



Aalborg Universitet

AALBORG UNIVERSITY
DENMARK

Manganese removal processes at 10 groundwater fed full-scale drinking water treatment plants

Lousinha Breda, Ines; Ramsay, Loren; Søborg, Ditte; Dimitrova, Reni; Roslev, Peter

Published in:
Water Quality Research Journal of Canada

DOI (link to publication from Publisher):
[10.2166/wqrj.2019.006](https://doi.org/10.2166/wqrj.2019.006)

Creative Commons License
CC BY 4.0

Publication date:
2019

Document Version
Publisher's PDF, also known as Version of record

[Link to publication from Aalborg University](#)

Citation for published version (APA):

Lousinha Breda, I., Ramsay, L., Søborg, D., Dimitrova, R., & Roslev, P. (2019). Manganese removal processes at 10 groundwater fed full-scale drinking water treatment plants. *Water Quality Research Journal of Canada*, 54(4), 326-337. <https://doi.org/10.2166/wqrj.2019.006>

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- ? Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- ? You may not further distribute the material or use it for any profit-making activity or commercial gain
- ? You may freely distribute the URL identifying the publication in the public portal ?

Take down policy

If you believe that this document breaches copyright please contact us at vbn@aub.aau.dk providing details, and we will remove access to the work immediately and investigate your claim.


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

I. L. Breda  (corresponding author)

R. Dimitrova

P. Roslev

Department of Chemistry and Bioscience,
Aalborg University,
Fredrik Bajers Vej 7H, 9220 Aalborg,
Denmark
E-mail: ilb@bio.aau.dk

I. L. Breda

Project and Development Group,
Skanderborg Forsyningsvirksomhed A/S,
Døjsøvej 1, 8660 Skanderborg,
Denmark

L. Ramsay

D. A. Søborg

Research Group for Energy and Environment,
VIA University College,
Chr. M. Østergaards Vej 4, 8700 Horsens,
Denmark

This article has been made Open Access thanks to the kind support of CAWQ/ACQE (<https://www.cawq.ca>).

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

This is an Open Access article distributed under the terms of the Creative Commons Attribution Licence (CC BY 4.0), which permits copying, adaptation and redistribution, provided the original work is properly cited (<http://creativecommons.org/licenses/by/4.0/>).

doi: 10.2166/wqrj.2019.006

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, Hovedværket, 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 triplicates of three different types of additions: (i) 1 mg/L Mn (control), (ii) 1 mg/L Mn and 1 mg/L NH₄ and (iii) 1 mg/L Mn and 25 mM NaN₃. Aliquots (2.5 mL) were collected after 30 and 60 min, filtered (0.22 µm) and analysed for Mn according to the manufacturer's instructions (kit LCW532, Hach, and a Multiskan FC Microplate Photometer, Thermo Fisher Scientific). NH₄ was analysed using an autoanalyser (Technicon TRAACS 800). The bottles were shaken (100 rpm) at 16 °C during the experiment.

Batch experiment to assess the effect of P and TM on the Mn removal capacity

A batch experiment was conducted to investigate the Mn removal capacity in the presence of P, TM and both P and

TM, using filter material from each DWTP collected at the top 20 cm, middle 20 cm layer and bottom 20 cm. Filter material (5 g) was placed in serum bottles with 50 mL of treated water spiked with 1 mg/L Mn and 1 mg/L NH₄. Triplicate bottles were spiked with a concentrate of P (1 M P using NaHPO₄ and KH₂PO₄ buffered at 6.8–7.0 pH), TM (1.7 µg/L Zn, 2.4 µg/L Mo, 1.4 µg/L Mn, 2.5 µg/L B, 1.5 µg/L Co, 1.5 µg/L Ni, 6.4 µg/L Cu) and both P and TM. Concentrations of TM were selected based on a previous study by Wagner et al. (2017). A remaining set of triplicate bottles was used as a control. All bottles were then placed on a rotation table (100 rpm) and incubated for 7 days at 16 °C. The solutions of each bottle were renewed every 3 days to ensure the availability of substrate and nutrients. After the incubation period, the bottles were spiked with a concentrate of 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:

$$\frac{d[C_{\text{out}}]}{dt} = -k[C_{\text{in}}] \Rightarrow k = -\frac{\ln\left(\frac{[C_{\text{out}}]}{[C_{\text{in}}]}\right)}{t} \quad (1)$$

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:

$$\text{EBCT} = \frac{\text{depth interval}}{v} \quad (2)$$

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 ($\mu\text{g}/\text{min}/\text{g}$) 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} (μg) and the mass of the filter material sample used in the batch m_{fm} (g), as follows:

$$R_c = k \frac{m_{\text{sub}}}{m_{\text{fm}}} \quad (3)$$

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 $\ln([\text{Mn}(\text{II})]_{\text{f}}/[\text{Mn}(\text{II})_{\text{o}}])$ 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 $\ln([\text{Mn}(\text{II})]_{\text{f}}/[\text{Mn}(\text{II})_{\text{o}}])$ 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 (Tekerekopoulou & 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

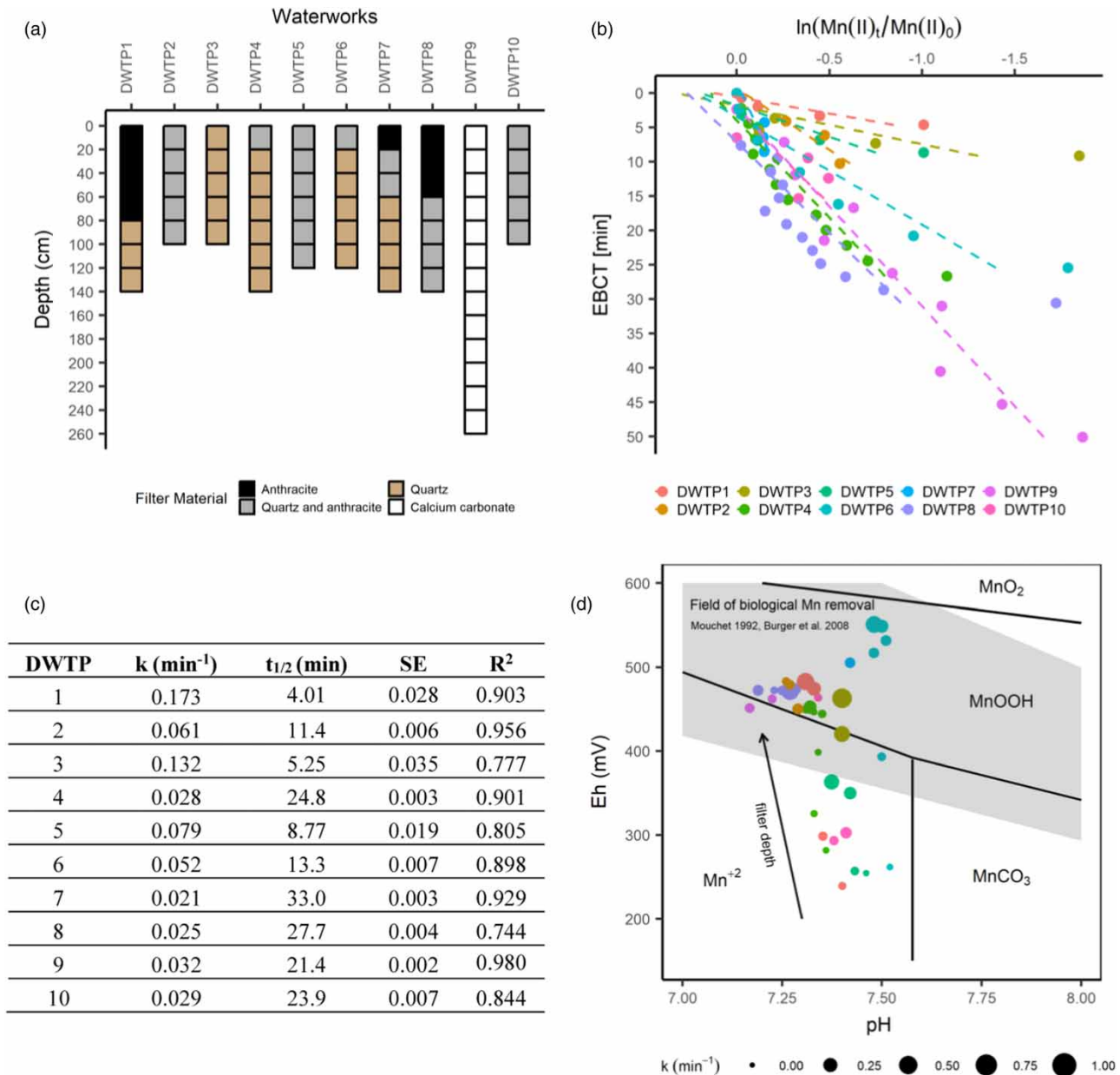


Figure 1 | (a) Filter material distribution over depth at each DWTP. (b) Analysis of linearity between $\ln([\text{Mn(II)}_t]/[\text{Mn(II)}_0])$ and EBCT in water samples with Mn concentration above 0.05 mg/L. (c) First-order removal constant k at each DWTPs, $t_{1/2}$ is the half-life and SE and the R^2 are the standard error and multiple R-squared of the linear regression, respectively. (d) Pourbaix diagram with data points indicating pH and redox in the water at each 10 cm depth of the filters until the Mn criterion was met. Colour distinguishes DWTPs. Size distinguishes removal rates at each 10 cm depth of the filter. Grey shading shows the field of biological Mn removal (Mouchet 1992; Burger et al. 2008). Pourbaix diagram is based on equilibrium constants given by PHREEQC using *wateq4f* database (Parkhurst & Appelo 1999) and the following conditions: 10 °C, 0.260 mg Mn(II)/L, 275 mg HCO_3^- /L. Please refer to the online version of this paper to see this figure in colour: <http://dx.doi.org/10.2166/wqrj.2019.006>.

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 NaN_3 on the Mn R_c

The Mn R_c 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 R_c ($p > 0.05$ 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 R_c of matured filters. One should consider that the R_c of virgin filter materials varies with the filter material type. For example, the Mn R_c 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 R_c 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.

NaN_3 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 NaN_3 showed a limited effect on the Mn R_c 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 NaN_3 on the Mn R_c was investigated using the filter material samples collected over filter depth. Mn removal attained by filter material samples without NaN_3 was assumed to be due to biological and physico-chemical processes, whereas Mn removal attained by filter material samples with NaN_3 was assumed to be mainly due to physico-chemical processes alone.

In the present study, the Mn R_c was statistically lower in the presence of NaN_3 ($p < 0.05$, Mann-Whitney test). Mn removal by physico-chemical processes dominated in most filters, representing approximately 77% of the Mn R_c of the matured filter material (Figure 3(a)). The effect of NaN_3 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.

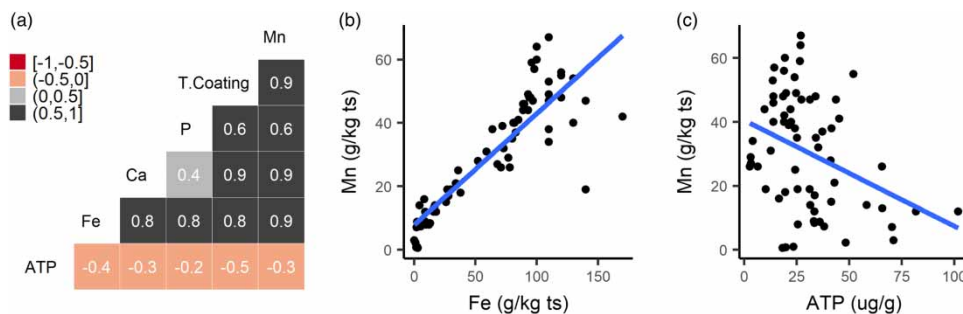


Figure 2 | (a) Pearson correlation between selected filter material properties from filter medium samples collected at 20 cm depth intervals of each filter. (b) Correlation plot between the amount of Mn and the amount of Fe. (c) Correlation plot between the amount of Mn and the concentration of ATP.

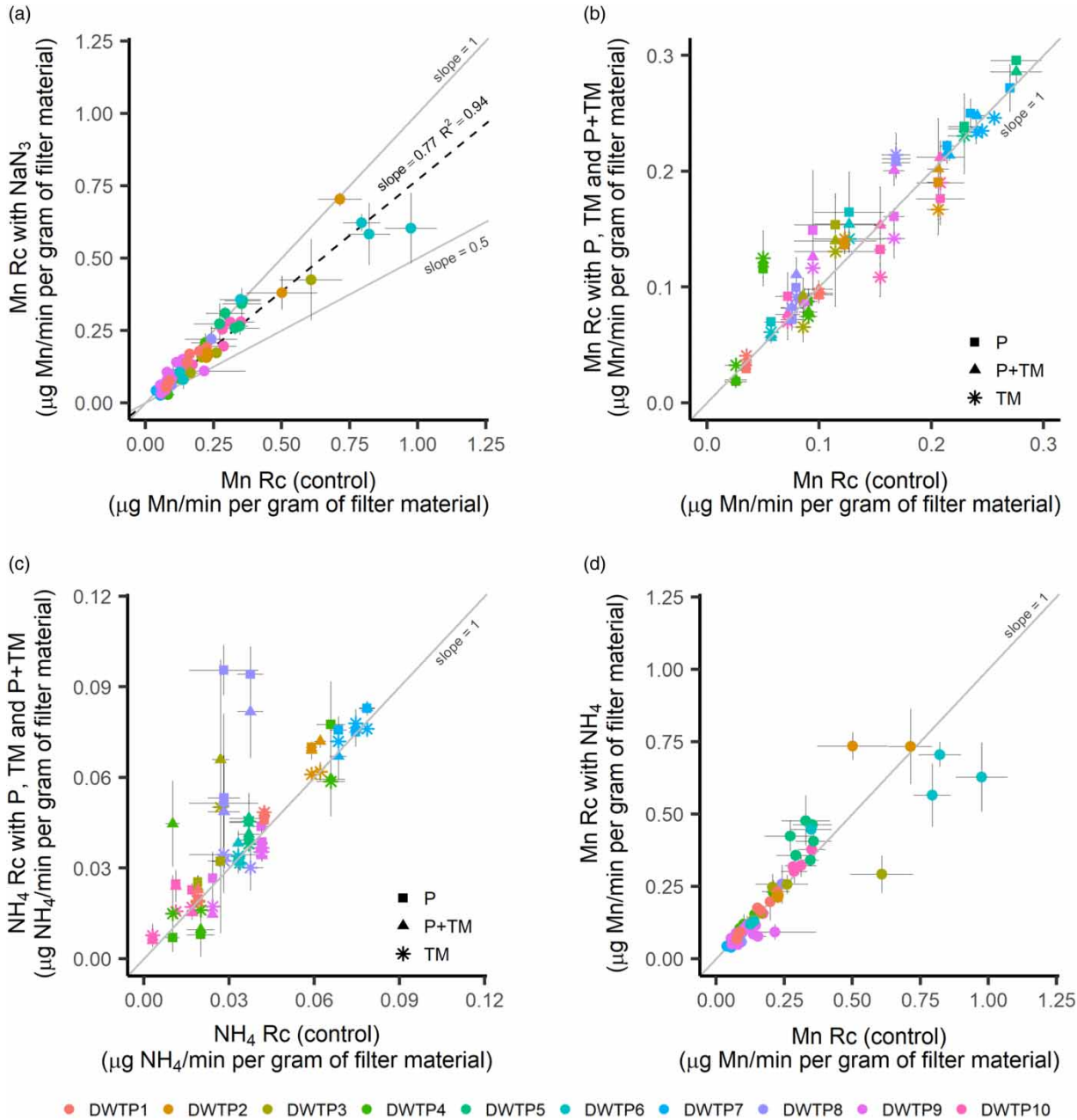


Figure 3 | (a) Mn R_c with NaN_3 versus Mn R_c without NaN_3 (control). Dashed black line represents linear regression. (b) Plot of Mn R_c with P, TM and P+TM versus Mn R_c without potential enhancers (control). (c) Plot of NH_4 R_c with P, TM and P+TM versus NH_4 R_c without potential enhancers (control). (d) Plot of Mn R_c with NH_4 versus Mn R_c without NH_4 (control). Colour distinguishes DWTPs. Error bars show the standard deviation of triplicates. Please refer to the online version of this paper to see this figure in colour: <http://dx.doi.org/10.2166/wqrj.2019.006>.

The effect of NaN_3 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 NaN_3 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 $\text{NH}_4 R_c$ 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 $\text{NH}_4 R_c$. Furthermore, enhancers showed a stronger effect on $\text{NH}_4 R_c$ than on Mn R_c . Nonetheless, and despite Mn removal being mostly dominated by physico-chemical processes (Figure 3(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 DWTP3, 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

Table 1 | Operational conditions of the 10 filters

Operational conditions	Bruins et al. (2014)	DWTP									
		1	2	3	4	5	6	7	8	9	10
Manganese removal (%)	–	99	97	92	80	99	99	98	99	99	99
Ammonium removal (%)	>85	97	98	67	45	97	99	85	85	87	65
Iron loading per filter run (kg/m ²)	<2.7	0.2	0.2	0.3	0.3	0.1	0.2	0.4	0.7	0.2	0.8
pH of filtrate	>7.1	7.4	7.5	7.4	7.4	7.5	7.3	7.4	7.3	7.3	7.4
Empty bed contact time (min)	>11	19	23	15	31	27	55	27.8	34	69	48
Filtration rate (m/h)	<10.5	4.5	2.9	3.3	2.7	3.2	1.3	2.8	3.1	2.5	2.0
Oxygen in filtrate (mg/L)	>1	9.9	10.7	9.9	9.4	11.1	9.3	9.5	8.1	6.7	10.8

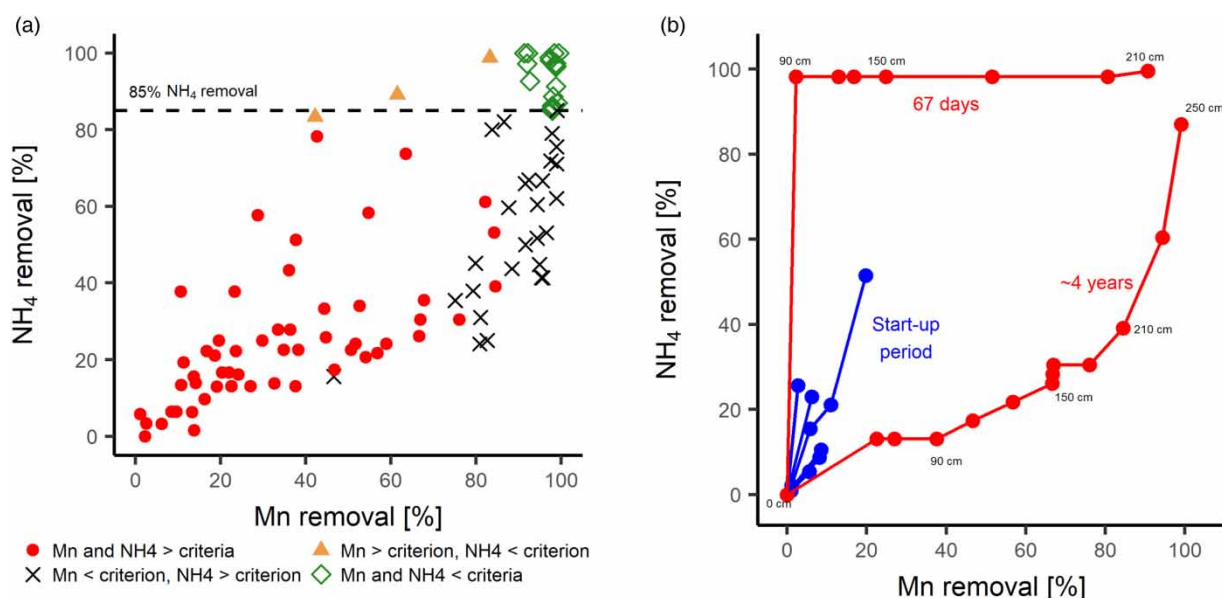


Figure 4 | (a) Mn versus NH₄ removal (percentage) from water samples collected at every 10 cm depth of the 10 DWTPs in relation to inlet concentrations at each DWTPs. Colour and shape distinguish criterion conditions for Mn and NH₄ (national criteria of 0.05 mg/L for both Mn and NH₄). (b) Mn versus NH₄ 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>.

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. 2013).

Recent studies have indicated that the contribution of biological processes for the removal of Mn varies with the age of the filter (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.

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.

ACKNOWLEDGEMENTS

This work was financed by Skanderborg Forsyningsvirksomhed A/S, Innovationsfonden (5016-00134B). Technicians at Aarhus Water and VandCenter Syd are acknowledged for assistance during sampling. Kirsten L. Thomsen from VIA University

College (Horsens), Helle Blendstrup, Lotte Trillingsgaard and Edmundas Maksimavicius from Aalborg University are acknowledged for technical assistance. Finally, the MUDP project 'Smart Redesign of Drinking Water Production' is acknowledged for supplying the data.

REFERENCES

- APHA/AWWA/WEF 1989 *Standard Methods for the Examination of Water and Wastewater*, 17th edn. American Public Health Association, American Water Works Association and Water Environment Federation, Washington, DC, USA.
- BEK 1068 2018 *Bekendtgørelse om Vandkvalitet og Tilsyn med Vandforsyningsanlæg*. Danish Ministry of the Environment, Denmark (in Danish).
- Brandhuber, P., Clark, S., Knocke, W. & Tobiason, J. 2013 *Guidance for the Treatment of Manganese*. Water Research Foundation, Denver, CO.
- Breda, I. L., Ramsay, L. & Søborg, D. A. 2016 *The role of backwash in start-up of full-scale drinking water biofilters*. *Journal of Water Supply: Research and Technology – AQUA* **65** (3), 234–243. doi:10.2166/aqua.2016.093.
- Breda, I. L., Søborg, D. A., Ramsay, L. & Roslev, P. 2018 *Manganese removal processes during start-up of inoculated and non-inoculated drinking water biofilters*. *Water Quality Research Journal*. https://doi.org/10.2166/wqrj.2018.016
- Bruins, J. H., Vries, D., Petrusevski, B., Slokar, Y. M. & Kennedy, M. D. 2014 *Assessment of Mn removal from over 100 groundwater treatment plants*. *Journal of Water Supply: Research and Technology – AQUA* **63** (4), 268–280. https://doi.org/10.2166/aqua.2013.086.
- Bruins, J. H., Petrusevski, B., Slokar, Y. M., Huysman, K., Joris, K., Kruithof, J. C. & Kennedy, M. D. 2015 *Biological and physico-chemical formation of Birnessite during the ripening of manganese removal filters*. *Water Research* **69**, 154–161. doi:10.1016/j.watres.2014.11.019.
- Burger, M. S., Mercer, S. S., Shupe, G. D. & Gagnon, G. A. 2008 *Mn removal during bench-scale biofiltration*. *Water Research* **42** (19), 4733–4742. https://doi.org/10.1016/j.watres.2008.08.024.
- Dangeti, S., Roshani, B., Rindall, B., McBeth, J. M. & Chang, W. 2017 *Biofiltration field study for cold Fe(II)- and Mn(II)-rich groundwater: accelerated Mn(II) removal kinetics and cold-adapted Mn(II)-oxidizing microbial populations*. *Water Quality Research Journal of Canada* **52** (4), 229–242. https://doi.org/10.2166/wqrj.2017.006.
- de Vet, W. W. J. M., Rietveld, L. C. & Van Loosdrecht, M. C. M. 2009 *Influence of iron on nitrification in drinking water filters*. *Journal of Water Supply: Research and Technology – AQUA* **58** (4), 247–256.
- de Vet, W. W. J. M., Van Loosdrecht, M. C. M. & Rietveld, L. C. 2012 *Phosphorus limitation in nitrifying groundwater filters*. *Water Research* **46** (4), 1061–1069. https://doi.org/10.1016/j.watres.2011.11.075.
- Islam, A., Goodwill, J., Bouchard, R., Tobiason, J. & Knocke, W. 2010 *Characterization of filter and media MnOx (s) surfaces and Mn removal capability*. *Journal of the American Water Works Association* **102** (9), 71–85.
- Katsoyiannis, I. A. & Zouboulis, A. I. 2004 *Biological treatment of Mn(II) and Fe(II) containing groundwater: kinetic considerations and product characterization*. *Water Research* **38** (7), 1922–1932. https://doi.org/10.1016/j.watres.2004.01.014.
- Marcus, D. N., Pinto, A., Anantharaman, K., Ruberg, S. A., Kramer, E. L., Raskin, L. & Dick, G. J. 2016 *Diverse Mn(II)-oxidizing bacteria are prevalent in drinking water systems*. *Environmental Microbiology Reports* **9**, 120–128. https://doi.org/10.1111/1758-2229.12508.
- Mouchet, P. 1992 *From conventional to biological removal of iron and Mn in France*. *Journal of American Water Works Association* **84** (4), 158–167.
- Parkhurst, D. L. & Appelo, C. A. J. 1999 *User's Guide to PHREEQC (Version 2) – A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations*. U.S. Geological Survey Water-Resources Investigations Report 99-4259, p. 312.
- Ramsay, L., Breda, I. L. & Søborg, D. A. 2018 *Comprehensive analysis of the start-up period of a full-scale drinking water biofilter provides guidance for optimization*. *Drinking Water Engineering and Science* **11** (2), 87–100. https://doi.org/10.5194/dwes-11-87-2018.
- R Core Team 2017 *R: A Language and Environment for Statistical Computing*. R Foundation for Statistical Computing, Vienna, Austria. http://www.R-project.org.
- Rosson, R. A., Tebo, B. M. & Neelson, K. H. 1984 *Use of poisons in determination of microbial manganese binding rates in seawater*. *Applied and Environmental Microbiology* **47** (4), 740–745.
- Sahabi, D. M., Takeda, M., Suzuki, I. & Koizumi, J. i. 2009 *Removal of Mn²⁺ from water by 'aged' biofilter media: the role of catalytic oxides layers*. *Journal of Bioscience and Bioengineering* **107** (2), 151–157. https://doi.org/10.1016/j.jbiosc.2008.10.013.
- Tekerlekopoulou, A. G. & Vayenas, D. V. 2008 *Simultaneous biological removal of ammonia, iron and Mn from potable water using a trickling filter*. *Biochemical Engineering Journal* **39** (1), 215–220. https://doi.org/10.1016/j.bej.2007.09.005.
- Vandenabeele, J., Vande Woestyne, M., Houwen, F., Germonpré, R., Vandesande, D. & Verstraete, W. 1995 *Role of autotrophic nitrifiers in biological manganese removal*. *Ecology* **29** (1), 83–98.
- Vries, D., Bertelkamp, C., Schoonenberg Kegel, F., Hofs, B., Dusseldorp, J., Bruins, J. H. H., de Vet, W. & van den Akker, B. 2017 *Iron and manganese removal: recent advances in modelling treatment efficiency by rapid sand filtration*. *Water Research* **109**, 35–45. https://doi.org/10.1016/j.watres.2016.11.032.

Wagner, F. B., Albrechtsen, H.-J. & Boe-Hansen, R. 2017 *Importance of Copper for Nitrification in Biological Rapid Sand Filters for Drinking Water Production*. Department of Environmental Engineering, Technical University of Denmark (DTU), Kgs. Lyngby.

Zhang, R., Huang, T., Wen, G., Chen, Y., Cao, X., Zhang, B. & Wang, B. 2018 *Phosphate dosing to sustain the ammonium removal activity of an iron-manganese co-oxide filter film at pilot scale: effects on chemical catalytic oxidation*. *Chemical Engineering Journal* **334**, 1186–1194. doi:10.1016/j.cej.2017.11.010.

First received 27 February 2019; accepted in revised form 31 May 2019. Available online 14 June 2019