Manganese removal processes at 10 groundwater fed full-scale drinking water treatment plants
I. L. Breda, L. Ramsay, D. A. Søborg, R. Dimitrova and P. Roslev

ABSTRACT

Manganese (Mn) removal in drinking water filters is facilitated by biological and physico-chemical processes. However, there is limited information about the dominant processes for Mn removal in full-scale matured filters with different filter materials over filter depth. Water and filter material samples were collected from 10 full-scale drinking water treatment plants (DWTPs) to characterise the Mn removal processes, to evaluate the potential use of enhancers and to gain further insight on operational conditions of matured filters for the efficient Mn removal. The first-order Mn removal constant at the DWTPs varied from $10^{-2}$ to $10^{-1}$ min$^{-1}$. The amount of Mn coating on the filter material grains showed a strong correlation with the amount of iron, calcium and total coating, but no correlation with the concentration of ATP. Inhibition of biological activity showed that Mn removal in matured filters was dominated by physico-chemical processes (59–97%). Addition of phosphorus and trace metals showed limited effect on Mn removal capacity, indicating that the enhancement of Mn removal in matured filters is possible but challenging. There was limited effect of the filter material type (quartz, calcium carbonate and anthracite) on Mn removal in matured filters, which can be relevant information for the industry when assessing filter designs and determining returns of investments.

Key words | ammonium, filter material, phosphorus, removal capacity, sodium azide, trace metals

INTRODUCTION

Drinking water treatment from groundwater sources in Denmark is based on aeration and biofiltration (single or double stage). Bacteria play an essential role in the removal of ammonium (NH$_4$), while iron (Fe) may be removed chemically following aeration. Removal of manganese (Mn) involves both biological and physico-chemical processes, but knowledge regarding the role of these mechanisms is very limited in fully matured, full-scale filters (Sahabi et al. 2009; Bruins et al. 2015; Breda et al. 2018).

Recent studies suggest that after a short initial sorption phase, Mn removal by a non-coated virgin filter material is initially biological, evolving to a predominantly physico-chemical removal process over time (Sahabi et al. 2009; Bruins et al. 2015; Breda et al. 2018). Sahabi et al. (2009) characterised the Mn removal processes in a drinking water treatment plant (DWTP) using filter material samples collected from a specific depth of six full-scale matured filters with 3 and 15 years of maturation. Bruins et al. (2015) characterised the origin of Mn oxides coating filter material samples collected from the top layer of a virgin quartz filter column during the initial 2 years of maturation. To the authors’ knowledge, characterisation of the Mn removal processes occurring at different depths of matured filters using different filter materials and located at different full-scale drinking water treatment plants (DWTPs) has not been reported.

Inadequate Mn removal in previously well-functioning, fully matured filters has been reported in the previous study (Bruins et al. 2014). Review of operational conditions for
efficient Mn removal in matured filters and investigation of possible performance enhancers could potentially help utilities combat Mn breakthrough and/or increase the resilience to variations in flow and concentration in functional filters.

Enhancement strategies promoting NH$_4$ removal capacity of matured filters have been investigated in previous studies, especially the addition of trace metals (TM) and phosphorus (P) to enhance nitrification (de Vet et al. 2012; Wagner et al. 2017). Hence, the addition of key elements to nutrient-limited matured filters could potentially enhance Mn oxidation facilitated by biological processes.

The changes observed in the Mn removal process over time (Sahabi et al. 2009; Bruins et al. 2015) suggest that the filter maturation period continues after the end of the start-up period. Full maturation is a state in which only limited variation over time occurs with respect to the physico-chemical and biological aspects of the surface of the filter material coating, e.g., surface area and charge, surface composition and microbial community (abundance, diversity and activity). The duration of the period between completed start-up and full maturation is unknown and likely dependent on operational conditions and source water quality.

The present study contributes to the overall knowledge of drinking water filters by collecting both water and filter material samples over depth at 10 full-scale DWTPs with different stages of maturation. This study aimed to characterise the Mn removal processes (biological or physico-chemical) occurring at different filter depths and to evaluate the potential use of TM and phosphorus to enhance the Mn removal capacity of matured filters. In addition, this study provides practical advice that can be used by water utilities to manage operations and to obtain efficient Mn removal, such as the role of filter material coating and the importance of filter material selection.

**MATERIALS AND METHODS**

**Sampling at 10 DWTPs**

This study investigated 10 DWTPs treating groundwater in Denmark: five located in Aarhus and five located in Odense (Dalum, Elsted, Holmehaven, Hovedverket, Kasted, Lindved, Lunde, Stavtrup, Truelsbjerg and Østerby DWTP, labelled DWTP1–10). Location and multivariate analysis of the groundwater quality feeding each DWTP is available in the Supplementary Materials (available with the online version of this paper). The effluent water of each DWTP complies with the drinking water national criteria (BEK 1068 2018). Mn was efficiently removed to below the national criterion of 0.05 mg/L at all DWTPs over the last 20 years.

The removal of iron (Fe), NH$_4$ and Mn by the DWTPs included in this study occurs in the first filter. In the present investigation, water and filter material samples were collected from the first filter of each DWTP before backwash, i.e., at the end of the ripening cycle of the filter.

Water samples (100 mL) were collected at the filter's inlet, every 10 cm within the filter bed and at the filter's outlet. Collection of filter bed water samples was accomplished by a multiple-depth sampling device with separate screens every 10 cm, which was lowered into the filter bed during backwash and left in the filter until the following backwash. Water samples were withdrawn from the screens with a multichannel peristaltic pump (Cole Parmer, USA). Samples for analysis of chemical parameters were collected after pH, redox, oxygen (O$_2$) and temperature levels were stable in the withdrawn water. Inline measurements of pH, redox and temperature were recorded using a digital pH electrode (SENTIX940), a redox sensor (ORP-T900), an optical dissolved O$_2$ sensor (FDO 925) and a Multi 3,430 meter (WTW GmbH, Germany). Redox measurements were corrected to temperature conditions of 10 °C. Filtered (0.45 μm) and non-filtered water samples were analysed for Fe and Mn (DIN EN ISO 17294-2: 2017-01, Agrolab, Germany), and non-filtered water samples were analysed for NH$_4$ (DIN ISO 15923-1: 2014-07, Agrolab, Germany). Treated water (15 L) was collected at each DWTP to use in batch experiments (described later in this section).

Filter material was sampled after draining of the filters overnight. Filter material samples (approximately 500 g) were collected from the filter bed over 20 cm depth intervals. This was accomplished with a sampling device constructed with a 50-mm PVC pipe lowered into the sand bed and a shop vac to lift the sand through the pipe and into a 500 mL blue-cap sampling flask, after separating sand and air/water in a hydrocyclone. After the pipe was lowered 20 cm, the flask was replaced with a new one, and the pipe was lowered another 20 cm.
Characterisation of matured filter material

The filter material total coating mass was calculated by subtracting the mass of the grains before and after acid digestion and drying. Acid digestion was conducted at room temperature in triplicates using approximately 2 g of dried filter material in a 50 mL mixture of 4 M hydrochloric acid (HCl, Merck KGaA) and 2 g/L oxalic acid (C₂H₂O₄, Merck KGaA) as described by De Vet et al. 2009. The filter material type (e.g., sand, anthracite) was classified visually after acid digestion. The filter material coating composition (Fe, Mn, Ca and P) was determined by Eurofins (Denmark), after acid digestion, following Standard Methods 3120 (APHA/AWWA/WEF 1989).

Batch experiment to assess the effect of NaN₃ and NH₄ on the Mn removal capacity

A batch experiment was conducted to investigate the Mn removal capacity in the presence of NaN₃ and NH₄ using filter material from each DWTP collected over 20 cm depth intervals. Filter material (5 g) was placed in nine serum bottles with 50 mL treated water (collected at the same DWTP as the filter material). Three of the bottles were pretreated by spiking with a 25 mM solution of NaN₃ (Merck KGaA) to inhibit biological activity. All bottles were then placed on a shaker (100 rpm) and incubated overnight at 16 °C. After the incubation period, the bottles were spiked with Mn (MnCl₂·4H₂O, Emsure ACS) and NH₄ (NH₄Cl, Bie&Berntsen), resulting in an initial concentration of 1 mg/L Mn and 1 mg/L NH₄. Aliquots (2.5 mL) were collected after 1 h and 1 h and 30 min, filtered (0.22 μm), and analysed for Mn and NH₄ as described previously. The bottles were shaken (100 rpm) at 16 °C during the experiment.

First-order removal constant and removal capacity

The removal constant was calculated for each full-scale filter at each 10 cm depth interval assuming the first-order removal, as follows:

\[
\frac{d[C_{\text{out}}]}{dt} = -k[C_{\text{in}}] \Rightarrow k = -\frac{\ln\left(\frac{C_{\text{out}}}{C_{\text{in}}}ight)}{t}
\]

where \(k\) is the first-order removal constant (min⁻¹), \(C_{\text{in}}\) and \(C_{\text{out}}\) are the total concentration of C in water samples collected at the top and bottom of each depth interval (mg/L), and \(t\) is the empty bed contact time (EBCT) at each depth interval (min), which can be calculated as follows:

\[
\text{EBCT} = \frac{\text{depth interval}}{v}
\]

where depth interval is the distance between sampling ports placed across the full-scale filter depth (0.01 m) and \(v\) is the filtration rate of the full-scale filter (m/min).
The removal capacity $R_c$ of the filter material ($\mu$g/min/g) was determined through the batch assays (previously described). The constant $k$ (min$^{-1}$) was determined as the slope of the first-order regression of $C$ (mg/L) over time $t$ (min) by replacing $C_{in}$ and $C_{out}$ with $C_{initial}$ and $C_{final}$, respectively in Equation (1). $R_c$ was then calculated by multiplying $k$ (min$^{-1}$) by the quotient of the initial mass of the substrate $m_{sub}$ (g) and the mass of the filter material sample used in the batch $m_{fm}$ (g), as follows:

$$R_c = k \frac{m_{sub}}{m_{fm}}$$  \hspace{1cm} (3)

Statistics

Data analysis was performed in R (R Core Team 2017). The difference between conditions in batch assays was evaluated using the non-parametric Mann–Whitney test. Correlations between variables were examined with a scatterplot and calculation of the Pearson correlation coefficient. Shapiro test was used to evaluate the normality of Mn $R_c$ of each DWTP. Analysis of variance (ANOVA) was used to investigate the effect of filter material type on Mn removal capacity and filter material age on Mn coating.

RESULTS AND DISCUSSION

First-order removal constant at each DWTP

Drinking water filters are often composed of single or dual filter material. In the present study, two filters were composed of single filter material (DWTP3 with sand and DWTP9 with calcium carbonate), and eight filters were composed of dual filter materials (sand and anthracite). Some of those filters showed a complete mix of filter material throughout the filter depth (DWTP2, DWTP5 and DWTP10), while others showed a strong stratification (DWTP1 and DWTP8; Figure 1(a)).

Water samples collected from each 10 cm depth intervals of the filters at the 10 DWTPs were used to calculate $k$. Figure 1(b) shows approximate linearity between ln($[\text{Mn(II)}_t]/[\text{Mn(II)}_0]$) and EBCT for each DWTP, suggesting that Mn removal can be approximated by a first-order removal. The first-order removal constant $k$ (min$^{-1}$) was determined for each DWTP as the slope from the linear regression between ln($[\text{Mn(II)}_t]/[\text{Mn(II)}_0]$) and EBCT and varied from 0.02 to 0.17 min$^{-1}$ between DWTPs (Figure 1(c)). Similar values (0.0001–0.120 min$^{-1}$ and 0.17 min$^{-1}$) were reported by Vries et al. (2017) for heterogeneous Mn removal at five DWTPs and by Katsoyiannis & Zouboulis (2004) in a column, filter treating groundwater, respectively.

The pH and redox measurements in water samples at each 10 cm depth from the 10 DWTPs showed an increase in redox potential with filter depth (Figure 1(d)). A similar increase of redox potential along with the filter depth in filters removing Fe, Mn and NH$_4$ has been reported previously (Tekerlekopoulou & Vayenas 2008).

Some studies in Mn removal by drinking water filters suggest that there is a ‘Field of biological Mn removal’ limited by pH and redox potential (shaded area in Figure 1(d), Mouchet 1992; Burger et al. 2008; Dangeti et al. 2017). The pH and redox at most depths investigated in the present study fall within this field, suggesting that the filters investigated in this study were running under pH and redox values suitable for the biological removal of Mn. Furthermore, higher values of removal constants were registered within the ‘Field of biological Mn removal’ than outside of this area, indicating that biological conditions for Mn removal could potentially contribute to higher values of $k$.

Characterisation of filter material coating with relation to physico-chemical Mn removal

Mn present on the coating of filter material grains collected over depth at each DWTP varied from 0.58 to 67 g/kg. A large variation in Mn from 0.01 to over 120 g/kg in filter material samples collected at 14 DWTPs was also reported by Islam et al. (2010).

The Mn coating present in filter material from DWTPs under 10 years of operation was statistically lower than from the ones running for over 10 years ($p < 0.05$ after ANOVA). This can be caused by an accumulation of Mn on the filter grains over time. A previous investigation using backwash samples from DWTP8 indicated that over
90% of Mn entering the filter was accumulated on the filter grains (Breda et al. 2016). Although the autocatalytic properties of Mn oxides present in the coating of the grains contribute to the Mn removal, the amount of Mn in a thick coating does not represent the amount of Mn in contact with the water phase. Thus, a higher amount of Mn in the coating does not necessarily mean higher Mn removal efficiency.

The coating was dominated by Fe and Mn, with a Fe/Mn ratio median of 2 ranging from 0.7 to 2.9 (10th–90th
percentile, respectively). The correlation coefficients between elements present in the coating of the filter grains were determined using the Pearson method (Figure 2(a)). Mn present in the coating showed a strong positive correlation with total coating, Fe, Ca and P but no correlation with adenosine triphosphate (ATP) concentration (Figure 2(a) and 2(b)). The lack of correlation between ATP and Mn does not preclude that biological activity has no effect on the presence of Mn in the coating of the grains since ATP is influenced by many microorganisms in addition to Mn oxidising bacteria (MnOBs).

**Effect of the biological inhibitor NaN₃ on the Mn Rₗ**

The Mn Rₗ was determined in batch assays using filter material collected over 20 cm depth intervals of each filter. Even though there was a change in filter material type through depth at some of the DWTPs (Figure 1(a)), the filter material type showed no significant effect on the Mn Rₗ (p > 0.05 after ANOVA). Water utilities often select a dual or alternative filter material to improve the operation conditions of the filters, e.g., reduction of cost and/or improvement of removal efficiency. However, results from the present study question the value of the type of filter material with regards to the Mn Rₗ of matured filters. One should consider that the Rₗ of virgin filter materials varies with the filter material type. For example, the Mn Rₗ of a virgin Mn sand is approximately 30 times superior to the one from virgin sand (Supplementary Materials, available with the online version of this paper). Thus, the selection of the filter material type can be important during the initial stages of the filter maturation, more specifically during the start-up period. In contrast, the present investigation suggests that there is no effect of the filter material type on Mn Rₗ after a maturation time of 3 years (which is the age of the youngest filter, DWTP1, Figure 1(a)). This information is of interest to the industry for assessing the filter design and determining the return of investments.

NaN₃ is an inhibitor of respiratory activity in microorganisms, while it does not appear to affect the autocatalytic properties of Mn oxide coatings (Rosson et al. 1984). This was observed in an additional assay, in which NaN₃ showed a limited effect on the Mn Rₗ of virgin quartz sand and virgin Mn sand (Supplementary Materials). To characterise the Mn removal processes occurring at functional full-scale filters, the effect of NaN₃ on the Mn Rₗ was investigated using the filter material samples collected over filter depth. Mn removal attained by filter material samples without NaN₃ was assumed to be due to biological and physico-chemical processes, whereas Mn removal attained by filter material samples with NaN₃ was assumed to be mainly due to physico-chemical processes alone.

In the present study, the Mn Rₗ was statistically lower in the presence of NaN₃ (p < 0.05, Mann–Whitney test). Mn removal by physico-chemical processes dominated in most filters, representing approximately 77% of the Mn Rₗ of the matured filter material (Figure 3(a)). The effect of NaN₃ for each DWTP (average of triplicates over depth) ranged from 7% to 30% (DWTP5 < DWTP1 < DWTP8 < DWTP9 < DWTP2 < DWTP4 < DWTP10 < DWTP6 < DWTP7 < DWTP3). As all the 10 DWTP were efficiently removing Mn, the results suggest that dominance of biological removal of Mn is not required to attain efficient removal of Mn in full-scale filters with over 3 years of maturation.

![Figure 2](http://i.waponline.com/wqrj/article-pdf/54/4/326/669592/wqrjc0540326.pdf)

(a) Pearson correlation between selected filter material properties from filter medium samples collected at 20 cm depth intervals of each filter. (b) Correlation plot between the amount of Mn and the amount of Fe. (c) Correlation plot between the amount of Mn and the concentration of ATP.
The effect of NaN₃ on the Mn \( R_c \) of samples collected over 20 cm depth intervals ranged from 3% to 41% (10th–90th percentile, respectively), with no correlation between filter depth and effect of NaN₃ at any DWTP (correlation factor of 0.3 after Pearson).

Sahabi et al. (2009) concluded that Mn removal in filter material matured for more than 3 years is mostly due to physico-chemical processes, and Bruins et al. (2015) concluded that Birnessite (Mn oxide) formation became a predominantly physico-chemical process with the progress
of filter maturation and development of the filter material coating. Even though the highest removal rates were registered within the ‘Field of biological Mn removal’ (Figure 1(d)), and previous investigations suggesting that MnOBs are prevalent in drinking water systems (Marcus et al. 2016), batch tests indicate that physico-chemical processes dominate the Mn removal in the DWTPs (Figure 3(a)). Biological removal of Mn may still be of importance in maintaining the filter function over time since Mn oxides of biogenic origin show higher autocatalytic properties (Bruins et al. 2015). Inadequate Mn removal in previously well-functioning fully matured filters might be related to the absence of biogenic Mn oxides, resulting in limited biological removal of Mn. Classification of Mn removal processes over depth in filters experiencing Mn breakthrough could provide further insight into the causes for such events.

Effect of potential enhancers P, TM and P + TM on the Mn $R_c$

To investigate the effect of potential enhancers on the Mn $R_c$ of fully matured filters, filter material samples collected from the top, middle and bottom 20 cm of the filters at each DWTP were used in a batch assay to determine the Mn $R_c$ with and without the addition of P, TM and P + TM. Concentration profiles of water samples from individual DWTPs showed that Mn and NH$_4$ are removed around the same filter depths. For that reason, the batch assay used a spike of both NH$_4$ and Mn to investigate the effect of the referred compounds on the $R_c$ of the filter material. Collectively the results indicated no statistical difference in Mn $R_c$ with and without potential enhancers ($p > 0.05$, Mann–Whitney test). However, the Mn $R_c$ increased in the presence of the potential enhancers (P, TM and P + TM) in filter material samples collected at 120–140 cm filter depth from DWTP4 and DWTP8, by a factor of 2.4 and 1.2, respectively (Figure 3(b)). These results can be relevant for the water utilities managing DWTP4 and DWTP8, as the respective Mn removal constant $k$ at both DWTPs were among the lowest (Figure 1(c)).

Regarding the overall effect of the potential enhancers on NH$_4$, results showed that the NH$_4$ $R_c$ was statistically greater when P and P + TM were added ($p < 0.05$), but not for TM alone ($p > 0.05$). Previous studies have reported performance enhancement in NH$_4$ removal when individually dosing P and TM (de Vet et al. 2012; Wagner et al. 2017; Zhang et al. 2018). Wagner et al. (2017) concluded that Cu dosing enhanced nitrification of poorly performing full-scale rapid sand filters while remarking that pilot column filters could not always successfully reproduce full-scale filter behaviour.

DWTPs showing a positive effect of the potential enhancers on the Mn $R_c$ were not the same as the ones showing a positive effect on the NH$_4$ $R_c$. Furthermore, enhancers showed a stronger effect on NH$_4$ $R_c$ than on Mn $R_c$. Nonetheless, and despite Mn removal being mostly dominated by physico-chemical processes (Figure 5(a)), our results suggest that there might be possibilities to increase the Mn $R_c$ of matured filters through enhancement strategies.

Operational conditions

Bruins et al. (2014) carried out a multivariate statistical analysis using principal component analysis (PCA) on 34 parameters of 100 DWTPs treating groundwater followed by univariate statistics to determine the limiting operational conditions for efficient Mn removal. The study concluded that efficient removal of Mn correlated with six parameters: NH$_4$ removal efficiency, Fe loading per filter run, pH of the filtrate, EBCT, filtration rate and oxygen in the filtrate. These six operational parameters for the 10 DWTPs investigated in the present study and corresponding Mn removal efficiencies are summarised in Table 1.

Efficient Mn removal was achieved in all DWTPs included in this study, and nearly all operational conditions were within the operational conditions determined by Bruins et al. (2014). However, the operational condition >85% NH$_4$ removal was not met at DWTP5, DWTP4 and DWTP10. For DWTP3, a low NH$_4$ removal efficiency (67%, Table 1) was observed even though this DWTP had the second highest $k$ for Mn (Figure 1(b) and 1(c)). This suggests that Mn removal efficiency is not always dependent on the compliance of the 85% NH$_4$ removal minimum established by Bruins et al. (2014).

In the present study, the concentration of Mn and NH$_4$ measured in water samples collected over filter depth clearly showed that the Mn criterion was often met before the 85% NH$_4$ removal was reached (Figure 4(a)). More specifically, half of the observations with Mn below the criterion are
found in samples with 60% NH₄ removal (Figure 4(a)). In addition to the observations, in situ batch tests using matured filter material collected over 20 cm depth intervals of the filters at the 10 DWTPs showed that 1 mg/L NH₄ had no significant detrimental effect on the Mn $R_c$ ($p > 0.05$ after Mann–Whitney test, Figure 3(d)).

Both negative and positive effects of simultaneous NH₄ and Mn removal have been reported (Vandenabeele et al. 1995). Furthermore, previous research has demonstrated that the presence of nitrite can have an inhibitory effect on microbial oxidation of dissolved Mn (Brandhuber et al. 2015).

Recent studies have indicated that the contribution of biological processes for the removal of Mn varies with the age of the filters (maturation time). To the authors’ knowledge, the age of the filter maturation was not included as a parameter in the PCA conducted by Bruins et al. (2014). It can be hypothesised that the degree of importance of the six operational parameters varies with the filters’ ages.

Table 1 | Operational conditions of the 10 filters

<table>
<thead>
<tr>
<th>Operational conditions</th>
<th>Bruins et al. (2014)</th>
<th>DWTP 1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
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<tr>
<td>Manganese removal (%)</td>
<td>–</td>
<td>99</td>
<td>97</td>
<td>92</td>
<td>80</td>
<td>99</td>
<td>99</td>
<td>98</td>
<td>99</td>
<td>99</td>
<td>99</td>
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<tr>
<td>Ammonium removal (%)</td>
<td>&gt;85</td>
<td>97</td>
<td>98</td>
<td>67</td>
<td>45</td>
<td>97</td>
<td>99</td>
<td>85</td>
<td>85</td>
<td>87</td>
<td>65</td>
</tr>
<tr>
<td>Iron loading per filter run (kg/m²)</td>
<td>&lt;2.7</td>
<td>0.2</td>
<td>0.2</td>
<td>0.3</td>
<td>0.3</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.7</td>
<td>0.2</td>
<td>0.8</td>
</tr>
<tr>
<td>pH of filtrate</td>
<td>&gt;7.1</td>
<td>7.4</td>
<td>7.5</td>
<td>7.4</td>
<td>7.4</td>
<td>7.5</td>
<td>7.3</td>
<td>7.4</td>
<td>7.3</td>
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<td>7.4</td>
</tr>
<tr>
<td>Empty bed contact time (min)</td>
<td>&gt;11</td>
<td>19</td>
<td>23</td>
<td>15</td>
<td>31</td>
<td>27</td>
<td>55</td>
<td>27.8</td>
<td>34</td>
<td>69</td>
<td>48</td>
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<tr>
<td>Filtration rate (m/h)</td>
<td>&lt;10.5</td>
<td>4.5</td>
<td>2.9</td>
<td>3.3</td>
<td>2.7</td>
<td>3.2</td>
<td>1.3</td>
<td>2.8</td>
<td>3.1</td>
<td>2.5</td>
<td>2.0</td>
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<td>Oxygen in filtrate (mg/L)</td>
<td>&gt;1</td>
<td>9.9</td>
<td>10.7</td>
<td>9.9</td>
<td>9.4</td>
<td>11.1</td>
<td>9.3</td>
<td>9.5</td>
<td>8.1</td>
<td>6.7</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Figure 4 | (a) Mn versus NH₄ removal (percentage) from water samples collected at every 10 cm depth of the 10 DWTPs in relation to inlet concentrations at each DWTPs. Colour and shape distinguish criterion conditions for Mn and NH₄ (national criteria of 0.05 mg/L for both Mn and NH₄). (b) Mn versus NH₄ removal (percentage) over time (days 11, 27, 35, 39, 43, 67 and approximately 4 years) calculated based on the concentration of each substance in water samples collected over 20 cm depth intervals in relation to the inlet concentrations at DWTP9. All data were retrieved from Ramsay et al. (2018) with the exception of observations at 4 years. Please refer to the online version of this paper to see this figure in colour: http://dx.doi.org/10.2166/wqrj.2019.006.
A comprehensive description of the start-up period after construction of DWTP9 was conducted by Ramsay et al. (2018), including measurements of Mn and NH4 in water samples collected over the filter depth during the start-up period and shortly after the conclusion of the start-up period. According to the observations in this study, NH4 complied with the national criterion before the commencement of Mn removal (Figure 4(b), 67 days). On the contrary, the present study shows that after 4 years of maturation, the same filter removes Mn at a lesser depth than NH4 (Figure 4(b)). This can be explained by a sequence of events. Complete nitrification is required for the onset of Mn removal during the start-up period of a virgin filter. Thus, by the end of the start-up period, Mn removal often takes place in the bottom section of the filter, preceding NH4 removal. Shortly after the start-up period, Mn continues to be removed in the bottom section of the filter, and Mn oxides start to coat the filter grains. During normal operations, the filters run in a sequence of ripening cycles and backwash procedures. The backwash promotes the transport of filter grains and deposits from the bottom section of the filter to the upper section of the filter. By the end of the backwash, Mn oxides initially accumulated in the bottom section of the filter are spread and attached to grains across the filter depth. As the ripening cycle restarts, Mn in the water phase starts to be removed across the filter depth due to the autocatalytic properties of Mn oxides. Consequently, the amount of Mn oxides coating the grains increases, promoting the further autocatalytic removal of Mn across the filter depth. This study indicates that the shift in the location of Mn removal from bottom to upper sections of the filter can lead to a change in the spatial order of the main removal processes occurring over the filter depth: from an initial stratification of Fe, NH4 and Mn removal to Fe, Mn and NH4 removal.

On a practical note, it is important to clarify that the end of the start-up period is not the end of the filter’s maturation (Ramsay et al. 2018). During the start-up period, virgin filter material matures into a functional filter that can remove substances to drinking water criteria. However, the maturation of the filter continues, changing not only the category of the removal processes occurring in the filter (e.g., Mn removal from biological to mostly physico-chemical) but also the stratification of the removal of specific substances over the filter depth (e.g., Mn and NH4 removal, Figure 4(b)).

**CONCLUSIONS**

After characterisation of Mn removal at 10 full-scale DWTPs efficiently removing Mn, this study concludes the following:

- The first-order removal constant for Mn in 10 fully matured DWTPs varied from $10^{-2}$ to $10^{-1}$ min$^{-1}$.
- Mn coating the filter material grains showed a strong positive correlation (Pearson correlation coefficient 0.9) with the amount of Fe, Ca and total coating, but no correlation with the concentration of ATP (Pearson correlation coefficient, −0.3).
- Mn removal was mostly mediated by physico-chemical processes in the matured filters. Addition of a known biological inhibitor (NaN3) resulted in an approximately 23% reduction of the Mn removal capacity, ranging from 3% to 41% (10th–90th percentile, respectively) in filter material collected over filter depth at the different DWTPs. Collectively the results suggested that dominance of biological removal of Mn is not required to attain the efficient removal of Mn.
- Addition of P and TM showed a limited overall effect on the Mn removal capacity of matured filters. However, at 120–140 cm filter depth of DWTP4 and DWTP8, an increase in the Mn removal capacity was observed by a factor of 2.4 and 1.2, respectively, suggesting that the enhancement of Mn removal in matured filters is possible but challenging.
- In addition, this investigation provides practical guidance to the design and operation of drinking water filters for the efficient Mn removal. Results showed a limited detrimental effect of NH4 and a limited effect of filter material type (quartz sand, anthracite and calcium carbonate) on the Mn removal capacity of matured filters. Furthermore, results indicate a switch in the spatial stratification of Mn and NH4 removal processes over filter depth as the filter ages.

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