determine pathogen risks in an unconfined carbonate aquifer used for managed aquifer recharge. *Water Res.* **2010**, *44* (4), 1038–1049.

(16) Hoppe-Jones, C.; Oldham, G.; Drewes, J. E. Attenuation of total organic carbon and unregulated trace organic chemicals in U.S. riverbank filtration systems. *Water Res.* **2010**, *44* (15), 4643–4659.

(17) Massmann, G.; Dünnbier, U.; Heberer, T.; Taute, T. Behaviour and redox sensitivity of pharmaceutical residues during bank filtration - Investigation of residues of phenazone-type analgesics. *Chemosphere* **2008**, *71* (8), 1476–1485.

(18) Thomas, N. E.; Kan, K. T.; Bray, D. I.; MacQuarrie, K. T. B. Temporal changes in manganese concentrations in water from the fredericton aquifer, New Brunswick. *Ground Water* **1994**, *32* (4), 650–656.

(19) Hässelbarth, U.; Lüdemann, D. Biological incrustation of wells due to mass development of iron and manganese bacteria. *Water Treat. Exam.* **1972**, *21*, 20–29.

(20) de Vet, W. W. J. M.; van Genuchten, C. C. A.; van Loosdrecht, M. C. M.; van Dijk, J. C. Water quality and treatment of river bank filtrate. *Drinking Water Eng. Sci.* **2010**, 3 (1), 79–90.

(21) Bouchard, M. F.; Sauvé, S.; Barbeau, B.; Legrand, M.; Brodeur, M.-.; Bouffard, T.; Limoges, E.; Bellinger, D. C.; Mergler, D. Intellectual impairment in school-age children exposed to manganese from drinking water. *Environ. Health Perspect.* **2011**, *119*, 1.

(22) Wasserman, G. A.; Liu, X.; Parvez, F.; Ahsan, H.; Levy, D.; Factor-Litvak, P.; Kline, J.; van Geen, A.; Slavkovich, V.; LoIacono, N. J.; Cheng, Z.; Zheng, Y.; Graziano, J. H., Water manganese exposure and children's intellectual function in Araihazar, Bangladesh. *Environ. Health Perspect.* **2006**, *114*, (1).

(23) van Beek, C. Restoring Well Yield in the Netherlands. *J. Am. Water Works Assoc.* **1984**, *76* (10), 66–72.

(24) van Beek, C.; Breedveld, R.; Stuyfzand, P. Preventing two types of well clogging. *J. Am. Water Works Assoc.* **2009**, *101* (4), 125–134.

(25) von Gunten, H. R.; Kull, T. P. Infiltration of inorganic-compounds from the Glatt River, Switzerland, into a Groundwater Aquifer. *Water Air Soil Poll.* **1986**, *29* (3), 333–346.

(26) Massmann, G.; Nogeitzig, A.; Taute, T.; Pekdeger, A. Seasonal and spatial distribution of redox zones during lake bank filtration in Berlin, Germany. *Environ. Geol.* **2008**, *54* (1), 53–65.

(27) von Gunten, H. R.; Karametaxas, G.; Krahenbuhl, U.; Kuslys, M.; Giovanoli, R.; Hoehn, E.; Keil, R. Seasonal biogeochemical cycles in riverborne groundwater. *Geochim. Cosmochim. Ac.* **1991**, *55* (12), 3597–3609.

(28) Bourg, A. C. M.; Bertin, C. Biogeochemical processes during the infiltration of river water into an alluvial aquifer. *Environ. Sci. Technol.* **1993**, *27* (4), 661–666.

(29) Massmann, G.; Sültenfuss, J. Identification of processes affecting excess air formation during natural bank filtration and managed aquifer recharge. *J. Hydrol.* **2008**, *359* (3−4), 235–246.

(30) Kohfahl, C.; Massmann, G.; Pekdeger, A. Sources of oxygen flux in groundwater during induced bank filtration at a site in Berlin, Germany. *Hydrogeol. J.* **2009**, *17* (3), 571–578.

(31) Post, J. E. Manganese oxide minerals: Crystal structures and economic and environmental significance. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96* (7), 3447–3454.

(32) Lloyd, J. R. Microbial reduction of metals and radionuclides. *FEMS Microbiol. Rev.* **2003**, *27* (2−3), 411–425.

(33) Lovley, D. R. Dissimilatory Fe(III) and Mn(IV) reduction. *Microbiol. Mol. Biol. Rev.* **1991**, *55* (2), 259–287.

(34) Tebo, B. M.; Bargar, J. R.; Clement, B. G.; Dick, G. J.; Murray, K. J.; Parker, D.; Verity, R.; Webb, S. M. Biogenic manganese oxides: Properties and mechanisms of formation. *Annu. Rev. Earth Planet. Sci.* **2004**, *32* (1), 287–328.

(35) Corstjens, P. L.; de Vrind, J. P.; Westbroek, P.; de Vrind-de Jong, E. W. Enzymatic iron oxidation by *Leptothrix discophora*: Identification of an iron-oxidizing protein. *Appl. Environ. Microbiol.* **1992**, *58* (2), 450–454.

(36) Morgan, J. J. Kinetics of reaction between O_2 and Mn(II) species in aqueous solutions. *Geochim. Cosmochim. Ac.* **2005**, *69* (1), 35–48.

(37) Luther, G. W. Manganese(II) oxidation and Mn(IV) reduction in the environment—Two one-electron transfer steps versus a single two-electron step. *Geomicrobiol. J.* **2005**, *22* (3), 195–203.

(38) Davies, S. H. R.; Morgan, J. J. Manganese(II) oxidation kinetics on metal oxide surfaces. *J. Colloid Interface Sci.* **1989**, *129* (1), 63–77.

(39) Hastings, D.; Emerson, S. Oxidation of manganese by spores of a marine bacillus: Kinetic and thermodynamic considerations. *Geochim. Cosmochim. Acta* **1986**, *50* (8), 1819–1824.

(40) Jacobs, L. A.; von Gunten, H. R.; Keil, R.; Kuslys, M. Geochemical changes along a river-groundwater infiltration flow path—Glattfelden, Switzerland. *Geochim. Cosmochim. Acta* **1988**, *52* (11), 2693–2706.

(41) Berner, R. A., *Early Diagenesis: A Theoretical Approach*; Princeton University Press: Princeton, NJ, 1980.

(42) Greskowiak, J.; Prommer, H.; Massmann, G.; Nutzmann, G. Modeling seasonal redox dynamics and the corresponding fate of the pharmaceutical residue phenazone during artificial recharge of groundwater. *Environ. Sci. Technol.* **2006**, *40* (21), 6615–6621.

(43) Bourg, A. C. M.; Richard-Raymond, F. Spatial and temporal variability in the water redox chemistry of the M27 experimental site in

the Drac River calcareous alluvial aquifer (Grenoble, France). *J. Contam. Hydrol.* **1994**, *15* (1−2), 93–105.

(44) Hoffmann, A.; Gunkel, G. Carbon input, production and turnover in the interstices of a Lake Tegel bank filtration site, Berlin, Germany. *Limnologica* **2011**In Press, Corrected Proof.

(45) Kedziorek, M. A. M.; Geoffriau, S.; Bourg, A. C. M. Organic matter and modeling redox reactions during river bank filtration in an alluvial aquifer of the Lot River, France. *Environ. Sci. Technol.* **2008**, *42* (8), 2793–2798.

(46) Massmann, G.; Greskowiak, J.; Dünnbier, U.; Zuehlke, S.; Knappe, A.; Pekdeger, A. The impact of variable temperatures on the redox conditions and the behaviour of pharmaceutical residues during artificial recharge. *J. Hydrol.* **2006**, *328* (1−2), 141–156.

(47) Greskowiak, J.; Prommer, H.; Massmann, G.; Johnston, C. D.; Nutzmann, G.; Pekdeger, A. The impact of variably saturated conditions on hydrogeochemical changes during artificial recharge of groundwater. *Appl. Geochem.* **2005**, *20* (7), 1409–1426.

(48) Hoffmann, A.; Gunkel, G. Bank filtration in the sandy littoral zone of Lake Tegel (Berlin): Structure and dynamics of the biological active filter zone and clogging processes. *Limnologica* **2011**, *41* (1), 10–19.

(49) Gunkel, G.; Hoffmann, A. Clogging processes in a bank filtration system in the littoral zone of Lake Tegel (Germany), In *5th International Symposium on Managed Aquifer Recharge*, Berlin, 2005; pp 599−604.

(50) Doussan, C.; Ledoux, E.; Detay, M. River-groundwater exchanges, bank filtration, and groundwater quality: Ammonium behavior. *J. Environ. Qual.* **1998**, *27* (6), 1418–1427.

(51) Doussan, C.; Poitevin, G.; Ledoux, E.; Detay, M. River bank filtration: Modelling of the changes in water chemistry with emphasis on nitrogen species. *J. Contam. Hydrol.* **1997**, *25* (1−2), 129–156.

(52) Beliaev, A. S.; Saffarini, D. A. *Shewanella putrefaciens* mtrB encodes an outer membrane protein required for Fe(III) and Mn(IV) reduction. *J. Bacteriol.* **1998**, *180* (23), 6292–6297.

(53) Blakeney, M. D.; Moulaei, T.; DiChristina, T. J. Fe(III) reduction activity and cytochrome content of *Shewanella putrefaciens* grown on ten compounds as sole terminal electron acceptor. *Microbiol. Res.* **2000**, *155* (2), 87–94.

(54) Ruebush, S. S.; Icopini, G. A.; Brantley, S. L.; Tien, M. In vitro enzymatic reduction kinetics of mineral oxides by membrane fractions from *Shewanella oneidensis* MR-1. *Geochim. Cosmochim. Ac.* **2006**, *70* (1), 56–70.

(55) Burdige, D. J.; Dhakar, S. P.; Nealson, K. H. Effects of manganese oxide mineralogy on microbial and chemical manganese reduction. *Geomicrobiol. J.* **1992**, *10* (1), 27–48.

(56) Petrunic, B. M.; MacQuarrie, K. T. B.; Al, T. A. Reductive dissolution of Mn oxides in river-recharged aquifers: a laboratory column study. *J. Hydrol.* **2005**, *301* (1−4), 163–181.

(57) Davranche, M.; Bollinger, J.-C. Heavy metals desorption from synthesized and natural iron and manganese oxyhydroxides: effect of reductive conditions. *J. Colloid Interface Sci.* **2000**, *227* (2), 531–539.

(58) Lienert, C.; Short, S. A.; von Gunten, H. R. Uranium infiltration from a river to shallow groundwater. *Geochim. Cosmochim. Acta* **1994**, *58* (24), 5455–5463.

(59) Williams, M. D.; Oostrom, M. Oxygenation of anoxic water in a fluctuating water table system: an experimental and numerical study. *J. Hydrol.* **2000**, *230* (1−2), 70–85.

(60) Senn, D. B.; Hemond, H. F. Nitrate controls on iron and arsenic in an urban lake. *Science* **2002**, *296* (5577), 2373–2376.

(61) Boogerd, F. C.; de Vrind, J. P. Manganese oxidation by *Leptothrix discophora*. *J. Bacteriol.* **1987**, *169* (2), 489–494.

(62) Morgan, J. J., Manganese in natural waters and earth's crust: Its availability to organisms. In *Manganese and its role in biological processes*; Sigel, A. S. Ed.; Marcel Dekker, Inc.: New York, 2000.

(63) Bourg, A. C. M.; Bertin, C. Seasonal and spatial trends in manganese solubility in an alluvial aquifer. *Environ. Sci. Technol.* **2002**, *28* (5), 868–876.

(64) Kedziorek, M. A. M.; Bourg, A. C. M. Electron trapping capacity of dissolved oxygen and nitrate to evaluate Mn and Fe reductive dissolution in alluvial aquifers during riverbank filtration. *J. Hydrol.* **2009**, *365* (1−2), 74–78.

(65) Manning, B. A.; Fendorf, S. E.; Bostick, B.; Suarez, D. L. Arsenic(III) oxidation and arsenic(V) adsorption reactions on synthetic birnessite. *Environ. Sci. Technol.* **2002**, *36* (5), 976–981.

(66) Murray, K. J.; Webb, S. M.; Bargar, J. R.; Tebo, B. M. Indirect oxidation of Co(II) in the presence of the marine Mn(II)-oxidizing bacterium *Bacillus* sp. strain SG-1. *Appl. Environ. Microbiol.* **2007**, *73* (21), 6905–6909.

(67) Gandy, C. J.; Smith, J. W. N.; Jarvis, A. P. Attenuation of mining-derived pollutants in the hyporheic zone: A review. *Sci. Total Environ.* **2007**, *373* (2−3), 435–446.

(68) Massmann, G.; Pekdeger, A.; Merz, C. Redox processes in the Oderbruch polder groundwater flow system in Germany. *Appl. Geochem.* **2004**, *19* (6), 863–886.

(69) Herczeg, A. L.; Rattray, K. J.; Dillon, P. J.; Pavelic, P.; Barry, K. E. Geochemical processes during five years of aquifer storage recovery. *Ground Water* **2004**, *42* (3), 438–445.

(70) Massmann, G.; Tichomirowa, M.; Merz, C.; Pekdeger, A. Sulfide oxidation and sulfate reduction in a shallow groundwater system (Oderbruch Aquifer, Germany). *J. Hydrol.* **2003**, *278* (1−4), 231–243.

(71) Petkewich, M. D.; Parkhurst, D. L.; Conlon, K. J.; Campbell, B. G.; Mirecki, J. E. *Hydrologic and Geochemical Evaluation of Aquifer Storage Recovery in the Santee Limestone/Black Mingo Aquifer, Charleston, South Carolina, 1998−2002*, SIR 2004−5046; U.S. Geological Survey: Reston, VA, 2004.

(72) van Breukelen, B. M.; Appelo, C. A. J.; Olsthoorn, T. N. Hydrogeochemical transport modeling of 24 years of Rhine water infiltration in the dunes of the Amsterdam Water Supply. *J. Hydrol.* **1998**, *209* (1−4), 281–296.

(73) Rinck-Pfeiffer, S.; Ragusa, S.; Sztajnbok, P.; Vandevelde, T. Interrelationships between biological, chemical, and physical processes as an analog to clogging in aquifer storage and recovery (ASR) wells. *Water Res.* **2000**, *34* (7), 2110–2118.

(74) Patterson, B. M.; Shackleton, M.; Furness, A. J.; Pearce, J.; Descourvieres, C.; Linge, K. L.; Busetti, F.; Spadek, T. Fate of nine recycled water trace organic contaminants and metal(loid)s during managed aquifer recharge into a anaerobic aquifer: Column studies. *Water Res.* **2010**, *44* (5), 1471–1481.

(75) Morel, F. M. M.; Hering, J. G., *Principles and Applications of Aquatic Chemistry*; Wiley-Interscience: New York, 1993.

(76) Johnson, J. S.; Baker, L. A.; Fox, P. Geochemical transformations during artificial groundwater recharge: soil-water interactions of inorganic constituents. *Water Res.* **1999**, *33* (1), 196–206.

(77) Tessier, A.; Campbell, P. G. C.; Bisson, M. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51* (7), 844–851.

(78) Rimstidt, J. D.; Balog, A.; Webb, J. Distribution of trace elements between carbonate minerals and aqueous solutions. *Geochim. Cosmochim. Acta* **1998**, *62* (11), 1851–1863.

(79) Jensen, D. L.; Boddum, J. K.; Tjell, J. C.; Christensen, T. H. The solubility of rhodochrosite (MnCO3) and siderite (FeCO3) in anaerobic aquatic environments. *Appl. Geochem.* **2002**, *17* (4), 503–511.

(80) *MINTEQA2/PRODEFA2, Geochemical Assessment Model for Environmental Systems, Version 4.03*, 4.03; U.S. Environmental Protection Agency,National Exposure Research Laboratory, Ecosystems Research Division: Athens, GA, 2006.

(81) Mettler, S.; Abdelmoula, M.; Hoehn, E.; Schoenenberger, R.; Weidler, P.; Gunten, U. Characterization of iron and manganese precipitates from an in situ ground water treatment plant. *Ground Water* **2001**, *39* (6), 921–930.

(82) von Gunten, H. R.; Karametaxas, G.; Keil, R. Chemical processes in infiltrated riverbed sediments. *Environ. Sci. Technol.* **1994**, *28* (12), 2087–2093.

(83) Descourvières, C.; Hartog, N.; Patterson, B. M.; Oldham, C.; Prommer, H. Geochemical controls on sediment reactivity and buffering processes in a heterogeneous aquifer. *Appl. Geochem.* **2009**, *25* (2), 261–275.

(84) Mirecki, J. E.; Campbell, B. G.; Conlon, K. J.; Petkewich, M. D. Solute changes during aquifer storage recovery testing in a limestone clastic aquifer. *Ground Water* **1998**, *36* (3), 394–403.

(85) Parkhurst, D. L.; Petkewich, M. D. Geochemical modeling of an aquifer storage recovery experiment, Charleston, South Carolina. In *U.S. Geological Survey Artifical Recharge Workshop Proceedings, Sacramento, CA, April 2−4*, 2002; Aiken, G. R.; Kuniansky, E. L., Eds. U.S. Geological Survey, 2002.

(86) Bourg, A. C. M.; Darmendrail, D. Effect of dissolved organic-matter and pH on the migration of zinc through river bank sediments. *Environ. Technol.* **1992**, *13* (7), 695–700.

(87) Axe, L.; Trivedi, P. Intraparticle surface diffusion of metal contaminants and their attenuation in microporous amorphous Al, Fe, and Mn oxides. *J. Colloid Interface Sci.* **2002**, *247* (2), 259–265.

(88) Gadde, R. R.; Laitinen, H. A. Heavy metal adsorption by hydrous iron and manganese oxides. *Anal. Chem.* **1974**, *46* (13), 2022–2026.

(89) Murray, J. W. The interaction of metal ions at the manganese dioxide-solution interface. *Geochim. Cosmochim. Acta* **1975**, *39* (4), 505–519.

(90) Lee, G.; Bigham, J. M.; Faure, G. Removal of trace metals by coprecipitation with Fe, Al, and Mn from natural waters contaminated with acid mine drainage in the Ducktown Mining District, Tennessee. *Appl. Geochem.* **2002**, *17* (5), 569–581.

(91) Kay, J. T.; Conklin, M. H.; Fuller, C. C.; O'Day, P. A. Processes of nickel and cobalt uptake by a manganese oxide forming sediment in Pinal Creek, Globe Mining District, Arizona. *Environ. Sci. Technol.* **2001**, *35* (24), 4719–4725.

(92) Fuller, C. C.; Harvey, J. W. Reactive uptake of trace metals in the hyporheic zone of a mining-contaminated stream, Pinal Creek, Arizona. *Environ. Sci. Technol.* **2000**, *34* (7), 1150–1155.

(93) Wehrli, B.; Stumm, W. Vanadyl in natural waters: Adsorption and hydrolysis promote oxygenation. *Geochim. Cosmochim. Acta* **1989**, *53* (1), 69–77.

(94) Oren, O.; Gavrieli, I.; Burg, A.; Guttman, J.; Lazar, B. Manganese mobilization and enrichment during soil aquifer treatment (SAT) of effluents, the Dan Region Sewage Reclamation Project (Shafdan), Israel. *Environ. Sci. Technol.* **2007**, *41* (3), 766–772.

(95) Spiteri, C.; Slomp, C. P.; Regnier, P.; Meile, C.; Van Cappellen, P. Modelling the geochemical fate and transport of wastewater-derived phosphorus in contrasting groundwater systems. *J. Contam. Hydrol.* **2007**, *92* (1−2), 85–106.

(96) Appelo, C. A. J.; Drijver, B.; Hekkenberg, R.; de Jonge, M. Modeling *in situ* iron removal from ground water. *Ground Water* **1999**, *37* (6), 811–817.

(97) Stuyfzand, P. J.; Juhàsz-Holterman, M. H. A.; Lange, W. J., Riverbank filtration in the netherlands: well fields, clogging and geochemical reactions. In *Riverbank Filtration Hydrology*; Hubbs, S. A., Ed.; Springer: Netherlands: 2006; Vol. 60, pp 119−153.

(98) Sontheimer, H. Experience with riverbank filtration along the Rhine river. *J. Am. Water Works Assoc.* **1980**, *72* (7), 386–390.

(99) Schmidt, C. K.; Lange, F. T.; Brauch, H.-J.; Kühn, W. *Experiences with Riverbank Filtration and Infiltration in Germany*; DVGW-Water Technology Center (TZW): Karlsruhe, Germany, 2003; p 17.

(100) Gupta, V.; Johnson, W. P.; Shafieian, P.; Ryu, H.; Alum, A.; Abbaszadegan, M.; Hubbs, S. A.; Rauch-Williams, T. Riverbank filtration: Comparison of pilot scale transport with theory. *Environ. Sci. Technol.* **2009**, *43* (3), 669–676.

(101) Tufenkji, N.; Ryan, J. N.; Elimelech, M. The promise of bank filtration. *Environ. Sci. Technol.* **2002**, *36* (21), 422A–428A.

(102) Klump, S.; Cirpka, O. A.; Surbeck, H.; Kipfer, R. Experimental and numerical studies on excess-air formation in quasi-saturated porous media. *Water Resour. Res.* **2008**, 44.

(103) Cey, B. D.; Hudson, G. B.; Moran, J. E.; Scanlon, B. R., Impact of artificial recharge on dissolved noble gases in groundwater in California. *Environ. Sci. Technol.* **2008**.

(104) Ayotte, J. D.; Szabo, Z.; Focazio, M. J.; Eberts, S. M. Effects of human-induced alteration of groundwater flow on concentrations of naturally-occurring trace elements at water-supply wells. *Appl. Geochem.* **2011**, *26* (5), 747–762.

(105) Dillon, P.; Pavelic, P.; Toze, S.; Rinck-Pfeiffer, S.; Martin, R.; Knapton, A.; Pidsley, D. Role of aquifer storage in water reuse. *Desalination* **2006**, *188* (1−3), 123–134.

(106) Gino, E.; Starosvetsky, J.; Kurzbaum, E.; Armon, R. Combined chemical-biological treatment for prevention/rehabilitation of clogged wells by an iron-oxidizing bacterium. *Environ. Sci. Technol.* **2010**, *44* (8), 3123–3129.

(107) Borch, T.; Kretzschmar, R.; Kappler, A.; Cappellen, P. V.; Ginder-Vogel, M.; Voegelin, A.; Campbell, K. Biogeochemical redox processes and their impact on contaminant dynamics. *Environ. Sci. Technol.* **2010**, *44* (1), 15–23.

(108) Sprenger, C.; Lorenzen, G.; Hülshoff, I.; Grützmacher, G.; Ronghang, M.; Pekdeger, A. Vulnerability of bank filtration systems to climate change. *Sci. Total Environ.* **2010**, *409* (4), 655–663.

(109) Lorenzen, G.; Sprenger, C.; Taute, T.; Pekdeger, A.; Mittal, A.; Massmann, G. Assessment of the potential for bank filtration in a water-stressed megacity (Delhi, India). *Environ. Earth Sci.* **2010**, *61* (7), 1419–1434.

(110) Schubert, J. Hydraulic aspects of riverbank filtration--field studies. *J. Hydrol.* **2002**, *266* (3−4), 145–161.

(111) Abiye, T.; Sulieman, H.; Ayalew, M. Use of treated wastewater for managed aquifer recharge in highly populated urban centers: a case study in Addis Ababa, Ethiopia. *Environ. Geol.* **2009**, *58* (1), 55–59.

(112) Singh, P.; Kumar, P.; Mehrotra, I.; Grischek, T. Impact of riverbank filtration on treatment of polluted river water. *J. Environ. Manage.* **2010**, *91* (5), 1055–1062.

(113) Massmann, G.; Sültenfuss, J.; Dünnbier, U.; Knappe, A.; Taute, T.; Pekdeger, A. Investigation of groundwater residence times during bank filtration in Berlin: a multi-tracer approach. *Hydrol. Process.* **2007**, *22* (6), 788–801.

(114) Clark, J. F.; Hudson, G. B.; Davisson, M. L.; Woodside, G.; Herndon, R. Geochemical imaging of flow near an artificial recharge facility, Orange County, California. *Ground Water* **2004**, *42* (2), 167–174.

(115) Jimenez, B.; Chavez, A. Quality assessment of an aquifer recharged with wastewater for its potential use as drinking source: "El Mezquital Valley" case. *Water Sci. Technol.* **2004**, *50* (2), 269–276.

(116) Gaus, I.; Shand, P.; Gale, I. N.; Williams, A. T.; Eastwood, J. C. Geochemical modelling of fluoride concentration changes during aquifer storage and recovery (ASR) in the Chalk aquifer in Wessex, England. *Q. J. Eng. Geol. Hydrogeol.* **2002**, 35, 203–208.

(117) Price, R. E.; Pichler, T. Abundance and mineralogical association of arsenic in the Suwannee Limestone (Florida): Implications for arsenic release during water-rock interaction. *Chem. Geol.* **2006**, *228* (1−3), 44–56.

(118) Wallis, I.; Prommer, H.; Simmons, C. T.; Post, V.; Stuyfzand, P. J. Evaluation of conceptual and numerical models for arsenic mobilization and attenuation during managed aquifer recharge. *Environ. Sci. Technol.* **2010**, *44* (13), 5035–5041.

(119) Prommer, H.; Barry, D. A.; Zheng, C. MODFLOW/MT3DMS-based reactive multicomponent transport modeling. *Ground Water* **2003**, *41* (2), 247–257.

(120) MacQuarrie, K. T. B.; Al, T. A. The influence of seasonal temperature variation and other factors on the occurrence of dissolved manganese during bank filtration In *Proceedings of the 6th International Groundwater Quality Conference*, Freemantle, Australia, 2007; Trefry, M. G., Ed. IAHS: Freemantle, Australia, 2007; pp 467−474.

(121) Konikow, L. F.; August, L. L.; Voss, C. I. Effects of clay dispersion on aquifer storage and recovery in coastal aquifers. *Transp. Porous Media* **2001**, *43* (1), 45–64.

(122) Wiese, B.; Nützmann, G. Transient leakance and infiltration characteristics during lake bank filtration. *Ground Water* **2009**, *47* (1), 57–68.

(123) Eusuff, M. M.; Lansey, K. E. Optimal operation of artificial groundwater recharge systems considering water quality transformations. *Water Resour. Manage.* **2004**, *18* (4), 379–405.