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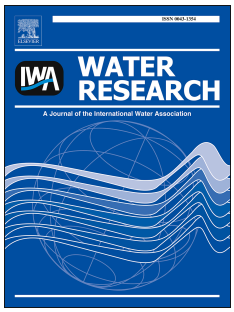

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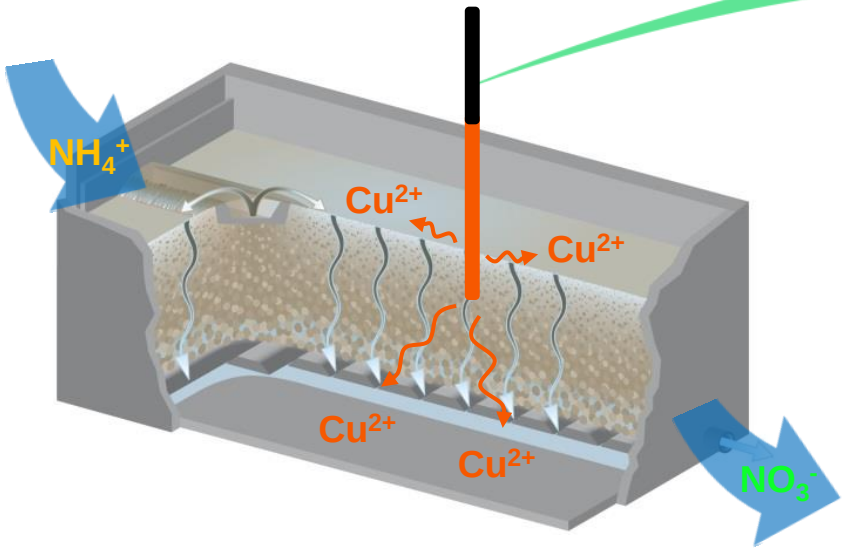

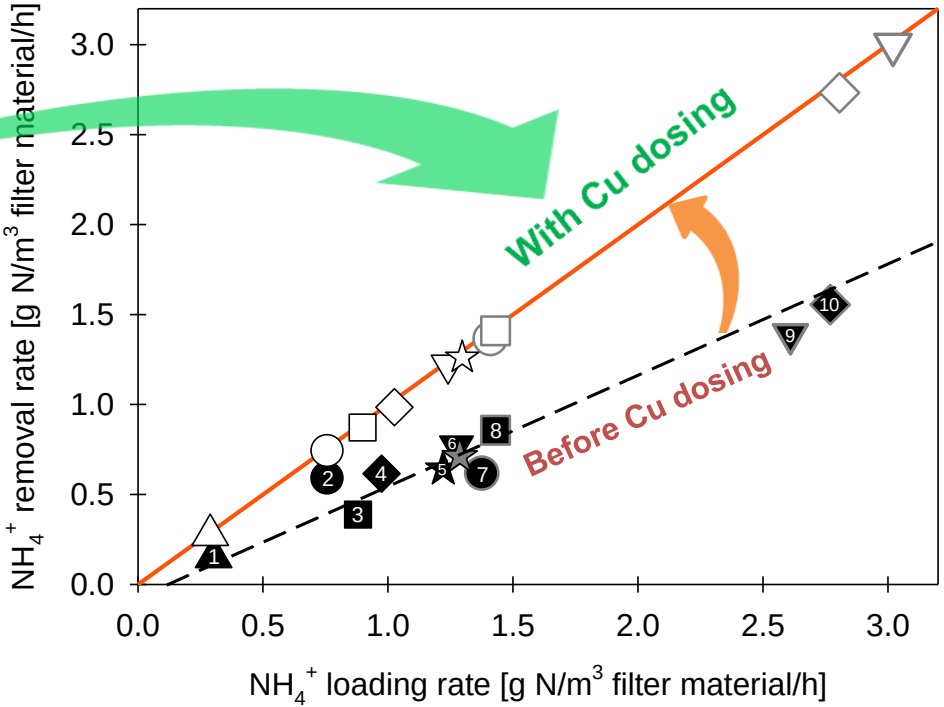

Remediation of incomplete nitrification and capacity increase of biofilters at different drinking water treatment plants through copper dosing

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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 ≤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.

Keywords

Ammonium, biological water treatment, copper deficiency, granular media filtration, groundwater, nutrient limitations

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

45 been reported (Daims et al., 2015). Presence of nitrifying microorganisms in biological filters treating
46 groundwater is well studied (de Vet et al., 2011; Gülay et al., 2014; Lee et al., 2014; Palomo et al., 2016).

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

58 Ammonium is the parameter that challenges Danish water utilities by far the most. Between 2002 and 2013, out
59 of 5,826 analyzes of effluent water at the larger Danish drinking water treatment plants (treating >350,000 m^3/y),
60 13.2 % exceeded the ammonium guideline value (Danish Nature Agency, 2014, 2012, 2009, 2007). With the
61 legal water quality demand, poor nitrification performance constrains water utilities in the way they operate their
62 treatment plants. As a result, the hydraulic loading rate (i.e. treatment flow) is often decreased until the effluent
63 guideline is met, which means that the utilities have a reduced treatment capacity. Besides the constraints with
64 regards to production capacity, it furthermore leaves no room for buffering sudden (and sometimes unexpected)
65 loading increases (Lee et al., 2014). Problems with incomplete nitrification have been known for long (Stamer
66 and Nielsen, 2005) and expensive and time-consuming experience based approaches are taken to remediate the
67 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 like e.g. 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 minute frequency with an ammonium auto-analyzer (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 dosing to determine depth specific ammonium and nitrite removal rates.

2.2. *Water sampling*

Filter effluent water was sampled from sampling taps and influent water was sampled from either taps or from the water on top of the filters. Water depth samples of the filter with dosing at Holmehave DWTP was collected through a PTFE tube inside a supporting rigid stainless steel sampling probe, inserted into the filter at an angle of 45º, and extracted from depths of 10, 20, 30, 40, 50, 60, and 75 cm with a peristaltic pump (Ole Dich, 101 ACR) at a rate of 25 mL min^{-1}. The hydraulic loading rate to the filter was constant during sampling of a complete water depth profile, which was accomplished within 1 h. Depth sampling was always carried out at the same time within a filtration cycle, one day after the filter was backwashed. Water for ammonium and nitrite analyses was immediately filtered through a sterile 0.2 µm filter (Sartorius, Minisart®), stored at 4 °C, and analyzed within 24 h; or frozen at -20 ºC and analyzed within 2 weeks. Samples for determination of total copper concentration were collected unfiltered into acid washed PTFE vials and immediately acidified with 65 % nitric acid (Merck, Suprapur®) to pH <2, and stored at 4 °C until analysis.

2.3. *Analytical methods*

Ammonium and nitrite were determined by colorimetric methods analogous to APHA 4500-NH3-F and APHA 4500-NO2-B (APHA et al., 2005), with quantification limits of 0.01 and 0.002 mg N L^{-1}. For the ammonium auto-analyzer, the quantification limit was 0.02 mg NH_4-N L^{-1}. Unless otherwise noted (Table 2), copper concentrations were determined by inductively coupled plasma mass spectrometry (Agilent Technologies, 7700 Series ICP-MS), according to EPA method 6020A (USEPA, 2007), with a detection limit of 0.01 µg Cu/L.

2.4. *Calculation of nitrification performance indicators and operational parameters*

The volumetric Ammonium Loading Rates of the filters were calculated as $ALR = Qc_{a,in}/A\Delta z$, where Q is the filter flow rate, $c_{a,in}$ is the influent concentration of ammonium, A is the filter cross section area, and Δz is the depth of the active layers of the filters (see Table 2). The volumetric Ammonium Removal Rate was defined as $ARR = Q(c_{a,in}-c_{a,out})/A\Delta z$, where $c_{a,out}$ is the filter effluent concentration of ammonium. From information of water depth profiles at Holmehave DWTP, depth specific volumetric ammonium and nitrite removal rates were calculated and are denoted ARR_{ds} and NRR_{ds}. When referring to ARR_{ds} of a specific layer of the filter, $c_{a,in}$ and $c_{a,out}$ are the ammonium influent and effluent concentrations to and from this layer. Δz is the thickness of that specific layer (e.g.: for calculating the ARR_{ds} of the layer from 10-20 cm depth, $c_{a,in}$ and $c_{a,out}$ are the ammonium concentrations at 10 and 20 cm depth, respectively, and Δz is 0.1 m). The depth specific Nitrite Removal Rate was calculated as $NRR_{ds} = Q[(c_{a,in}-c_{a,out})+(c_{n,in}-c_{n,out})]/A\Delta z$, where $c_{n,in}$ and $c_{n,out}$ are the nitrite influent and effluent concentrations to and from the respective layer. The unit of the ALR and the $ARR_{(ds)}$ is [g NH_4^+-N/m^3/h], where m^3 refers to volume of filter material. The NRR_{ds} has the unit [g NO_2^--N/m^3/h]. The filter velocity [m/h] was calculated as u = Q/A, and the empty bed contact time [h] was calculated as EBCT = $(A\Delta z)/Q$.

3. Results and discussion

3.1. *Characteristics of the investigated treatment plants prior to dosing*

The investigated DWTPs were chosen because they all have long histories of incomplete nitrification (except for Skive DWTP, which was newly started up). The plants have had problems with incomplete ammonium removal for several years (Fig. 1), and numerous attempts to remediate nitrification performance failed. Right before onset of copper dosing, all DWTPs exceeded an ammonium effluent concentration of 0.05 mg NH_4^+/L (expressed as ammonium-N: 0.039 mg NH_4^+-N/L), with filter effluent concentrations from 0.08 mg NH_4^+-N/L (Skindermarken DWTP) to values as high as 0.49 mg NH_4^+-N/L (Bakkebølle DWTP; Table 2). Copper concentrations were very low in the filter influent at any of the DWTPs, where copper could not be detected with detection limits of <0.01 to <0.04 µg Cu/L (Table 2).

Besides the low copper influent concentrations, common for all DWTPs, the plants varied substantially regarding site-specific characteristics. If DWTPs shared similarities, e.g. in filter construction, the plants differed in other features such as treatment configuration, empty bed contact times (EBCT) and ammonium loading rates (Table 2) or raw water chemistry (Table 1). The investigated DWTPs were also contrasted in terms of treatment volumes, with smaller plants such as Bakkebølle DWTP treating 0.2 * 10^6 m^3/y, and the larger Holmehave DWTP treating 3.56 * 10^6 m^3/y (Table 2), showing that both smaller and larger facilities struggle. Ammonium influent concentrations to the filters ranged fairly broadly from 0.15 to 1.17 mg NH_4^+-N/L, but not extraordinarily high. The investigated plants were diverse, but they all had in common that the nitrification was incomplete.

Filtration rates ranged from 1.07 to 2.80 m/h, except Mørkeskov DWTP (6.46 m/h), and were thus lower than the typical range for many rapid granular media filters of 5-15 m/h (Crittenden et al., 2005). Correspondingly, contact times in the filters were quite high, with 0.27 to 0.73 h of empty bed contact time (EBCT; Table 2). Despite the long contact times, volumetric ammonium removal rates (ARR) were not high enough to completely remove the influent ammonium loadings (Fig. 2). Filters at Skive DWTP removed 0.10 g NH_4^+-N/m^3/h,

equivalent to only 33 % of influent ammonium. Before copper dosing, the ARR was highest at Langerød treatment plant at 1.55 g NH_4^+-N/m^3/h, corresponding to 56 % removal. The ARRs were very low compared to rates as high as 3.4 g NH_4^+-N/m^3/h reported for pilot columns with rapid sand filter material treating prefiltered groundwater (Lee et al., 2014), or compared to 4.35 g NH_4^+-N/m^3/h for biological GAC filters treating river water (Laurent et al., 2003), and up to 5 g NH_4^+-N/m^3/h for trickling filters treating groundwater (de Vet et al., 2011), thereby emphasizing the poor nitrification performance of the studied biofilters.

The low filtration rates and low ammonium loading rates at the investigated DWTPs were partly a result of the poor performance. Initially, the filters were designed for higher loading rates, because usually a "worst-case situation" determines the design, where the water quality which requires the most treatment is combined with a situation where the highest possible water flow needs to be treated. Furthermore, some treatment plants were designed with an expectation of an increasing water demand, which was however never realized. At the investigated DWTPs, the actual loading rates were lower than the design, and due to problems with low ammonium removal capacity, operators had decreased the filter flow even further (if ALRs cannot be lowered by switching to a raw water source with lower ammonium concentrations). Filters are generally designed for removal capacities in the range of 2-8 g NH_4^+-N/m^3 filter material/h. At the investigated DWTPs however, the given very low ALRs of 0.30 to 2.8 g NH_4^+-N/m^3/h still resulted in incomplete ammonium removal, which accentuates the poor function of the filters before copper dosing. Violations of the nitrite effluent guideline of 0.003 mg NO_2^--N/L were much less frequent at the investigated DWTPs (Table 2), probably because the oxidation of ammonia is the rate-limiting step of nitrification (Martens-Habbena et al., 2009). However, at DWTPs Nærum and Mørkeskov, effluent concentrations violated the water quality standard of 0.003 mg NO_2^--N/L.

3.2. *Generic resolving of insufficient ammonium removal*

Copper dosing stimulated ammonium removal at all investigated DWTPs. Removal rates increased rapidly (Fig. 2), and within approximately 2-3 weeks, most filters removed ammonium to levels lower than the method

208 detection limit of 0.01 mg NH_4^+-N/L (Table 2). Autotrophic nitrifying bacteria have relatively low growth rates
209 and yields (Zhang et al., 2009) compared to heterotrophs, especially at low temperatures of approx. 9 °C, as in
210 this study (Table 1). The time span of 2-3 weeks therefore indicates that the mechanism of stimulation is
211 probably related to growth of ammonia oxidizing microorganisms. This is in agreement with an earlier study,
212 where ammonia oxidizing bacteria grew as a result of the dosing (Wagner et al., 2016b). Continuous dosing
213 resulted in long-term low effluent concentrations (Fig. 1), thereby improving biological stability (van der Kooij,
214 2000) of the treated water. At Nærum (Wagner et al., 2016a) and Mørkeskov DWTPs, dosing also decreased
215 nitrite effluent concentrations (Table 2). In control filters without copper dosing at Nærum (Wagner et al.,
216 2016a), Langerød, Glostrup, Holmehave, and Frederiksgade DWTPs, nitrification activity was not increased in
217 the investigated period (data not shown). At Glostrup DWTP, initial, passive copper dosing had no effect on the
218 removal, in contrast to Langerød, Bakkebølle and Skindermarken DWTPs, where application of passive dosing
219 was successful. However, after switching the dosing method in Glostrup to active dosing by an electrode,
220 nitrification activity increased (Table 2). With active dosing by electrode, the release of copper is controlled by
221 electrical current and is generally higher compared to passive dosing, where no current is used (Albrechtsen et
222 al., 2015). The fact that the plants Langerød, Bakkebølle and Skindermarken have de-ironing prefiltration, and
223 Glostrup does not, probably also played a role in the successful application of passive dosing at those plants (see
224 also section 3.3).
225 The hydraulic loading rates at the DWTPs were unchanged when comparing before and after dosing (except for
226 treatment plants Glostrup and Skive, where hydraulic loading rates were increased after dosing);
227 correspondingly, contact times were not increased after dosing (Table 2). Nevertheless, after the onset of dosing,
228 the filters managed to completely remove the ammonium load (Fig. 2), meaning that the removal efficiency was
229 improved by the dosing. ARRs increased until complete removal of ammonium was achieved, where ARRs were
230 equal to the ALRs, as indicated in Fig. 2 by the diagonal 'complete removal' line. Removal rate increased from
231 26 % at Skindermarken to 150 % at Skive DWTP, with an average increase for all plants of 87 %.

Copper dosing concentrations at the DWTPs were ≤1.5 µg Cu/L (Table 2) and were therefore several orders lower than international health-based guidelines for drinking water of 2000 µg Cu/L (European Comission, 1998; WHO, 2011).

Nitrification was successfully stimulated by the rather low concentrations of total copper, regardless of very high alkalinity (e.g. 448 mg HCO_3^-/L at Glostrup), which can decrease the concentration of free Cu^{2+} (Zhang and Edwards, 2010), the available form of copper (Amin et al., 2013). Furthermore, when pH increases from 7 to 8, the fraction of Cu^{2+} decreases from approx. 60 to as little as 10% (Sylva, 1976). Despite a pH generally >7 and values as high as 8.2 at Skindermarken and 8.0 at Skive DWTPs, low concentration copper dosing generically remediated nitrification at all poorly functioning systems, regardless of other different site-specific characteristics of the studied DWTPs (Table 2).

Some of the DWTPs (e.g. Nærum and Langerød) had nitrification problems since they were renovated (new filter material and replacement of piping at the plants). It should be further studied, to what extend the use of different materials, for example a trend to replace cast iron pipes with stainless steel or plastic pipes, can aggravate trace metal deficiencies.

3.3. *Effect on filters with vs. without primary filtration*

When copper was dosed to filters receiving prefiltered water, it took less time until ammonium removal was complete (Fig. 3). For DWTPs with primary filter, the full effect was reached after 12 (Langerød) to 20 days (Valbygård), with an average duration of 15 ± 3 days. Two-sample t-test ($\alpha = 0.05$) showed that for plants without primary filtration, it took significantly longer (p-value = 0.004) to reach a full effect. The average duration was 53 % higher (23 ± 4 days), with times ranging from 21 (Holmehave and Mørkeskov) to 30 days (Glostrup). Durations until complete removal were not correlated with the ammonium loadings of the filters (r = -0.23; Fig. 3). Iron influent concentrations in the filters receiving dosing at plants without primary filtration were substantially higher (Table 2). The slower response of the filters without de-ironing pretreatment may be

255 explained by sorption of copper to iron oxides (Benjamin et al., 1996), which reduced the availability for the
256 nitrifying microorganisms.
257 We furthermore investigated possible correlations of the effect of dosing (expressed as change in ARR divided
258 by the time to reach the full effect) with other operational parameters. The change in ARR over time was not
259 correlated with parameters such as filter velocity or EBCT, or ammonium influent concentrations. However, as
260 expected, ARR correlated positively with the ALR (r = 0.94), meaning that the change in ARR induced by
261 copper dosing was higher when the ALR was higher.

262 3.4. *Increasing the filter's robustness towards loading rate increases*

263 To investigate if copper dosing could increase the ammonium removal rate even beyond the normal ALR of a
264 filter, the ALR to the filter at Glostrup DWTP was increased 20 % from a normal average 1.23 to an average
265 ALR of 1.49 g NH_4^+-N/m^3/h. Short term loading rate upshifts as high as 1.85 g NH_4^+-N/m^3/h were conducted.
266 And yet, the filter completely removed the increased loads, showing that with copper dosing the filter had extra
267 capacity to remove ammonium beyond the normal load. For example, an ARR of 1.84 g NH_4^+-N/m^3/h was
268 achieved under an ALR of 1.85 g NH_4^+-N/m^3/h, on day 127 (Fig. 4). Such an extra capacity is needed to buffer
269 shifts in loading rate, which is especially relevant because nitrifying biological filters at drinking water treatment
270 plants are frequently subject to such variations. The upshifts can be caused by either a change in ammonium inlet
271 concentrations (Kors et al., 1998), by a changing water flow to be treated (hydraulic load) (Lee et al., 2014), or a
272 combination of both (Lopato et al., 2013). At another site, Holmehave DWTP, ammonium influent
273 concentrations were rather constant at 0.39 ± 0.01 mg NH_4^+-N/L (n=32, sampled between April 2014 and
274 October 2015), and the ALR in this experiment was increased by increasing hydraulic loading rates. Prior to the
275 upshifts, the filter at Holmehave DWTP had been operated with an ALR of 1.00 ± 0.09 g NH_4^+-N/m^3/h for
276 approximately 7 months. The maximum ammonium removal rate of the filter was 0.64 g NH_4^+-N/m^3/h,
277 regardless of being operated at normal ALRs, or at 1.50 g NH_4^+-N/m^3/h (Fig. 5B) under a loading rate upshift.
278 Nitrification was incomplete already at low hydraulic loading rates: Ammonium effluent concentrations were as

279 high as 0.11 mg NH_4^+-N/L, at relatively low filter velocities of approximately 1.5 m/h (Fig. 5A). Increasing
280 hydraulic loading rate further increased ammonium effluent concentrations (Fig. 5A). For example, an increase
281 in filter velocity of 75 % increased the effluent concentrations by 109 % to 0.23 mg NH_4^+-N/L. With increasing
282 ammonium effluent concentrations under increasing ALRs, the filter clearly reached its removal capacity,
283 meaning that the filter had no further buffer capacity. This is problematic from a practical point of view, since it
284 constrains treatment plant operation. In order to reduce the effluent concentration, water utilities decrease the
285 water throughput, which in turn makes it challenging to maintain production.
286 Before dosing, the copper concentrations in the filter influent were <0.01 µg Cu/L, and increased to 0.85 µg
287 Cu/L (n=8) after dosing onset. The dosing not only facilitated complete ammonium removal at normal ALRs of
288 approximately 1.0 g NH_4^+-N/m^3/h (Fig. 2 & Fig. 5B), but it also enabled the filter to better cope with loading rate
289 increases (Fig. 5A&B). Ammonium was completely removed when the ALR was upshifted from 1.0 to 1.34 g
290 NH_4^+-N/m^3/h, only 29 days after dosing onset. In contrast to before copper dosing, ammonium effluent
291 concentrations remained stable at values around the detection limit of 0.01 mg NH_4^+-N/L, with increasing
292 hydraulic loading ranging from 1.8 to 2.9 m/h (Fig. 5A). At a filter velocity of 2.6 m/h for example, the effluent
293 concentrations were decreased more than 20 times after dosing. However at a filter velocity of 3.9 m/h
294 (corresponding to an ALR of 2.05 g NH_4^+-N/m^3/h), ammonium effluent concentration was 0.066 mg NH_4^+-N/L
295 (Fig. 5B), indicating the new (maximum) removal capacity at this time after dosing start was around 1.70 g
296 NH_4^+-N/m^3/h, more than 2.6 times higher than before the dosing. Nonetheless, the ARR was still lower than
297 ARRs of other biological groundwater filters of for example 3.4 (Lee et al., 2014) or 5 g NH_4^+-N/m^3/h (de Vet et
298 al., 2011), probably because those filters had been operated under generally higher ALRs. In theory, operating
299 the filter at Holmehave DWTP under continuously higher ALRs and with copper dosing will lead to increased
300 biomass growth, given constant biomass yield and no other growth limiting factors. Factors such as alkalinity
301 (5.39 meq/L), pH (7.4), dissolved oxygen (8.32 mg DO/L), and phosphorus (0.053 mg PO_4^{3-}-P/L) in the filter
302 influent were not limiting; hence, the increased capacity points towards an opportunity of adding more
303 ammonium to increase ARR even further.

3.5. *Location of extra ammonium removal capacity over filter depth*

To examine the filter layers active for ammonium removal, the ammonium concentration over filter depth was investigated at Holmehave DWTP at the normal ALR of 1.0 g NH_4^+-N/m^3/h, before and after dosing. To determine if the extra removal capacity at increased load can be attributed to a specific location in the filter, concentrations over depth were furthermore investigated for the increased ALR of 1.50 g NH_4^+-N/m^3/h. The depth specific volumetric ammonium removal rates were calculated from the depth concentrations and are denoted ARR_{ds}.

Before copper dosing, at an ALR of 1.0 g NH_4^+-N/m^3/h (filter velocity of 1.92 m/h), ammonium concentrations decreased over filter depth following an almost linear profile (Fig. 6A). The highest ARR_{ds} was achieved between 60 and 75 cm filter depth (Fig. 6C), where ammonium concentrations dropped from 0.196 to 0.121 mg NH_4^+-N/L, which was in accordance with previous observations (Wagner et al., 2016a) where ammonium oxidation also was slightly higher in the deeper regions of the investigated filter. Removal in the filter was not stratified, unlike reported for well-performing nitrifying filters (Lee et al., 2014; Tatari et al., 2016). Nitrite produced from the oxidation of ammonium was oxidized further; hence NRR_{ds} was almost equal to ARR_{ds} (Fig. 6C&D). Concentrations were low (Fig. 6B), because ammonium oxidation was limiting the rate of nitrification (Martens-Habbena et al., 2009).

When copper had been dosed for 67 days, ammonium oxidation was significantly increased in the top layer of the filter, leading to highly stratified removal, where all ammonium was removed within 30 cm depth (Fig. 6A). ARR_{ds} from 0 to 10 cm depth increased by more than 7-fold, from 0.67 to 4.90 g NH_4^+-N/m^3/h. The ARR_{ds} from 0 to 10 cm was therefore substantially different from the ARR of 0.98 g NH_4^+-N/m^3/h, when integrated over the whole active layer of the filter (75 cm), which shows the value of depth profile information. Nitrite concentrations increased to 0.021 mg NO_2^--N/L at 10 cm, after which concentrations decreased again (Fig. 6B) and nitrite was safely removed to <0.002 mg NO_2^--N/L after 40 cm depth. NRR_{ds} in the top of the filter were also

327 greatly increased compared to before the dosing, and NRR_{ds} from 0 to 10 cm depth was slightly lower than the
328 ARR_{ds} (Fig. 6C&D), due to the nitrite peak which was not oxidized further to nitrate at that depth.
329 On day 68 of the dosing, the ALR was increased by 50 % to 1.50 g NH_4^+-N/m^3/h (filter velocity of 2.88 m/h).
330 Ammonium removal moved downwards in the filter and 60 cm filter depth were necessary for complete
331 removal, compared with 30 cm under normal loading (Fig. 6A); hence, a slightly longer contact time was
332 necessary. At the normal ALR after dosing, ammonium was removed at 30 cm depth. Hence, ARR_{ds} below this
333 depth were 0, but interestingly, under increased load, the filter exhibited substantial ARR_{ds} between 30 and 60
334 cm depth (Fig. 6C). ARR_{ds} under increased loading were highest between 15 and 55 cm (Fig. 6D), showing that
335 some of the above mentioned extra ammonium removal capacity was located in this layer of the filter. The nitrite
336 concentration profile was also pushed downwards, but nitrite was removed to <0.002 mg NO_2^--N/L after 60 cm
337 (Fig. 6B). Nitrogen balances over filter depth showed that oxidized ammonium and nitrite was present as nitrite
338 and/or nitrate, confirming nitrification was the governing process.
339 The depth profile investigation revealed that the increased nitrification efficiency stemmed from a faster
340 oxidation of ammonium in the upper layers of the filter. Additional capacity for ammonium removal at increased
341 ALR was located between 15 and 55 cm, showing that copper dosing stimulated nitrification activity also in the
342 deeper parts of the filter. Average effluent copper measurements (67 and 68 days with dosing) of 0.52 µg Cu/L
343 confirmed that copper fully penetrated the filter. The findings document that copper dosing activated the whole
344 filter, which is important for practical dosing applications.
345

346 **4. Conclusions**

347 Overall, copper dosing increased nitrification efficiency at different full-scale drinking water treatment plants,
348 which had struggled with poor nitrification performance for several years. The stimulation of ammonium
349 removal was generic - regardless of differences in raw water chemistry, treatment plant configuration, filter
350 design and operation, and ammonium loading rates.

- At 10 out of 10 different DWTPs, copper dosing at ≤1.5 µg Cu/L fully remediated nitrification within only 2-3 weeks. With dosing, ammonium removal rates increased on average by 87 %, and most filters achieved very low effluent ammonium concentrations of <0.01 mg NH_4^+-N/L.
- Full nitrification was established relatively quickly (19 days on average). Dosing filters receiving prefiltered water achieved complete ammonium removal faster, than filters without primary filtration, possibly related with that those filters received considerably higher iron loads, which may have precipitated or bound the copper.
- Poor nitrification performance can constrain DWTPs operation. When the filter velocity was increased by 75 % in a filter operating at its ammonium removal capacity, the ammonium effluent concentrations increased by 109 %, causing a deterioration of the finished water quality. With dosing, at the same increased filter velocity, effluent concentrations were <0.01 mg NH_4^+-N/L and more than 20 times lower than without the dosing.
- With dosing, biofilters could efficiently remove ammonium at loadings even beyond the loading rates the filters were normally operated under. Under short-term loading rate upshifts, the removal capacity of a filter was increased by more than 2.6 times, showing that copper dosing can not only remediate existing problems, but also increase the robustness of these filters. The extra capacity makes filters resilient towards loading rate upshifts/fluctuations.
- The increased resilience was brought about by ammonium and nitrite oxidation being shifted further up in the filter. Under increased loading rates, extra removal capacity was located at the depth of 15 to 55 cm, showing that copper dosing activated the whole filter. Water depth sampling furthermore revealed significant, but transient nitrite peaks. These were subsequently oxidized further to effluent concentrations <0.002 mg NO_2^--N/L, thereby preventing problematic nitrite breakthrough.

Our results suggest copper dosing as a technology with the potential of solving many cases of insufficient nitrification at drinking water treatment plants, with the perspective of achieving even lower ammonium and nitrite effluent concentrations and operation under higher flow rates. Higher rates and increased nitrification efficiency in general indicate the possibility of treating the same amount of water with less filter area, thereby decreasing the geographical footprint.

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Table and figure captions:

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Figure 1: Long-term time series of ammonium effluent concentrations at the investigated DWTPs. Data points were normalized to the onset of copper dosing on day 0. The shaded area visualizes the dosing period. Long-term data for Skive DWTP was not available, as the plant was just newly started up. (with data adapted from Geological Survey of Denmark and Greenland, 2016)

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499 Figure 5: Effect of copper dosing on ammonium removal at increased loading rates (Holmehave DWTP). A:
500 Ammonium effluent concentrations for different filter velocities. B: Volumetric ammonium removal rates
501 (ARR) vs. volumetric ammonium loading rates (ALR). Different symbols depict three phases in relation to
502 copper dosing.

503 Figure 6: Effect of dosing on ammonium and nitrite removal over filter depth, at normal and increased
504 ammonium loading rates (Holmehave DWTP). A: Ammonium, B: nitrite concentrations, C: depth specific
505 ammonium removal rate, and D: depth specific nitrite removal rate, before and after copper dosing at a filter
506 velocity of 1.92 m/h, and after copper dosing with increased loading rate at 2.88 m/h.

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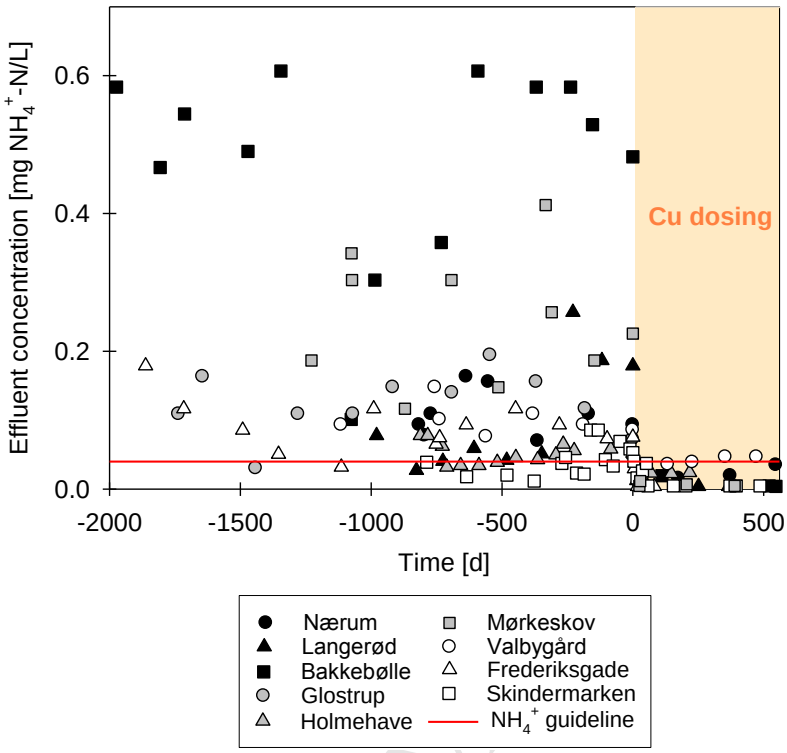
DWTP	Nærum	Langerød	Bakkebølle	Skindermarken	Glostrup	Holmehave	Mørkeskov	Valbygård	Frederiksgade	Skive
Temp [ºC]	9.2	9.3	9.4	9.0	9.9	9.4	9.8	9.0	9.4	8.3
pH [-]	7.5	7.4	7.1	8.2	7.5	7.4	7.2	7.4	7.3	8.0
Dissolved oxygen [mg/L]	0.6	0.9	0.4	0.5	0.4	1.5	<0.1	0.3	1.2	<0.1
NH_4^+ [mg N/L]	0.34	1.05	1.10	0.87	0.77	0.39	1.34	0.70	0.63	0.17
NO_2^- [mg N/L]	0.002	0.005	0.002	0.002	<0.001	0.002	0.002	0.005	<0.001	<0.001
NO_3^- [mg N/L]	0.07	0.01	0.08	0.07	0.05	0.06	0.11	0.07	0.02	0.09
total Fe [mg/L]	2.50	3.05	1.43	0.27	1.89	1.56	0.70	1.99	1.50	0.51
total Mn [mg/L]	0.09	0.12	0.01	0.05	0.06	0.32	0.01	0.09	0.03	0.28
H_2S [mg/L]	<0.02	0.03	0.47	0.03	0.03	NA	0.26	0.04	0.04	<0.05
CH_4 [mg/L]	0.01	0.03	2.11	0.23	0.02	NA	1.26	0.03	1.04	0.02
P [mg/L]	0.020	0.251	0.031	0.210	0.032	0.088	0.022	0.153	0.051	0.148
Alkalinity [as mg HCO_3^- /L]	342	358	406	265	448	308	408	398	349	150
Ca^{2+} [mg/L]	114	86	86	45	105	89	93	70	68	61
Mg^{2+} [mg/L]	18	14	21	16	39	12	24	16	25	5
Cl^- [mg/L]	56	52	31	66	108	41	99	117	46	33
SO_4^{2-} [mg/L]	49	8	13	0.3	60	34	16	23	6	51
NVOC [mg/L]	2.1	2.6	2.5	1.0	2.0	2.0	2.7	2.4	2.9	1.1

NA: not available

Table 2: Characteristics and nitrification performance indicators of all investigated DWTP

DWTP	Water abstracted [10^6 m^3] in (year)	Treatment train	Filter material of filter with dosing	Depth of active layer [m]	Filter velocity before/ after Cu [m/h]	EBCT [h]*	Cu dosing method	Cu influent conc. before/after dosing [µg/L]	Ammonium influent conc. before/after dosing [mg N/L]	Ammonium effluent conc. before/after dosing [mg N/L]	Nitrite effluent conc. before/after dosing [mg N/L]	Total iron conc. in the influent to the filter with dosing [mg Fe/L]	Volumetric ammonium loading rate before/after dosing [g N/m^3/h]	Response for complete ammonium removal [days]
Nærum (Wagner et al., 2016)	0.85 (2014)	stairs aeration → single stage rapid sand filtration	0.8-1.4 mm quartz	0.60	1.56	0.38	Active (solid electrode)	<0.01 /0.97	0.34/0.35	0.19/<0.01	0.009/ 0.006	2.06	0.88/0.90	22
Langerød	1.47 (2015)	stairs aeration → rapid sand prefiltration → rapid sand afterfiltration	0.8-1.4 mm quartz	0.65	2.40	0.27	Passive (solid structure)	<0.03/0.42	0.75/0.76	0.33/<0.02	<0.002/NA	0.14	2.77/2.81	12
Bakkebølle	0.20 (2015)	INKA aeration → rapid sand prefiltration → rapid sand afterfiltration	1-3 mm granular calcium carbonate	0.70	1.07	0.65	Passive (solid structure)	<0.03/1.50	0.89/0.91	0.49/0.03	<0.002	0.08	1.37/1.41	17
Skinder-marken	0.61 (2016)	plate aeration → rapid sand prefiltration → rapid sand afterfiltration	0.4-0.8 mm quartz (20 cm) → 0.8-1.4 mm quartz (25 cm) → 1.3-2.0 mm quartz (15 cm)	0.60	1.30	0.46	Passive (solid structure)	<0.04/ 0.29 (effluent)	0.35	0.08/<0.01	0.003/ <0.002	0.06	0.76	13
Glostrup	0.54 (2016)	stairs aeration → contact basin → single stage rapid sand filtration	0.8-1.4 mm quartz	0.80	2.57/2.71	0.31/ 0.30	Passive (solid structure)	<0.01/0.36	0.38	0.18/0.17	<0.002	1.32	1.22/1.29	no effect
					2.71/2.80	0.30/ 0.29	Active (solid electrode)	<0.01/0.91	0.38/0.37	0.17/<0.01	<0.002		1.29/1.30	30
Holmehave	3.56 (2015)	plate aeration → single stage rapid sand filtration	0.8-1.4 mm quartz	0.75	1.92	0.39	Active (solid electrode)	<0.01/1.34	0.38/0.40	0.14/<0.01	<0.002	1.46	0.97/1.03	21
Mørkeskov	0.40 (2015)	stairs aeration → contact basin → single stage pressurized sand filtration	0.8-1.4 mm quartz (200 cm) → 1.2-2.0 mm quartz (50 cm)	2.50	6.46	0.39	Active (solid electrode)	NA/NA	1.01/1.17	0.47/<0.01	0.006/ <0.002	0.7+	2.61/3.02	21
Valbygård	1.67 (2015)	INKA aeration → rapid sand prefiltration → rapid sand afterfiltration	1.6-2.2 mm quartz	0.80	1.62	0.49	Active (solid electrode)	<0.02/ 0.15 (effluent)	0.70	0.28/<0.01	<0.002	NA	1.43	20
Frederiks-gade	1.36 (2015)	Cascade aeration → rapid sand prefiltration → rapid sand afterfiltration	1.0-2.0 mm quartz	0.72	2.41	0.30	Active (solid electrode)	<0.01/0.66	0.38/0.37	0.15/<0.01	<0.002	0.01	1.27/1.24	14
Skive	1.38 (2016)	O_2 injection → single stage pressurized sand filtration	0.8-1.4 mm quartz	1.20	1.62/2.43	0.74/ 0.49	Active (liquid from $CuSO_4$)	<0.04/1.50	0.22/0.15	0.15/0.03	NA/NA	0.51+	0.3	22

Cu analyses for Langerød, Bakkebølle, Valbygård, Skindermarken, Skive according to ICP/MS ISO 17294:2 ; * EBCT: Empty Bed Contact Time ; NA: not available ; +values from raw water



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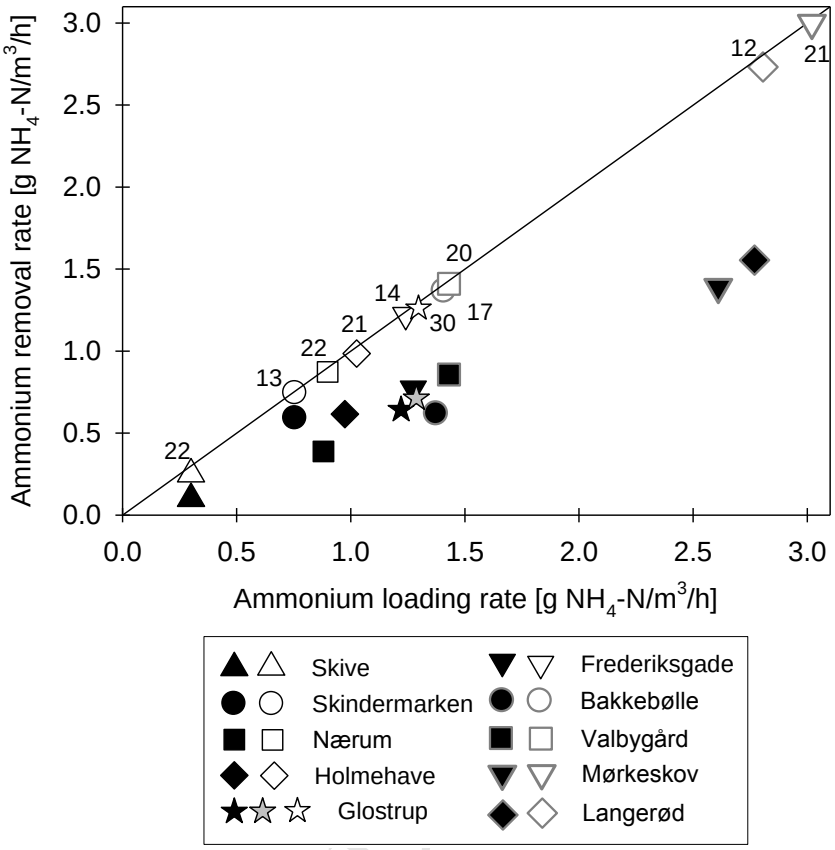

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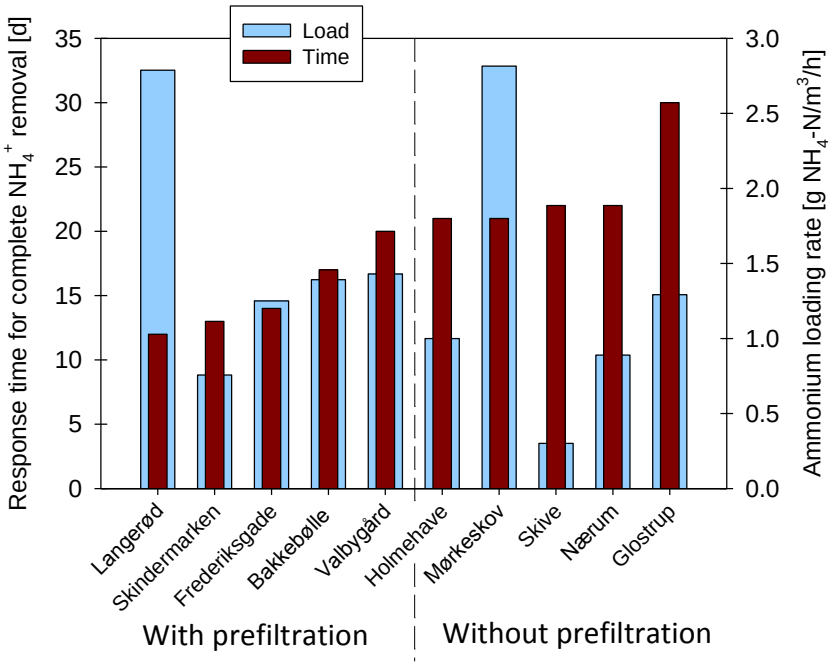

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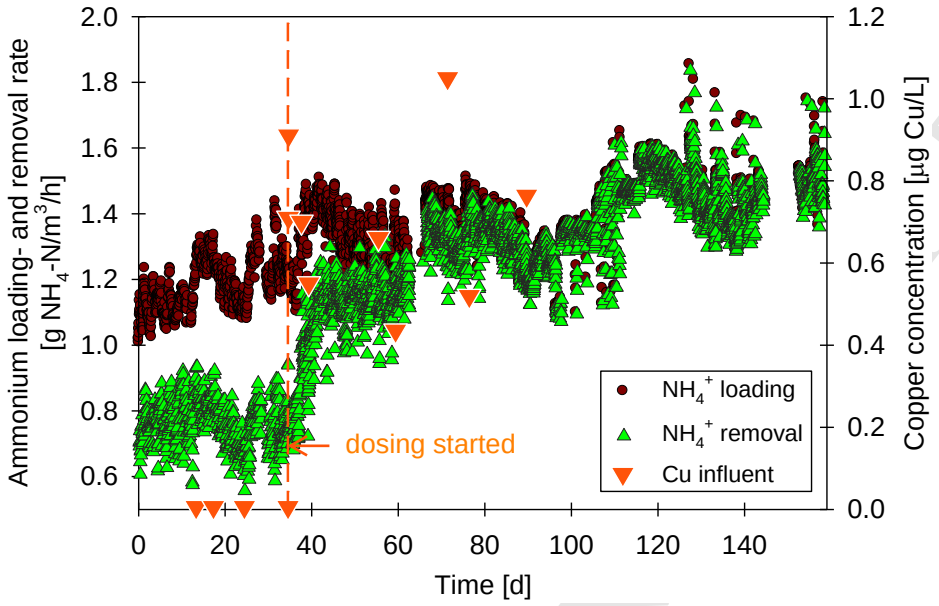

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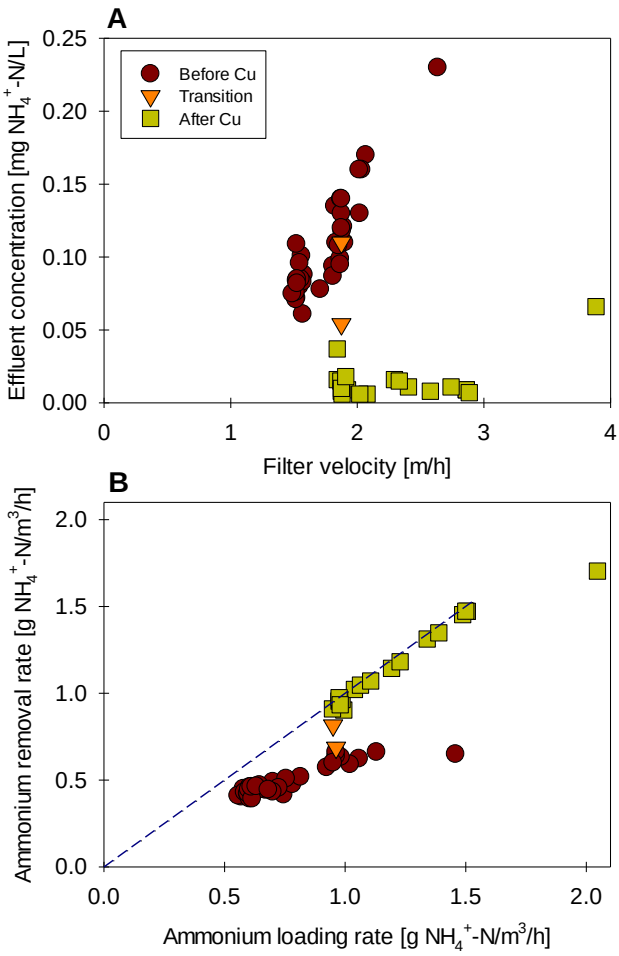

Figure 5: Effect of copper dosing on ammonium removal at increased loading rates (Holmehave DWTP). A: Ammonium effluent concentrations for different filter velocities. B: Volumetric ammonium removal rates (ARR) vs. volumetric ammonium loading rates (ALR). Different symbols depict three phases in relation to copper dosing.

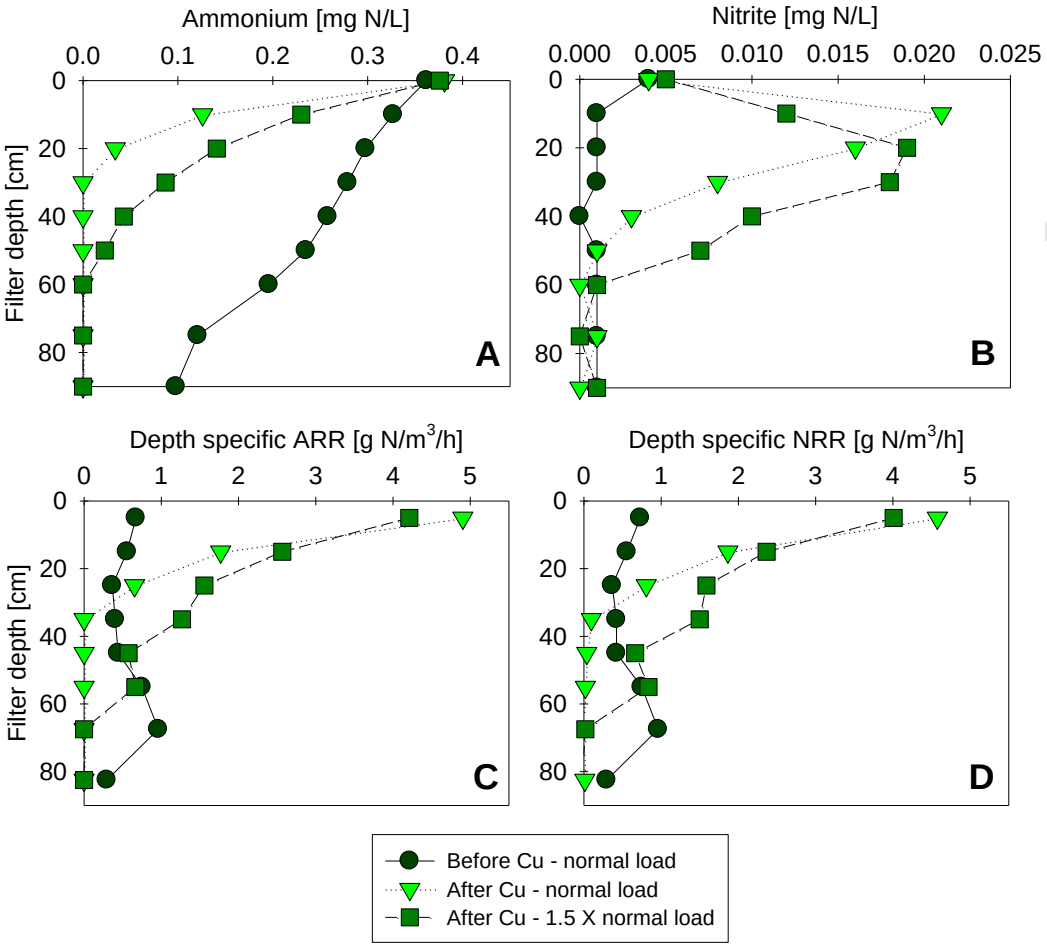

Figure 6: Effect of dosing on ammonium and nitrite removal over filter depth, at normal and increased ammonium loading rates (Holmehave DWTP). A: Ammonium, B: nitrite concentrations, C: depth specific ammonium removal rate, and D: depth specific nitrite removal rate, before and after copper dosing at a filter velocity of 1.92 m/h, and after copper dosing with increased loading rate at 2.88 m/h.

Highlights

- At 10 out of 10 water works, copper dosing remediated incomplete nitrification
- It took only 3 weeks on average until complete ammonium removal was achieved
- Stimulation occurred despite variation in water chemistry, plant design and operation
- With dosing, filters completely nitrified even at increased ammonium loading rates
- Increased capacity buffered loading rate variations, thereby increasing robustness