

Influence of iron on nitrification in full-scale drinking water trickling filters

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ABSTRACT

In the production of drinking water from groundwater, iron removal in filters may interfere with nitrification. Microbial nitrification might decline because of irreversible accumulation of iron deposits in pores and on filter material. This paper shows the successful application of two experimental techniques applied at a full-scale water treatment plant in the Netherlands to maintain sustainable nitrification. Filter performances were evaluated by measurements of ammonium in the filter effluent, accumulation of deposits and their removal during backwash, development of the mainly inorganic filter coating and media expansion curves. The application of dual-media drinking water trickling filters, in combination with filter backwash with media expansion, minimizes the irreversible accumulation of iron deposits in the filter. Subsurface aeration results in a lower iron content of the filter coating.

Key words | backwash, drinking water, dual-media trickling filter, iron removal, nitrification, subsurface aeration

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INTRODUCTION

In the Netherlands and Flanders, the production of drinking water (DW) from groundwater containing ammonium usually comprises nitrification in rapid sand filters by immobilized microorganisms attached to the sand. No oxidizing chemicals are applied. Incomplete nitrification may lead to regrowth in the (non-chlorinated) DW distribution systems since ammonium is a nutrient for many microorganisms (Chu *et al.* 2005). Both the presence of ammonium itself and the biological instability resulting from it may deteriorate water quality and lead to health risks. Therefore, strict standards for ammonium are applied (0.20 and 0.10 mg L⁻¹ for the Dutch and the company's standards, respectively); research focuses on maintaining sufficient nitrification capacity by optimizing the process design and/or its operation and maintenance. In a rapid sand filter system, a sufficient surface for the attachment of microorganisms exists, hydraulic conditions are such that contact time is sufficient and short-circuit flows do not occur. The nitrifying population adapts to the local ammonium

supply and, in standard downward flow filters, activity is highest at the top of the filter bed. During the start-up period of 1–5 months with new filter material, nitrifying microorganisms have to multiply first to form sufficiently large populations. Seeding is not mandatory for the start-up, so it must be concluded that nitrifying microorganisms are sufficiently present in the raw water, ventilation air or filter material for inoculation. Trickling filters in full-scale water treatment plants (WTP) at Oasen Drinking Water Company (Oasen) in the province of South Holland, The Netherlands, show an efficient nitrification directly after the start-up period. In many cases, however, this is not a sustainable situation and the ammonium concentration in the filter effluent starts to rise after some years or even months of production. Figure 1 shows a typical pattern for ammonium removal in an Oasen DW trickling filter. Iron removal is always nearly complete in this filter (>98%).

In the first period after start-up, there is almost full ammonium removal and about 90% of ammonium nitrogen

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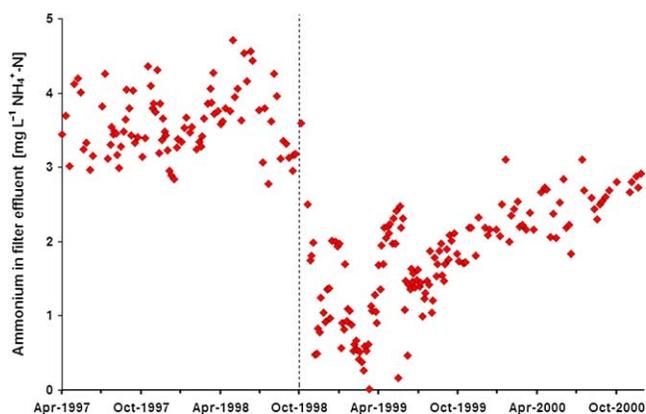


Figure 1 | Typical start-up and fallback pattern for ammonium removal in an Oasen single-medium DW trickling filter. The filter was filled with fresh filter material (sand 1.7–2.5 mm, bed height 2 m) on October 15, 1998. Average ammonium in raw groundwater over the shown period was $4.1 \text{ mg L}^{-1} \text{ NH}_4^+\text{-N}$. Fluctuations before October 15, 1998 were caused by fluctuations in raw water quality.

is converted to nitrate nitrogen. After approximately 6 months, the nitrifying activity slowly declines, resulting in increasing ammonium levels in the filter effluent. The remaining ammonium is always converted in a subsequent DW trickling filter.

Nitrification in the DW trickling filters is not limited by oxygen, due to an intensive gas exchange by forced ventilation with air through the filter bed, resulting in oxygen concentrations always above 8 mg L^{-1} in the filtrate. The filter ventilation also removes methane very efficiently (de Vet *et al.* 2002), preventing the extensive growth of methane-oxidizing bacteria in the filter. The same can be assumed for hydrogen sulfide in the raw water. Biological degradation of dissolved organic matter (DOC) is not likely to be the cause of the relapse in nitrification. In the two sequential filters, only $0.4 \text{ mg L}^{-1} \text{ C}$ as DOC is removed from the raw water (containing $2.5\text{--}2.8 \text{ mg L}^{-1} \text{ C}$). Even in the worst case, where no adsorbed DOC is flushed out during backwash and all is being converted in the filters, the oxygen demand for it is marginal compared to that for oxidation of over 5 mg L^{-1} of ammonium.

Since full nitrification can occur, it is hypothesized that the decline in nitrifying activity is caused by interference with deposits built up during the ageing of the filter.

Anaerobic groundwater usually contains ammonium, iron and manganese (and sometimes methane). Information on the interaction between ammonium, iron and

manganese removal in DW filters is still limited. Most references to combined iron, manganese and ammonium removal in DW filters focus on the biological processes. In pilot research on biological groundwater treatment in northern Croatia, Štembal *et al.* (2005) found increased removal at higher flow rates for all three removal processes, and therefore concluded that processes are mass transfer rather than reaction limited. Different flow-rate dependences of the removal efficiency for the three compounds require optimization of the filter design and operational actions depending on the raw water quality. Some authors elaborate on biological iron and manganese removal in filters without nitrification (Mouchet 1992; Li *et al.* 2005). Others deal with the influence of nitrification on biological manganese removal. Vandenaabeele *et al.* (1995b) demonstrated a stimulating effect of *Nitrosomonas europaea* and *Nitrobacter winogradskyi* on biological manganese removal, compared to inhibition of biological manganese oxidation and even the reduction of MnO_2 by nitrite. Vandenaabeele *et al.* (1995a) found nitrate having a stabilizing effect on the removal of manganese by preventing the microbial reduction of MnO_2 to Mn^{2+} . Bray & Olańczuk-Neyman (2001) studied the combined ammonium and manganese removal in DW production from groundwater in Poland in full- and pilot-scale long-term experiments of over half a year. They found a negative impact of long-lasting low oxygen concentrations on manganese removal, but did not find any interaction between nitrification and manganese removal. Adverse effects from manganese removal on nitrification are not reported in literature. References concerning the combination of nitrification and biological iron oxidation in DW filters are scarce. Štembal *et al.* (2005) found bacteria of the genus *Siderocapsa* present in comparable cell counts as nitrifying bacteria and suggested its role in iron and manganese oxidation. Their research did not focus on possible interactions between the removal processes. Other studies emphasize the inhibiting effect of ammonium on biological iron removal (e.g. Twort *et al.* 2000). Tekerlekopoulou *et al.* (2006) reported on biological and physicochemical iron oxidation in combination with nitrification in a pilot-scale trickling filter for DW production during a test period of eight months. High raw water concentrations (up to 4 mg L^{-1}) of iron

and ammonium reduced removal efficiency significantly for iron, but not for ammonium.

None of the references demonstrates a direct adversarial effect of iron removal on nitrification in DW filters. Iron accumulation, however, influences nitrification in at least one indirect way: filter clogging as a result of iron accumulation requires frequent backwashing of the filter, which might result in detachment of the (nitrifying) biomass. References on this subject show a broad array of impacts because of variations in filter materials, water quality and backwash procedures (Miltner *et al.* 1995; Laurent *et al.* 2003).

This paper focuses on the interference of iron removal with the nitrifying microorganisms in trickling filters for DW production, resulting in decreased nitrifying activity. Two distinct techniques are presented in long-duration experiments in a full-scale WTP to prevent the negative impact of iron removal and maintain sustainable nitrification in the DW trickling filters.

MATERIALS AND METHODS

Description of WTP Lekkerkerk (Oasen)

The source for DW production for Oasen is riverbank infiltrate from the River Lek into fenland soils, resulting in concentrations of methane, iron, ammonium and manganese in the raw water well above DW standards. In the Oasen WTP, methane is effectively stripped before or during trickling filtration by forced aeration. The other compounds, however, are deposited or converted in the DW trickling filters.

Two separate long-term experiments took place at Oasen WTP Lekkerkerk. The WTP comprises two comparable but separate DW trickling filtration systems for two separate well fields. This paper focuses on the first DW trickling filters only. To prevent interference, each of the full-scale experiments took place in a different treatment system. More details of the two experimental set-ups, dual-media DW trickling filtration with backwash in expansion mode and subsurface aeration, will be given later in this section. Raw and filtrate water quality parameters for both

full-scale systems during the experimental periods are summarized in Table 1.

In both systems, each DW trickling filter has a bed area of 18 m² and a bed depth of 2 m. The average superficial water velocity is 2.2 m h⁻¹. Figure 2 shows Oasen DW trickling filters with spraying of the raw water onto the dry filter bed. The second filter is being backwashed.

Experiment 1: dual-media DW trickling filtration with backwash in expansion mode

The application of dual-media DW trickling filters is rare. Dual-media filters consist of a layer of coarse material with a lower density on top of a finer material with a higher density. With downflow filtration the coarse material on top guarantees a large storage volume for suspended matter such as iron flocs, while the fine bottom layer supplies a good effluent water quality. The fractions of both materials are chosen such that the expansion during backwashing for the top layer is slightly larger than for the bottom layer. In the full-scale experiment, a combination of anthracite (1.4–2.5 mm, dry density 700 kg m⁻³) on top of normal filter sand (0.8–1.25 mm, dry density 1600 kg m⁻³) has been used. Each layer was 1 m in height (de Vet & Burger 2006).

Experiment 2: subsurface aeration

Another way for Oasen to maintain sound nitrification is by subsurface aeration, a mild form of *in situ* iron removal (Appelo *et al.* 1999). In this technique, limited amounts of tap water (oxygen content > 8 mg L⁻¹) are periodically injected over two days into one of the six wells on average used in the well field for extraction of groundwater, followed by 40 days of extraction from the same well. Because of this, the total amount of injection water is only 1% of the total extracted raw water. Subsurface aeration has a limited effect on the total iron concentrations in the raw water and only at the beginning of the extraction period. During subsurface aeration, mobile iron colloids are formed in the aquifer (Appelo & de Vet 2003; Wolthoorn *et al.* 2004a). Former research on subsurface aeration proved that these colloids are extracted with the raw water (Wolthoorn *et al.* 2004a). In lab-scale filtration experiments, Wolthoorn *et al.* (2004b) demonstrated that synthetically formed

Table 1 | Raw and filtrate water qualities for both experimental full-scale DW trickling filtration systems

		Dual-media filter with backwash in expansion*		Subsurface aeration†	
		Influent	Effluent	Influent	Effluent
Ammonium	mg L ⁻¹ NH ₄ ⁺ -N	4.5	0.41	1.7	0.05
Nitrite	mg L ⁻¹ NO ₂ ⁻ -N	<0.002	0.02	<0.002	0.01
Nitrate	mg L ⁻¹ NO ₃ ⁻ -N	<0.1	n.a.	<0.1	n.a.
Iron	mg L ⁻¹ Fe ²⁺	5.4	0.01	3.6	0.02
Manganese	mg L ⁻¹ Mn ²⁺	0.54	0.02	0.95	0.07
Methane	mg L ⁻¹ CH ₄	1.1‡	n.a.	0.59	n.a.
Bicarbonate	mg L ⁻¹ HCO ₃ ⁻	229	n.a.	229	n.a.
TOC	mg L ⁻¹ C	2.7	n.a.	2.2	n.a.
Temperature	°C	12	12	12	13
pH at 20°C	pH	7.24	7.41	7.33	7.75

*Average September 2004–2006.

†Average September 2005–2006.

‡Average 2003–2006.

n.a. = not analyzed.

analogues of these natural colloids also enhance nitrification. The filter material in the DW trickling filter on which the subsurface aerated groundwater was treated was coarse river sand (fraction 1.7–2.5 mm).

Measurements

Ammonium has been determined by colorimetric measurement. The method used has a detection limit of 0.03 mg L⁻¹ NH₄⁺-N and an accuracy of 0.019 at 0.16 mg L⁻¹ NH₄⁺-N.

**Figure 2** | Oasen DW trickling filters in production (in the front) and during backwash (in the background).

Nitrification capacity was calculated at every data point from the measured ammonium concentrations in the filter influent and effluent, and the water flow through the filter divided by the fixed gross volume of the filter bed.

Separate column experiments with samples from the full-scale filter, as shown in Figure 3, have been used to directly measure the expansion curves for the dual-media materials used. The measurements were performed twice: once with new filter material and once with coated materials from the full-scale DW trickling filter after more than a year of production. Measurements took place at 20 ± 2°C. Expansion was expressed as expanded bed height divided by bed height without expansion in the test column.

In order to determine the amount of deposits accumulated, 20 mL of filter material was flushed four times with 100 mL of demineralized water and the wash water was filtered over a glass fiber filter (Ø 90 mm, DoubleWeigh, F93490mm-X, T.J. Environmental) each time. The deposits' content was then calculated by measuring the dry weight of the clean filter and the filter with the deposits. The deposits content is expressed in g L⁻¹.

The composition of the coatings was determined in two ways. For most experiments, the washed, coated material was first dried after removing the deposits (see Methods for deposits' content). Next, all the coating of 4 g of dried filter material was dissolved in 100 mL 4M hydrochloric acid



Figure 3 | Diagram (left) and photos (fresh materials top right and coated materials bottom right) of experimental set-up for media expansion measurements.

with 2 g L^{-1} oxalic acid. The total coating weight was determined by measuring the dry weight before and after acidification and is expressed as mass-% of the dried, uncoated filter material. The calcium, iron, magnesium and manganese concentrations in the decanted acid solution were measured by ICP-MS. Only for the comparison of the coatings on subsurface aerated and non-subsurface aerated filter materials was Scanning Electron Microscopy combined with X-Ray Micro-Analysis (SEM/XRMA) used.

RESULTS

Existing single-media filters without subsurface aeration as pre-treatment

The full-scale DW trickling filters removed virtually all iron, ammonium and manganese during the first period after start-up. The calculated average nitrification capacity for a whole filter reached values of over $4.5\text{ g NH}_4^+\text{-N per h per m}^3$ of filter material. Long-term measurements of the

filter material from a full-scale DW trickling filter demonstrate that increased inorganic deposits on the filter material accompany the decline of nitrifying activity. Examination of the top 1 m depth of the filter shows a decrease of nitrification capacity and a growing coating of mainly iron deposits over time (Figure 4).

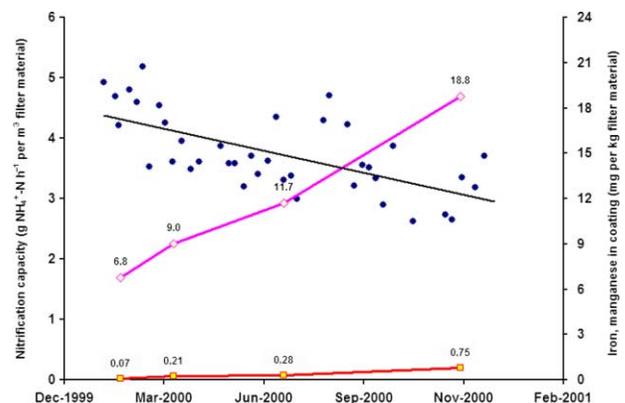


Figure 4 | Change in nitrification capacity (●) and amount of iron (◇) and manganese (□) coating in a single-medium DW trickling filter over time.

Dual-media DW trickling filtration with backwash in expansion

One way of delaying the deterioration of nitrification might be by reducing iron deposition on the filter material by improving backwashing. In the same treatment system, a dual-media filter with bed expansion during backwash was compared with a single-medium filter (coarse sand 1.7–2.5 mm) without bed expansion during backwash. For expansion of the reference single-medium filter material, a much higher superficial backwash velocity of over 90 m h^{-1} is required, which is physically impossible in the full-scale filters. To enhance deposit removal, a long backwash period with a water flow of 4 m h^{-1} and air scour was applied. Figure 5 shows that nitrification remained significantly better in the filter with backwash under bed expansion as compared to the filter backwashed without expansion over a period of almost two years' time. Run time for the dual-media filter was 96 h. For the single-medium filter, the run time was only 48 h due to clogging.

For efficient deposit removal during backwash, a minimum of preferably 10% expansion of the filter bed is required. Measured expansions of the filter materials used are shown in Figure 6. Bed expansion (measured in the laboratory at $20 \pm 2^\circ\text{C}$) increased during production,

probably due to the low density or the higher drag coefficient of the coating. In the full-scale filters, bed expansion will be even higher as a result of the higher water viscosity at the lower water temperature ($12\text{--}13^\circ\text{C}$).

In order to assess the efficiency of deposit removal during backwash, the deposits' content was determined by sampling at three depths in the filter bed. The removed deposits mainly consisted of iron (hydr)oxides (data not shown). Figure 7 illustrates the removal of deposits during backwash in the first year of production. The data points shown are the averages of 50 cm depths of the filter bed, so the 25 cm depth point is the value determined from samples over depths ranging from 0–50 cm, etc. Deposit removal after 12 months of production appeared to have become less efficient, and more deposits seemed to accumulate in the lower sand layer. The coating on the filter material also increased disproportionately in this period (Figure 8). However, the growth of the coating was overall much greater in the top anthracite layer.

Influencing the iron removal mechanisms by subsurface aeration

Coating of the filter material does not lead, *per se*, to nitrification problems. In full-scale filters, a comparable

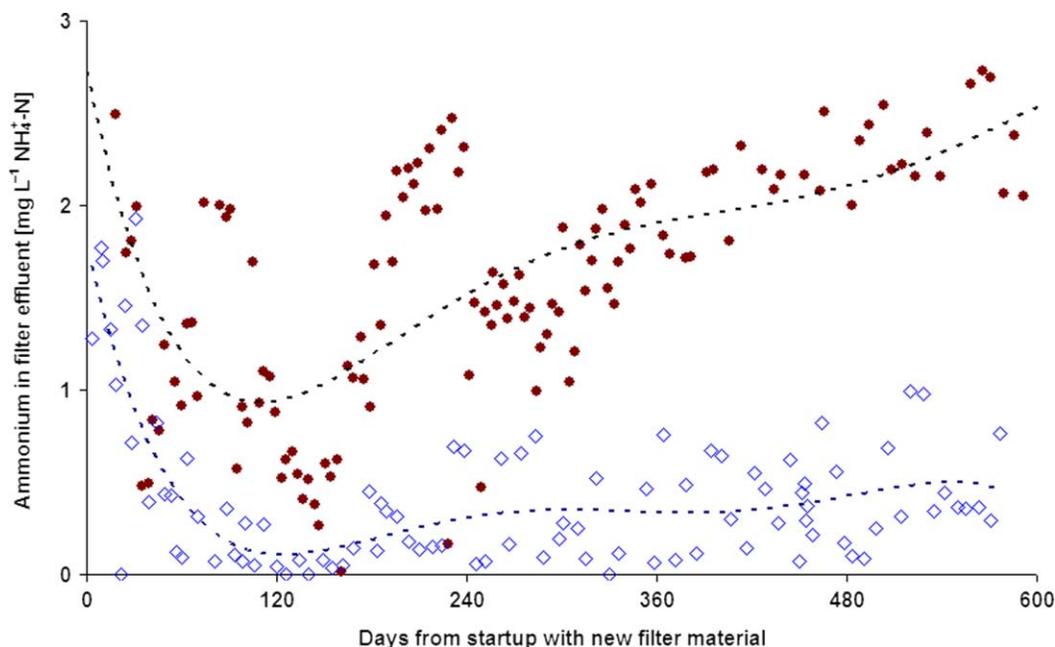


Figure 5 | Ammonium in the effluent of a filter with backwashing without expansion (●) and a filter with backwashing with bed expansion (◊).

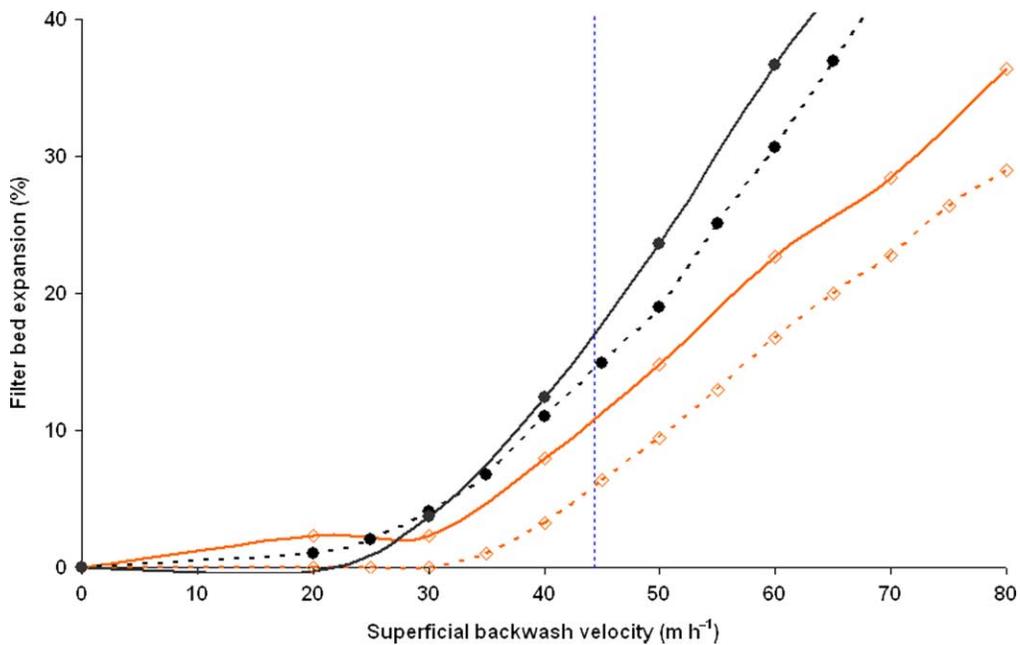


Figure 6 | Filter bed expansion for anthracite (●) and sand (◇) filter medium as a function of backwash velocity. Dotted lines are for fresh medium, solid lines for media after 13 months of operation. Actual backwash velocity at full-scale filter 44 m h⁻¹.

fraction, between 31–34%, of iron from the raw water was deposited as a filter coating in both a subsurface aerated filter and a filter without subsurface aeration after a production period of 2.5 years. Figure 9 illustrates both the

beneficial effect of subsurface aeration on nitrification in a single-medium DW trickling filter as well as the autonomous deterioration during a moratorium without subsurface aeration. This major improvement of the nitrification by

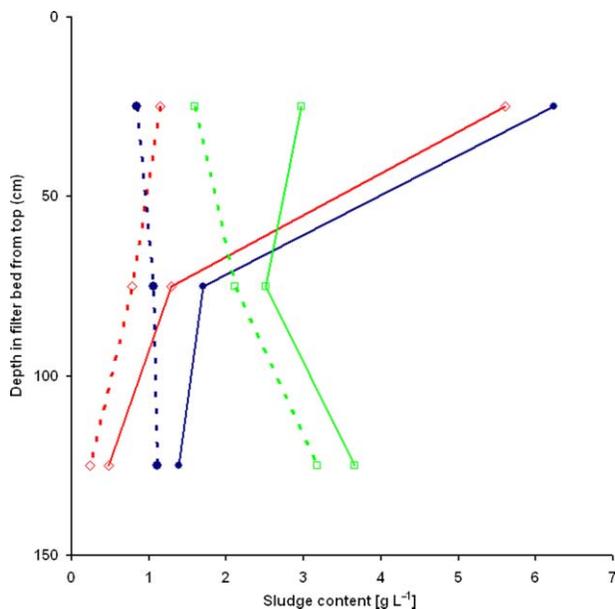


Figure 7 | Accumulated deposit amounts in the dual-media filter just before (solid lines) and after (dotted lines) backwashing. Operational times after filling with new filter medium were 3 months (◇), 6 months (●) and 12 months (□).

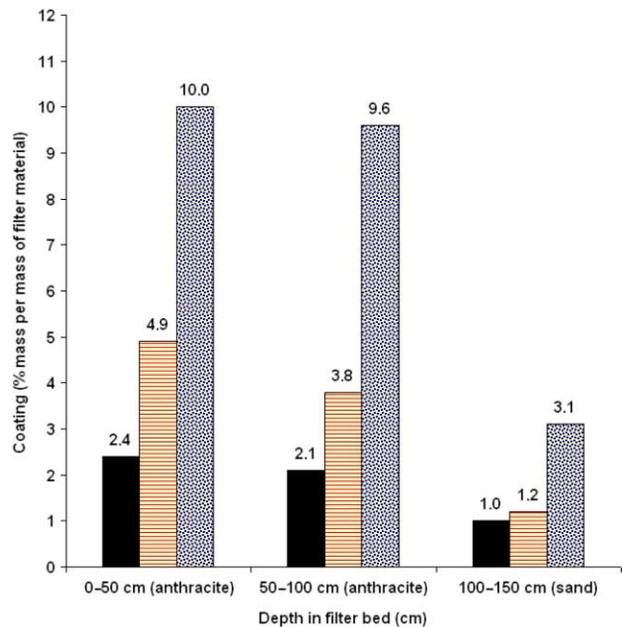


Figure 8 | Formation of mainly inorganic coating in three layers of the dual-media filter over time. Operational times after filling with new filter medium were 3 months (solid bars), 6 months (striped bars) and 12 months (dotted bars).

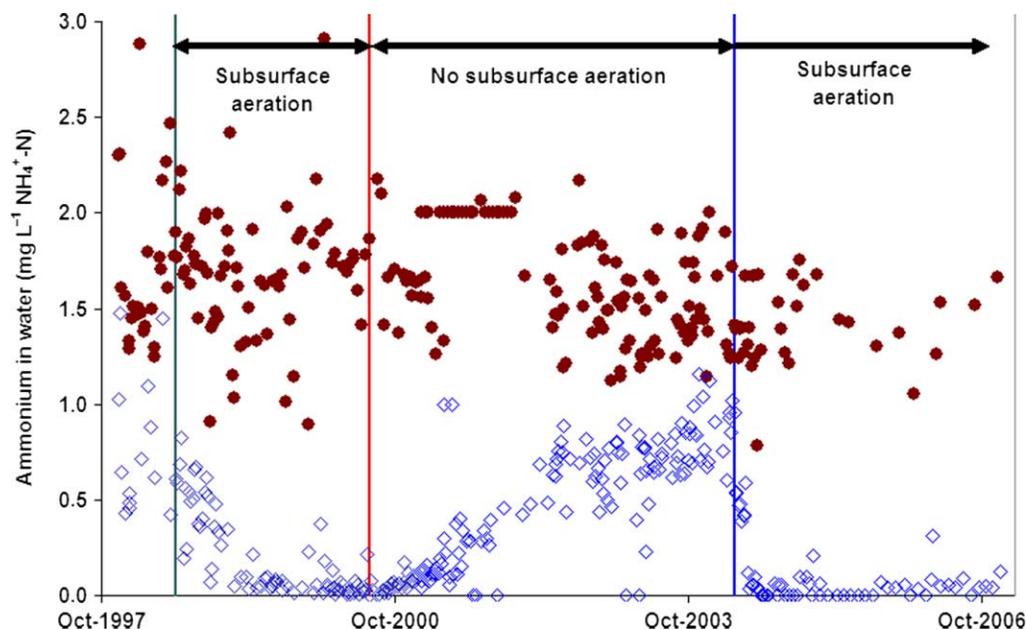


Figure 9 | Ammonium concentration in the influent (●) and effluent (◊) of a full-scale groundwater trickling filter during periods with and without subsurface aeration.

subsurface aeration has been reproduced in over 10 DW trickling filters at three full-scale Oasen WTPs during the last decade. It is emphasized that the effect is not caused by subsurface removal of iron or ammonium. Only 2–3% of the iron and no ammonium is removed in the aquifer due to subsurface aeration (data not shown).

The exact mechanism by which iron deposits influence nitrifying microorganisms is yet unknown. However, it is assumed that the characteristics of the filter coating play a determining role as the major attachment sites for nitrifying microorganisms. The composition of the main elements in the coatings of filter sand from a subsurface aerated and a non-subsurface aerated filter at Oasen is shown in Figure 10. In the subsurface aerated filter, the iron content is lower and the manganese content higher than in the non-subsurface aerated filter.

DISCUSSION

The decline of nitrifying activity in full-scale groundwater trickling filters can effectively be prevented by the application of dual-media filters backwashed with expansion or by the application of subsurface aeration. The observations presented throw some light upon the possible mechanisms

for the improved nitrification. The binding element appears to be iron deposition, iron being the quantitatively most important substance in these filters. All the iron hydroxides formed will consist of the unstable, low-crystalline ferrihydrite as a result of the rapid oxidation (in fact: hydrolysis) process.

Ferrihydrite – generally, but wrongly, called “amorphous iron oxide” – exists in different grades of crystallinity, ranging from two to eight peaks or lines in x-ray diffraction (XRD). The poorest crystalline ferrihydrite is formed at the highest rate of hydrolysis. Only the two-line ferrihydrite may transform into higher crystalline phases like goethite. Ferrihydrite has a larger surface area compared to the crystal forms that lack internal surfaces (Schwertmann & Cornell 2000). Using XRD, Sharma *et al.* (2002) found in all but one case only low-crystalline phases of iron hydroxides in full-scale filter samples in the Netherlands, but the crystalline gradation is not shown in that paper.

In DW trickling filters, reduced iron from groundwater is removed by a combination of two mechanisms: floc filtration and adsorptive oxidation. During the rapid hydrolysis in the water phase, primary ferrihydrite oxidation products of the lowest crystallinity are formed, which polymerize into agglomerations of voluminous, hydrated flocs during flocculation. In the adsorptive oxidation

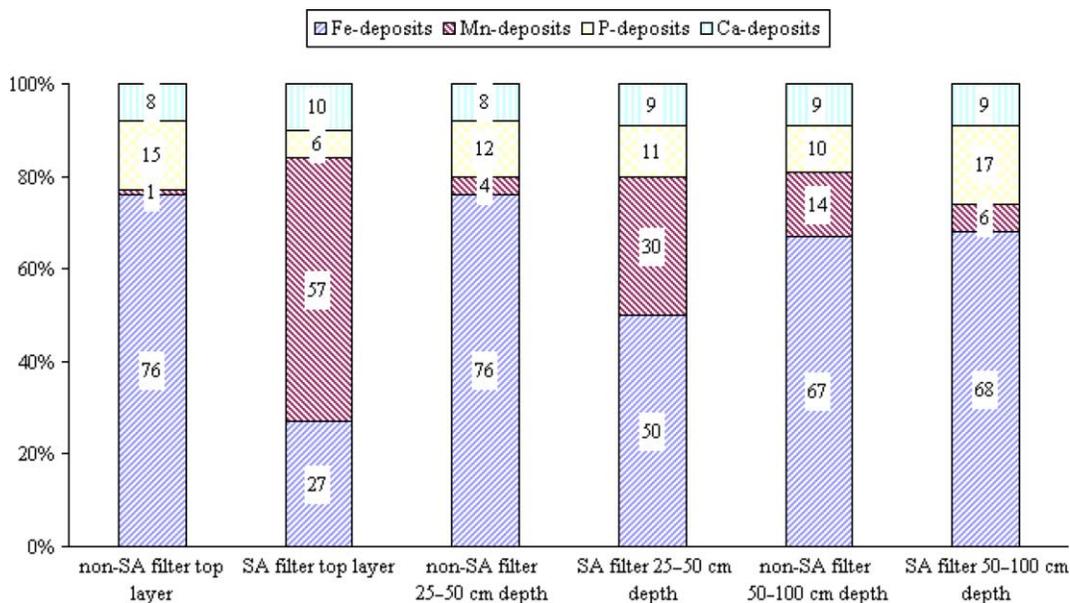


Figure 10 | Mass distribution of the major components in the coatings in a subsurface aerated and a non-subsurface aerated filter as determined by x-ray micro-analysis.

removal process, iron hydroxides grow by consecutive adsorption and oxidation, are therefore more compact, and possibly more crystalline. In DW trickling filters, adsorptive oxidation will prevail due to short pre-oxidation time, but both iron removal mechanisms will occur. During an effective backwash, the flocs formed by oxidation in the water phase are mostly flushed out of the filter bed. Without expansion, the removal is incomplete; flocs stay trapped in the filter bed and the iron may then be transformed onto the surfaces of the filter grains. Pedersen *et al.* (2005) demonstrated that, in the presence of Fe^{2+} , ferrihydrite is transformed within days into stable iron oxides such as lepidocrocite and goethite. The combination of both forms of iron is available in DW trickling filters. The standard backwash frequency for iron removing filters is once every 1–4 days, so in case of an ineffective backwash, the transformation of flocs may occur. On the one hand, this rapid transformation of ferrihydrite from the flocs into stable iron oxides on the filter coating might lower the porosity and permeability of the filter coating significantly. Direct growth of a ferrihydrite coating by adsorption and oxidation, on the other hand, will occur more gradually and result in a stable coating with larger pore area. An increase in the coating surface area by adsorptive oxidation was also found by Sharma *et al.* (2002).

When subsurface aeration is applied, nitrification remains good despite the presence of the coating. The composition and structure of the coating can be influenced by changing the oxidation regime of iron. One hypothesis based on research by Wolthoorn (2003) is that complex colloids formed by subsurface aeration might change the iron removal mechanism in the filters. The colloids might alter the ratio of iron removed by floc formation to adsorption by changing the homogeneous oxidation rate of iron or directly change the coating by attachment. The higher manganese content of the coating of subsurface aerated filters might be an indication of a larger surface area.

Further research into the effect of components other than iron in the filter coating (especially manganese) on nitrification is still necessary.

High porosity of the filter coating might alter the availability of, for example, substrates or trace elements or the attachment of microorganisms.

CONCLUSIONS

Nitrification problems in trickling sand filters for the production of drinking water from iron-containing groundwater usually occur through ageing of the filter

bed. The accumulation of iron hydroxide deposits between the filter material and the growth of mainly iron-based coatings on the filter material coincide with these problems and are their probable cause. Two full-scale techniques have proven successful in the long term to prevent the negative impact of iron removal on nitrification in the DW trickling filters. On the one hand, the irreversible accumulation of removed iron deposits can be prevented by using dual-media filtration in combination with backwashing with adequate filter bed expansion. On the other hand, the iron content of the coating can be reduced by changing the iron oxidation process through subsurface aeration. Both techniques maintain sound and almost complete nitrification in the first filtration step, thus contributing to the biological stability of the drinking water leaving the WTP.

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