Effect of oxygen deprivation on treatment processes in a full-scale drinking water biofilter

D. A. Søborg, I. L. Breda and L. Ramsay

ABSTRACT

Dissolved oxygen is critical for proper operation of waterworks that utilize anaerobic groundwater and rely on biofilters to remove iron, manganese and ammonium. In these biofilters, planned or inadvertent oxygen deprivation may occur for a variety of reasons. The water quality effects of oxygen deprivation on the function of drinking water biofilters, however, have not previously been reported. In this study, a 5-day oxygen deprivation period in full-scale biofilters was found to affect iron, manganese and ammonium concentrations differently. During the oxygen deprivation period, iron continued to be removed, although a greater depth of filter media was required to carry out the removal. Manganese oxide in filter media was mobilized, causing manganese water concentrations to increase well above raw water levels. The ammonium in the raw water passed through the biofilters unchanged, indicating the dependence of nitrification microorganisms on oxygen as their sole electron acceptor. Stringent national drinking water criteria were exceeded during the deprivation period but were once again met within hours after oxygenation was recommenced. Manganese and nitrite recovery to pre-deprivation concentrations, however, required days. The results illustrate the interdependence of treatment parameters and provide valuable practical information to waterworks that experience or plan oxygen stoppage.

Key words | aeration, drinking water, oxygenation, oxygen deprivation, rapid biofilter, treatment processes

INTRODUCTION

Dissolved oxygen (DO) is a critical parameter for the proper operation of many drinking water treatment systems. Often, production of drinking water is based on groundwater that contains iron, manganese and ammonium and is completely devoid of oxygen. In this situation, the treatment process may consist of two simple steps; an oxygenation step in which air or pure oxygen is dissolved into the source water followed by a filtration step that utilizes water saturated, rapid biofilters (AWWA & ASCE 2012). DO is the major electron acceptor for the chemical and microbiological processes that take place on the inorganic coating and in the biofilm that form on the granular support media in these biofilters.

Oxygen deprivation in biofilters may occur due to inadequate treatment system design, source water with high oxygen demand, faulty equipment, improper operation of the aeration step, down-time in connection with maintenance, etc. Since oxygen is required for the treatment of anaerobic groundwater, one would expect oxygen deprivation to have negative effects on the finished water quality. It is important to fully understand these effects. In addition, study of water quality deterioration during oxygen deprivation and subsequent recovery when oxygen is again added to the water is expected to provide valuable insight into the processes that take place in biofilters under normal, oxic conditions.

Effects of oxygen deprivation

The effects of low-oxygen conditions on biofilters have been studied previously (e.g. Bray & Olanczuk-Neyman 2001;
Van Beek et al. 2012). However, no studies regarding the effects of complete oxygen deprivation were found in the field of drinking water. At first glance, one might expect that the removal of iron, manganese and ammonium in drinking water biofilters would simply cease at the onset of oxygen deprivation conditions. The following examples, however, demonstrate that this is not necessarily the case.

One potential negative effect of oxygen deprivation is the reduction and dissolution of the large pool of iron and manganese precipitates that is present in mature biofilters. A study on iron oxide sludge from lime treatment of acid mine drainage (Beauchemin et al. 2010) showed, however, no dissolution of the iron oxide under anoxic conditions and therefore no release of iron oxide bound arsenic to the environment. Conversely, the study showed that manganese oxide present in the sludge was dissolved, suggesting that iron oxide was protected from dissolution as long as a significant amount of manganese oxide remained in the sludge. In another study, groundwater levels were raised, covering sediments in a drinking water aquifer that were previously oxic with anoxic water (Larsen & Postma 1997). This resulted in the reduction and dissolution of manganese oxide in the sediments with simultaneous release of manganese oxide bound nickel to the aquifer. Here, the reduction of manganese oxide was attributed to concomitant oxidation of iron (II) ions. A study on drinking water treatment found increasing manganese concentration in the water after filtration when conditions of low DO (0.4–1.8 mg L\(^{-1}\)) were maintained for more than 4 days (Bray & Olanczuk-Neyman 2001). Other studies have identified several bacterial species in water systems that are able to reduce, e.g. iron and manganese oxide under aerobic as well as anaerobic conditions (Weber et al. 2006; Vandieken et al. 2012).

Another potential negative effect of oxygen deprivation is the obstruction of ammonium conversion. In simplified geochemical models, ammonium is oxidized to nitrite by ammonium oxidizing bacteria (AOB) and further to nitrate by nitrite oxidizing bacteria (NOB) in the presence of oxygen. Without a suitable electron acceptor, ammonium in the raw water would simply pass through the biofilters to the finished water without oxidation. These simplified models, however, do not take into account that alternative electron acceptors for ammonium oxidation include nitrite (the anammox wastewater treatment process) (Mulder et al. 1995), nitrogen dioxide (Schmidt & Bock 1997), sulfate (Rikmann et al. 2012), manganese oxide (Javaud et al. 2011) and iron oxide (Clement et al. 2005). For various reasons, these alternative electron acceptors may be irrelevant under oxygen deprivation conditions in drinking water biofilters: some are not expected to be found in the anaerobic groundwater used as source water (nitrite, nitrogen dioxide) while others may require special conditions or acclimatization periods (manganese oxide, iron oxide, sulfate).

In a drinking water treatment system, water quality deterioration during a period of oxygen deprivation may be superseded by water quality improvement during a subsequent period of recovery when oxygen addition is recommenced. Wastewater treatment systems with cyclic aerobic/anaerobic conditions provide information about this recovery period. In a study by Mota et al. (2005), accumulation of the highest nitrite concentrations in effluent from digested swine manure laboratory reactors was observed for the longest non-aerated period (4 hours) indicating that NOB were more sensitive than AOB to oxygen deprivation. The longest non-aerated periods also resulted in the lowest ratio of total NOB to total rRNA suggesting that these periods have a strong effect on NOB biomass levels (Mota et al. 2005). In other studies, however, AOB and NOB have been found to survive oxygen deprivation for years (Biswas et al. 2011; Yan et al. 2012).

The water quality effects of oxygen deprivation on the function of full-scale drinking water biofilters have not previously been reported. One barrier to performing such experiments in full-scale is that the quality of the finished water may immediately deteriorate and no longer meet water quality criteria. An opportunity was afforded for this study at a newly completed waterworks near Aarhus, Denmark, which had just completed the start-up period, but had not yet begun to pump the finished water to the consumers.

Waterworks used in the experiment

Truelsbjerg waterworks (Aarhus Water Ltd, Denmark) has three identical production lines. Water treatment starts
with the addition of 93–95% pure oxygen to the raw water. This oxygenation is followed by filtration through two stainless steel pressure filters in series (Filter 1 and 2). The filters are backwashed with air and water in an up-flow direction. The procedure consists of three steps: (1) 3 minutes of compressed air alone; (2) 10 minutes of compressed air and treated, oxic water simultaneously; and (3) 9 minutes of treated, oxic water alone. The oxygen deprivation experiment described in this paper was carried out on Production Line 1 (Figure 1).

**METHODS**

**Experimentation**

Addition of oxygen to the raw water during regular operation (see Figure 1) was stopped abruptly in Production Line 1 at Truelsbjerg waterworks on 8 October 2014 by closing the appropriate ball valve. The valve remained closed for 5 days (deprivation period). It was re-opened on October 13 and remained open for the rest of the experiment (recovery period). The flow was $42 \pm 9 \text{ m}^3\text{ h}^{-1}$ and both filters were backwashed once on October 10. During backwash, the water in the filters was completely replaced with finished water with an oxygen content of approximately 10 mg L$^{-1}$.

**Field measurements**

The oxygen concentration in water between filters and in finished water was logged during the entire experiment (optical dissolved oxygen sensor FDO 925 and Multi 3430 meter, WTW GmbH, Germany). Ammonium concentrations were logged at-line in the same two locations (Amtax SC Ammonium Analyzer, Hach Lange Ltd, Denmark). Commonplace in-line physical and chemical parameters (flow, temperature, pressure, turbidity, pH and conductivity) were also logged.

**Sampling**

Water samples were collected manually using standard procedures (ISO 5776-5:2006) from stainless steel taps in 29 locations (Figure 1): from raw water, water between filters and finished water as well as from 13 taps distributed at 20 cm depth intervals on each filter. Water was collected 11 times from the first-mentioned locations: under baseline (pre-deprivation) conditions, during the deprivation period (1, 2 and 3 hours, 2, 3, 4 and 5 days) and during the recovery period (3 and 5 hours, 3 days). Water samples from the 13 taps on each filter were collected four times: baseline, deprivation 3 hours, deprivation 5 days, recovery 3 hours. All samples were stored at 5°C and analyzed within 24 hours.
Chemical analyses

Iron, manganese and ammonium were analyzed by colorimetry (DR 3900, Hach Lange Ltd, Denmark) according to the manufacturer’s instructions with the kits LCK321/521, LCK304, and LCW532, respectively. Nitrite was analyzed by colorimetry using Standard Method 4500-NO2 (B) (APHA et al. 1989).

Filter media characteristics

Filter 1 contained calcium carbonate (Nevtraco®) from Silhorko Eurowater Ltd. Filter 2 contained a thin layer of manganese oxide (Demantax®) from Silhorko Eurowater Ltd and quartz (DanaKvarts®) from Dansk Kvarts Industri A/S. Both filters contained support material (DanaKvarts®) (Figure 1). The particle density and porosity of the filter media were calculated using a gravimetric method in which a graduated cylinder was tared, filled with 100 mL dried media, and weighed again. Water was added until the pores were filled, the cylinder shaken to settle the sand, excess water above the sand removed, and the cylinder weighed again. Grain size was determined by Dynamic Image Analysis (Camsizer® 2006, Retsch Technology GmbH, Germany).

RESULTS AND DISCUSSION

Source water quality

The source water at Truelsbjerg waterworks is anaerobic groundwater abstracted from eight wells. All wells were active during the experiment, although some wells were stopped during night hours, reflecting variations in consumer demands. The water quality of the mixed raw water varied therefore only slightly during the experiment. Calcium (91 ± 9 mg L⁻¹) and hydrogen carbonate (293 ± 23 mg L⁻¹) were the dominating ions, the redox conditions were reduced (no oxygen, nitrate or nitrite, but traces of methane and hydrogen sulfide) and the pH conditions were near neutral (7.5 ± 0.2). The source water concentrations of the main treatment parameters iron, manganese and ammonium (1.5 ± 0.6, 0.47 ± 0.23 and 0.23 ± 0.03 mg L⁻¹) exceeded the respective Danish drinking water criteria of 0.1, 0.02 and 0.05 mg L⁻¹ (BEK 292 2014; GEUS 2014). These criteria are considerably more stringent than in many countries, reducing the risk of overlooking important concentration changes that might otherwise be considered trivial.

Filter media

The grain size ranges (10–90% fractiles) were found to be 2.3–4.1, 0.5–0.8 and 1.6–3.2 mm for calcium carbonate, quartz and manganese oxide, respectively. The calcium carbonate in Filter 1 was found to have a larger porosity (40.3%) than the quartz (33.3%) in Filter 2, justifying the selection of calcium carbonate for Filter 1 where iron oxides are formed. Granular manganese oxide was placed in a layer at the top of Filter 2 (Figure 1) to help remove manganese ions from the raw water in a manner similar to manganese greensand, a more frequently used filter media. Due to its higher particle density (3.32 kg L⁻¹), the manganese oxide sank through the quartz (2.51 kg L⁻¹) during backwashes prior to the experiment.

Baseline conditions

The term baseline is used here to describe normal operation under oxic conditions. The biofilters had been performing well under baseline conditions for more than three weeks prior to the experiment. A sampling event just prior to the on-set of oxygen deprivation confirmed that the biofilters removed iron, manganese and ammonium below the stringent national drinking water criteria. Furthermore, no nitrite from the conversion of ammonium was observed in concentrations above the detection limit in water samples collected between the two filters or in the finished water. The DO in the finished water was approximately 8 mg L⁻¹.

Turning off the oxygenation

Addition of oxygen near the inlet of Filter 1 was stopped abruptly (i.e. input of oxygen to Filter 1 was described by a decreasing step function). Shortly thereafter, the DO between filters decreased exponentially to anoxic conditions, see Figure 2. The breakthrough of oxygen-depleted...
water indicated a median residence time of water in Filter 1 of 29 minutes and a residence time distribution ranging from 15 to 56 minutes (5 and 95% fractiles).

The breakthrough of oxygen-depleted water between the filters was accompanied by an increase in ammonium (Figure 2). The increase did not begin until anoxic conditions were reached. Within 60 minutes of the onset of anoxic conditions, the ammonium concentration between filters reached about 90% of the raw water level of 0.24 mg L\(^{-1}\). No change in iron and manganese concentrations was observed between filters during the first 120 minutes following the oxygen stoppage (Figure 2).

The deprivation period

The oxygen deprivation period was continued for 5 days. During the entire deprivation period, DO levels of 0.1–0.4 mg L\(^{-1}\) were measured in water between filters and in finished water. These low values likely represent the detection limit, caused by small amounts of vagrant oxygen entering the measurement set-up. An exception was seen during backwash at both sampling locations. Here, the DO concentration increased to the level of DO in the water used for the backwash and dropped immediately when normal operation was resumed. The first water samples were collected 24 hours after backwash. Any effects due to the introduction of oxygen during backwash would be expected to be short-lived and not traceable in these samples.

Table 1 shows that concentrations of iron, manganese and ammonium in the raw water exceeded the national criteria in all samples, hence the need for water treatment.

In samples collected between the two filters and in the finished water, iron was in compliance with the national drinking water criterion at all times during oxygen deprivation and recovery. In these same locations, however, manganese concentrations started to exceed the criterion within the first 3 days of the deprivation period. Ammonium exceedances in the finished water began with the sample collected 2 hours after the oxygen stoppage. A single nitrite

![Figure 2](https://iwaponline.com/ws/article-pdf/15/4/825/413776/ws015040825.pdf)

**Figure 2** Concentration of DO and treatment parameters as a function of minutes after oxygen stoppage at the sampling location between Filters 1 and 2.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Compound</th>
<th>Baseline (mg L(^{-1}))</th>
<th>Deprivation (mg L(^{-1}))</th>
<th>Recovery (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>1 h</td>
<td>2 h</td>
<td>3 h</td>
</tr>
<tr>
<td>Raw water</td>
<td>Fe(^{2+})</td>
<td>1.39</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>Mn(^{2+})</td>
<td>0.530</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NH(_4)(^+)</td>
<td>0.236</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td>NO(_2)(^-)</td>
<td>&lt;0.005</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Between Filters 1 and 2</td>
<td>Fe(^{2+})</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Mn(^{2+})</td>
<td>0.005</td>
<td>0.005</td>
<td>0.006</td>
</tr>
<tr>
<td></td>
<td>NH(_4)(^+)</td>
<td>&lt;0.015</td>
<td>0.038</td>
<td>0.215</td>
</tr>
<tr>
<td></td>
<td>NO(_2)(^-)</td>
<td>&lt;0.005</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Finished water</td>
<td>Fe(^{2+})</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td></td>
<td>Mn(^{2+})</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
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<tr>
<td></td>
<td>NH(_4)(^+)</td>
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<td>0.149</td>
<td>0.211</td>
</tr>
<tr>
<td></td>
<td>NO(_2)(^-)</td>
<td>&lt;0.005</td>
<td>NA</td>
<td>NA</td>
</tr>
</tbody>
</table>

NA, not analyzed.

Shading indicates concentrations above national drinking water criteria.
exceedance was seen 5 hours into the recovery period between filters. The exceedances of drinking water criteria demonstrate that oxygen deprivation can have important practical implications.

**Depth profiles of iron, manganese and ammonium**

Under baseline conditions, removal of iron, manganese and ammonium was complete in Filter 1 at filter media depths of 90, 170 and 130 cm, respectively (Figure 3(a)–3(c)). This means that Filter 2 was not necessary for the water treatment process (Figure 3(d)–3(f)).

The iron depth profile after 3 hours of oxygen deprivation (Figure 3(a)) shows that a greater filter media depth (150 cm) compared to baseline conditions (90 cm) was required to achieve iron concentrations in the water below the national drinking water criterion of 0.1 mg L\(^{-1}\). After 5 days of oxygen deprivation, the entire filter depth of Filter 1 was needed to meet this criterion. If the oxygen deprivation period had been longer, one would expect the dissolved iron in the raw water eventually to pass through both filters, causing the finished water to exceed the iron criterion.

Manganese was still removed completely in Filter 1 after 3 hours of oxygen deprivation and there was no noteworthy difference in the removal depth compared to the baseline (Figure 3(b)). However, after 5 days of oxygen deprivation, about twice the concentration of manganese (about 1 mg L\(^{-1}\)) was found in the water between filters compared to the raw water (about 0.5 mg L\(^{-1}\)). Looking at the profile, the increase took place at a media depth of 70–190 cm (tap 7–13) in Filter 1 (Figure 3(b)) and was most likely related to reduction and mobilization of previously precipitated manganese oxide on the filter media to manganese (II) ions. The electron donor utilized for this reduction reaction was not investigated directly. Thermodynamically, however, manganese oxide reduction takes place at a higher oxidation–reduction potential than iron oxide reduction and

![Figure 3](https://iwaponline.com/ws/article-pdf/15/4/825/413776/ws015040825.pdf)
may therefore be more redox active in biofilters (Petrunic et al. 2005). Stoichiometrically, iron (II) ions in the raw water may result in the mobilization of manganese (II) ions in a ratio of 2:1 according to the redox reaction equation below.

\[
2\text{Fe}^{2+} + \text{MnO}_2 + \text{H}_2\text{O} + 3\text{H}_2\text{O} = 2\text{Fe(OH)}_3 + \text{Mn}^{2+} + 2\text{H}^+
\]

Five days into the deprivation period, Filter 1 lowered the iron concentration from 1.31 mg L\(^{-1}\) (raw water) to 0.266 mg L\(^{-1}\) (tap 13), a change of 18.7 meq L\(^{-1}\). Correspondingly, the manganese concentration increased from 0.456 to 1.107 mg L\(^{-1}\), a change of 11.8 meq L\(^{-1}\). This results in an iron/manganese equivalent ratio of 1.6:1, which is in reasonable agreement with the theoretical ratio of 2:1. This suggests that continued oxidation of iron in the raw water was made possible by manganese oxide acting as the electron acceptor, a view supported by the study of Larsen & Postma (1997).

The 1 mg L\(^{-1}\) manganese in the water entering Filter 2 decreased to a concentration of 0.4 mg L\(^{-1}\) in the finished water. The decrease happened at a media depth of 110–190 cm (tap 9–13) of Filter 2 (Figure 3(e)) with the largest decrease found at a media depth of 170–190 cm (tap 12–13) corresponding to the approximate location of granular manganese oxide filter media at the time of the experiment. This illustrates the advantage of including manganese oxide as a filter medium.

The ammonium depth profiles (Figure 3) clearly show that ammonium was not removed during the oxygen deprivation period and that ammonium removal recovered completely shortly after oxygen addition recommenced. This indicated that the AOB required oxygen to carry out the first step of nitrification and that no compensating mechanism using other electron acceptors or other microorganisms was found in the system.

The recovery period

After 5 days of oxygen deprivation, oxygenation was recommenced. The concentration of oxygen reached the median oxygen concentration of 4 mg L\(^{-1}\) within 45 minutes and returned to the baseline value of approximately 8 mg L\(^{-1}\) within a few hours. This was in contrast to the 29 minutes required for the oxygen to decrease to 4 mg L\(^{-1}\) at the start of the deprivation period. This discrepancy may be due to a reduction capacity in the precipitated oxides that was accumulated in the filter during the deprivation period.

After 3 hours of recovery, the following changes were observed (Figure 3). Iron concentrations fell below 0.05 mg L\(^{-1}\) in the first 90 cm of media in Filter 1 (tap 8), comparable to baseline conditions (Figure 3(a)). Similarly, ammonium depth profiles corresponding to those at baseline conditions were achieved (Figure 3(c)). For manganese, the removal took place beginning at a media depth of 50 cm in Filter 1 (tap 6, Figure 3(b)) as was the case during baseline conditions. In contrast to baseline concentrations, however, manganese concentrations in the water between filters (0.152 mg L\(^{-1}\)) and in the finished water (0.085 mg L\(^{-1}\)) did not meet the national drinking water criterion of 0.02 mg L\(^{-1}\). During baseline conditions, the criterion was met at a media depth of 170 cm (tap 12) in Filter 1 (Table 1 and Figure 3(e)). After 5 hours of recovery, both filters were still required to achieve complete removal of manganese. The concentrations of manganese in the water between the filters and the finished water were 0.075 and 0.052 mg L\(^{-1}\), respectively. Additional samples taken 3 days after the start of the recovery period showed that manganese was once again completely removed in Filter 1, as seen at baseline.

During recovery, the ammonium concentration decreased as soon as oxic conditions were reestablished in the filters. The drinking water criterion for ammonium was reached in water between filters and the finished water in less than 2 hours. There was a clear accumulation of nitrite in Filter 1 5 hours after start of the recovery period. The concentration of nitrite in water between the filters (0.040 mg L\(^{-1}\), Table 1) greatly exceeded the criterion of 0.01 mg L\(^{-1}\). Selected profile samples for nitrite showed that this took place in the bottom half of Filter 1 (from tap 8, data not shown) which corresponded well to the depth at which ammonium was oxidized to nitrite (primarily between tap 7 and 9, see Figure 3(c)). This indicates that AOB recovers more quickly than NOB. This means that the similar observations made in wastewater systems (Mota et al. 2005) are now confirmed in drinking water systems.
CONCLUSIONS

In the experiment performed, oxygen deprivation at a full-scale waterworks caused deterioration of the finished water quality. Due to stringent drinking water criteria, this deterioration resulted in the very practical problem of non-compliant finished water.

The effect of oxygen deprivation was different for each of the individual treatment parameters. Iron continued to be removed during the entire 5-day oxygen deprivation period, although a greater depth of filter media was required to effect the removal. Manganese was mobilized from the manganese oxide already present on the mature filter media, causing the manganese concentration in the water between the filters to be approximately twice as high as in the raw water. The continued removal of iron and the mobilization of manganese appear to be directly related through a reaction in which manganese oxide acts as a surrogate electron acceptor for the oxidation of iron in the absence of oxygen. The ammonium in the raw water simply passed through the filters unchanged during oxygen deprivation, indicating the exclusive dependence of nitrification on oxygen as the sole electron acceptor.

The recovery period illustrated that the stringent national drinking water criteria were once again met for iron, manganese and ammonium within hours after oxygenation was recommenced. However, complete manganese and nitrite recovery to pre-deprivation concentrations required days. The delayed nitrite recovery indicates that NOB are more sensitive to oxygen deprivation than AOB. The rapid recovery following oxygen deprivation is important information for waterworks that experience an oxygen stoppage or who intentionally stop the aeration/oxygenation for a period of time.

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