Elevated manganese concentrations in groundwater wells after longtime abstraction with bank filtration: developing and testing of a sorption model for Ringerike waterworks, Norway

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Abstract
Groundwater abstraction wells located in aquifers hydraulically connected with rivers or lakes will induce bank filtration if the water level in the aquifer is lowered below the surface-water level. Many groundwater works utilize this induced infiltration to increase the abstraction capacity of their wells. Unfortunately, infiltration of organic-rich surface water may alter the aquifer’s redox geochemistry, and mobilize iron and/or manganese. Ringerike groundwater works in southeastern Norway operates with bank filtration. Manganese concentrations in the abstracted water began to increase 19 years after the start of operations, and stabilized at an elevated level 8 years later. The estimated manganese retardation \( R_{\text{sorp}} = 45 \pm 18 \) from a simplified advection-sorption model is comparable to the observed manganese retardation range \( 36 < R_{\text{obs}} < 50 \), assuming a groundwater residence time \( t_{\text{gw}} \sim 200 \) days. The advection-sorption model is based on limited sediment composition and hydrochemical data, which introduces significant uncertainty to \( R_{\text{sorp}} \). However, \( R_{\text{sorp}} \) and \( R_{\text{obs}} \) in the same range, and the good fit between PHREEQC simulated and observed data, indicates that sorption is a possible explanation for the delayed breakthrough of elevated manganese concentrations in Ringerike waterworks’ production wells. Comparable bank filtration schemes are advised to establish observation well(s) between the bank filtration and production well field for early detection of sorption fronts. This would facilitate (1) longer time available for remediation measures and their evaluation, and (2) less manganese to be desorbed during the remediation stage.

Keywords Manganese · Water supply · Bank filtration · Reactive transport · Retardation

Introduction
Bank filtration refers to infiltration of surface water into an unconfined aquifer, induced by groundwater abstraction. Groundwater abstraction will draw down the water level in the aquifer, whereby infiltration is induced if the water level in the aquifer is lowered below the water level of a hydraulically connected river or lake. The filtration through the aquifer sediments will improve the infiltrated water quality hygienically (e.g., remove pathogens and organic matter; Hiscock and Grischek 2002; Kvitsand et al. 2017). Furthermore, the induced infiltration will increase the abstraction capacity from small aquifers, by supplementing the groundwater recharge from precipitation and natural groundwater flow (Knutsson 2008). Bank filtration is therefore often used for drinking-water pretreatment (Dillon 2005).

A downside to bank filtration is the possible alteration of redox conditions in the aquifer, which may increase the iron (Fe\(^{2+}\)) and manganese (Mn\(^{2+}\)) concentrations in the abstracted water (Farnsworth and Hering 2011). Elevated iron and manganese concentrations lead to undesired color and taste, which needs costly treatment if the water is to be used for drinking purposes (Ellingsen 1992). This is because iron and manganese are oxidized and precipitate as oxide minerals in contact with oxygen. The precipitates may furthermore incrust and clog well filters, distribution pipes, etc., forcing costly remediation (Houben and Treskatis 2007). Followingly, groundwater sources with high iron and manganese concentrations are sought avoided for drinking-water purposes.

The alteration of redox conditions in aquifers during bank filtration can be ascribed to an increased influx of
If enough organic matter infiltrates, the degradation will deplete the water of oxygen and nitrate, and in turn reduce manganese (Mn$^{3+/4+}$) oxides and iron (Fe$^{3+}$) oxides to soluble Fe$^{2+}$ and Mn$^{2+}$ ions (Stumm and Morgan 1996; see Fig. 1), resulting in a reducing zone near the bank, characterized by high dissolved Fe$^{2+}$ and Mn$^{2+}$ concentrations. The degradation of organic matter also produces carbon dioxide gas which is dissolved in water to form carbonic acid. The acid dissolves carbonate minerals, which may further increase dissolved iron and manganese concentrations. The transport of iron and manganese toward the abstraction well may be delayed by sorption to aquifer sediments. The composition of ions adsorbed to aquifer sediments reflects the dissolved concentrations (Appelo and Postma 2005). Thus, increasing dissolved manganese concentrations would lead to ion exchange of manganese for other cations initially adsorbed to the aquifer sediments, causing a manganese “sorption front” moving towards the production well area, with a velocity that is slower than the average groundwater flow rate (Fig. 1). Water-table oscillations around the abstraction well(s) will oxygenate the groundwater, leading to a more oxic zone in this part of the aquifer. Precipitation of oxide minerals in the aquifer around the abstraction wells may hinder the breakthrough of elevated iron and manganese concentrations in the abstracted water (Farnsworth and Hering 2011). If, however, dissolved iron and manganese reaches the abstraction well, they may be oxidized in the well filter through mixing with shallow, oxygen-rich groundwater, causing the aforementioned clogging issues (Houben and Treskatis 2007).

The redox characteristics of iron and manganese differ from one another. Manganese is more easily reduced than iron, and requires more oxygen to be oxidized. Furthermore, oxidation of manganese is kinetically slower than oxidation of iron (Stumm and Morgan 1996), which explains why elevated dissolved concentrations of manganese is more common than elevated concentrations of iron in bank filtration abstraction wells (Farnsworth and Hering 2011).

Some bank filtration schemes abstract water low in manganese for many years before manganese concentrations start to increase (see Table 1). The retardation $R$ of manganese transport can be defined as (Appelo and Postma 2005)

$$R_{\text{obs}} = \frac{t_{\text{Mn}}}{t_{\text{gw}}}$$

where $t_{\text{Mn}}$ is the bank filtration operation time before elevated manganese concentrations occurred and $t_{\text{gw}}$ is the aquifer residence time of the abstracted groundwater. The data in Table 1 indicate retardation $R_{\text{obs}}$ ranging from single- to three-digit magnitude.

Delayed occurrences of elevated manganese concentrations in bank filtration settings have demanded numerous and often complex explanations (see Table 1 and Fig. 1). Many authors have attributed the retardation of manganese transport to sorption to aquifer sediments (Thomas et al. 1994; Petrunic et al. 2005; Farnsworth and Hering 2011). Oren et al. (2007) developed a manganese sorption model for sewage infiltration into an aquifer in the Dan Region, Israel, based on the composition of cations in solution and the aquifer sediments’ cation exchange capacity. The aim was to assess whether the modeled manganese retardation due to sorption resembled the observed retardation in nearby observation wells. Since the modeled manganese retardation resembled the observed one, Oren et al. (2007) concluded that sorption was the probable cause of manganese breakthrough after a time lag of 8–12 years.

The organic content of the infiltrating surface water and the aquifer sediments can also induce changes to manganese concentrations with time. Seasonal changes in the organic loading of recharge water and lithological variation led to seasonal and spatial changes in dissolved manganese.
concentrations, respectively, in an alluvial aquifer connected to the Lot River in south of France (Bourg and Bertin 1994). The spatial changes were due to low-permeability clay lamellas, which impeded the groundwater flow rate and led to longer residence time and more reducing conditions. Variation in lithology and the drilling of a new production well that induced new groundwater flow paths were used to explain increasing manganese concentrations after longtime operation at Lillehammer waterworks, Norway (Holmström et al. 2010). Similarly, increasing recharge of organic-rich river water to the aquifer, following drilling of a new production well and increasing pumping rate, was used to explain increasing groundwater manganese concentrations in New Brunswick, Canada, between 1971–1989 (Thomas et al. 1994).

Thomas et al. (1994) and Petrunic et al. (2005) also pointed to the microbial community as part of the explanation for elevated manganese concentrations. The microbial community needs time to adapt to a new redox regime (i.e., build a community of manganese-reducing bacteria), which will increase the reduction rate of manganese oxides with time.

Well clogging also may induce changes to the abstracted water quality. Incrustations usually form in the top portion of the well filter first, where inflow rates are highest, and then gradually expand downwards as the well filter clogs. This will lead to abstraction of deeper groundwater, which is often more anoxic and higher in iron and manganese, with time (Houben and Treskatis 2007).

It is also noteworthy that all occurrences listed in Table 1 are related to glaciofluvial aquifers, though previous studies have had limited emphasis on this aspect. Despite many possible explanations for increasing manganese concentrations after longtime operation, the retardation explanation is often not properly settled (see Table 1). This article investigates whether sorption can explain the elevated manganese concentrations after longtime groundwater abstraction with bank filtration at Ringerike waterworks. A simplified advection-sorption model is developed based on existing aquifer sediment data and new hydrochemical field and laboratory measurements of the abstracted water. The model is validated by comparison with records of manganese concentrations in the production wells in the period 2006–2021, and other geochemical data. Strategies to monitor future bank filtration schemes with regards to disclosing risk of and source of elevated manganese concentrations are also presented.

### Study area

#### The Kilemoen aquifer and Ringerike waterworks

The study area comprises the Holocene ice marginal delta Kilemoen, deposited ~10,500 years ago during the last
deglaciation (Vorren and Mangerud 2006). The deposit consists of glaciofluvial, unconsolidated sand and gravel, partially covered by and with lamellas of marine clay deposited when seawater inundated the area (see Fig. 2). The glaciofluvial deposit makes up an unconfined aquifer hydraulically connected to River Begna, with >30 m saturated thickness (Vestland 2012). The regional natural groundwater gradient follows the river from north to south, with groundwater recharge north of and discharge south of Kilemoen. Kilemoen comprises many kettle holes, with one of these deemed favorable for Ringerike waterworks’ production well field (Klemetsrud 1985).

Ringerike waterworks started its operation in 1987 with three production wells (no. 1–3) pumping 80–90 L/s on average (see Table 2). Initially, the riverbed was deemed too impermeable for bank filtration; thus, a sand filter for pretreatment of river water and two infiltration wells were established near the riverbank (see “Tjorputten” in Fig. 2) to increase the abstraction capacity (Ellingsen and Finsrud 1990). Though, the sand filter and infiltration wells have been used very sparsely. The precipitation recharge is estimated to be 13 L/s at Kilemoen (Vestland 2012). Stable water levels, while water is pumped out at 80–90 L/s from the aquifer, indicate that bank filtration is active somewhere along the Kilemoen-Begna interface. Now it is assumed that most of the bank filtration occurs north of the production well and in the Tjorputten area.

| Well | Operational since (year) | Total depth (m) | Screened depth (m) | Q (L/s) |
|------|-------------------------|----------------|-------------------|--------|
| PW1  | 1987                    | 47             | 27–47             | 16–21  |
| PW2  | 1987                    | 43             | 23–43             | 16–21  |
| PW3  | 1987                    | 47             | 27–47             | 16–21  |
| PW4  | 2007                    | 33             | 23–33             | a      |
| PW5  | 2007                    | 27             | 16–26             | 14–19  |
| PW6  | 2009                    | 33             | 23–33             | 14–19  |

*aCurrently not in operation due to problems with sand production

Fig. 2  a Map of the study area. Production wells at Ringerike waterworks in enlarged section. Modified from (Geological Survey of Norway 2021). b Profile of the Kilemoen aquifer. Based on drilling logs by Skarphagen (1982) and Klemetsrud (1985). Production well (PW) screen depths are indicated by horizontal lines. Proportional groundwater flow is indicated conceptually. Elevation data retrieved from Norwegian Mapping Authority (2021)
Elevated manganese concentrations: Previous investigations

The dissolved manganese concentrations in the production wells started to increase in 2006 (Fig. 3a), initiating investigations to disclose the problem cause. Test drillings in 2006–2007 showed increasing iron and manganese levels with depth both in the production well kettle hole and near the riverbank at Tjørputten (see Fig. 3b). The total organic carbon (TOC) levels in the aquifer (TOC = 0.1–1.2 mg/L; Fig. 3b) were lower than the yearly average in River Begna in the period 1994–2014 (TOC = 3.27±0.84 mg/L; sampled at Hensfossen in Fig. 2; Lindholm et al. 2015). The depletion of TOC is probably due to oxidation of organic matter from the river water, coupled with the reduction of iron and manganese oxides in a zone near the riverbank. However, this requires that oxygen and nitrate are depleted during infiltration. The river TOC levels equal a chemical oxygen demand COD = 8.72±2.23 mg/L, which is below the oxygen saturation at 5–10 °C (11–13 mg/L). The infiltrating water may however not be fully oxygen saturated, which would facilitate reductive dissolution of oxides.

Elevated manganese concentrations in PW1–PW3 and increasing manganese concentrations with depth (Fig. 3b) led to the drilling of three new, shallower production wells south of the existing wells in 2007 (PW4 and PW5) and 2009 (PW6; see Table 2 and Fig. 2). The new production wells have consistently measured lower manganese concentrations than the older ones. Problems with sand pumping in PW4, probably due to the PW4 well screen’s proximity to a clay lamella, see Fig. 2(b), has kept this well partly out of operation. Meanwhile the manganese concentrations in PW1–PW3 continued to increase after 2006, unconstrained by operational measures, including increased use of infiltration wells and installing variable speed drive pumps in the production wells. Each production well comprises a piezometric well drilled right next to it. None of these piezometric wells have indicated substantial production well clogging (i.e., increasing difference in drawdown in piezometric and production well). Nevertheless, mechanical rehabilitation by brushing and jetting was deployed in 2007 without affecting the manganese concentrations. Eventually, the problems of elevated manganese concentrations constrained a new 100 million NOK (~10 million EUR) water treatment facility in 2018, which has delivered water of satisfactory quality to the water distribution system (Brugger and Paskert 2020). The lack of detailed calculations and hydrochemical measurements hampered this analysis, but set the stage for a more in-depth analysis of the manganese issues at Ringerike waterworks.

Materials and methods

Hydrochemistry data

The raw groundwater quality from five pumping wells (PW1–PW3, PW5, PW6) at Ringerike waterworks was investigated separately by field measurements and water sampling in October 2021. Sensors measuring dissolved
Oxygen (DO; WTW FDO 925), pH (WTW Sensolyt 900-P), electrical conductivity (EC; WTW TetraCon 925/C), oxidation-reduction potential (ORP) (Sensolyt ORP 900-P) and temperature (all sensors) were submerged in a flow-through cell and connected to a WTW Multi 3630 IDS digital meter (Fig. 4). The digital meter performed automatic readings every 30 s for ~1 h, while the flow rate through the cell was kept at ~0.1 L/s. ORP was recalculated to redox potential relative to the standard hydrogen electrode (Eh) by a correction factor given by the electrode supplier. Alkalinity was determined by GRAN titration (Stumm and Morgan 1996) with a Merck MColorTest. Additionally, water samples were taken from each of the field measured production wells. The water samples were first filtered with a 0.45-μm membrane, then acidified with 0.1M HNO₃, and analyzed for major cations and anions by inductively coupled mass spectrometry (ICP-MS; Agilent 8800 ICP-MS Triple Quad) at the Department of Chemistry, NTNU, Norway. The accuracy of the ICP-MS instrument (i.e., % error (absolute) between expected and measured value) was determined from analysis of freshwater reference material.

Results from field measurements and water samples were used as input for the geochemical software PHREEQC v. 3.7.2a (Parkhurst and Appelo 2013) to calculate mineral saturation indices and the electrical balance between cations and anions. Equilibrium constants used for calculating mineral saturation indices were retrieved from the “PHREEQC. DAT” database.

**Manganese sorption model**

One-dimensional (1D) transport of manganese in an aquifer, assuming neglectable dispersion, can be described with the *advection-reaction* equation:

\[
\frac{\partial [\text{Mn}^{2+}]}{\partial t} = \pm \sum_{i=1}^{n} P_i - \text{v} \frac{\partial [\text{Mn}^{2+}]}{\partial x} - S
\]  

where [Mn²⁺] is the manganese concentration, t is time, x is distance from the riverbank in the flow direction, P_i is the rate of chemical precipitation/dissolution reaction involving manganese, v is the average groundwater flow velocity and S is the rate of manganese adsorption.

Adsorption and desorption of dissolved ions (ion exchange) occur instantaneously and can be treated as equilibrium processes if the flow rate is slow enough and if there are no stagnant zones in the porous medium (Appelo and Postma 2005). The groundwater flow velocity at Ringørkile is relatively high (v = 2.5 m/day, Vestland 2012), but comparable to the flow velocity (v = 1.5 m/day) in the Dan Region, Israel, where ion exchange equilibrium was assumed for a similar transport model (Oren et al. 2007). The ion exchange equilibrium assumption facilitates relating the change in dissolved concentration with time (\(\frac{\partial [\text{Mn}^{2+}]}{\partial t}\)) to the adsorption rate S with a manganese *distribution coefficient* K_d (Appelo and Postma 2005):

\[
S = K_d \cdot \frac{\partial [\text{Mn}^{2+}]}{\partial t}
\]  

Equation 2 can be further simplified by assuming that reductive dissolution of manganese oxides only occurs near the riverbank (i.e., at x = 0), and that no other manganese precipitation/dissolution reaction occurs in the aquifer. Inserting Eq. (3) into Eq. (2), combined with mathematical manipulation and the definition of retardation from Eq. (1), yields the *sorption retardation equation* (Appelo and Postma 2005):

\[
\sum_{i=1}^{n} P_i - \text{v} \frac{\partial [\text{Mn}^{2+}]}{\partial x} - S = K_d \cdot \frac{\partial [\text{Mn}^{2+}]}{\partial t}
\]
where \( L \) (~500 m) is the length from the recharge area to the production well area. \( K_d \) depends on the total cation exchange capacity (CEC) of the aquifer sediments, and the composition of cations in solution and their relative tendency to ion exchange for each other:

\[
K_d = \frac{\beta_{Mn} \cdot \text{CEC}}{[\text{Mn}^{2+}]} \tag{5}
\]

where \( \beta_{Mn} \) is the proportion of sorption sites taken up by manganese. Under circum-neutral pH conditions, the CEC primarily depends on the organic matter and clay (<2 μm) concentration of the aquifer matrix (Breeuwsma et al. 1986, in Appelo and Postma 2005):

\[
\text{CEC} \left( \frac{\text{meq}}{100 \text{ g dry soil}} \right) = 0.7 \times (\text{wt.} - \% \text{ clay}) + 3.5 \times (\text{wt.} - \% \text{ organic carbon}) \tag{6}
\]

Grain-size distributions from 40 test drillings in the Kilemoen aquifer demonstrated 39 drillings with no clay, and one with ~10% clay content (Klemetsrud 1985; Skarphagen 1982). The mean ± 2 × standard deviations clay content was approximated to 0.25±0.25%, since the clay did not appear to be normally distributed. The organic carbon content was not measured in any of the sediment samples from Kilemoen. However, two sediment samples from a glaciofluvial aquifer (Gardermoen, ~50 km direct distance away) of the same age as Kilemoen contained 0.17 and 0.21% (0.19±0.06%) organic carbon (Woyessa 2012). These values, together with an effective porosity \( n = 20\% \) (Vestland 2012) and bulk dry aquifer density \( \rho_b = 2.12 \text{ g/cm}^3 \) (i.e., assuming an aquifer matrix consisting of pure quartz), were used to estimate \( \text{CEC} = 0.089\pm0.029 \text{ eq/L water} \). The estimated CEC, together with measured [Mn\(^{2+}\)] and \( \beta_{Mn} \), calculated from cation concentrations in PW1–PW3, were used to calculate \( K_d \) (Eq. 5) and \( R_{\text{sorp}} \) (Eq. 4). See section S1 in the electronic supplementary material (ESM) for calculation of \( \beta_{Mn} \) and detailed deduction of equations.

The sorption processes for PW1–PW3 were also simulated with the ADVECTION, EXCHANGE, and SOLUTION modules in PHREEQC (see Fig. 5). The 500 m aquifer section between the riverbank and production well area was represented by 50 reaction cells, with each cell representing a groundwater solution in equilibrium with cation exchange sites with the average CEC = 0.089 eq/L water. Cell 1–50 was initially equilibrated with groundwater quality as measured in PW1–PW3, except for the manganese concentrations. A [Mn\(^{2+}\)] = 0.007 mg/L measured at Hofsfossen (Bækken et al. 2011) in River Begna (Fig. 2) was chosen to represent the prebank filtration (\( t = 0 \)) aquifer conditions. This value resembled the minimum manganese concentrations measured in the production wells (Fig. 3a). Thus, initially very little manganese was adsorbed. The bank filtration process was simulated by shifting the solutions to increasing cell numbers, and the introduction of a new groundwater quality (cell 0) into cell 1. The solution in cell 0 did not change during the simulation, and comprised manganese concentrations as measured in PW1–PW3. The simulation comprised 4,000 shifts, which equaled 4,000/50 = 80 abstracted pore volumes. Abstracted pore volumes equal time since the start of the simulation/operation (\( t \)) divided by groundwater residence time (\( t_{gw} \)). See section S2 of the ESM for the PHREEQC script.

### Results

The measured raw groundwater chemistry of the production wells at Ringerike waterworks is presented in Table 3. The water samples’ charge balance between cations and anions was not always satisfactory, with imbalance decreasing with increasing total dissolved solids (electrical conductivity). The accuracy of the ICP-MS instrument was generally higher for cations (1.2–4.3 %-error) than anions (66.4 %-error for SO\(_4^{2-}\); 7.1 %-error for Cl\(^-\); see section S3 of the ESM for details). Comparing with previous water samples (Hilmo 2007; Vestland 2012), the field measured alkalinity values were slightly higher in this study. The charge imbalances could thus be due to systematic errors in the anion measurements. Still, the charge imbalances for
the production wells of highest interest (PW1–PW3) were between –5.5 and –10.1%, and thus deemed acceptable for further analysis.

All production wells abstract a circumneutral, Ca–HCO₃ water quality. There is however a marked difference between the deeper (PW1–PW3) and shallower (PW5–PW6) wells, both with regards to electrical conductivity and concentrations of redox-sensitive species. The deeper wells display higher electrical conductivity, higher manganese and lower dissolved oxygen values, indicative of a more reductive redox environment in the deeper parts of the aquifer. Still, wells of similar depth display different hydrochemistry—for instance, the manganese concentrations were two times higher in PW1 than PW3. This could relate to the ratio of bank filtration to native groundwater in the abstracted water. PW1–PW2 probably produce higher ratios of bank filtrated water than PW3 (Fig. 2).

Calculations of mineral saturation indices (SI) with PHREEQC show that all abstracted water at Ringerike waterworks is undersaturated (i.e., SI < 0) both with respect to manganese oxides (MnOOH) and manganese and calcium carbonates (MnCO₃, CaCO₃, see Table 4). Thus, the groundwater will tend to dissolve rather than precipitate these minerals. It is also noteworthy that redox potentials (0.3 ≤ Eh ≤ 0.4 V) were comparable for all wells, despite oxygen concentrations ranging from 0.3 to 6.7 mg/L (Table 4). Oxidation of manganese at pH ~7 occurs at Eh ≥ 0.6 V (Appelo and Postma 2005). This implies that oxygenation, which probably occurs in the vicinity of the abstraction wells (Farnsworth and Hering 2011), is not sufficient to trigger oxidation of manganese. This can be explained by oxidation of manganese’s slow kinetics, as compared with iron (Stumm and Morgan 1996). The redox potentials are well within levels where oxidation of iron is expected to occur (Eh > 0 V), indicating iron oxides as the stable iron phase (Appelo and Postma 2005), and explaining the low iron concentrations in the abstracted water (see Table 3).

\[
\begin{align*}
\text{Table 3 Raw groundwater chemistry 12–14 October 2021 at Ringerike waterworks. } Eh \\
\text{redox potential referring to the normal hydrogen electrode, } DO \text{ dissolved oxygen, } EC \text{ electrical conductivity, } Temp. \text{ temperature, } Alk \text{ alkalinity}
\end{align*}
\]

| Parameter | PW1 a | PW2 a | PW3 a | PW5 a | PW6 a |
|-----------|-------|-------|-------|-------|-------|
| pH b      | 6.77 ±0.04 | 7.00 ±0.03 | 6.94 ±0.02 | 6.74 ±0.02 | 6.80 ±0.03 |
| Eh (mV) c | 362 ±5 | 343 ±7 | 337 ±5 | 404 ±28 | 365 ±23 |
| DO (mg/L) b | 1.23 ±0.01 | 0.31 ±0.01 | 0.67 ±0.01 | 6.73 ±0.01 | 2.38 ±0.20 |
| EC (μS/cm) b | 1.49 ±1 | 1.89 ±3 | 1.60 ±0.1 | 0.82 ±0.1 | 1.20 ±0.1 |
| Temp. (°C) b | 7.4 ±0.2 | 7.2 ±0.1 | 6.9 ±0.1 | 6.7 ±0.1 | 7.2 ±0.1 |
| Alk (mmol/L) c | 1.3 ±0.2 | 1.6 ±0.1 | 1.4 ±0.2 | 0.9 ±0.2 | 1.2 ±0.4 |
| Fe²⁺ (mg/L) d | 0.01 ±0.00 | 0.00 ±0.00 | 0.01 ±0.00 | 0.00 ±0.00 | 0.01 ±0.00 |
| Mn²⁺ (mg/L) d | 0.68 ±0.01 | 0.85 ±0.02 | 0.30 ±0.00 | 0.00 ±0.00 | 0.03 ±0.00 |
| Na⁺ (mg/L) d | 3.88 ±0.02 | 5.58 ±0.09 | 5.47 ±0.03 | 2.35 ±0.03 | 3.39 ±0.06 |
| Mg²⁺ (mg/L) c | 3.84 ±0.06 | 4.46 ±0.06 | 4.35 ±0.03 | 1.92 ±0.03 | 2.93 ±0.09 |
| Ca²⁺ (mg/L) d | 15.41 ±0.12 | 20.12 ±0.22 | 15.43 ±0.09 | 8.38 ±0.12 | 13.30 ±0.21 |
| K⁺ (mg/L) d | 2.22 ±0.03 | 2.29 ±0.04 | 1.98 ±0.02 | 1.41 ±0.01 | 1.82 ±0.03 |
| Cl⁻ (mg/L) d | 2.80 ±0.40 | 4.59 ±0.25 | 4.81 ±0.29 | 1.03 ±0.09 | 1.97 ±0.08 |
| SO₄²⁻ (mg/L) d | 6.02 ±0.04 | 8.15 ±0.08 | 9.53 ±0.13 | 4.61 ±0.04 | 6.26 ±0.11 |
| Charge balance e | –8.0% | –5.5% | –10.1% | –17.9% | –11.6% |

Each well was sampled and field measured once (n = 1)

Values given as mean ± 2 × standard deviations (SD) during ~1 h of continuous measurement (every 30 s) in flow through cell.

Values given as mean ± 2 × SD of three Gran titrations

Values given as mean ± root square deviation of ICP-MS instrument measurements

\[
\sum\text{Cations} - \sum\text{Anions} \text{ (in equivalents)}
\]

The \( K_d \) and \( R_{sorp} \) for production wells PW1–PW3 were estimated to be 44±18 and 45±18, respectively. The uncertainties in the estimates were relatively large (~40%) and depend on (1) the uncertainty of clay content, (2) the uncertainty of organic matter content of the soil, and (3) variation in the cation composition (\( \beta_{Mn} [\text{Mn}^{2+}] \)) of the groundwater (see Eqs. 4–6). Their relative importance to the uncertainty were calculated to be 25% (clay), 36% (organic

\[
\begin{align*}
\text{Table 4 Saturation indices for rhodochrosite (MnCO₃), manganite (MnOOH) and calcite (CaCO₃)}
\end{align*}
\]

| Production well | Saturation index (SI) |
|----------------|----------------------|
|                | MnCO₃    | MnOOH    | CaCO₃    |
| PW1           | –0.56    | –3.57    | –1.68    |
| PW2           | –0.17    | –3.16    | –1.26    |
| PW3           | –0.73    | –3.86    | –1.49    |
| PW6           | –1.91    | –4.79    | –1.75    |
matter) and 39% (cation composition), demonstrating that the cause of uncertainty is relatively evenly distributed.

PHREEQC-simulated concentrations of calcium, chloride and manganese in PW2 are displayed in Fig. 6. Calcium first increases due to ion exchange, with manganese replacing calcium at exchange sites. Chloride values remain constant since anions do not participate in sorption processes. Manganese concentrations start to increase after ~20–30 abstracted pore volumes. The “S-shaped” curvature of the simulated manganese concentrations, with a gradual increase in manganese concentrations up until a maximum level, is due to $K_d$’s dependency on the solute concentration of manganese and other cations (Eq. 5). Ca$^{2+}$ and other major cations (Mg$^{2+}$, K$^+$, Na$^+$) decrease, while manganese concentrations increase. This is because cation exchange sites are becoming saturated with respect to manganese. Consequently, less major cations become desorbed. When ion exchange equilibrium is reached in the entire aquifer (i.e., after ~50 abstracted pore volumes), manganese concentrations stabilize meanwhile Ca$^{2+}$ and other cations return to its level at time zero (= 0 abstracted pore volumes).

Discussion

Simulated manganese concentrations from the PHREEQC sorption model are plotted versus observed concentrations in Fig. 7. The simulated ($R_{\text{sim}}$) and observed ($R_{\text{obs}}$) manganese retardation is read off as the number of abstracted pore volumes before manganese concentrations start to increase and stabilize at an elevated level. The observed manganese concentrations resemble the curvature of the simulated ones. An especially good fit is observed for PW2 ($R^2 = 0.90$), while simulations for PW1 ($R^2 = -0.08$) and PW3 ($R^2 = -0.82$) predict breakthrough of the sorption front later than the observed increase in manganese concentrations. This indicates that the sorption capacity of the aquifer sediments is sufficient to delay manganese transport to the production wells in the Kilemoen aquifer, and that it serves as a possible explanation for the observed retardation of manganese.

**Fig. 6** PHREEQC simulated concentrations of Ca$^{2+}$, Cl$^-$ and Mn$^{2+}$ in production well PW2 versus numbers of abstracted pore volumes $= t/t_{gw}$, where $t$ = time since start of simulation and $t_{gw}$ = groundwater residence time.

**Fig. 7** PHREEQC-simulated (“model”) and observed manganese concentrations in production wells PW1–PW3 plotted vs. abstracted pore volumes $= t/t_{gw}$, where $t$ = time since start of operation/simulation and $t_{gw}$ = groundwater residence time. Abstracted pore volumes matched with date, assuming $t_{gw} = 200$ days, and start of operation on 1 January 1987.
strengthen the hypothesis of sorption controlling the elevation of manganese concentrations after longtime operation. Firstly, the model assumes that neither mineral precipitation nor dissolution occurs between the riverbank and production well area (0 < x ≤ L). The manganese mineral subsaturations (Table 4) indicate that manganese may be (reductively) dissolved in the water phase near the abstraction wells, in addition to near the riverbank. The manganese retardation due to sorption $R_{\text{sorp}}$ would represent an underestimate if manganese-containing minerals dissolve closer to the abstraction well than the model assumes. Furthermore, silicate and carbonate dissolution adding cations to the groundwater is expected to occur between the riverbank and abstraction wells. For instance, all water samples in Table 4 are undersaturated with respect to calcite. Water samples indicate higher ratios of dissolved manganese to other cations in test wells near the riverbank (Hilmo 2007) than in the production wells (Table 3). A larger proportion of manganese to other cations would increase the relative tendency of manganese to occupy sorption sites ($\mu_{\text{Mn}}$), and thus increase the manganese sorption retardation $R_{\text{sorp}}$.

Furthermore, the clay concentrations vary considerably, as shown on the map and in drilling logs in Fig. 1. In all, 39 out of 40 test sediment samples displayed no clay present, which could indicate groundwater flow paths with no clay present. In this case, the average $R_{\text{sorp}}$ for PW1–PW3 would be reduced to 36±14, which would lead to a better fit of the modeled to observed data for PW1 and PW3 (see Fig. 7).

Lastly, no organic matter measurements were available for the Kilemoen aquifer. Instead, the analysis relied on two sediment samples from another aquifer (Gardermoen, ~50 km direct distance away) of the same age (~10,500 years old).

Other retardation explanations should also be tested before concluding whether sorption is the main controller of manganese transport in the Kilemoen aquifer. Since the abstraction wells have not experienced severe clogging issues, changes in water quality due to new inflow paths around the production wells are thus not probable. This is also as expected from the subsaturation with respect to manganese oxides and carbonates (Table 4) and low iron concentrations (Table 3). Manganese oxide and carbonate subsaturations also increase the risk of a manganese sorption front reaching the production wells, since no precipitation sequestration of manganese can be expected (Farnsworth and Hering 2011). Thus, mineral saturation calculations strengthen the hypothesis of sorption controlling the elevated manganese concentrations after longtime operation.

Additionally, the operational scheme did not change (e.g., establishing of new production wells or increasing pumping rate) prior to the increasing manganese concentrations in 2006. The introduction of a new groundwater flow path leading to extraction of groundwater with longer residence time and/or more reductive conditions is thus deemed unlikely. This further points to sorption as the most probable cause of delayed manganese increase in the production wells.

Laboratory experiments by Petrunic et al. (2005) showed that the microbial community needed time to adapt to changing redox conditions. Still, the microbial activity could not explain the delayed manganese enrichment alone, neither in the laboratory experiments nor the bank filtration scheme at New Brunswick, Canada (see Table 1). Regular measurements of the inorganic (CO$_2$, Ca$^{2+}$, alkalinity, pH) and organic (TOC) carbonate system would be valuable to assess delays in microbial community growth, as one would expect more CO$_2$ and less TOC in the water when the microbial activity intensifies. Unfortunately, however, sparse carbonate-system measurements have been collected from the Ringerike waterworks.

The authors deem sorption as the most probable cause of delayed elevated manganese concentrations. This is because neither introduction of a new flow path, either locally around the production wells or in the aquifer, nor changes in the microbial community seem to be able to explain the retardation alone and/or in a more satisfactory manner than the presented sorption model shown in Fig. 7. Still, more data on sediment composition (organic and clay content) and water quality over time would have reduced the uncertainty associated with this conclusion.

The estimated TOC value for the Kilemoen aquifer seems representative of other glaciofluvial aquifers in Norway. Five sediment samples from a younger glaciofluvial aquifer (~10,200–10,500 years old, Olsen 2008) in Lillehammer, Norway, displayed a median (range) of TOC = 0.26% (0.08–1.07%; Holmstrøm et al. 2010). Two sediment samples from an older glaciofluvial deposit (~12,500 years old (Vorren and Mangerud 2006)) displayed loss on ignition LOI = 0.15 and 0.42% (Riise 2015; Stenvik et al. 2022). TOC values of 0.09 and 0.24% could be estimated from the LOI values by dividing with van Bemmels’s factor (= 1.724) (Holmstrøm et al. 2010). Despite relatively sparse data, the measured TOC values indicate that Norwegian glaciofluvial aquifers can have a significant Mn$^{2+}$ sorption retardation capacity, which may be further increased if clay is present (Eq. 6).

Mn$^{2+}$ retardation due to sorption and changes in the microbial community may explain why all occurrences (known to the authors) of elevated manganese concentrations after longtime bank filtration have occurred in glaciofluvial deposits (see Table 1). Additionally, manganese retardation due to sorption was observed during sewage reclamation by infiltration to the aquifer in the Dan Region, Israel (Oren et al. 2007). For all these manganese retardation cases, there seems to be limited or at least less organic
material in the depositional environment than the infiltrating water. This implies that more oxic groundwater conditions prevailed during natural prebank filtration conditions, which limited dissolved and hence adsorbed manganese in the aquifer. Furthermore, the aquifer formations had excess manganese sorption capacity available when the redox geochemistry changed (i.e., when abstraction wells in the aquifer induced bank filtration).

**Monitoring of sorption fronts in bank filtration settings**

If the elevated manganese concentrations are due to a sorption front moving from the bank filtration to the production well area, water quality sampling in an observation well between the bank filtration and production well area would be valuable.

The observation well would facilitate both detection of the sorption before it reaches the production well(s) and assessment of the degree of success of in-situ remediation measures. The location of the observation well has certain implications: the closer to the infiltration area the observation well is located, the longer time is available to implement the remedies and the sooner remediation actions can be evaluated, if these actions are applied in the bank filtration area (e.g., establishing an infiltration basin/well). Sooner implementation of remedies is also of great significance, since the amount of adsorbed manganese must first be desorbed and flushed out of the aquifer before the aquifer returns to its original state with low manganese concentrations. This could explain why measures that were undertaken at Ringerike waterworks in 2006–2007 (i.e., running the sand filter and infiltration wells near the riverbank) did not reduce the manganese concentrations in the short term.

According to Fig. 6, a manganese sorption front would result in a gradual increase in manganese, meanwhile other cation concentrations gradually decrease. Thus, major cations versus dissolved manganese time series could indicate whether sorption causes the delayed breakthrough of manganese in observation/production wells. Regular water quality sampling should be performed in the observation wells, both by field measurements (pH, O₂, EC, Eh, T, alkalinity) in a flow-through cell and water samples for laboratory analysis (major cations and anions, iron and manganese, TOC), to keep track of the water quality versus time. The authors suggest at least one full water quality assessment per year.

The example from Ringerike waterworks demonstrates the value of water quality monitoring of bank filtration schemes. Issues with elevated Mn²⁺ concentrations, the operational scheme and aquifer conditions at Ringerike are representative of many other Norwegian waterworks (Table 1). Similar bank filtration waterworks in glaciofluvial aquifers in Norway and abroad are thus advised to implement the aforementioned monitoring during operation.

**Conclusions**

The elevated concentrations of manganese in the Kilemoen aquifer are most likely caused by reductive dissolution of manganese oxides near the riverbank, induced by bank filtration of organic-rich river water. This is deduced from depth-specific water sampling near the riverbank, which displays higher iron and manganese and lower TOC values in the groundwater compared with the river water.

Manganese concentrations in the production wells at Ringerike waterworks ~500 m away from the riverbank started to increase 19–27 years after start of operation, depending on the well location. This equals a retardation in the range 36 < R_{obs} < 50, assuming groundwater residence time t_{gw} ~200 days. Similar retardation (R_{sorp} = 45±18) was estimated with a simplified advection-sorption model, considering sorption as the only retardation factor. This shows retardation due to sorption is a possible explanation to the observed manganese retardation, although rather large uncertainty is associated with the rather sparse input data and simplified advection-reaction model.

For similar bank filtration schemes, it is recommended to establish an observation well between the production well area and the riverbank that is water sampled and field measured regularly to monitor possible manganese sorption fronts moving toward the production well field. This would enable planning and evaluation of measures to reduce manganese concentrations before they break through to the production well field. Locating the observation well closer to the riverbank will (1) allow more time to execute remediation measures and more rapid evaluation of these and (2) require less manganese to be desorbed and flushed out of the aquifer during remediation.

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References

Appelo CAJ, Postma D (2005) Geochemistry, groundwater and pollution, 2nd edn. Balkema, Amsterdam

Bærken T, Kile MR, Skryseth LM, Eriksen TE (2011) Resipienttunderdsøkelse av Begna, Randselela og Tyrifjorden i 2010 i forbindelse med utslipp fra Norske Skog Follum ASA og Huhtamäki Norway AS [Recipient survey of Begna, Randselela and Tyrifjorden in 2010 in response to pollution from Norske Skog Follum ASA and Huhtamäki Norway AS]. NIVA report 6189-2011, Norwegian Institute for Water Research (NIVA), Oslo, Norway. https://niva.braga.unit.no/niva-xmuli/bitstream/handle/11250/2155206189-2011_72dpi.pdf. Accessed Sept 2022

Bourg ACM, Bertin C (1994) Seasonal and spatial trends in manganese solubility in an alluvial aquifer. Environ Sci Technol 28(5):868–876. https://doi.org/10.1021/es930054d018

Breeuwsma A, Wüsten H, Vleschouwer J, Slobbe A, Bouma J (1986) Derivation of land qualities to assess environmental problems from soil surveys. Soil Sci Soc Am J 50(1):186–190. https://doi.org/10.2136/sssaj1986.0361599500500010035x

Bruggen P, Paskert P (2020) Groundwater plant with treatment system to remove manganese. Water Solutions (2). https://www.hydrogroup.de/fileadmin/redakteur/pdf/fachberichte/twa/2020-02-water-solutions-groundwater-plant-with-system-to-remove-manganese.pdf. Accessed Sept 2022

Dawre MR (2006) Assessing infiltration velocities during riverbank filtration. MSc Thesis, University of New Brunswick, Fredericton, NB, Canada

Dillon P (2005) Future management of aquifer recharge. Hydrogeol J 13(1):313–316. https://doi.org/10.1007/s10040-004-0413-6

Ellingsen K (1992) Grunnvannskvalitet: problemer og tiltak [Groundwater quality: problems and preventive measures]. GIN guide no. 12. Skriften 106, Geological Survey of Norway, Trondheim, Norway. https://www.ngu.no/upload/Publikasjoner/Skrifter/GIN-veileder_nr12.pdf. Accessed Sept 2022

Ellingsen K, Finsrud R (1990) Grunnvannsanlegg - eksempler [Groundwater works: examples] GIN-guide no. 5, Skriften 101, Geological Survey of Norway, Trondheim, Norway. https://www.ngu.no/upload/Publikasjoner/Skrifter/GIN-veileder_nr5.pdf. Accessed Sept 2022

Farnsworth CE, Hering JG (2011) Inorganic geochemistry and redox dynamics in bank filtration settings. Environ Sci Technol 45(12):5079–5087. https://doi.org/10.1021/es2001612

Geological Survey of Norway (2021) GRANADA: Nasjonal grunnvannsdatabase [GRANADA: national groundwater database]. http://geo.ngu.no/kart/granada_mobil/. Accessed 23 June 2021

Hilmo BO (2007) Undersøkelsesboringer ved Tjortputten: oppsummering av resultater og forslag til videre arbeid [Test drillings at Tjortputten: summary of results and proposals for further work]. 514555 – Nye brønner til Ringerike vannverk, Asplan Viak AS, Trondheim, Norway. https://www.ngu.no/upload/Publikasjoner/Eksterne-grunnvannsrapporter/VRL46_2008_010a_ful.pdf. Accessed Sept 2022

Hiscock KM, Grischek T (2002) Attenuation of groundwater pollution by bank filtration. J Hydrod 266(3):139–144. https://doi.org/10.1016/S0022-1694(02)00158-0

Holmström P, Rudolph-Lund K, Sørlie JE (2010) Korgen vannverk: hydrogeologisk og vannkjemisk tilstandsvurdering av brønner [Korgen waterwork: hydrogeological and chemical assessment of groundwater wells]. NGI report 20081232-00-1-R, Norwegian Geotechnical Institute (NGI), Oslo

Houben G, Treskatis C (2007) Water well rehabilitation and reconstruction. McGraw-Hill, New York

Klemetsrud T (1985) Ringerike vannverk - Kilemoen: pilotboringer i grop 8, og ved Tjortputten [Ringerike waterwerk - Kilemoen: pilot drilling in kettle hole 8 and at Tjortputten]. NGU report 86009, Geological Survey of Norway, Oslo, Norway. https://www.ngu.no/publikasjoner/riinkerievein-kilemoen-pilotboringer-i-grop-8-og-ved-tjortputten. Accessed Sept 2022

Knutsen G (2008) Hydrogeology in the Nordic countries. Episode 31. https://doi.org/10.18814/epiusgs/2008v31/020

Kraft P (2011) Beskyttelse av røvannskilden til Bø vannverk [Protection of Bø waterworks’ groundwater source]. 522947 – Reguleringsplan for beskyttelse av Bø vannverk, Asplan Viak AS, Ås, Norway. http://webhost3.is.gisline.no/GisLinePlanarkiv/082102_32_2009/Dokumenter/Beskyttelsesplan.pdf. Accessed Sept 2022

Kvitsand HML, Mørkel M, Fiksdal L, Østerhus SW (2017) Evaluation of bank filtration as a pretreatment method for the provision of hygienically safe drinking water in Norway: results from monitoring at two full-scale sites. Hydrogeol J 25(5):1257–1269. https://doi.org/10.1007/s10040-017-1576-2

Lindholm M, Vogelsang C, Engebretsen A, Kverna S, Eggstedt HO, Selvik JR (2015) Forurensningsregnskap for Ringerike kommune [Accounting for pollution in Ringerike municipality]. NIVA report 6873-2015, NIVA, Oslo, Norway. https://niva.braga.unit.no/niva-xmuli/bitstream/handle/11250/285876/6873-2015_72dpi.pdf?sequence=3&isAllowed=y. Accessed Sept 2022

Norwegian Mapping Authority (2021) Høydedata [Elevation data]. https://hydrodata.no/LaserInnsyn/. Accessed 27 Oct 2021

Olsen L (2008) Kvartærgeologi i Lillemammer kommune: beskrivelse til løsmassekart M 1:50 000 [Quaternary geology in Lillemam-mer municipality: description to map M 1:50 000]. NGU report 2008.031, Geological Survey of Norway, Trondheim, Norway. https://www.ngu.no/upload/Publikasjoner/Rapporter/2008/2008_031.pdf. Accessed Sept 2022

Oren O, Gavrieli I, Burg A, Gutman J, Lazar B (2007) Manganese mobilization and enrichment during soil aquifer treatment (SAT) of effluents, the Dan Region Sewage Reclamation Project
Riise MH (2015) Praktisk guide for grunnvarmeanlegg basert på oppumpet grunnvann [Practical guide for ground water heat pump systems]. MSc Thesis, Norwegian University of Science and Technology, Trondheim, Norway. https://ntuopen.ntnu.no/ntnu-xmui/handle/11250/2350389. Accessed Sept 2022

Petrunic BM, MacQuarrie KTB, Al TA (2005) Reductive dissolution of Mn oxides in river-recharged aquifers: a laboratory column study. J Hydrol 301(1):163–181. https://doi.org/10.1016/j.jhydrol.2004.10.1021

Silvey WD, Johnston HE (1977) Preliminary study of sources and processes of enrichment of manganese in water from University of Rhode Island supply wells. US Geological Survey Open file Rep 77 561. http://pubs.er.usgs.gov/publication/ofr77561. Accessed Sept 2022

Stenvik LA, Gjengedal S, Ramstad RK, Frengstad BS (2022) Hydrochemical and biotic control on iron incrustations in groundwater heat pump systems: case study from a saline, anoxic aquifer in Melhus, Norway. Geothermics 100. https://doi.org/10.1016/j.geothermics.2022.102349

Stenvik LA, Gjengedal S, Ramstad RK, Frengstad BS (2022) Hydrochemical and biotic control on iron incrustations in groundwater heat pump systems: case study from a saline, anoxic aquifer in Melhus, Norway. Geothermics 100. https://doi.org/10.1016/j.geothermics.2022.102349

Vestland M (2012) Klausuleringsplan for Ringerike vannverk Kilemoen [Protection plan for Ringerike waterworks Kilemoen]. 529119 – 2-%C3%A9vensutkast med eksempler fra Ringerike og Sunndal vannverk [Iron and manganese problems under groundwater abstraction with cases from Ringerike and Sunndal waterworks]. Vann 55(2):151–161. https://vannforeningen.no/dokumentarkiv/jern-og-manganproblem-avdeling-vannavdeling-med-eksempler-fer-avdeling-vannavdeling/

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