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Remediation of incomplete nitrification and capacity increase of biofilters at different drinking water treatment plants through copper dosing

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ABSTRACT

Drinking water treatment plants based on groundwater may suffer from incomplete ammonium removal, which deteriorates drinking water quality and constrains water utilities in the operation of their plants. Ammonium is normally removed through nitrification in biological granular media filters, and recent studies have demonstrated that dosing of copper can stimulate the removal of ammonium. Here, we investigated if copper dosing could generically improve ammonium removal of biofilters, at treatment plants with different characteristics. Copper was dosed at $\leq$1.5 μg Cu/L to biofilters at 10 groundwater treatment plants, all of which had displayed several years of incomplete nitrification. Plants exceeded the Danish national water quality standard of 0.05 mg NH_4^+/L by a factor of 2–12. Within only 2-3 weeks of dosing, ammonium removal rates increased significantly (up to 150%). Nitrification was fully established, with ammonium effluent concentrations of <0.01 mg NH_4^+-N/L at most plants, regardless of the differences in raw water chemistry, ammonium loading rates, filter design and operation, or treatment plant configuration. However, for filters without primary filtration, it took longer time to reach complete ammonium removal than for filters receiving prefiltered water, likely due to sorption of copper to iron oxides, at plants without prefiltration. With complete ammonium removal, we subjected two plants to short-term loading rate upshifts, to examine the filters' ability to cope with loading rate variations. After 2 months of dosing and an average loading rate of 1.0 g NH_4^+-N/m^3 filter material/h, the loading rate was upshifted by 50%. Yet, a filter managed to completely remove all the influent ammonium, showing that with copper dosing the filter had extra capacity to remove ammonium even beyond its normal loading rates. Depth sampling revealed that the ammonium removal rate of the filter's upper 10 cm increased more than 7-fold from 0.67 to 4.90 g NH_4^+-N/m^3/h, and that nitrite produced from increased ammonium oxidation was completely oxidized further to nitrate. Hence, no problems with nitrite accumulation or breakthrough occurred. Overall, copper dosing generically enhanced nitrification efficiency and allowed a range of quite different plants to meet water quality standards, even at increased loading rates. The capacity increase is highly relevant in practice, as it makes filters more robust towards sudden ammonium loading rate variations.

1. Introduction

Ammonium (NH_4^+) is often a concern when anoxic groundwater is used for drinking water production. Generally, ammonium is removed biologically during water treatment, through nitrification in rapid granular media filters. The process is mediated by ammonia oxidizing bacteria (Prosser, 1989) or archaea (Martens-Habbena et al., 2009), which oxidize ammonia to nitrite, and nitrite oxidizing bacteria (Prosser, 1989), which oxidize nitrite to nitrate. Recently, complete oxidation of ammonia to nitrate in one organism (comammox) has been reported (Daims et al., 2015). Presence of nitrifying microorganisms in biological filters treating

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groundwater is well studied (de Vet et al., 2011; Gülay et al., 2014; Lee et al., 2014; Palomo et al., 2016).

Unfortunately, nitrification is sometimes incomplete, leading to ammonium and/or nitrite residues in the treated water. This can cause microbial aftergrowth in distribution systems without disinfection (van der Kooij, 2000), which may cause oxygen depletion, unpleasant taste and odor, and technical problems such as corrosion (Zhang et al., 2009). Furthermore, in systems with chlorine-based disinfection, ammonium can reduce the disinfection efficiency (Zhang et al., 2009). Incomplete nitrification during treatment therefore poses a risk to drinking water quality and safety. Especially for systems without disinfectant residual, such as in Denmark, efficient removal of growth-promoting nutrients to concentrations as low as possible is essential for preventing microbial aftergrowth (Prest et al., 2016; van der Kooij, 2000). Hence, to ensure safe drinking water, a guideline value for ammonium is set at 0.5 mg NH_4^+/L by the EU drinking water directive (European Comission, 1998). Some EU member states enforce stricter guideline values; like Denmark, with 0.05 mg NH_4^+/L for ammonium and 0.01 mg NO_2^-/L for nitrite (Ministry of Environment and Food of Denmark, 2016).

Ammonium is the parameter that challenges Danish water utilities by far the most. Between 2002 and 2013, out of 5,826 analyzes of effluent water at the larger Danish drinking water treatment plants (treating >350,000 m^3/y), 13.2% exceeded the ammonium guideline value (Danish Nature Agency, 2014, 2012, 2009, 2007). With the legal water quality demand, poor nitrification performance constrains water utilities in the way they operate their treatment plants. As a result, the hydraulic loading rate (i.e. treatment flow) is often decreased until the effluent guideline is met, which means that the utilities have a reduced treatment capacity. Besides the constraints with regards to production capacity, it furthermore leaves no room for buffering sudden (and sometimes unexpected) loading increases (Lee et al., 2014). Problems with incomplete nitrification have been known for long (Stamer and Nielsen, 2005) and expensive and time-consuming experience based approaches are taken to remediate the deficiencies – often without success.

Recently, we demonstrated that poor nitrification performance could be resolved by dosing of copper as micronutrient to a rapid sand filter (Wagner et al., 2016a). The metal is vital for the enzyme ammonia monooxygenase, responsible for the oxidation of ammonia (Sayavedra-Soto and Arp, 2011). When copper was dosed to the deficient biofilter, ammonium removal activity rapidly increased (Wagner et al., 2016a). Yet, this investigation focused on a single treatment plant, and parameters affecting the availability of copper such as alkalinity (Zhang and Edwards, 2010), pH (Sylva, 1976), and iron load (Benjamin et al., 1996), can vary from plant to plant. It is therefore of great importance to investigate whether these observations (Wagner et al., 2016a) are generic and applicable at different treatment plants with diverse features. With a stimulation of nitrification, the further question arises whether the dosing can increase biofilters' robustness, and thus enable filters to completely nitrify ammonium even under ammonium loading rate upshifts which exceed the normal loading rates.

In light of the problems with poor nitrification performance constraining treatment plant operation, our study had two main aims: (I) to investigate if copper dosing can generically increase ammonium removal efficiency and thereby remediate incomplete nitrification, at various treatment plants with individual features such as different treatment units, filter designs and operation, ammonium loading rates, raw water chemistry, etc., and (II) to elucidate whether the dosing can increase ammonium removal rates further, beyond the ammonium loading rates typical for the filters. Here, we present a comprehensive investigation on the effect of copper dosing on nitrification at 10 full-scale drinking water treatment plants in Denmark.

2. Materials and methods

2.1. Investigated drinking water treatment plants

The investigated 10 drinking water treatment plants (DWTPs) are located across Denmark and abstract groundwater from anaerobic aquifers with different raw water chemistry (Table 1). The selected DWTPs all failed to completely remove the influent ammonium loadings, leaving ammonium residues in the finished water, and they represented a wide range of different characteristics. The main treatment steps at the plants were aeration of groundwater, followed by granular media filtration. Five plants had primary and subsequent secondary filtration; the other five had single filtration only (Table 2). At all DWTPs, filter material was quartz of variable grain size (except for Bakkebølle DWTP, where calcined flint was used). The depth of active layers (assumed active for removal of ammonium) of the filters varied, as did the hydraulic and ammonium loading rates (Table 2).

2.1.1. Investigations with copper dosing

To characterize nitrification performance prior to copper dosing, samples for ammonium, nitrite, and copper were collected from the filters' influent and effluent water. Then copper dosing to one or more filters at the DWTPs started. Copper was dosed by different methods: passive dosing with a solid copper structure releasing copper to the water through contact between fluid and solid, active dosing through electrolysis (Albrechtsen et al., 2015), or as liquid solution prepared from $CuSO_4$ (technical grade, VWR chemicals) (Table 2). Whenever a plant was equipped with primary filtration, copper was dosed to a secondary filter. At the onset of copper dosing, ammonium influent and effluent concentrations were analyzed with a 30 min frequency with an ammonium autoanalyzer (Hach Lange, AMTAX™ sc) at Nærum (Wagner et al., 2016a), at Langerød, and Glostrup DWTPs, and elsewhere with at least one sampling per week. During the dosing, operational parameters (such as hydraulic loading, etc.) were maintained constant. Effects of the dosing on nitrification were assessed by comparing dosing filters' effluent ammonium concentrations before and during dosing. Additionally, volumetric ammonium removal rates (ARRs) were calculated to compare the filters performance, at the respective volumetric ammonium loading rates (ALRs) (see 2.4 for calculation). Reference filters, which were operated under the same conditions as the dosing filters, but without dosing, were monitored at DWTPs Nærum (Wagner et al., 2016a), Langerød, Glostrup, Holmehave, and Frederiksgade.

2.1.2. Ammonium loading rate upshift experiments

To investigate robustness of ammonium removal during ammonium loading rate upshifts, ALRs were increased above the normal loading rates at DWTPs Glostrup and Holmehave. Prior to the upshifts, normal loading rates were: 1.23 ± 0.15 g NH_4^+-N/m^3/h at Glostrup, during approximately 8 months, and 1.00 ± 0.09 g NH_4^+-N/m^3/h at Holmehave DWTP, during approximately 7 months. Upshifts started when ammonium removal was complete with dosing, under normal ALRs. During upshifts, average ALRs were 1.49 ± 0.08 and 1.18 ± 0.28 g NH_4^+-N/m^3/h, with peak ALRs as high as 1.85 and 2.05 g NH_4^+-N/m^3/h, at Glostrup and Holmehave DWTPs. Ammonium influent concentrations to the filters were relatively stable, so that the loading upshifts were conducted by increasing the filters' hydraulic loading. ARRs at respective ALRs were calculated to compare nitrification performance. Additionally, at Holmehave DWTP, water was collected over depth of the filter with